APPENDIX 1
SOP FOR NEAR-FIELD TRANSECT MONITORING

APPENDIX 1
STANDARD OPERATING PROCEDURE FOR NEAR-FIELD TRANSECT MONITORING

1.1 Scope and Application

This Standard Operating Procedure (SOP) is applicable to the collection of real-time surface water quality data and water column samples along transects located in the near-field monitoring area.

1.2 Summary of Method

Surface water quality data (turbidity, conductivity, pH, temperature, and dissolved oxygen) will be obtained at numerous locations along transects located in the vicinity of dredging operations. Additionally, water samples for total suspended solid (TSS) and metals analyses will be collected at mid-depth using a submersible pump at the maximum turbidity value point along designated transects. TSS analysis will be performed in accordance with the procedures specified in Appendix 29; analytical procedures for metals analyses are presented in Appendices 32 through 35.

1.3 Health and Safety Warnings

Health and safety issues are addressed in the project Health and Safety Plan (HASP; Parsons 2008).

1.4 Contamination and Interferences

Sources of interferences for surface water quality data collection include calibration drift and instrument error. Potential sources of TSS contamination during sampling include the presence of residual solids within sample collection equipment. Thorough rinsing of sampling equipment with distilled water prior to use will minimize the potential for contamination of samples during collection.

Potential sources of trace metals contamination during sampling include metallic or metal-containing sampling equipment, containers, personal protective equipment (PPE; e.g., gloves that contain zinc due to the presence of talc), reagent water, and improperly cleaned and

stored equipment. Additionally, atmospheric inputs such as dirt and dust from engine exhaust, tobacco smoke, nearby roads, bridges, wires, and poles can result in sample contamination. Before samples are collected for metals analysis, the sample collection vessels and sample containers will be cleaned using detergent, mineral acids, and reagent water. Reagent water is defined as water prepared by the laboratory in which the analytes of interest and potentially interfering substances are not detected at the Method Detection Limit (MDL) of the analytical method(s). After cleaning, sample containers will be filled with weak acid solution, and individually double-bagged using resealable plastic bags. Sample collection vessels will be placed in plastic bags to minimize contact with metal or atmospheric deposition of particles containing metal.

1.5 Personnel Qualifications

All field personnel are required to take a 40-hour OSHA Hazardous Waste Operations training course and annual refresher courses, and participate in a medical monitoring program prior to engaging in any field collection activities as required in 29 CFR 1910.120. Additionally, field personnel will be under the direct supervision of qualified professionals who are experienced in performing the tasks required for sample collection.

1.6 Equipment and Supplies

Equipment needed includes:

- Sampling vessel
- Submersible pump equipped with a flow-through cell and a sample tap.
- Depth finder
- Sample containers (plastic for TSS)
- Pre-cleaned sample containers (plastic for metals; additional glass containers may be required if analysis for mercury or hexavalent chromium is required)
- Laboratory supplied reagent water (free of metals)
- Plastic (polyethylene) resealable food storage bags
- Plastic (polyethylene) trash bags
- Dedicated, clean cooler with ice (metals samples)
- Disposable gloves (talc free)
- Distilled water
- Cooler with ice (TSS samples)

- Laptop computer and printer
- Field database
- Surface water quality (SWQ) sonde
- GPS

1.7 Water Sample Collection

1.7.1 Sampling Locations

Real-time data will be collected from transects located in the vicinity of dredging operations. The locations of these transects will be provided to the field crew once or twice daily by the field sampling manager (as needed). Water sampling will be conducted at a point along each near-field monitoring transect that exhibits the highest turbidity, If an area of increased turbidity cannot be identified during the transect monitoring, the water sampling will be conducted at a point that is the same approximate distance from shore as the dredging operation being monitored on the cross-channel transects, and at a point on the transect that is approximately parallel to the downstream end of the dredge on the in-channel transects.

1.7.2 Procedures

1. Synchronize the field database with the environmental Data Management System (eDMS) and download transect IDs.
2. Use the GIS field application depicting the monitoring transects and realtime vessel position and navigate the vessel to the furthest upstream transect. Approach one end of the transect as close to shore as water depth permits.
3. Lower the submersible pump to mid-depth of the water column and activate to provide a continuous flow of water. The water will be pumped through a flow-through cell equipped with a calibrated SWQ sonde.
4. Activate the sonde, GPS, and data logger. Allow the water quality sonde to stabilize and GPS coordinates to resolve.
5. Set the data logger to record SWQ data and GPS coordinates every 10 seconds. Traveling at idle speed, move the sampling vessel along the transect, using the GIS display as a guide. Raise or lower the submersible pump as appropriate to maintain the intake at approximately mid-depth of the water column. When the end of the transect is reached, stop data collection.

6. Upload the SWQ data to the field application. Using the ArcPad application, display the SWQ. Navigate the sampling vessel to the point with the highest turbidity value displayed in the GIS application. Hold the vessel within approximately 10 ft. of this position using the engine.
7. Verify sample collection requirements for the transect. Record information associated with sample collection in the field database, and print labels for sample containers for TSS (and metals if required) analysis, and prepare sample container(s).
8. Ensure that the submersible pump is at mid-depth, and record the turbidity in the field database (key in one turbidity number from visual read-out; do not record other water quality parameters).
9. Open the sample port on the discharge line, allow approximately one liter of water to flush through the port prior to sample collection.
10. Put on new disposable gloves.
11. For TSS samples, fill the appropriate containers and place filled containers in a cooler with ice. Repeat sampling procedure to fill containers needed for QA/QC samples, as required. Metals samples will be collected in a manner generally consistent with the "Clean Hands/Dirty Hands" technique described in Appendix 21, except that it will be modified to allow the samples to be collected by one person while the second crew member navigates the sampling vessel. The design of the sample collection system (i.e., filling containers from a tap) will minimize the potential for sample contamination. Therefore, metals samples will be collected as follows:
    - Open the outer resealable plastic bag and remove and open the inner resealable plastic bag containing sample container and remove the cap.
    - Open the sample tap and fill the sample container.
    - Once sufficient sample volume is collected, place a top on the container.
    - Label the container, and then place it back into its resealable plastic bag. The container and bag are then placed into a second resealable plastic bag.
    - Seal the outer bag, and place the double-bagged sample bottle into a cooler (dedicated for metals samples) for subsequent delivery to the field laboratory for filtration.
    - Repeat procedures above to fill containers needed for QA/QC samples, as required.

12. Upon completion of operations monitoring, return to the Work Support Marina and filter metals samples in accordance with the procedures specified in Appendix 21.
13. Using field application, generate an XML file for upload to the eDMS.
14. Upload field sample information (in XML format) to the eDMS.
15. Use the field database to generate field logs and chain of custody forms, and coordinate with shore-based staff to submit samples to the appropriate laboratory.

1.8 Sample Handling and Preservation

Sample containers will be labeled in accordance with labeling requirements specified in Section 10.1. Samples will be collected and placed in containers in accordance with the procedures described above. Each container for metals analysis will be placed in two resealable food storage bags (double-bagged: one inside the other), and placed in a clean cooler dedicated to metals analysis for the Hudson River. The samples will be chilled with ice to approximately 4°C. A temperature blank will be placed in each cooler for use by the laboratory to measure the temperature of samples upon submittal. Filtrations will be performed as soon as practical after collection at a field laboratory. Samples will be shipped or transported to the laboratory at the end of each day and dissolved samples will be preserved with nitric acid upon arrival at the laboratory. Chain of custody procedures will be followed, as specified in Section 10.1 of this QAPP.

1.9 Data and Records Management

Data from water sample collection will be recorded in the field database provided by GE using a laptop computer. Blank field log sheets can also be used to record information manually in case difficulties with the data entry computer. Manually recorded data will be transcribed into the field database at the end of each day.

1.10 Quality Control and Quality Assurance (QA/QC)

QA/QC procedures are defined in Section 10.2 of this QAPP, and include the collection of field QA/QC samples. Field QA/QC samples to be collected for TSS samples will be blind duplicate samples. Field QA/QC samples to be collected for metals samples are blind duplicate samples and matrix spike samples. Field QA/QC samples will be collected at the frequency specified in Section 10.2. Blind duplicate samples and matrix spike samples will be

prepared by filling additional appropriately marked containers at pre-selected sampling stations (both samples will not be collected at the same station). The station where these samples are collected will be rotated randomly for each sampling event. Equipment blanks will not be collected with the exception of filter blanks for dissolved metals which will be collected once per 24-hour period of sample collection. Additional equipment blank samples will not be required due to the configuration of the sample collection system. The continuous flow of river water through the sampling system will minimize any potential for contamination from the system.

1.11 References

Parsons, 2008. Phase 1 Remedial Action Health and Safety Plan, Hudson River PCBs Superfund Site. Prepared for General Electric Company, Albany, NY. August 2008.

APPENDIX 2
SOP FOR NEAR-FIELD BUOY MONITORING

APPENDIX 2
STANDARD OPERATING PROCEDURE FOR NEAR-FIELD BUOY MONITORING

1.1 Scope and Application

This Standard Operating Procedure (SOP) is applicable to the collection of real-time surface water quality data and water column samples from monitoring buoys in the near-field area.

1.2 Summary of Method

Surface water quality data (turbidity, conductivity, pH, temperature, and dissolved oxygen) will be obtained from monitoring buoys located in the vicinity of dredging operations. Additionally, water samples for total suspended solid (TSS) and metals analyses will be collected using automated samplers mounted on the buoys at mid-depth in the water column. TSS analysis will be performed in accordance with the procedures specified in Appendix 29; analytical procedures for metals analyses are presented in Appendices 32 through 35.

1.3 Health and Safety Warnings

Health and safety issues are addressed in the project Health and Safety Plan (HASP; Parsons 2008).

1.4 Contamination and Interferences

Sources of interferences for surface water quality data collection include calibration drift and instrument error. Potential sources of TSS contamination during sampling include the presence of residual solids within sample collection equipment. Replacing automatic sampler intake tubing whenever significant visible residue is observed will minimize the potential for contamination of samples during collection.

Potential sources of trace metals contamination during sampling include metallic or metal-containing sampling equipment, containers, personal protective equipment (PPE; e.g., gloves that contain zinc due to the presence of talc), reagent water, and improperly cleaned and stored equipment. Additionally, atmospheric inputs such as dirt and dust from engine

exhaust, tobacco smoke, nearby roads, bridges, wires, and poles can result in sample contamination. Procedures followed during the BMP for the collection of metals samples have successfully addressed these concerns; therefore the methods specified in this SOP are generally consistent with the BMP methods.

1.5 Personnel Qualifications

All field personnel are required to take a 40-hour OSHA Hazardous Waste Operations training course and annual refresher courses, and participate in a medical monitoring program prior to engaging in any field collection activities as required in 29 CFR 1910.120. Additionally, field personnel will be under the direct supervision of qualified professionals who are experienced in performing the tasks required for sample collection.

1.6 Equipment and Supplies

Equipment needed includes:

1. Sampling vessel appropriately sized and equipped to deploy, maintain, and operate monitoring buoys.
2. Monitoring buoy equipped with:
   - ISCO 6712 portable sampler
   - YSI 6920 multiparameter sonde
   - Campbell Scientific CR850 datalogger
   - Garmin GPS-18 receiver
   - GE 50 watt solar panel and 96ah battery
   - Sierra Wireless Airlink Raven Verizon compatible modem
   - Rolyan Buoys 4 x 6 ft Pontoon Float
   - Anchoring system and chain
3. Depth finder
4. Laboratory supplied reagent water (free of metals)
5. Sample containers (plastic for TSS)

6. Pre-cleaned sample containers (plastic for metals; additional glass containers may be required if analysis for mercury or hexavalent chromium is required)
7. Plastic (polyethylene) resealable food storage bags
8. Plastic (polyethylene) trash bags
9. Dedicated, clean cooler with ice (metals samples)
10. Disposable gloves (talc free)
11. Distilled water.
12. Cooler with ice (TSS samples)
13. Laptop computer and printer
14. Field database
15. GPS

1.7 Buoy deployment and relocation

Monitoring buoys will be deployed at predetermined approximate distances upstream and downstream of dredging operations. Once deployed, data obtained during the transect monitoring (Appendix 1) will be used to identify the center of any resuspended sediment plume originating from the dredging operation(s) being monitored. The buoys will be relocated up to two times per day (during the day work shift) to keep them located within the plume.

1.7.1 Buoy Deployment

1. Obtain coordinates for buoy locations from the field sampling manager two times per day (at morning coordination meeting and in the early afternoon).
2. Transport the buoys to the target locations with the sampling vessel.
3. Navigate the sampling vessel to within approximately 10 ft. of the target coordinates and hold in position using spuds or anchors.
4. Cut a length of mooring chain approximately 8 ft. longer than the water depth; attached one end to a 70 lb. cast iron anchor and the other end to an 18 in. diameter orange float. Place the anchor approximately 15 ft. upstream of the target location.

5. Place the buoy in the water and attach one end of a 10 ft. length of mooring chain to the orange float and the other end to the upstream side of the buoy. The solar panel should be facing downstream, oriented south. Allow the buoy to drift downstream until the slack in the mooring chain is pulled out, and the buoy is held in position by the anchor.
6. Place a 35 lb. anchor approximately 10 ft. downstream of the buoy. Connect the downstream orange float to the buoy with a piece of mooring chain.
7. Attach the sonde and sampler intake tubing to a 10 lb. downrigger. Attach a length of chain to the downrigger, and lower the sonde and end of the sampler intake tubing to the approximate mid-depth of the water column (minimum of 2 ft. off the bottom in shallow water).
8. Activate the sonde, datalogger, gps, cellular signal booster, and cellular modem system. The sonde will have been calibrated on shore prior to deployment. Confirm that the buoy is collecting and transmitting data.
9. Remove the top of the ISCO sampler and confirm that the plastic containers in the tray are clean.
10. Set the time delay on the ISCO sampler to begin Program A at the next time interval that corresponds to 6:00, 12:00, 18:00, or 24:00.
11. Confirm that the sampler is programmed to run Program A continuously. The sampler should dispense approximately 150 ml into three 1-L plastic containers once every hour; after 6 hours, the first three containers will be complete and the sampler will begin filling the next three containers automatically.
12. Confirm that the flashing warning beacon on the top of the buoy is operable.

1.7.2 Buoy Relocation

Buoys will be relocated (as necessary) each time the transect data (Appendix 1) are obtained on transects where buoys are also deployed. The transect turbidity data will be reviewed upon completion of running the transect. If the buoy is more than approximately 25 ft. from the point where the highest turbidity was measured, it will be relocated to within approximately 10 ft. of this point and redeployed as described in Section 1.7.1 above, with the exception that the sampler will be allowed to continue to run (will not be reprogrammed

to restart at the next 6 hour time interval) and data collection by the sonde will not be interrupted.

1.8 Water Sample Collection

Water samples will be collected from all buoys for TSS analysis and from a subset of buoys for metals analysis. The buoys that will collect samples for metals analysis will be determined by the Field Sampling Manager and communicated to the field crew at the daily morning coordination meeting.

1.8.1 Procedures

1. Synchronize the field database with the environmental Data Management System (eDMS) and download buoy IDs.
2. Verify sample collection requirements for the buoy. Record information associated with sample collection in the field database, and print labels for sample containers for TSS (and metals if required) analysis, and prepare sample container(s). The length of time the sampler has been deployed on one day (one, two, three, or four 6-hour composite periods) will determine the number of TSS samples to be submitted, and how the daily composite samples for metals analysis will be prepared. As metals samples will be daily composites, mark the outside of the container in increments that correspond to the number of 6-hour composite periods that will be included in the daily composite. For a sample comprised of four 6-hour periods, mark the container at the approximate ¼, ½, ¾, and full levels.
3. For metals samples, sampling will be conducted in general accordance with the "Clean Hands/Dirty Hands" technique described in Appendix 21, as follows:
   - Identify one person to be "Clean Hands" and one person to be "Dirty Hands".
   - "Dirty Hands" removes top of the ISCO sampler to expose the filled containers in the sampler tray.
   - "Dirty Hands" opens outer resealable plastic bag.
   - "Clean Hands" removes and opens inner resealable plastic bag containing sample container and prepares for collection.

- "Dirty Hands" removes the first 6-hour composite ISCO container from the sampler tray, swirls the container to resuspend any materials that have settled out, and then fills the container held by "Clean Hands" up to the first increment marked on the container. Repeat as necessary using subsequent 6-hour composite ISCO containers until the sample container is full.
- Once sufficient sample volume is collected, "clean hands" places a top on the container.
- "Clean hands" places the label on the container, and then places it back into its resealable plastic bag. The container and bag are then placed into a second resealable plastic bag held by "dirty hands".
- "Dirty hands" seals the outer bag, and places the double-bagged sample bottle into the cooler (dedicated for metals samples) for subsequent delivery to the field laboratory for filtration.

4. For TSS samples, remove the first 6-hour composite ISCO container from the sampler tray. Swirl this container to resuspend any settled solids, and then pour the entire contents into a 1L plastic container for TSS analysis. Place filled containers in a cooler with ice.
5. The third 6-hour composite ISCO container will be available for use to fill additional sample containers for QA/QC samples (TSS or metals), as needed using the procedures above.
6. Upon completion of operations monitoring, return to the Work Support Marina and filter metals samples in accordance with the procedures specified in Appendix 21.
7. Using field application, generate an XML file for upload to the eDMS.
8. Upload field sample information (in XML format) to the eDMS.
9. Use the field database to generate field logs and chain of custody forms, and coordinate with shore-based staff to submit samples to the appropriate laboratory.

1.9 Sample Handling and Preservation

Sample containers will be labeled in accordance with labeling requirements specified in Section 10.1. Samples will be collected and placed in containers in accordance with the procedures described above. Each container for metals analysis will be placed in two resealable food storage bags (double-bagged: one inside the other), and placed in a clean cooler dedicated to metals analysis for the Hudson River. The samples will be chilled with ice to approximately 4°C. A temperature blank will be placed in each cooler for use by the laboratory to measure the temperature of samples upon submittal. Filtrations will be performed as soon as practical after collection at a field laboratory. Samples will be shipped or transported to the laboratory at the end of each day and dissolved samples will be preserved with nitric acid upon arrival at the laboratory. Chain of custody procedures will be followed, as specified in Section 10.1 of this QAPP.

1.10 Data and Records Management

Data from water sample collection will be recorded in the field database provided by GE using a laptop computer. Blank field log sheets can also be used to record information manually in case difficulties with data entry using the computer are encountered. Manually recorded data will be transcribed into the field database at the end of each day.

1.11 Quality Control and Quality Assurance (QA/QC)

QA/QC procedures are defined in Section 10.2 of this QAPP, and include the collection of field QA/QC samples. Field QA/QC samples to be collected for TSS samples will be blind duplicate samples. Field QA/QC samples to be collected for metals samples are blind duplicate samples, and matrix spike samples. Field QA/QC samples will be collected at the frequency specified in Section 10.2. Blind duplicate samples and matrix spike samples will be prepared by filling additional appropriately marked containers at pre-selected sampling stations (both samples will not be collected at the same station). The station where these samples are collected will be rotated randomly for each sampling event. Equipment blanks will not be collected with the exception of filter blanks for dissolved metals which will be collected once per 24-hour period of sample collection. Additional equipment blank samples will not be required due to the configuration of the sample collection system. The use of the ISCO sampler will minimize any potential for contamination from the system as the sample

collection tubing is made of non-metallic materials and the tube will be rinsed with river water before and after collection of each sample aliquot.

1.12 References

Parsons. 2008. *Phase 1 Remedial Action Health and Safety Plan, Hudson River PCBs Superfund Site.* Prepared for General Electric Company, Albany, NY. August 2008.

APPENDIX 3
SOP FOR FAR-FIELD WATER COLUMN SAMPLING

APPENDIX 3
STANDARD OPERATING PROCEDURE FOR FAR-FIELD WATER SAMPLING

1.1 Procedures

1.1.1 Scope and Application

This Standard Operating Procedure (SOP) is applicable to the collection of water samples at far-field monitoring stations.

1.2 Summary of Method

At automated far-field monitoring stations, samples will be collected using a programmable automatic sampler. The sampler will withdraw samples from a stilling well that is supplied with river water with pumps on a continuous basis. This sampler will be programmed to collect aliquots at specified time intervals to provide composite samples over the required time period, depending on the level of sampling (routine or contingency). At non-automated far-field monitoring stations, samples will be collected using a multiple-aliquot depth integrating sampler (MADIS), consistent with the sample collection method used in the Baseline Monitoring Program (BMP; QEA and ESI 2004) with the exception of the Rogers Island station, which will be a grab sample due to shallow water conditions.

Upon collection, samples will be submitted for polychlorinated biphenyls (PCBs), particulate organic carbon/dissolved organic carbon (POC/DOC), and total suspended solid (TSS) analysis; at a subset of locations, hardness, and total and dissolved metals will be added to the analyte list. Laboratory analyses will be performed in accordance with the procedures specified in Appendices 28, 29, and 31 through 36.

1.3 Health and Safety Warnings

Health and safety issues are addressed in the project Health and Safety Plan (HASP; Parsons 2008).

1.4 Contamination and Interferences

Potential sources of contamination and interferences during sampling at automated sampling stations include the presence of residual analytes and/or accumulation of solids within the sample collection system. The stilling well and automatic sampler tubing will be inspected each time the automatic sampler is serviced. If a significant layer of solids is observed in the stilling well, it will be cleaned by brushing the walls with a dedicated scrub brush, draining, and rinsing with river water. If the automatic sampler tubing shows indications of solids accumulation, discoloration, or wear, the tubing will be replaced.

Potential sources of contamination and interferences using the MADIS sampler include cross-contamination between sampling locations due to inadequate decontamination of sample collection vessels and nozzles. Decontamination procedures used during the BMP have adequately addressed these concerns, and will continue to be followed during the Remedial Action Monitoring Program (RAMP).

1.5 Personnel Qualifications

All field personnel are required to take a 40-hour OSHA Hazardous Waste Operations training course and annual refresher courses, and participate in a medical monitoring program prior to engaging in any field collection activities as required in 29 CFR 1910.120. Additionally, field personnel will be under the direct supervision of qualified professionals who are experienced in performing the tasks required for sample collection.

1.6 Equipment and Supplies

Equipment needed for collection of water samples at automated far-field monitoring stations includes:

- Operational automated sampling station (in-river piping, pumps, stilling well, ISCO automatic sampler[s], gravity feed automatic sampler), continuous water quality measurement instrumentation
- Sample containers
- Disposable gloves (talc free)
- Laboratory supplied organic free water
- Cooler with ice

- Resealable food storage bags
- Laptop computer and printer
- Field database

Equipment needed for water sample collection at non-automated far-field stations includes:

- Multiple aliquot depth-integrating sampler
- Boat and motor equipped w/anchors or spuds
- Safety equipment for boat as required to meet USCG regulations
- Portable electric winch w/two-directional line speed and distance control
- Global Positioning System (GPS; WAAS enabled)
- Sample containers
- Disposable gloves (talc free)
- Laboratory supplied organic free water;
- Laptop computer and printer
- Field database
- Multi parameter water quality meter
- Cooler with ice
- Hardhats
- Reflective safety vests
- Resealable food storage bags
- Trash bags

1.7 Water Sample Collection

1.7.1 Sampling Locations

The following far-field stations will be automated:

- Thompson Island
- Schuylerville at Lock 5
- Waterford

The remaining far-field stations will be sampled manually:

- Bakers Falls
- Rogers Island
- Stillwater

- Mohawk River
- Lower Hudson at Albany
- Lower Hudson at Poughkeepsie

1.7.2 Sampling Procedures at Automated Far-Field Stations:

1. Prior to sample collection, the Field Sampling Manager will determine the proper time intervals for sample composite timing at the far-field stations and communicate that information to the field crew. Sampling intervals will vary at each station. When flow conditions are less than approximately 8,000 cfs at Fort Edward, samples at all automated far-field stations will be 24-hour composites. If flow is above 8,000 cfs, or is predicted to increase to over 8,000 cfs, two 12-hour composites will be collected at the Thompson Island station, as directed by the Field Sampling Manager. If the Thompson Island station becomes inoperable, and flow at Fort Edward is above 5,000 cfs, or is predicted to increase to over 5,000 cfs, two 12-hour composites will be collected at the Schuylerville station. Additionally, if PCB concentrations at Thompson Island or Schuylerville are greater than or equal to 500 ng/L, samples will be submitted in triplicate the following day. To provide sufficient sample volume to meet these potential contingencies, the automated gravity feed sampling system will be programmed to collect two 12-hour composites and three 24-hour composites at Thompson Island and Schuylerville each day. The 12-hour composites or the triplicate 24-hour composites will be submitted to the laboratory on an as needed basis as determined by the Field Sampling Manager. Sample composite periods for all other parameters will be 24 hours with the exception of metals. If metals concentrations at a far-field station exceeds EPA criteria, the sample composite periods will be reduced to four 6-hour composites per day (as directed by the Field Sampling Manager). PCB composite periods at Waterford will always be 24 hours.
2. Upon arrival at a far-field station, confirm that the pumps are operating and are discharging at approximately the same flow rate, and that the water quality sonde is operating properly. If necessary, adjust the valves on the pump discharges to balance the flow rates to within approximately 5% of each other. Pumps should operate at a flow in the range of 4-5 gal/min.

3. Check the sampler display to identify when the next sample aliquot is scheduled for collection. Ensure that sufficient time exists (approximately 5 to 10 minutes) to remove collected samples from the sampler and replace with new containers prior to collection of the next sample aliquot. If necessary, wait until the next aliquot is collected prior to servicing the sampler.
4. For PCB samples (gravity feed automated system):
   - Confirm that the sampler has operated properly. The sampler should dispense approximately 40 ml into three 1-L glass containers once every hour for 24 hours and approximately 40 ml every 30 minutes into two 1-L glass containers (filled sequentially, one every 12 hours). At the end of the 24-hour compositing period, the first five containers will be filled and the sampler will begin filling the next set of containers automatically.
   - Put on new disposable gloves.
   - Remove the containers that have been filled over the last 24 hour compositing period (or 12 hours if directed by the Field Sampling Manager) from the refrigerator and cap.
   - Select which samples need to be submitted for laboratory analysis.
   - Enter the required information in the field database.
   - Use the field database to generate and print a label for the containers.
   - Dry the outside of the containers with a paper towel, and label appropriately.
   - Place the labeled containers in a cooler with ice for transport to the analytical laboratory.
   - Confirm that the sampling system is operating and the next 12-24 hour composite containers are being filled.
   - Replace the removed sample containers with new 1L glass containers (supplied by the laboratory).
5. For TSS and POC/DOC samples:
   - Remove the upper half of the ISCO sampler from the sampler base.

- Check to make sure that sample containers have been filled to the desired level, and that the next set of containers are being filled equally. If sample volumes are not correct, check the sampler program and sampler pump tubing. Replace the sampler pump tubing if signs of wear are observed.
- For TSS samples, remove the first 24-hour composite ISCO container from the sampler tray. Swirl this container to resupend any settled solids, and then pour the entire contents into a 1L plastic container for TSS analysis. Place filled containers in a cooler with ice.
- Repeat for POC/DOC, metals, and QA/QC samples (as required)

6. Rinse the ISCO containers with distilled water and return to sampler tray for reuse.
7. Enter the required information in the field database.
8. Use the field database to generate and print a label and field log for the containers.
9. Dry the outside of the containers with a paper towel, and label appropriately.
10. Place the labeled container in a cooler with ice for transport to the field or analytical laboratory.
11. Upon completion of sample retrieval, return to the Work Support Marina and filter metals samples in accordance with the procedures specified in Appendix 21.
12. Using field application, generate an XML file for upload to the environmental Data Management System (eDMS).
13. Upload field sample information (in XML format) to the eDMS.
14. Use the field database to generate field logs and chain of custody forms, and coordinate with shore-based staff to submit samples to the appropriate laboratory.

1.7.3 Sampling Procedures at Non-Automated Far-Field Stations

(Bakers Falls)

1. Locate the desired sampling station (approximate center channel).
2. Obtain measurements for temperature, dissolved oxygen (DO), pH, conductivity and turbidity using a YSI 6920 (or equivalent) probe as described in the SOP for probe measurements included as Appendix 22 of this QAPP.
3. Maneuver a portable electric winch into position above the sampling location.

4. Put on a new pair of disposable gloves.
5. Place a set of 12, pre-cleaned sample collection vessels in the MADIS sampler. The sample collection vessels will consist of a 500-ml glass container equipped with a Teflon lined cap. The cap will contain a ¼-in. ID Teflon inlet nozzle for water and a 1/32-in. ID Teflon/stainless steel outlet nozzle for air to escape as the vessel fills. A clean set of sample collection vessels will be used at each station. The glass collection vessels will be cleaned by the laboratory between sampling events. The caps and nozzles will be dedicated to each site. After each use the caps and nozzles will be rinsed with DI water in the field and placed in a plastic container labeled with the station name.
6. Tighten the caps on the sample collection vessels.
7. Determine the amount of sample that will be required from each station to fill all sample containers, including any duplicate or split samples. The volume of sample will be adjusted so that, to the extent possible, all of the sample collected will be put into containers (collection of excess sample will be avoided).
8. Prior to actual sample collection, the sampler must be calibrated to water depth and river flow conditions in a manner that will produce the desired sample volume following Steps 9 through 11, below.
9. Lower the sampler using an electric winch equipped with line speed and distance control through the water column to within two feet of the river bottom.
10. Once the sampler is deployed to within two feet of the river bottom, retrieve the sampler using the same approximate line speed used to deploy the sampler. Repeat as necessary to achieve target sample volume.
11. When the sampler is retrieved, remove the sample collection vessels and inspect to confirm that the vessel is filled to the desired level. If the target sample volume is not collected, the winch line speed will either be increased (to reduce sample volume) or decreased (to increase sample volume). Discard the sample and adjust sampling procedures accordingly. Repeat as necessary to obtain an appropriate sample volume.

12. Once the sampler is calibrated so that an acceptable sample volume is collected, the sample containers will be filled. Each time the sampler is retrieved, the contents of the sample collection vessels will be poured into the sample containers, including duplicate or split samples. Depending on the analytical program being followed for a sampling event, the contents of one or more of the sample collection vessels may not be needed. When this occurs, the unused sample will be poured out prior to deploying the sampler again.
13. Place one of the sample collection vessels used at each station in a re-sealable plastic bag, and label with date, time, and station. At Bakers Falls, multiple sample collection vessels will be used to form the large-volume (8-L) composite for PCB analysis required for this site. At this location, eight of the sample collection vessels used to obtain aliquots for the 8-L composite will be placed in a resealable plastic bag and labeled. These containers will be submitted to the laboratory for a hexane rinse, which will be combined with the composite sample submitted for PCB analysis.
14. The remaining sample collection vessels will be placed in a storage rack and delivered to the laboratory for cleaning. Enough sample collection vessels will be available to allow sampling at all stations during a single sampling event. Two full sets of vessels will be maintained to allow the laboratory sufficient time to clean the vessels. Decontamination using organic solvents (acetone, hexane) will only be performed under controlled conditions in the laboratory due to waste management issues in the field and concerns related to residual solvent biasing organic carbon analyses.
15. Rinse the sample collection vessel caps and nozzles thoroughly with DI water in the field and place in a plastic container labeled with the station name.

(Rogers Island, Stillwater, Albany and Poughkeepsie)

1. 1. Navigate the sampling boat to the coordinates of the sampling station or sub-station using GPS (WAAS enabled) and anchor the boat in a manner that will hold the boat within approximately 10 ft. of the target coordinates. Field conditions may be such that anchoring is not practical (rocky bottom, high flow velocity, etc.). At these locations, the boat engine will be used to hold the boat in position as close as possible to the sampling location.

2. If anchors are used, allow a minimum of 5 minutes to elapse before starting sampling to allow any suspended sediment to settle or pass downstream.
3. Collect field data as specified for Bakers Falls (Step 2), above.
4. Set up a winch with line speed control on the sampling boat.
5. Calibrate the sampler and collect samples in the same manner specified in Steps 4 through 15, above. At Rogers Island, there is not sufficient water depth to deploy the depth integrating sampler; therefore, a grab sample will be collected.
6. Using field application, generate an XML file for upload to the eDMS.
7. Upload field sample information (in XML format) to the eDMS.
8. Use the field database to generate field logs and chain of custody forms, and coordinate with shore-based staff to submit samples to the appropriate laboratory.

1.8 Sample Handling and Preservation

Sample containers will be labeled in accordance with labeling requirements specified in Section 10.1 of this QAPP. Samples will be collected and placed in containers in accordance with the procedures described above. Each container will be placed in a re-sealable food storage bag and placed in a cooler. The samples will be chilled with ice to approximately 4°C. A temperature blank will be placed in each cooler for use by the laboratory to measure the temperature of samples upon submittal. Samples will be transported to the laboratory as soon as practical. Chain of custody procedures will be followed, as specified in Section 10.1 of this QAPP.

1.9 Data and Records Management

All data from water sample collection will be recorded in the field database provided by GE using a laptop computer. Upon completion of sampling at one location, all data from the location will be entered into the database. Blank field log sheets can also be used to record information manually in case difficulties with data entry using the computer are encountered. Manually recorded data will be transcribed into the field database at the end of each day.

1.10 Quality Control and Quality Assurance (QA/QC)

QA/QC procedures are defined in Section 10.2 of this QAPP, and include the collection of field QA/QC samples. Field QA/QC samples to be collected are blind duplicate samples, equipment blank samples, and matrix spike samples. One set of field QA/QC samples will be collected at the rates defined in Section 10.2.1. Blind duplicate samples and matrix spike samples will be prepared by filling additional appropriately marked containers at pre-selected sampling stations (both samples will not be collected at the same station). The station where these samples are collected will be rotated randomly for each set of QA/QC samples collected. After collection, QA/QC samples will be handled in a manner that is consistent with all other environmental samples. Equipment blank samples will be prepared as follows:

1.10.1 Automated Far-Field Stations

Equipment blanks will not be collected with the exception of filter blanks for dissolved metals which will be collected once per 24-hour period of sample collection. Additional equipment blank samples will not be required due to the configuration of the sample collection system. The use of the ISCO sampler will minimize any potential for contamination from the system as the sample collection tubing is made of non-metallic materials and the tube will be rinsed with river water before and after collection of each sample aliquot.

1.10.2 Non-Automated Far-Field Stations

1. Put on new disposable gloves.
2. Place a set of clean sample collection vessels in the depth integrating sampler.
3. Slowly pour laboratory supplied organic free water into the collection vessels and fill enough of the sample collection vessels to provide sufficient sample volume to fill the sample containers.
4. When nearly full, remove the sample collection vessels and distribute to appropriately labeled sample containers.
5. After collection, handle equipment blank samples in a manner that is consistent with all other environmental samples.

6. After preparation of equipment blank samples, the sample collection vessels may be reused to collect river water samples without cleaning.

1.11 References

QEA and ESI. 2004. *Quality Assurance Project Plan for the Hudson River PCBs Site. Baseline Monitoring Program*. May 28, 2004.

Parsons. 2008. *Phase 1 Remedial Action Health and Safety Plan, Hudson River PCBs Superfund Site.* Prepared for General Electric Company, Albany, NY. August 2008.

APPENDIX 4
SOP FOR ANNUAL FISH SAMPLING

APPENDIX 4
STANDARD OPERATING PROCEDURES FOR FISH SAMPLE COLLECTION AND PROCESSING

1.1 Scope and Application

The purpose of this document is to provide a procedure for sampling largemouth or smallmouth bass (*Micropterus salmoides* and *M. dolomiueu*), striped bass (*Morone saxatilis*), brown or yellow bullhead (*Ameiurus nebulosus*, *A. natlis*), channel or white catfish (*Ictalurus punctatus*, *A. catus*), yellow or white perch (*Perca flavescens* and *Morone americana*) pumpkinseed (*Lepomis gibbosus*), and spottail shiner (*Notropis hudsonius*), or other substitute resident species from the Upper and Lower Hudson River. This SOP will detail the sample collection, preparation for contaminant analysis, and age estimation.

1.2 Summary of Method

Black bass (largemouth or smallmouth), bullhead (yellow or brown), yellow perch, yearling pumpkinseed, and spottail shiner or other forage fish will be sampled from four locations in the Upper Hudson River; Above the Feeder Dam, Thompson Island Pool, Ft. Miller/Northumberland Pools, and the Stillwater Pool. Black bass (largemouth or smallmouth), ictalurids (bullhead [brown and/or yellow] and catfish [white and/or channel]), perch (yellow or white), striped bass, yearling pumpkinseed, and spottail shiner or other forage fish will be sampled from Albany/Troy in the Lower Hudson River. Black bass (largemouth or smallmouth), ictalurids (bullhead [brown and/or yellow] and catfish [white and/or channel]), and striped bass will be sampled from Catskill in the Lower Hudson River. Striped bass will be sampled from the Tappan Zee area in the Lower Hudson River. The collection methods may include electrofishing, netting, and angling. Sampling at Catskill and Tappan Zee will be conducted biennially, starting the spring following Phase 1 dredging; sampling at the Upper Hudson River and Albany/Troy will be conducted annually. Conditions such as water depth and target species will determine the appropriate sampling method.

Definitions:

- Beach seine – net used in shallow water to capture fish.
- Caudal fin – "tail" of the fish.
- Cranium – skull of the fish.
- Dorsal fin – located at the top (dorsal side) of the fish.
- Gill net – Passive sampling device designed to capture fish as they swim through the water column.
- Netting – Method for capturing fish that includes the use of a gill net or seine.
- Otolith – small ear bone in fish used for age estimation.
- Pectoral fin – first fin from the head that correspond to the arms of a land animal.

1.3 Health and Safety Warnings

Health and safety issues are addressed in the project Health and Safety Plan (HASP; Parsons 2006).

1.4 Contamination and Interferences

Potential interferences include inclement weather or equipment failure. In these instances sampling will be rescheduled so as to not compromise the integrity of the fish samples.

1.5 Personnel Qualifications

All sampling personnel are required to complete the 40-Hour HAZWOPER 29 CFR 1910.120(e) and the 8-hour refresher courses before commencing sample collection or equipment decontamination.

1.6 Equipment and Supplies

Equipment needed for fish sample collection includes:

- Beach seine
- Buoys
- Anchors
- Line
- Collection buckets
- Gill net

- Global positioning system (GPS)
- Sampling boat
- Aluminum electrofishing boat with fenders
- DC Generator
- Variable voltage pulsator
- Dip nets
- Electrodes
- Conductivity meter
- Volt meter
- Rubber gloves and boots
- Personal flotation devices (PFDs)
- Thermometer
- Secchi disk/turbidimeter
- Measuring board
- Scale
- Watch
- Scale envelope
- Otolith vial
- Fish collection record
- Chain of Custody form
- Analysis request form
- Cooler(s)
- Ice
- Aluminum Foil
- Resealable bags
- First aid kit
- Polarized sunglasses (for daytime sampling)
- Coast Guard safety equipment (e.g., flares, distress flag)
- Fire extinguisher

2 FISH SAMPLE COLLECTION

Collect fish with standard methods of electrofishing, netting, or angling. Fish retained for analysis must be within the size ranges specified in the QAPP.

2.1 Electrofishing

Electrofishing uses electrical currents to immobilize fish for capture. Electrofishing is the preferred method for fish collection. Electrofishing will not occur where populations of endangered species are present unless approved by NYSDEC. All electrofishing personnel will be sufficiently trained and attend daily Health and Safety meetings reviewing procedures prior to starting work. The following outlines the procedures for electrofishing:

1. Personnel performing the electrofishing should wear appropriate health and safety gear (rubber soled boots, rubber gloves, PFD).
2. Starting upstream and working downstream (depending on flow conditions), position the electrofishing boat in the water.
3. Optional use of a "fish finder" may increase efficiency and aid in targeting locations for sampling.
4. Measure the water conductivity and temperature to determine the appropriate operating voltage and amperage.
5. Adjust the output voltage and amperage dials until the desired output setting is obtained without harming fish. Use pulsed output to reduce stress on fish.
6. Maintain the output for a predetermined amount of time or until desired area is sampled.
7. Collect the fish with dip nets and place in bucket of water or live well for processing; unselected fish will be released.
8. Release all unselected fish following processing.
9. Process fish retained for analysis according to the procedures described below.

2.2 Netting

2.2.1 Seining

For near shore shallow study areas, a beach seine may be used for the resident forage fish. The beach seine is typically used in shallow water where the net wall can extend from the surface of the water to the bottom. It is useful in the capture of near-shore species or for species that use the near-shore area seasonally or daily. In addition, the substrate needs to be relatively smooth so that the lead line of the seine drags along the bottom of the river preventing fish escapement. The fish are herded into the net as it is swept through the

water. Seining will be conducted by a minimum of two people. The following outlines the procedures for seine netting:

1. Two people start together at the downstream edge of the sample location (wading or in boats).
2. One person begins extending the seine perpendicular to the shoreline until the net is straightened out or the water becomes too deep.
3. Both people begin walking parallel to the shoreline for a set distance before the deep end person begins to swing the end of the net back towards the shoreline.
4. Both ends of the net are brought together and the net hauled onto the shoreline with the captured fish.
5. Fish are removed from the net and placed into buckets for identification.

2.2.2 Gill netting

For the collection of resident sport fish, gill nets should be used when there is 100 ft. of continuous depths of greater than 3 ft. Fish are captured when they swim into the gill net and become entangled in the mesh of the net. A gill net consists of a net vertically suspended between a float line on top and a weighted lead line at the bottom. The mesh size of the net can consist of different sized panels or one single size for the entire length of net. To keep the net in a vertical orientation, anchors are attached to either end of the lead line and buoys are attached to either end of the float line. The lengths of the anchor and buoy lines are adjusted so that the net is suspended at the target water depth. The following describe the procedure for sampling with gill nets:

Setting the gill net:

1. Stack the gill net in a large storage bucket by placing the end with the larger mesh size in the tub first (if the net has variable mesh sizes), and coiling the rest of the net into the tub. This procedure facilitates setting the net.
2. Beginning close to shore, or in water approximately 2-m deep, remove the outer end of the net from the storage bucket; attach an anchor and buoy to the lead line and float line, respectively; and drop the anchor (attached to the lead line) and buoy (attached to the float line) over the bow of the boat. Adjust the buoy line so that the buoy is floating and the line is relatively taut.

3. Begin slowly backing the boat away from the shore.
4. Carefully, play out the remainder of the net as the boat is moving backwards, shaking out any tangles.
5. Once the inner end of the net is reached, stop the boat and pull on the net until it is taut.
6. Attach the anchor and buoy to the lead line and float line, respectively.
7. Drop the anchor (attached to the lead line) overboard.
8. Pull on the float line to make sure the net is taut.
9. Drop the buoy that is attached to the float line into the water. Adjust the buoy line so that the buoy is floating and the line is relatively taut.
10. Allow the gill net to soak for the prescribed sampling period (e.g., 4 to 8 hours; use the shortest time necessary to minimize mortality and stress on fish).

Retrieving the gill net:

1. Arrive at the end of the net in deeper water and retrieve the buoy and anchor.
2. Begin pulling the net on board the boat and stacking it in coils in the storage bucket.
3. Remove fish from the net as it is brought aboard the boat and place in holding bucket. In inclement weather (e.g., storm approaching, high winds), retrieve entire gill net into boat without removing fish and remove fish in a protected area.

2.2.3 Angling

Angling uses rod and reel to passively capture fish. This method is not highly efficient and will only be used if all other methods prove to be unsuccessful. It is not anticipated that this method will be necessary, but the procedures below will be followed if this method is used:

1. Personnel performing the angling should wear appropriate health and safety gear (PFD, waders).
2. Fish will be sampled by attaching an appropriate lure to the line to catch the fish.
3. Fish caught by hook and line will be identified and assessed for the need to retain for tissue analysis. All unnecessary fish will be immediately returned to the water.
4. Process fish retained for analysis according to the procedures described below.

3 DATA COLLECTION

Record the following data on the fish data entry form (Figure 3-2) immediately after collection:

- The name of person(s) collecting the samples
- GPS coordinates of the sampling location
- Collection date, time, and duration
- Weather conditions – temperature, wind, precipitation
- Tidal stage (for lower Hudson River stations)
- Observations on river conditions (e.g., temperature, turbidity)
- Species identification (genus and species)
- Sample total length (nearest mm) and weight (nearest g for black bass, ictalurids, perch, yearling pumpkinseed, and forage fish; nearest 10 g for striped bass)
- Sample tag number
- Otolith ID number

Scales or spines and otoliths will be collected from each fish should the analysis of fish age be conducted. For bass, perch, and pumpkinseed remove at least 10 scales from appropriate area of body (Figure 1) and place in a scale envelope for storage. For bullhead, remove one of the pectoral spines and place in a scale envelope for storage. For otoliths, remove at least one otolith from the head, being sure not to compromise the fillet sample, and place in a labeled vial. Record the date, time, fish ID number, fish total length, weight, and location sampled on the envelope or the otolith ID on the vial. For fish for which whole body analysis will be conducted (i.e. fall yearling pumpkinseeds), only scales will be collected. Upon agreement between EPA and GE, the aging structure collected for all fish may be modified.

Place the individual fish (bass, perch, bullhead, and pumpkinseed) or the group of fish (forage fish; single species per composite; group by size to extent possible) on a clean piece of aluminum foil. Wrap the foil and attach an identification label that includes the fish tag number, date, and location sampled. Place the wrapped fish in a resealable plastic bag (have various sizes available) and place on wet ice in a cooler.

3.1 Sample Handling and Preservation

Sample containers will be labeled in accordance with labeling requirements specified in Section 10.1 of this QAPP. Samples will be collected and placed in containers in accordance with the procedures described in Section 1.1.7, above. Each container will be placed in a re-sealable food storage bag and placed in a cooler. The samples will be chilled with ice to approximately 4°C. A temperature blank will be placed in each cooler for use by the laboratory to measure the temperature of samples upon submittal. Samples will be transported to the laboratory as soon as practical. If samples are held longer than 24 hours from collection, they will be frozen prior to shipment. Chain of custody procedures will be followed for tissue samples and age estimation samples (scales or spines and otoliths), as specified in Section 10.1 of this QAPP.

Store fish at a temperature below 4°C and ship immediately to the analytical laboratory, along with the Fish Collection Records, Chain of Custody, and Analysis Request documents. Scales or spines and otoliths can be stored at ambient temperature until processing, along with the Chain of Custody.

3.2 Data and Records Management

Data from fish sample collection will be recorded in the field database provided by GE using a laptop computer. Upon completion of sampling at one location, data from the location will be entered into the database and the field log for that location printed and the hard copy stored in the field notebook. This will limit the risk of losing sample information due to computer failure. Blank field log sheets also can be used to record information manually in case difficulties with data entry using the computer are encountered. Manually recorded data will be transcribed into the field database at the end of each day.

4 FISH AGE ESTIMATION

Fish age can be estimated based on scales or spines and otoliths. Preparation varies based on the hard structure used as described below.

4.1 Scales and Spines

For scale samples, several scales will be removed from the envelope and placed between two microscope slides or pressed into acetate. When not in use, the acetate slides will be stored in the scale envelope. If necessary, larger scales will be briefly soaked in a 5% acetic acid solution to facilitate softening and clearing of the scale.

Pectoral spines will be sectioned just above the basal recess using either a Dremel cutting wheel or jewellers saw and generally should be less than 0.5-mm thick to see the annuli. Spine sections will be soaked in a 5% acetic acid solution for at least 24 h and placed between two microscope slides.

Scales will be magnified and viewed with a microfiche projector. Spine sections will be observed under either a compound or dissecting microscope. For scale samples, it will be assumed that annulus formation was either complete or was forming in June based on observations made by Maraldo & MacCrimmon (1979) for largemouth bass in Canada. Thus, the outer margin will be considered to be the final annulus (no "+" designation will be given). Scales and spines will be aged independently by two readers; if agreement of age assignment does not occur, then the two readers will re-examine the structure together and reach concurrence. If an age cannot be agreed upon, a third interpreter will assist in making the final age interpretation. The estimated age will be recorded in the fish database.

Otoliths for black bass, yellow perch, and pumpkinseed sunfish will be processed and aged following the procedures of Hoyer et al. (1985), Maceina & Betsill (1987) and Maceina (1988). For black bass, yellow perch, and pumpkinseed sunfish whole otoliths will be soaked in a 1:1 solution of ethanol and glycerine for about 4 weeks. Otoliths will be examined independently by two readers in whole view for fish displaying up to six or seven annuli. In older fish, or where annuli are not clearly visible, otoliths will be sectioned and annuli will be counted by two readers. Bullhead otoliths will be sectioned, processed, and viewed independently by two readers following the procedures of Buckmeier et al. (2002). If disagreement in enumeration of age occurs, two readers will re-examine the structure together and reach concurrence, without the assistance of a third reader. The outer edge will be considered an annulus as annulus formation would be completed shortly if fish were not collected.

5 REFERENCES

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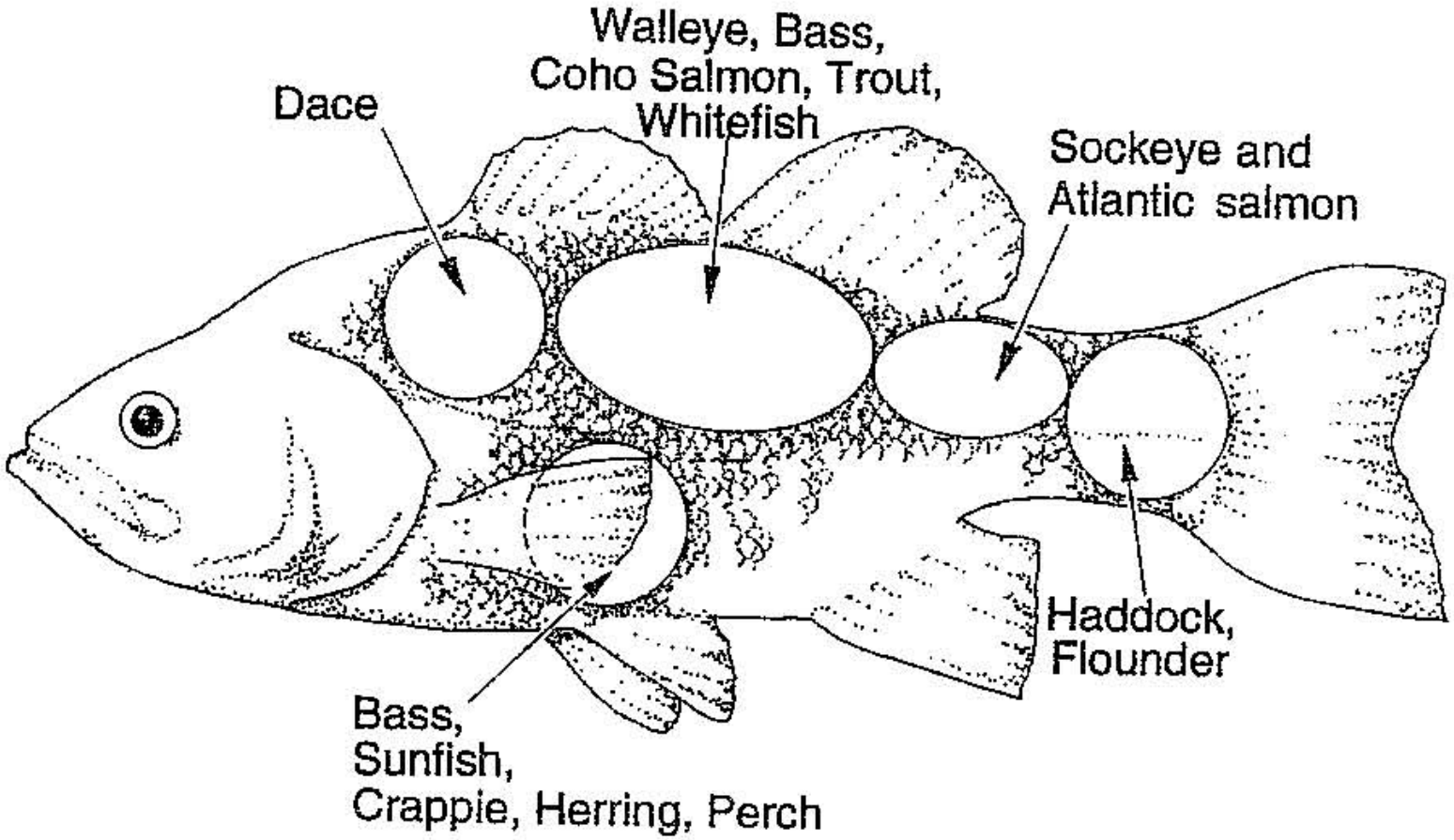

Figure 1. General body areas from which scales may be removed from fish of different taxa (from Murphy and Willis 1996).

APPENDIX 5
SOP FOR SEDIMENT RESIDUALS SAMPLE COLLECTION

APPENDIX 5
STANDARD OPERATING PROCEDURES FOR SEDIMENT RESIDUALS SAMPLE COLLECTION AND PROCESSING

1.1 Scope and Application

This Standard Operating Procedure (SOP) is applicable to the collection and processing of sediment samples for PCB analysis for the Hudson River Remedial Action Monitoring Program (RAMP).

This SOP describes the collection of sediment samples to assess Tri+ polychlorinated biphenyl (PCB) levels in:

- Residuals immediately following dredging (post-dredging residuals sampling)
- Residuals immediately following re-dredging (post-re-dredging residuals sampling)
- Backfill (backfill sampling); and to assess
- Tri+ PCB inventory in sediment remaining after dredging (post-dredging inventory)

Residuals sampling will be performed in each certification unit (CU), as described in Sections 4.4 and 4.5 of this QAPP, following the completion of dredging activities. The Tri+ PCB concentrations of the residual samples will be evaluated against the Residual Performance Standard action levels. For shoreline areas in which the dredging cut lines are shallower than the depth of contamination (DoC) because of slope stability requirements, Total PCB concentrations will be evaluated against the additional action level presented in the CDE.

1.2 Summary of Method

Sampling in a CU will be completed within 7 days of completion of each dredging attempt in that CU. Sample collection and processing procedures will generally follow the Sediment Sampling and Analysis Program (SSAP) protocols, with modifications to incorporate requirements of the RAMP. These sampling procedures will apply both to residual sediment and backfill sampling (after it has been placed). Sampling locations will be determined using Graphical Information Systems (GIS) software; coordinates for target sampling locations will be provided to field personnel in a field database. The sampling vessels will navigate to the

target sampling locations using a real-time kinematic differential global positioning system (RTK DGPS) capable of sub-meter accuracy. The shore-based control points established to perform the Sediment Sampling and Analysis Program (SSAP; QEA 2002) will be utilized to operate and perform quality control checks on this system. Samples will be collected using either vibracoring, or manual coring techniques. Cores in CUs will be advanced to a depth of 4 ft. The cores will be processed and samples obtained from the 0 to 6 in. interval for analysis. For cores collected from CUs, the remainder of the core will be archived according to similar procedures used during the SSAP. It may be necessary to resample some nodes for deeper samples, if the DoC has not been identified and the DoC cannot be estimated through extrapolation.

1.3 *Health and Safety Warnings*

Health and safety issues are addressed in the project Health and Safety Plan (RA HASP; Parsons 2008).

1.4 Interferences

- Cross contamination
- Inclement weather conditions

1.5 Personnel Qualifications

All field personnel are required to take a 40-hour OSHA Hazardous Waste Operations training course and annual refresher courses, and participate in a medical monitoring program prior to engaging in any field collection activities as required in 29 CFR 1910.120. Additionally, field personnel will be under the direct supervision of qualified professionals who are experienced in performing the tasks required for sample collection.

1.6 Equipment and Supplies

Equipment needed for collection of sediment samples includes:

- Sampling vessel equipped with spuds
- RTK DGPS capable of sub-meter accuracy
- Calibrated steel rod for probing
- 3 inches (o.d.) transparent polycarbonate tubes

- Vibracoring device
- Tubing cutters
- Hand coring apparatus
- Measuring stick w/foot
- Core caps
- Duct tape
- Core tube rack
- Ice
- Tarp/insulating blankets
- Ponar dredge
- Aluminum pans with lids
- Coolers, packing material and ice
- Laboratory grade detergent
- Acetone
- Hexane
- Distilled water
- Media for preparing equipment blanks
- Health and safety equipment (safety glasses, steel-toed boots, PFDs, gloves, etc.)

Equipment needed for processing of sediment samples for PCB analysis includes:

- Core tube clamping system
- Measuring stick w/foot
- Electric drill and bits
- Tubing cutters
- Vibratory saw
- Core draining tank
- Computer, printer, labels
- Disposable aluminum pans
- Stainless steel spoons
- Stainless steel broad knife
- Core caps
- Duct tape
- Resealable plastic bags
- Coolers, packing material and ice
- Laboratory grade detergent

- Acetone
- Hexane
- Distilled water
- Health and safety equipment (safety glasses, boots, gloves, aprons, etc.)

1.7 Sample Collection and Processing

Sample Collection

1. All data from sediment core collection will be recorded in the Sediment Residuals Sampling field database (provided by GE) using a laptop computer on the sampling vessel. Upon completion of sampling at one location, all data from the core will be entered into the database and the field log for that location, printed, and the hard copy stored in the field notebook. This will limit the risk of losing core information due to computer failure. Blank field log sheets that can be used to record information manually also will be provided in case of loss of computer power.
2. Using the on-board GPS system, maneuver the sampling vessel to within 10 ft of the pre-programmed target coordinates for each sample location. The target coordinates will be in northing and easting format, using the North American Datum of 1983 (NAD 83). Secure the vessel in place using spuds and/or anchors.
3. Use a sharpened ½ in. diameter steel rod marked in 6 in. intervals (or equivalent) to probe the sediment surface 3 to 5 ft. away from the target location to determine the sediment thickness and type. Advance the probe into the river bed, noting the depth of penetration and type of resistance met by the probe. Move the probe laterally several feet (while maintaining the 3 ft. minimum distance from the target sampling location) and repeat the procedure. The sediment will be probed a minimum of three times at each location, with the deepest penetration recorded in the field database. Each probing attempt will be a minimum of one foot away from any previous attempts. Record the approximate average sediment thickness and estimated sediment type (e.g., rock, fine-grained, coarse-grained) in the field database. If probing results are inconsistent between the 3 attempts, record the inconsistency in the manual description of the field database. Record the estimated sediment type as the most representative one of the 3 attempts.

4. If the estimated sediment thickness at the probing area is greater than 6 inches record probing information in the field log and attempt to collect a core using either manual coring techniques or a Rossfelder P3 vibracorer. The decision on which type of coring technique to follow will be made depending on the type of substrate that is encountered. If manual coring techniques are not successful in penetrating 4 ft. or more, core collection will be attempted using the vibracorer.
5. If the estimated sediment thickness at the probing area is less than 6 in. or if bedrock is present, additional probing of the sediment surface will be conducted within 20 ft of the target location for deeper sediments. If deeper sediments are found, relocate the boat to the new coordinates and attempt to collect a core. If sediment depth appears to be systematically less than 6 in., make a minimum of 3 attempts to collect a core. If a minimum recovery of 6 in. is not achieved, make up to 3 attempts to collect a sample with a ponar dredge.
6. Select a 3 in. (o.d.) core tube of appropriate length based on the probing information. (maximum length of 4 ft.). Use Lexan tubing for collecting manual cores, aluminum tubing for collecting vibracores.
7. Mount a clean coring tube onto the coring device.
8. Lower the coring apparatus (with the core tube attached) vertically through the water column, tube end first, until the river bottom is reached.
9. For vibracoring, activate the vibracorer at the sediment water interface. Continue to operate the vibracore (or apply force if using manual core collection technique) until the required penetration is achieved or refusal is met.
10. Measure and record the depth of core tube penetration into the sediment in the field database.
11. Pull the coring apparatus upward out of the river bottom (using a winch as needed), and raise it to the surface, while maintaining the core in a vertical position.
12. If it appears that the vibracorer head has come into contact with the surface sediments, discard the core and inspect the check valve and clean as necessary to remove any sediment. Reattempt the core in a manner that will prevent the vibracorer head from coming in contact with the sediment.
13. Before the bottom of the tube breaks the water surface, place a cap over the bottom to prevent the loss of material from the corer. Secure the cap in place with duct tape when brought onboard the vessel.

14. Estimate the recovered length of the sediment core and note it in the electronic field database. The length of the cores will be determined by inserting an aluminum measuring stick with a 2 in. by 2 in. aluminum foot attached to the lower end into the core tube. Measure the distance from the top of the core tube to the top of the sediment. Subtract this distance from the total length of the core tube to determine the length of the recovered core. The measuring tool will be decontaminated prior to reuse. A full day's supply will be provided to the coring crews each day. Place a line on the core tube using a permanent marker to indicate the length of field recovery and write the recovery in inches on the tube adjacent to this line.
15. Compare the length of the recovered core with the core penetration depth.
16. If the recovered length of the sediment core is more than 60% of the penetration depth, keep the core.
17. If recovery approaches 60% (e.g., approximately 50% or greater), temporarily retain the core. If an insufficient amount of material is recovered, discard the sediment contained in the core tube into a re-sealable 5-gallon pail and store for subsequent disposal at the field processing facility. Rinse the core tube with river water and prepare to make an additional attempt, or select another core tube for an additional attempt if the first core is retained. An additional attempt will be made at a minimum distance of 1ft. from previously attempted locations. A maximum of three attempts to collect a core will be made for a given location ID. Rinse the core tubes with river water between consecutive attempts.
18. If it appears that sediment was not retained in the core tube due to a leaking check valve in the vibracorer, the valve will be cleaned and collection of a core will be reattempted. Cores lost due to leaking check valves will not be counted as core collection attempts (i.e., three full attempts must be made with a properly operating check valve).
19. If all three attempts to collect a core are unsuccessful based on recovery alone (i.e., less than 60% recovery), retain the core with the highest recovery for analysis and put a flag in the database that indicates that the targeted recovery was not achieved.
20. If an acceptable core cannot be collected within 20 ft. of the node location, abandon the location and note conditions preventing core collection in the field database.
21. Discard the unusable cores by first decanting the water off the top back into the river and placing the sediment in a 5-gal. bucket for disposal.

22. After a successful core recovery enter additional information into the field database:
    - Date
    - Time of recovery
    - Actual coordinates of the sample location as determined by the RTK DGPS
    - Water depth (ft.)
    - Coring technique (vibracore or manual)
    - Core penetration depth (in.)
    - Observations, including probing results
23. Remove the core tube from the vibracorer or manual coring apparatus and place a second cap on the top of the core tube. Secure the cap in place with duct tape. Rinse the outside of the core tube with a small amount of river water to remove any residual sediment.
24. Draw an arrow on the core tube with permanent marker to mark the top of the core. Label the core with permanent marker indicating station ID, date, and time.
25. Store the core vertically in an insulated core tube storage rack (provided) on ice. Use the provided insulating blankets to keep the cores cool and out of direct sunlight until they are processed at the field processing facility.
26. At locations where grab samples will be collected, obtain a sediment sample by lowering a decontaminated ponar dredge until it comes in contact with the sediment and the release mechanism trips. Retrieve the ponar dredge and estimate the amount of sediment recovered. Enough sediment must be obtained to fill two 4 oz. containers (approximately ½ pint of sediment). If a sufficient amount of sediment is recovered, empty the contents into a new aluminum pan. Seal container with lid and duct tape. Label the container with permanent marker indicating station ID, date, and location. Place aluminum pan on ice in a cooler. If the amount of sediment recovered is insufficient, make up to two additional attempts with the ponar dredge and combine the sediment from each attempt in the aluminum pan. If sufficient sample cannot be collected after 3 attempts, abandon the location. Place the ponar dredge in a plastic bag for subsequent transport to the core processing facility for decontamination.
27. Decontaminate the ponar dredge (performed at the end of the day by GE contractors) according to the following decontamination procedure:

- Wash with laboratory grade detergent
- Rinse with distilled water
- Rinse with acetone and allow to air dry
- Rinse with hexane and allow to air dry
- Rinse with distilled water and air dry
- Contain rinsate for disposal at the field processing laboratory

28. At the end of each sampling day, field blanks will be prepared on each sampling vessel in accordance with the following procedure:
    - Put on a new pair of disposable gloves
    - Place an end cap on the lower end of an unused 36 in. core tube and secure with duct tape. Core tube should have been in the clean container of tubes for the entire day.
    - Pour approximately 6 in. of distilled water into the bottom of the tube.
    - Add play sand until there is insufficient water left in the tube to saturate the sand.
    - Add additional water and sand until there is a minimum of 30 in. of saturated sand in the tube. Standing water above the sand is acceptable.
    - Cap the top of the tube and secure with duct tape.
    - Label the tube with the proper field blank sample ID, date, and time.

29. At the end of each day, an electronic copy (disk or data stick) of the field log that includes the information recorded for each core sample collected that day will be provided to the processing laboratory coordinator. Additionally, a hard copy of the field log will be printed out. The hard copy will serve as a back-up to the electronic copy, as well as the chain of custody form from the field to the processing laboratory. This form will be signed by sample collection personnel and core processing personnel at the time that the core processing personnel take custody of the cores. A copy of the signed field log form will be maintained in the processing laboratory.

Sample Processing

1. Decontaminate all equipment prior to contact with core segments in a designated decontamination area. The decontamination steps are:
   - Remove visible sediment from equipment using paper towels. Dispose of the towels in appropriate containers labeled as PCB waste
   - Wash thoroughly using laboratory grade detergent and a scrub brush in the laboratory sink (wash water can go down the sink drain)
   - Rinse with distilled water
   - Rinse thoroughly with acetone under the hood in the laboratory, then allow to air dry
   - Rinse thoroughly with hexane under the hood in the laboratory, then allow to air dry
   - Rinse with distilled water

Acetone and hexane rinsate will be collected and placed in appropriate disposal containers.

2. Transport the cores from the field staging area to the field processing facility on a daily basis for core sectioning and sample preparation. The cores must be kept on ice and maintained in a vertical position during transport and handling.
3. Upon the delivery of the cores to the processing laboratory, a hard copy of the corresponding field data will be presented to the processing lab coordinator. The field data sheet will be signed by both the sample collection/delivery personnel and the processing lab coordinator, and will serve as the chain of custody form from the field to the processing facility. Transcribe either electronically (diskette or data stick) or manually the field data for each core into the field processing database.
4. The processing laboratory coordinator will dispense the cores to each sample processing custodian for processing.
5. Fasten the core tube in a clamping system and place a container below or next to the clamping system to collect water removed from the core and any spills that occur. Measure the total length of the core and record in the database.

6. Use the measuring device (4 ft aluminum measuring stick with aluminum foot attached to bottom) to measure to the top of the sediment inside the tubing. Subtract the distance from the top of sediment to the top of the core tube from the total core tube length to obtain core recovery and record in the database. If lab recovery differs from field recovery by more than 2 in. in the first 2 ft and 1 in. every 1 ft thereafter, discard the core and indicate as unusable in the database. It will be assumed for these cores that there was a void in the core that settled following collection and the sediment may be disturbed or displaced due to this. See step 17 of this SOP for details on voids encountered during core sectioning.
7. Drain the core by drilling a small hole about 1 in. above the estimated surface of the sediment and allow the water overlying the sediment core to drain, taking care not to disturb the surface of the sediment.
8. Cut the core tube off approximately 1 in. above the estimated surface of the sediment with a pipe cutter so the sediment/water interface can be seen
9. Mark the position of the top of the sediment on the outside of the core tube
10. Before sectioning, the mass of the sediment contained within the core will be determined. Place the upright core on the scale and weigh to the nearest gram. Measure and record the total length of the core tube. The mass of the core tubing can be determined from the volume and the density. Be sure to note the length of sediment, the length of water-filled tube above the sediment, and the length of air-filled tube above the water, if appropriate. The density of sediment in the core can be determined from the volume and the mass, after accounting for the mass of the tube itself.
11. Mark the core tube where the core will be cut into segments (6 in. intervals starting at the top of the core and working down). The sample processing custodian will print labels for each jar necessary for each segment of the core. If the total length of the core is greater than 6 in., segment the entire core and enter all required data in the database; however, archive samples greater than 6 in. for cores collected from CUs.

12. Each core segment will be analyzed for Aroclor PCBs in accordance with the method specified in Appendix 50. Approximately 4% of the samples will also be submitted for congener specific PCBs using the method specified in Appendix 46. These analyses will be assigned automatically in the database. Print container labels and place on appropriate containers. Container specifications are provided in the QAPP. Update the field processing database, and generate hard copies of chain of custody forms.
13. Prepare a set of clean, disposable aluminum pans (approximately 10 in. x 12 in. x 3 in.) for all sectioned core segments. Mark the pans with core segment location (i.e., 0-6"). When using a new shipment of aluminum pans get an average tare weight for 50 pans. Weigh each core segment on a calibrated scale. Create new entries in the field processing database by entering the top and bottom depth of each core segment.
14. Adjust the position of the core tube in the clamping system to provide adequate support and clearance for cutting the core into segments. For Lexan core tubes place a clean plastic cap on the top of the tube prior to each cut to minimize the loss of soft sediment during cutting.
15. Use a tubing cutter to cut the core tube at the bottom of the top core segment. Use a decontaminated tubing cutter to cut each segment (i.e., do not make two cuts with the same blade). Avoid disturbing the sediment. Use a clean stainless steel broad knife to separate the segment from the rest of the core after the core tube is cut, and place the segment into an aluminum pan (tare weight already established). Place the aluminum pan with the core segment on the balance and obtain a weight.
16. Extrude the sediment from the core tube, and dispose of the tube in appropriate containers labeled for PCB waste. When extruding sediments, attempt to keep the sediment intact to record stratigraphic changes within the section. For difficult to remove sediments, spoon out the sediment, trying to keep it intact to record stratigraphic changes.
17. Cores may occasionally contain voids; processing these cores will follow the protocol listed below. The protocol may be modified on a core-specific basis if field judgment indicates that alternative procedures are appropriate. Any such modifications will be made with the concurrence of USEPA oversight personnel.

- Cores containing voids with a length of 2 in. or less per the first 2 ft. and 1 in. per 1 ft. thereafter will be sectioned as though they were intact (e.g., push core together). The void length will be recorded in the database for future modification of the lab recovery value. If void appears to have disturbed the core (e.g., stratigraphic layers are mixed), the core will be discarded.
- If the void length is greater than the above values, the core will be discarded, unless the void is below 36 in. (see next bullet).
- For cores greater than 36 in. in length that contain voids below 36 in., segment the top 36 in. of sediment and discard the core below 36 in. If the void is much deeper in a longer core, use field judgment to determine whether or not to archive samples below 36 in. and above the void.

18. Give a physical description of each core segment to the sample custodian to record in the database. Characteristics include the general soil type based on the Unified Soil Classification System, approximate grain size, presence of observable biota, odor, and color. Classification of grain size will be a qualitative observation with the following types denoted: silt, fine sand, medium sand, coarse sand, clay, organic matter, and gravel. The approximate proportion of each soil type within each sample will be estimated (i.e., primary, some, little, trace).
19. Identify any changes in sediment character within each segment. If changes in stratigraphy are observed within a core segment, then the nature and approximate length of the various layers will be verbally relayed to the sample custodian for inclusion in the database. Evidence of changes in stratigraphy include an abrupt change in grain size (e.g., from silt to wood chip layer) or change in soil color which may indicate oxidized or reduced sediments. If objects of cultural significance are observed during the core processing, note them in the database and set them aside for inspection by a qualified geomorphologist or archaeologist.

20. The core sectioning scheme will be modified when glacial lake clay is encountered in a core. Split the appropriate section into two separate samples at the clay/sediment interface. Place into two separate aluminum pans and record the length of each section. Scrape off any coarse material from the clay segment to reduce cross contamination potential. Homogenize each as separate sample and reprint jar labels. Obtain a weight from each section with the appropriate length of tubing material to allow bulk density to be calculated. Collect the clay sample immediately below the section with the clay/sediment interface for submittal for PCB and moisture content analysis. Subsample this section by splitting the entire section longitudinally into quarters. Note any varves that are observed and homogenize one quarter for laboratory analysis. The remaining clay in the core tube can be properly disposed.
21. Homogenize the sediment in the aluminum pans using a stainless steel spoon. A 6 in. core segment will result in approximately 0.7 liters of sediment. Use the spoon to bring the sediment near the bottom of the bowl up to the top using a circular motion, similar to preparing food that requires mixing (e.g., cake batter). Repeat this procedure until all of the sediment near the bottom of the bowl has been brought to the surface at least twice. Continue mixing the contents of the bowl until an even texture and color is observed throughout the entire sample. Using the stainless steel spoon, manually break up large wood pieces that are too large to fit into the sample jar and are not required to be retained for cultural resources. Homogenize these smaller fragments with the rest of the sample to allow a representative portion to be placed in the sample jar. Be sure to thoroughly homogenize each segment.
22. Fill the appropriately labeled containers with sample and package them in a cooler for shipment to the laboratories. The samples will be shipped out in batches of 20 environmental samples accompanied by appropriate QA/QC samples. Chill samples to 4°C with ice packed in Ziploc® bags or equivalent.
23. Process the next core segment as described in steps 17-21 until the whole core is sectioned and all sample jars are filled.
24. Field blank processing will be conducted by sectioning the field blank in 6 in segments for each field blank needed. Using a vibratory saw or pipe cutters, depending on the core tube material, cut the 4 in section and place in the aluminum pan. Thoroughly homogenize the sample and place into an appropriately labeled 4 oz jar. Collect additional field blanks from the core in the same manner.

25. Prior to shipping the samples, confirm which project laboratory has capacity to receive samples the next day, and ship samples (with corresponding COC forms) accordingly *via* overnight delivery service or courier. All samples will be delivered to the analytical laboratories within 24 hours of processing, except for the samples for geotechnical characterization, which will be delivered to the laboratory on a less frequent basis.
26. Place all used spoons, vibratory saw blades, pipe cutters, and the measuring tool at the decontamination station for proper decontamination prior to reuse.

1.8 Sample Handling and Preservation

Store the core vertically in an insulated core tube storage rack (provided) on ice. Use insulating blankets to keep the cores cool and out of direct sunlight until they are processed at the field processing facility. Grab samples will be placed into a new aluminum pan. The pan is sealed with a lid and duct tape, labeled with permanent marker indicating station ID, date, and location and placed on ice in a cooler. Cores and grab samples will be delivered to the processing facility daily.

1.9 Data Records and Management

All data from sediment core collection will be recorded in the field database provided by GE using a laptop computer on the sampling vessel. Upon completion of sampling at one location, all data from the core will be entered into the database and the field log for that location, printed, and the hard copy stored in the field notebook. This will limit the risk of losing core information due to computer failure. Blank field log sheets that can be used to record information manually also will be provided in case of difficulties with data entry into the computer on the boat are encountered. Manually recorded data will be transcribed into the field database at the end of each day.

At the end of each day, an electronic copy (disk) of the field log that includes the information recorded for each core sample collected that day will be provided to the processing laboratory coordinator. Additionally, a hard copy of the field log will be printed out. The hard copy will serve as a back-up to the electronic copy, as well as the chain of custody form from the field to the processing laboratory. This form will be signed by sample

collection personnel and core processing personnel at the time that the core processing personnel take custody of the cores. A copy of the signed field log form will be maintained in the processing laboratory.

All data generated during sediment core processing will be recorded in the field database provided by GE using a computer in the processing laboratory. This database will also be used to generate container labels and chain of custody forms. The field database will be transmitted electronically to the DMS at the end of each day.

1.10 Quality Control and Quality Assurance

QA/QC procedures are defined in Section 10.2 of this QAPP, and include the collection of field QA/QC samples. Field QA/QC samples include equipment blanks and field duplicate samples. Equipment blanks will be prepared by processing a sample of laboratory grade sand in the same manner that environmental samples are processed, including placement in new core sample tubing, removal, mixing, and placing in containers.

Sediment field duplicates will be prepared in the field laboratory at the rate of 5% of the total number of environmental samples and will consist of two aliquots from the same segment of a sediment core (after homogenization).

1.11 References

Engineering Performance Standards (EPS) Volume 3, Section 4.1

Quantitative Environmental Analysis, LLC. 2002. *Design Support Sediment Sampling and Analysis Program, Field Sampling Plan*. Prepared for the General Electric Company.

Quantitative Environmental Analysis, LLC. 2005. *Hudson River PCBs Site Phase 1 Dredge Area Delineation Report*. Prepared for the General Electric Company.

Parsons. 2008. *Phase 1 Remedial Action Health and Safety Plan, Hudson River PCBs Superfund Site*. Prepared for General Electric Company, Albany, NY. August 2008.

APPENDIX 6
SOP FOR REMOTE NOISE MEASUREMENTS (INCLUDES DEPLOYMENT OF NOISE METERS AND LONG TERM COLLECTION OF DATA FOR COMPLIANCE AND POSSIBLY CONTINGENCY MONITORING AT THE PROCESSING FACILITY AND DURING DREDGING)

ARCADIS

Standard Operating Procedure: Remote Noise Measurements

I. Scope and Application

This Standard Operating Procedure (SOP) describes the procedures for remote sound monitoring during Phase 1 of the Hudson River remedial action. A sound level meter will used to perform sound monitoring (using a Larson Davis Model 820 or equivalent – see Attachment 1 for equipment description and specifications). Sound level meter calibration and maintenance are discussed in Appendix 56. Sound monitoring will be performed to document noise levels associated with of the following:

- Dredging and backfilling operations
- Processing facility operations
- Construction of the processing facility

II. Personnel Qualifications

Field sampling personnel will have current health and safety training, including 40-hour Occupational Safety and Health Administration (OSHA) Hazardous Waste Operations (HAZWOPER) training and an annual refresher course, site supervisor training, and site-specific training, as needed. In addition, personnel performing sound monitoring equipment installation and monitoring will be trained in the use of the sound level meter and other appropriate equipment (e.g., Global Positioning System [GPS] unit).

III. Equipment List

The following materials, as required, will be available while performing sound monitoring:

- Personal protective equipment (PPE), as required by the Health and Safety Plan (HASP)
- Sound level meter (Larson Davis Model 820 or equivalent), in environmental case, with appropriate batteries, cable, cellular modem, chain and lock, and all-weather microphone equipment
- Sound level meter manual

- GPS unit (Trimble XT or equivalent), as required
- Field notebook

IV. Cautions

Sound level meters and GPS units will be kept dry and within recommended operating temperatures. Failure to keep the sound level meter and GPS units dry and at optimal operating temperature may result in malfunction of the meter.

The following are other relevant cautions:

- Keep the environmental wind screen over the microphone sensor at all times when the meter is operational. Keep the microphone clean; dirt on the microphone may result in inaccurate measurements.
- Batteries must be checked before every installation; if battery levels are not sufficient, replacement batteries must be obtained and placed in the equipment.
- Always carry the GPS unit in its case and secure it. When riding unsecured in a vehicle, the GPS unit can be affected by shock and vibration.
- Keep the GPS plugs clean and dry. Blow away any dirt lodged in the plugs of the connecting cables.

V. Health and Safety Considerations

The HASP (Parsons, 2008) will be followed when performing sound monitoring.

VI. Procedures

The sound level meter will be installed according to the procedures contained in the operating manual. The procedure is summarized below:

1. Complete project and sample location information on the Noise Monitoring Form (Figure B-18) and field logbook.
2. Choose a meter location.

3. Connect the microphone to the sound level meter using the microphone cable.

4. Calibrate the meter and microphone system, using the SOP presented as Appendix 56.

5. Place the weather-resistant wind screen over the microphone, and mount the sound level meter on a tripod with the microphone aimed toward the sound source at an angle of about 10 degrees.

6. Install the modem by attaching it to the sound level meter, and taping the antenna to the pole containing the microphone.

7. Turn on the sound level meter.

8. Check that the measured sound levels and battery level are appropriate.

9. Check that the modem is working by using it to call the cell number of the field technician.

10. Turn on the sound level meter logging capability.

11. Close the environmental case, and chain and lock it to a secure ground point.

12. Obtain coordinates for monitoring location with the GPS unit.

13. Document the location of the sound level meter with digital photographs.

14. Return to field vehicle and clean and dry the sound level meter and GPS unit, as necessary.

The sound level meter will be removed according to the procedures contained in the operating manual and summarized below:

1. Unlock the environmental case, and stop the meter; do not turn it off.

2. Remove the environmental windscreen from meter.

3. Calibrate the system, using the SOP presented as Appendix 56.

4. Record the battery level and calibration level.

5. Turn off the sound level meter.

6. Disconnect the windscreen and the microphone cable.

7. Remove the microphone from the windscreen.

8. Remove the modem antenna, and unplug it from the sound level meter.

9. Unchain the environmental case.

10. Transport all equipment to field vehicle.

The GPS unit will be operated according to the procedures contained in the operating manual.

VII. Waste Management

Paper towels or other items used to maintain the sound level meter and GPS in clean and dry condition will be disposed of as municipal solid waste at the end of each monitoring event.

VIII. Data Recording and Management

The Noise Monitoring Form (Figure 7-4 in QAPP) will be used to record noise level data during this monitoring program. Additional field information, as necessary, will be recorded in the field notebook. Data will be telemetered to a storage computer every 24 hours. Exceedances will be telemetered immediately to onsite management personnel for appropriate action.

IX. Quality Assurance

The sound level meter will be maintained in accordance with this SOP and the operating manual. No additional quality assurance activities, such as collection of a duplicate measurement, are necessary.

The GPS unit will be maintained in accordance with this SOP and the operating manual. The GPS unit will have a daily check on a point with known coordinates.

X. References

Parsons, 2008. Phase 1 Remedial Action Health and Safety Plan, Hudson River PCBs Superfund Site. Prepared for General Electric Company, Albany, NY. August 2008.

Attachment 1

Larson Davis Models 812/820 Sound Level Meters

Source: http://www.larsondavis.com/820.html
Date: January 16, 2006

Models 812 / 820 Sound Level Meters

There exists a need to select an instrument that will do just what you need it to do. The 812 and 820 were designed with this in mind. For example, a consultant that works heavily in the industrial hygiene sector will greatly benefit from having the Model 812, a hand held data logging integrating sound level meter and a personal noise dosimeter. The Model 820 is the perfect environmental noise analyzer, maintaining all of the features of the 812 but with added memory, modem capability, daily and exceedance histories.

- *Sound Level Measurements*
- *Community Noise Assessment*
- *Environmental Noise Monitoring*
- *Statistical Analysis*
- *Transportation Noise/Passby Measurement*
- *Sonic boom/artillery fire measurements*
- *Production Line Testing*
- *Remote Outdoor Noise Monitoring (Model 820)*

The ½" condenser microphones used with our Models 812 and 820 allow for a wider dynamic range and greater level of accuracy. The Models 812 and 820 meet the IEC and ANSI requirements for Type 1, Precision Integrating Sound Level Meters.

Fundamental to each of these instruments is an integrating sound level meter. Each features true RMS and dual Peak detectors that operate simultaneously. Each has Slow, Fast, and Impulse detector rates. Each has A and C frequency weighting filters.

FEATURES

- *ANSI/IEC Type 1 integrating SLM*
- *110 dB dynamic range*
- *Long Term logging capabilities: Interval and Time histories (812 only); Interval, Time, Daily and Event histories (820 only)*
- *Statistics - user selectable Ln values: 4 in the 812, 6 in the 820*
- *Slow, Fast and Impulse Detectors*
- *True RMS with two separate Peak detectors*
- *A & C weighting*
- *½" condenser microphone - extension cables up to 20 feet available*
- *64K bytes of memory (812) / 256 K bytes of memory (820)*
- *AC/DC Output*
- *RS-232 Interface*
- *Remote communications via modem (820 only)*

Communications & AC/DC Outputs

Also common to this family of meters is a serial digital interface for communication with a computer or direct connection to a printer. Each meter also features AC and DC outputs for transferring data to DAT or chart recorder during data acquisition. The analog output can be weighted (A or C) or unweighted, independent of how the data is acquired and stored within the instrument.

Dynamic Range

Each of these instruments has a unique 110dB dynamic range without the need for range switching thus removing the problems of missed critical data.

Measurements

Measurements include instantaneous Sound Pressure Level, Lmin (rms), Lmax (rms), Lpeak and Unweighted Peak Levels, Ln (statistics), Leq, SEL, Time Weighted Average (TWA), and Taktmaximal 3 & 5. All of these parameters are measured simultaneously making this family very flexible in an extremely wide variety of applications.

Modem Capability (820)

The 820 can be connected to a modem for remote data acquisition from portable or permanent monitors. The modem control mode enables the 820 to automatically dial out upon a high level event or a low memory condition.

SPECIFICATIONS

Linearity range	> 107 dB
Max peak level	142 dB (based on normal sensitivity free field microphone)

RMS noise floor	17.5 dBA (based on high sensitivity random incidence microphone)
Time weighting	Slow, fast, and impulse
Frequency weighting	A and C
Microphone	½" air condenser
Microphone polarization	0, 28, & 200 volts DC
Memory	64KB
DC output	0 - 3 volts @ 600 ohms
AC output	
A - weight range	38.4 dBuV to 128.4 dBuV
C - weight range	36.3 dBuV to 126.3 dBuV
Linear range	36.1 dBuV to 126.1 dBuV
Output impedance	600 ohms
Gain	0 or 20 dB (user selectable)
Quartz clock/calendar	24 hour format (hh:mm:ss), 1 second resolution, 100 yr. calendar (mo/day/yr)
Power Supply	
Internal	9 Volt battery, 24 hr operation
External	7 to 16 Vdc, 30 ma current draw
Dimensions	13.2" L x 3.3" W x 1.1" D (with preamp connected)
Standards Met	

ANSI S1.4 - 1983
ANSI S1.25 - 1991
IEC 651
IEC 804
Directive 86/188/EEC
IEC/TC - 29

Accessories (included)

CCS009 Cordura nylon pouch

WS001 3 ½" windscreen

SWW_SLM_UTIL Windows software for instrument setup, data download, and data export 9V alkaline battery

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Operator's manual

Accessories (optional)

Acoustic calibrators
Outdoor environmental cases
Tripods
Software
Printer, computer and modem cable
Outdoor preamp (Model 820 only)

Go to LDE Environmental Noise Products Group

Go to LDL Research & Development Products Group

Go to LDI Industrial Hygiene Products Group

APPENDIX 7
SOP FOR MANUAL NOISE MEASUREMENTS (INCLUDES MANUAL NOISE MEASUREMENTS FOR BACKGROUND, PHASE 1 NOISE STUDY, AND POSSIBLY CONTINGENCY MONITORING AT THE PROCESSING FACILITY AND DURING DREDGING)

ARCADIS

Standard Operating Procedure: Manual Noise Measurements

I. Scope and Application

This Standard Operating Procedure (SOP) describes the procedures for sound monitoring during Phase 1 of the Hudson River remedial action. A sound level meter will used to perform sound monitoring (CEL Instruments Model 593 or equivalent – see Attachment 1 for equipment description and specifications). Sound level meter calibration and maintenance are discussed in Appendix 56. Sound monitoring will be performed to document noise levels of the following:

- Dredging and backfilling operations
- Processing facility operations
- Construction of the processing facility

II. Personnel Qualifications

Field sampling personnel will have current health and safety training, including 40-hour Occupational Safety and Health Administration (OSHA) Hazardous Waste Operations (HAZWOPER) training and an annual refresher course, site supervisor training, and site-specific training, as needed. In addition, personnel performing sound monitoring will be trained in the use of the sound level meter and other appropriate equipment (e.g., Global Positioning System [GPS] unit).

III. Equipment List

The following materials, as required, will be available while performing sound monitoring:

- Personal protective equipment (PPE), as required by the Health and Safety Plan (HASP; Parsons 2008)
- Sound level meter (CEL Instruments Model 593 or equivalent)
- Sound level meter manual
- GPS unit (Trimble XT or equivalent), as required

- Field notebook

IV. Cautions

Sound level meters and GPS unit will be kept dry and within recommended operating temperatures. Sound level meters and GPS unit may be exposed to inclement weather (such as rain or snow) or temperatures (such as temperatures below recommended operating temperatures) for short periods of time during measurements. Once a measurement is taken, the sound level meter and GPS unit will be returned to the field vehicle, where they will be dried off and kept within recommended operating temperatures. Failure to keep the sound level meter and GPS dry and at optimal operating temperature may result in malfunction of the meter.

The following are other relevant cautions:

- Keep the wind screen over the microphone sensor at all times when taking a reading. Keep the microphone clean. Dirt on the microphone may result in inaccurate measurements.

- Batteries must be checked before every installation; if battery levels are not sufficient, replacement batteries must be obtained and placed in the equipment.

- Always carry the GPS unit in its case and secure it. When riding unsecured in a vehicle, the GPS unit can be affected by shock and vibration.

- Keep the GPS plugs clean and dry. Blow away any dirt lodged in the plugs of the connecting cables.

V. Health and Safety Considerations

The HASP will be followed when performing sound monitoring.

VI. Procedures

The sound level meter will be operated according to the procedures contained in the operating manual and summarized below.

1. Complete project and sample location information on the Noise Monitoring Form (Figure 7-4) and field logbook.

2. Insert the microphone onto the sound level meter.

3. Turn on the sound level meter.

4. Place the wind screen over the microphone.

5. Select the range with the highest resolution (i.e., one with at least 20 decibels above and below the average sound level). For sample locations with lower sound levels, select a lower range.

6. Place the microphone approximately 5 feet off the ground on a tripod, aimed toward the source at an angle of about 10 degrees.

7. Turn the meter on for the specified time interval.

8. Record the result on the Noise Monitoring Form (Figure 7-4).

9. Take the wind screen off the microphone.

10. Turn off the sound level meter.

11. Obtain coordinates for monitoring location with the GPS unit.

12. Document the location of the sound level meter with digital photographs.

13. Return to field vehicle and clean and dry the sound level meter and GPS unit, as necessary.

The GPS will be operated according to the procedures contained in the operating manual.

VII. Waste Management

Paper towels or other items used to maintain the sound level meter and GPS unit in clean and dry condition will be disposed of as municipal solid waste at the end of each monitoring event.

VIII. Data Recording and Management

The Noise Monitoring Form (Figure 7-4) will be used to record noise level data during this monitoring program. Additional field information, as necessary, will be recorded in the field notebook. The sound level data will be downloaded daily via cable to a laptop computer in the field.

IX. Quality Assurance

The sound level meter will be maintained in accordance with this SOP and the operating manual. No additional quality assurance activities, such as collection of a duplicate measurement, are necessary.

The GPS unit will be maintained in accordance with this SOP and the operating manual. The GPS unit will have a daily check on a point with known coordinates.

X. References

Parsons, 2008. Phase 1 Remedial Action Health and Safety Plan, Hudson River PCBs Superfund Site. Prepared for General Electric Company, Albany, NY. August 2008.

Attachment 1

CEL-593 Sound Level Meter

Source:
http://www.afcintl.com/other/cel/celpdf/cel593_brochure.pdf
Date: January 16, 2006

CEL-593 Real time logging and event analyzer

Introduction

The CEL-593 models are the top of the range of CEL real time analyzers. These instruments are available with both full octave and third octave band filters that operate simultaneously across the whole audio spectrum. Manually controlled measurements allow the operator to use the analyzer for “Snapshot” recording. A versatile logging mode is included to store results at regular timed intervals. The CEL-593 also includes an event based data capture mode above a threshold.

Applications

Primary uses of this instrument include;

- Environmental noise surveys
- Workplace noise surveys
- Noise nuisance measurements
- Medium term monitoring
- Significant event recording

Operation

The CEL-593 Real time analyzer uses the concept of “Runs” and “Records” to make noise measurements. In this mode the instrument uses the built in calendar clock to control the capture of noise data. Up to 999 separate Runs can be stored in the instrument memory and each run can save up to 9999 regular period measurements. A run can then represent a measurement position with the records representing the regular period data sets. The run concept groups the individual period measurements together for easy analysis when recalled from memory or downloaded to a personal computer. Results can be viewed on screen in row and column format.

In addition to the regular collection of period data the CEL-593 range is also able to store even shorter profiles when used in the broadband mode. The profiles can be either the Leq or the maximum noise level saved at 1-second intervals. This operates as an effective digital level recorder and allows the operator to see the changing noise levels when exported to a PC.

A versatile event recognition system is available in all CEL-593 models that can be triggered from a level exceedance above a user-selected threshold or by the operator using the keypad. This can be made to switch on a tape recorder to record the audio signal when measurements are made in an un-attended situation. The event system can also be used to activate warning signs or other devices to daisy chain multiple instruments together. The Fastore option is included as standard with all CEL-593’s. This provides data capture rates up to 200 times per second.

All the CEL-593 models are provided with the CEL-502 RS232 serial interface and a copy of dB1 software. This allows the instrument to be controlled from the computer and to download run information at the end of a measurement for viewing, printing and export to standard spreadsheet programs.

CEL-593 Measurement parameters		
Acoustic standards	-	ANSI S1.4 Type 1 & 2, ANSI S1.43 Type 1 & 2, ANSI S1.11 IEC-651, IEC-804, IEC-225
Frequency weightings	-	A, C & Linear (unweighted 10 Hz to 25 kHz +0/–0.5dB) (choose 2 simultaneously from 3)
Time weightings	-	Slow, Fast, Impulse & Peak (choose 2 simultaneously from 3)
Amplitude weightings	-	Exchange rate Q = 3, 4, 5 & 6 (choose 2 simultaneously from 3)
Total measurement range (dB)	-	5 to 140 dB in 7 x 10 dB step intervals
Alternative measurement range (with 1/4in microphone)	-	30 to 165 dB (with CEL-302 ¼ in microphone)
Dynamic range (dB)	-	75 dB
Calculated results		
Broadband mode	-	SPL, Max, Min, Leq, Ileq, SEL, Lavg, TWA, LEP,d, Peak, 5 x LN%
Octave mode	-	2 selectable broadband results plus 11 simultaneous octave bands from 16 Hz to 16 kHz
Third octave mode	-	2 selectable broadband results plus 33 simultaneous octave bands from 12.5 Hz to 20 kHz
Storage method		
Manual mode	-	User control via tactile keypad, Start, Stop, Pause, variable measurement time
Regular timed interval mode	-	Preselectable fixed record times from 0.5, 1, 5, 10, 15, 30, 60 seconds 5, 10, 15, 20, 30 & 60 minutes
Storage capability	-	400,000 data results in broadband mode, or 22,800 third octave band spectra
Maximum number of Runs	-	999 Runs
Maximum number of Records	-	9999 Periods per Run
Maximum number of events	-	9999 Events per Run with separate 1 second time history profiles
Maximum number of time history profiles	-	1,000,000 regular 1 second values
Memory size	-	2 Mbytes
Measurement setups	-	1 factory default plus 6 user selectable configuration setups for each mode
Standard accessories included with instrument	-	CEL-250 1/2in Precision free field microphone capsule, CEL-500 Analog interface module, CEL-502 RS232 interface module, C6621 serial download cable to computer, CEL-510 Tripod shoe adapter, Operator Manuals, Getting Started Guide, 8 x AA batteries
Standard items included in kits	-	CEL-593.A/B/C1/K1 includes CEL-593.A/B/C1 RTA, CEL-284 Class 1 Acoustic calibrator, CEL-2962 Foam windscreen, CEL-6629 Attache kit case CEL-593.A/B/C2/K1 includes CEL-593.A/B/C2 RTA, CEL-282 Class 2 Acoustic calibrator, CEL-2962 Foam windscreen, CEL-6629 Attache kit case
Localization	-	Instrument firmware available in 5 languages, English, French, German, Italian & Spanish, specify at time of order

Instrument upgrades provided as standard		
Fastore recording	-	Rapid data capture of transient events such as impacts or gunfire etc.
Parameters recorded	-	Leq, SEL, duration, event start time
Sample rates for broadband	-	5, 10, 20, 50, 100, 125, 250, 500, 1000 millisec Leq samples
Sample rates for narrow band	-	10, 20, 50, 100, 250, 500, 1000 millisec Leq samples
Maximum number of events	-	9999 per run with optional time history recording

Instrument upgrades available		
CEL-5X3/UPTR	-	Adds the BUILDING ACOUSTICS option to the standard instrument (provides the building acoustics recording)
CEL-5X3/UPTL	-	Adds the LOUDNESS option to the standard instrument (provides the sound quality loudness recording)

APPENDIX 8
SOP FOR MANUAL LIGHT MEASUREMENTS

ARCADIS

Standard Operating Procedure: Manual Light Measurements

I. Scope and Application

This Standard Operating Procedure (SOP) describes the procedures for light monitoring during Phase 1 of the Hudson River remedial action. A light meter will used to perform light monitoring (Sper Scientific 840020 or equivalent – see Attachment 1 for equipment description and specifications). Light meter calibration and maintenance is discussed in Appendix 57. Light monitoring will be performed to document light levels associated with the following:

- Dredging operations
- Backfill operations
- Processing facility operations

II. Personnel Qualifications

Field sampling personnel will have current health and safety training, including 40-hour Occupational Safety and Health Administration (OSHA) Hazardous Waste Operations (HAZWOPER) training and an annual refresher course, site supervisor training, and site-specific training, as needed. In addition, personnel performing light monitoring will be trained in the use of the light meter and other appropriate equipment (e.g., Global Positioning System [GPS] unit).

III. Equipment List

The following materials, as required, will be available while performing light monitoring:

- Personal protective equipment (PPE), as required by the Health and Safety Plan (HASP; Parsons 2008)
- Light meter (Sper Scientific 840020 or equivalent)
- Light meter manual
- GPS unit (Trimble XT or equivalent), as required

- Field notebook

IV. Cautions

Light meters and GPS unit will be kept dry and within recommended operating temperatures. Light meters and the GPS unit may be exposed to inclement weather (such as rain or snow) or temperatures (such as temperatures below recommended operating temperatures) for short periods of time during measurements. Once a measurement is taken, the light meter and GPS unit will be returned to the field vehicle, where they will be dried off and kept within recommended operating temperatures. Failure to keep the light meter and GPS unit dry and at optimal operating temperature may result in malfunction of the meter.

The following are other relevant cautions:

- Keep the lens cap on the photo sensor at all times except when taking a reading.
- Keep the photo sensor clean. Dirt on the photo sensor may result in inaccurate measurements.
- When taking readings, do not cast a shadow on the photo sensor. Fluctuations in the light meter reading are generally due to shadows or fluctuations in the line voltage.
- When taking readings, shield the photo sensor from wind, if possible. Ambient temperature and wind can affect the luminous flux output.
- Always carry the GPS unit in its case and secure it. When riding unsecured in a vehicle, the GPS unit can be affected by shock and vibration.
- Keep the GPS plugs clean and dry. Blow away any dirt lodged in the plugs of the connecting cables.

V. Health and Safety Considerations

The HASP will be followed when performing light monitoring.

VI. Procedures

The light meter will be operated according to the procedures contained in the operating manual and summarized below.

1. Complete project and sample location information on the Light Monitoring Form (Figure 8-4) and field logbook.

2. Insert the photo sensor into the light meter.

3. Turn on the light meter.

4. Zero the light meter in accordance with the SOP presented as Appendix 55.

5. Remove the lens cap from the photo sensor.

6. Select footcandle as the unit of measurement.

7. Select the range with the highest resolution (i.e., the most number of digits after the decimal point). For sample locations with low light, select a lower range.

8. Hold the photo sensor approximately 3.5 feet off the ground and parallel to the ground with the photo sensor pointed up. Don not cast a shadow on the photo sensor.

9. Once the result is displayed, press the button on the meter to hold the result.

10. Record the result on the Light Monitoring Form (Figure 8-4).

11. Press the button to record the result electronically on the meter.

12. Place the lens cap on the photo sensor.

13. Turn off the light meter.

14. Obtain coordinates for monitoring location with the GPS unit.

15. Return to field vehicle and clean and dry the light meter and GPS unit, as necessary.

The GPS unit will be operated according to the procedures contained in the operating manual.

VII. Waste Management

Paper towels or other items used to maintain the light meter and GPS unit in clean and dry condition will be disposed of as municipal solid waste at the end of each monitoring event.

VIII. Data Recording and Management

The Light Monitoring Form (Figure 8-4) will be used to record light level data for this monitoring program. Additional field information, as necessary, will be recorded in the field notebook.

IX. Quality Assurance

The light meter will be maintained in accordance with this SOP and the operating manual. No additional quality assurance activities, such as collection of a duplicate measurement, are necessary.

The GPS unit will be maintained in accordance with this SOP and the operating manual. The GPS unit will have a daily check on a point with known coordinates.

X. References

Parsons, 2008. Phase 1 Remedial Action Health and Safety Plan, Hudson River PCBs Superfund Site. Prepared for General Electric Company, Albany, NY. August 2008.

Attachment 1

SPER Scientific Light Meter

Source: http://
http://www.sperscientific.com/images/broc_pdf/840022.pdf
Date: January 16, 2006

SPER SCIENTIFIC LTD

All of the functions of Light Meter 840020, plus max-min-avg functions, automatic power off, RS232C output and a detachable probe for easier replacement or repair. Higher range of up to 50,000 lux, 5,000 footcandles. A unique and very useful function is the meter's ability to compensate for the different colors of tungsten, fluorescent, mercury and sunlight, with the push of a button. The result is readings true to actual lighting conditions. Also able to compare the % difference between two light intensities. A special contrast control allows the LCD to be clearly read from different angles. Comes with a soft carrying case and 9V battery.

Measurement Range		
Unit	**Res**	**Accuracy**
0 - 1,999 Lux	1.0	±4% Reading + 2d
2,000 - 19,990 Lux	10	±4% Reading + 2d
20,000 - 50,000 Lux	100	±4% Reading + 2d
0 - 180.6 Footcandles	0.1	±4% Reading + 2d
200 - 1,806 Footcandles	1.0	±4% Reading + 2d
2,000 - 5,000 Footcandles	10	±4% Reading + 2d
Relativity		
0 to max 1999%	1%	

Dimensions (Meter)	7 x 3 x 1-1/4"
Dimensions (Sensor)	3 x 2 x 1/2"
Weight	11.6 oz.
Display	Dual Function, 4 digit display, 0.5" high
Light Type Selection	Tungsten, Fluorescent, Mercury and Sun Light
Sensor	Exclusive photo diode and color correction filter Spectrum designed to meet CIE
Sampling Time	Approximately 0.4 sec
Operating Temperature	0 - 50°C, (32 - 122°F)
Operating Humidity	Max 80% RH
Power Supply	006P DC 9V battery (Heavy duty alkaline type)
Power Current	Approximately DC 5.3 mA

APPENDIX 9
SOP FOR PCBS SAMPLING WITH HIGH VOLUME SAMPLERS (EPA TO-4A)

Standard Operating Procedures

Sampling for Polychlorinated Biphenyl (PCB) by EPA Method TO-4A Using a Polyurethane Foam (PUF) Cartridge

Revision 0
December 2006

_____
Author

_____
Technical Reviewer

_____
Project Manager

_____
QA Officer

TABLE OF CONTENTS

1.0 PURPOSE OF SOP

This SOP describes the procedures used to sample for polychlorinated biphenyls (PCBs) in ambient air using a high volume polyurethane foam (PUF) sampler employing EPA Method TO-4A.

2.0 SCOPE

This document describes a high volume PUF sampling procedure for PCBs in ambient air utilizing a TE-1000 PUF (or performance equivalent) Polyurethane Foam sampler. The TE-1000 draws ambient air through a quartz fiber filter and PUF cartridge at a rate of 200 - 300 liters/minute (LPM) for 24 hours. The suspended airborne particulates and vapor phase and particulate bound PCBs will be collected on the quartz fiber filter and PUF. These media will be combined and subsequently be extracted in the laboratory and the extracts analyzed for PCBs using a gas chromatograph equipped with an electron capture detector.

3.0 EQUIPMENT AND MATERIALS

3.1 Continuous-Flow Sampling Pump

The pump must be capable of pulling ambient air through a filter/adsorbent cartridge at a flow rate of approximately 200 - 300 standard liters per minute (LPM) to obtain a total sample volume of greater than 300 standard cubic meters over a 24-hour period. The TE-1000 PUF sampler is a dual chambered aluminum-sampling module. The upper chamber supports the airborne particulate filter media in a circular filter holder. The lower chamber encapsulates a glass cartridge, which contains the Polyurethane Foam (PUF) or PUF/XAD-2 for vapor entrapment. The dual chambered sampling module is designed for easy access to both upper and lower media. The threaded lower canister is removed with the cartridge intact for immediate exchange. Filter support screens and module components are equipped with gaskets providing a leak proof seal during the sampling process. The system is made up of eight primary parts: PUF Anodized

aluminum shelter, 7-Day Mechanical Timer, Flow Venturi & Calibration Valve, Motor Voltage Control, PUF Blower Motor Assembly, Dual Sampling Module, Exhaust Hose, Magnehelic Gauge and Gabled Roof (see Figures 1 & 2 for presentation of complete system). The operator will refer to the manufacturer's operation manual for pictorials and additional information to aid in performing maintenance and operation.

3.2 Sampling Module

The sampling module (Figure 3) consists of a metal filter holder capable of holding a 102-mm circular particle filter supported by a 16-mesh stainless-steel screen. The filter holder will screw on to a metal cylinder capable of holding a 65-mm O.D. by 125-mm borosilicate glass sorbent cartridge containing the sorbent (PUF or PUF/XAD). The filter holder is equipped with sealing gaskets placed on either side of the filter to achieve an air-tight seal. The glass sorbent cartridge is also sealed with gaskets which are located at the bottom of the metal cylinder and the bottom of the filter holder where the filter holder screws on to the metal cylinder. Two sampling modules should be made available for each high-volume sampler. This way the loading and recovery of filters and sorbent cartridges can be performed under controlled environmental conditions in a field office/laboratory.

3.3 Glass Sampling Cartridge

The sampling cartridge (sorbent cartridge) is a cylinder constructed of bososilicate glass which measures 65-mm O.D. by 125-mm in length. The cylinder is indented 20-mm from the lower end to provide support for a 16-mesh stainless-steel screen that holds the sorbent (PUF or PUF/XAD). These cartridges will be cleaned and loaded by the analytical laboratory. The loaded cartridges will be sealed in cleaned aluminum foil. Pre-loaded sorbent cartridges can be purchased from SKC (863 Valley View Road Eighty Four, PA 15330 tel: 800-752-8472).

3.4 Quartz Fiber Filter

The filter is a 102-millimeter bindless quartz microfiber filter. The laboratory will clean and dry the filters and provide them in a sealed glass petri dish for loading into the sampling module.

3.5 Polyurethane Foam (PUF)

The PUF should be of the polyether type with a density of 0.0225g/cm^3. This type of foam is used for furniture upholstery and mattresses. The PUF is cut in cylinders that will fit into the sampling cartridge under slight compression. The PUF must be solvent extracted and dried prior to use. The cleanliness of the PUF must be demonstrated prior to use. See the SOP *Preparation of TO-4A Samples for PCB Analyses* for details on the required cleaning and certification procedures for quartz filters and PUF sorbent traps.

3.6 High-Volume Sampler Calibrator Kit

The calibrator kit consists of an orifice and a slack tube water manometer. The orifice calibrator must be capable of providing multipoint resistance for the high-volume sampler. The slack tube water manometer should be capable of measuring pressures of up to 30 inches of water. The TISCH TE-5040A orifice calibrator with water manometer (or performance equivalent) will be used.

3.7 Gloves

White cotton or nitrile gloves will be used when loading or recovering sampling modules. It is highly recommended the white cotton or nitrile gloves be worn whenever handling sampling media.

4.0 HIGH-VOLUME SAMPLER OPERATION

In order to operate the TE-1000 PUF sampler, it is necessary to assemble the instrument.

4.1 Equipment Assembly

Shelter Box Assembly

1. Open the shelter box and remove Anodized Aluminum Shelter.

2. Inside of the shelter is the exhaust hose. Unwrap and insert end with speed clamp on end of blower motor discharge. Tighten with a flat edge screwdriver and put end of hose downwind of sampler.
3. Enclosed in the bottom of the shelter is the Dual Sampling Module. Remove from box.
4. Take out rubber plug inserted in quick disconnect on shelter. Insert Dual Sampling Module and lock in place by pushing rings down for a tight seal.
5. Take off cover that is on top of 4-in. filter holder. NOTE: Turning motor on with cover in place will damage motor.
6. Open lid box and remove Gabled Roof.

Gabled Roof Assembly

1. Secure front catch to the shelter using 2 (10-24 x ½-in.) pan head screws with stop nuts.
2. Secure roof back catch to the back of the shelter using a (10-24 x ½-in.) pan head screw with a stop nut.
3. Secure rear lid hasp inside the lid with the slotted end angled up using 2 (10-24 x ½-in.) pan head screws with stop nuts.
4. Remove 4 (10-24 x ½-in.) pan nutserts in back of shelter.
5. Attach the lid to the shelter by placing the lid hinge plates on the "OUTSIDE" of the shelter top and tighten the 4 – (10-24 x ½-in.) pan head screws into the nutserts.
6. Adjust the front catch to be sure that the lid slot lowers over it when closing the lid. NOTE: The rear lid hasp should align with the roof back catch when the lid is open.
7. Attach the chain and the "S" hook assembly to the side of the shelter with a (6-32 x ½-in.) pan head screw and nut.
8. The lid can be secured in an open or closed position with the "S" hook.

Electrical Hook-Up

(NOTE: An electrical source of 110 volts, 15 amps is required.)

1. The PUF Blower Motor male cord set plugs into the Motor Voltage Control Female cord set.

2. The male cord set of the Motor Voltage Control plugs into the 7-Day Mechanical Timer female cord set that is on the left side of the timer.
3. The other female cord set on the timer (on the right) is hot all the time and is an extra plug.
4. The male cord set of the timer plugs into the line voltage.

Once the TE-1000 PUF sampler is assembled correctly according to this section and connected to a power supply, the instrument is ready for operation.

4.2 Verifying Flow Rates

The flow rates are set with a Variac (motor voltage control) that controls the motor speed. (NOTE: For this ambient air program, the desired flow rate is 250 L/min.) Flow rates are recorded before and after sampling as discussed in Section 6.0.

5.0 CALIBRATION

The TE-1000 PUF Sampler should be calibrated:

1. Upon installation.
2. After motor maintenance or replacement.
3. After motor brush adjustment or replacement.
4. At least once every three months regardless of sampler use.

5.1 Calibration Procedure

1. Calibration of the PUF Sampler is performed WITHOUT a foam plug or filter paper in the sampling module. However, the empty glass cartridge must remain in the module to insure a good seal through the module.
2. Install the Calibrator (orifice) on top of the four-in. Filter Holder. Conduct a leak test by covering the holes on top of the orifice and pressure tap on the orifice with your hands. Listen for a high-pitched squealing sound made by escaping air. If this sound is heard, a

leak is present and the top loading adaptor hold-down nuts need to be re-tightened. Avoid running sampler for longer than 30 seconds at a time with the orifice blocked.

3. Open both ports on top of the water manometer and connect tubing from the water manometer port to the pressure tap on the orifice. Leave the opposite side of the water manometer port open to the atmosphere.
4. Open the ball valve fully (handle should be straight up); this is located inside of shelter directly above the blower motor.
5. Turn the system on by tripping the manual switch on the timer. Allow a few minutes for the motor to warm-up.
6. Adjust and tighten the voltage control screw (variac) on the motor voltage control to obtain a reading of 80 inches on the dial of the Magnehelic Gage or 89 whatever is desired. Do not change until completion of calibration.
7. With 80 inches on the magnehelic gage as your first calibration point, record this figure and the orifice water manometer reading on your data sheet (Figure 4) or log book.
8. Close the ball valve slightly to readjust the dial gage down to 70 inches. Record this figure and the orifice water manometer reading on your data sheet/lab notebook.
9. Using the above procedure, adjust the ball valve for readings at 60, 50, and 40 and record information.
10. Manually turn off sampler.
11. Using the high-volume calibration spreadsheet (Figure 5) enter each magnehelic and water manometer reading that was recorded during the calibration procedure. Also enter the current ambient temperature and pressure along with the current date and project specific information.
12. The spreadsheet will calculate the slope (*m*), intercept (*b*) and correlation coefficient (*r*). The *r* value must be ≥ 0.99 for the calibration to be valid. If the *r* does not meet acceptance limits, a leak is most likely the problem and the calibration procedure should be repeated. The spreadsheet will also calculate the desired setting for the magnehelic gage based on the desired flow rate (250 L/min for this example).

6.0 SAMPLING

The TE-1000 PUF Sampler may be operated at ground level or on rooftops. The exhaust hose should be stretched out in a downwind direction if possible. The sampler should be operated for 24 hours in order to obtain average daily levels of airborne PCBs. NOTE: On and off times and weather conditions during sampling periods should be recorded. Air concentrations may fluctuate with time of day, temperature, humidity, wind direction, and velocity.

6.1 Loading the Sampling Module

Loading of the sample module should be performed in the "clean" environment of the field office or field laboratory prior to performing the sampling. The following procedure should be followed to load the sampling module.

1. Release the three swing bolts on the 4-in. filter holder and remove the triangle cover (cover must be off when sampler is "ON") and hold down ring.
2. Using clean gloves, install a clean 102 mm diameter glass fiber filter on the support screen in between the Teflon gaskets and secure it with the hold down ring and swing bolts. (NOTE: The 102 mm diameter micro quartz fiber filters will be supplied and pre-certified by the analytical laboratory.)
3. Unscrew filter holder from the metal sampling cylinder.
4. Using clean nitrile or cotton gloves, load the glass cartridge with PUF and or PUF/XAD-2 into the metal sampling cylinder. Screw the filter housing and metal sampling tube loaded with the glass cartridge together making sure all fittings are snug.

6.2 Loading and Operating of High-Volume Sampler

1. Open Gable roof assembly and inspect internal sample housing for debris. Remove any debris with a brush or by other means.
2. Insert the loaded sampling module into high-volume sampler and secure.
3. Loosen the three swing bolts on the 4-in. filter holder and remove the triangle cover from the hold down ring. Tighten the swing bolts and lower the gable roof.

4. Start pump by turning it on. Record start time and adjust pump flow rate using the Motor Voltage Control until the magnehelic gage reads the desired magnenelic setting derived from the calibration spreadsheet. Record this reading on the data sheet (Figure 6).
5. Manually stop pump after desired sampling period by turning it off. (NOTE: For this ambient air program, the desired sampling period is 24 hours.) After sampling is completed, record the stop time and post pump flow rate from magnehelic.
6. Open Gable roof and loosen the three swing bolts on the 4-in. filter holder and insert the triangle cover on to the hold down ring. Tighten the swing bolts and lower the gable roof.

6.3 Recovery of Sampling Module

Recovery of the sample module should be performed in the "clean" environment of the field office or field laboratory. The following procedure should be followed to recover the sampling module.

1. Unscrew filter holder from the metal sampling cylinder.
2. Using clean nitrile or cotton gloves, remove the glass cartridge with PUF or PUF/XAD-2 from the metal sampling cylinder.
3. Release the three swing bolts on the 4-in. filter holder and remove the triangle cover and hold down ring.
4. Fold filter in half and in half again, then place the filter inside the glass cartridge.
5. Wrap the glass cartridge with aluminum foil and place back in the original shipping container.
6. Label the container and place sample in a temperature controlled (4°C ± 2°C) storage facility (refrigerator or cooler) until transport to an analytical laboratory.
7. A field blank (a loaded glass cartridge and quartz filter (folded and inserted into the glass cartridge) that has yet to be used to collect a field sample) should be labeled and placed along with the field samples being stored until transport to the laboratory.

7.0 SAMPLE VOLUME DETERMINATION

To determine the sample volume (corrected to actual temperature and pressure) that was collected the flow rate (corrected to actual temperature and pressure) must be multiplied by the duration of sampling. The duration of sampling is typically 24 hours or 1440 minutes. To determine flow rate, take the average of the initial magnehelic reading and final magnehelic reading recorded on the sample data sheet in combination with the ambient temperature and pressure recorded during the sampling event. Calculate as follows:

$$Flow\ rate\ (LPM) = [1/m([Sqrt\ (magn)(Pa/760)(298/Ta)]-b)]*[(760/Pa)(Ta/298)]$$

Where:

m	=	sampler slope (determined during calibration)
b	=	sampler intercept (determined during calibration)
magn	=	average magnehelic gage reading (average of initial and final readings)
Ta	=	average ambient temperature (°K) (during sample collection)
Pa	=	average ambient pressure (mm Hg) (during sample collection)
Sqrt	=	square root
760	=	Standard pressure (mmHg)
298	=	Standard temperature (°K)

With flow rate and sampling duration determined, volume is calculated as follows:

$$Volume\ (L) = flow\ rate\ (L/min) * sampling\ duration\ (1440\ min)$$

$$Volume\ (m^3) = volume\ (L) \div 1000$$

8.0 SAMPLE SHIPMENT AND CUSTODY

Prior to transferring the samples to the analytical laboratory, the samples must be packaged such that the samples will remain intact and at the proper temperature (4°C ± 2°C) during transport to

the laboratory. Documentation of the transfer of sample custody from the sampler to the laboratory must also be performed.

8.1 Chain of Custody Form

Prior to sample transfer a chain of custody form must be completed. This form will either be supplied by the sampler or the analytical laboratory. Refer to the RAMP QAPP for the chain of custody form. At a minimum, the following items must be completed for each sample:

1. Project Name.
2. Shipping Date.
3. Sample Identification (as specified by the RAMP QAPP and on the sample label).
4. Date of Sample Collection.
5. Sample Description (location, station #, etc.).
6. Sample volume (m^3).
7. Requested Analysis (PCBs).

When transferring the custody of the samples to the laboratory (or laboratory currier) sign and date/time the "Relinquished By:" section of the form and have the laboratory or currier sign and date/time the "Received By:" section. Keep a copy of each form for the project file.

8.2 Packing of Samples

The following procedure should be followed for packing of the samples for shipment:

1. Verify the sample ID against the chain of custody form.
2. Wrap the sample container in packing material (i.e., bubble wrap, bubble bags).
3. Place wrapped container into cooler which is lined with cushioning material.
4. Place bags of ice or blue ice on top and around the sample containers such that the sample temperature will be maintained.
5. Place a water filled vial labeled "Temperature blank" in among the samples to act as a representative sample. Upon receipt at the laboratory, the laboratory will measure the

temperature of the water contained in this vial to determine if the temperature of the samples was maintained at 4°C ± 2°C.

6. Secure the cooler lid closed.

9.0 MAINTENANCE

Most of the routine maintenance items can be done in the field. If more time is needed to fix or troubleshoot a problem, replace the whole unit with a spare and finish working on it in the repair lab. This will minimize the station down time. All work on the equipment will be documented in the site equipment log, signed, and dated by the person performing the work.

9.1 Preventative Maintenance

1. TE-1000 PUF Sampler- Power cords should be checked for crimps, cracks or exposed junctions each sample day. Inspect the Dual Sampling Module for: (a) all gaskets are sealing properly; replace if necessary; (b) clean any dirt that is built up around the module and filter holder; and (c) make sure quick disconnect is working correctly by making a good seal.
2. Blower Motor Assembly - Inspect and replace the motor flange gasket and motor cushion routinely and replace the motor carbon brushes every 400 to 500 hours of operation. It is imperative that the brushes be replaced before the brush shunt touches the motor commutator.
3. Motor Brush Replacement – Ensure all power is disconnected from the TE-PUF Sampler prior to opening the motor housing and unplug the motor power cord.
    a. Remove the Motor Mounting Cover by removing the four bolts. This will expose the flange gasket and the motor. Turn motor over.
    b. Remove ground wires from backplate and carefully lift the metal housing from the motor.
    c. With a screwdriver carefully remove the plastic fan cover by prying in between brush and cover until both sides pop loose.
    d. With a screwdriver carefully pry the brass quick disconnect tabs from the expended brushes.

e. With a screwdriver remove brush holder and release brushes.
f. With new brushes, carefully slide quick disconnect tabs firmly into tab slot until seated.
g. Push brush carbon against commutator until plastic brush housing falls into place on commutator end bracket.
h. Replace brush holder clamps onto brushes.
i. Assemble motor after brush replacement: snap plastic fan cover into place, feed ground wires back through backplate, put housing back on motor, pull cord set back to normal position, fasten ground wires to backplate, turn motor over, tighten flange on top of housing and gasket. NOTE: Make sure wires do not get smashed between metal ring and housing.

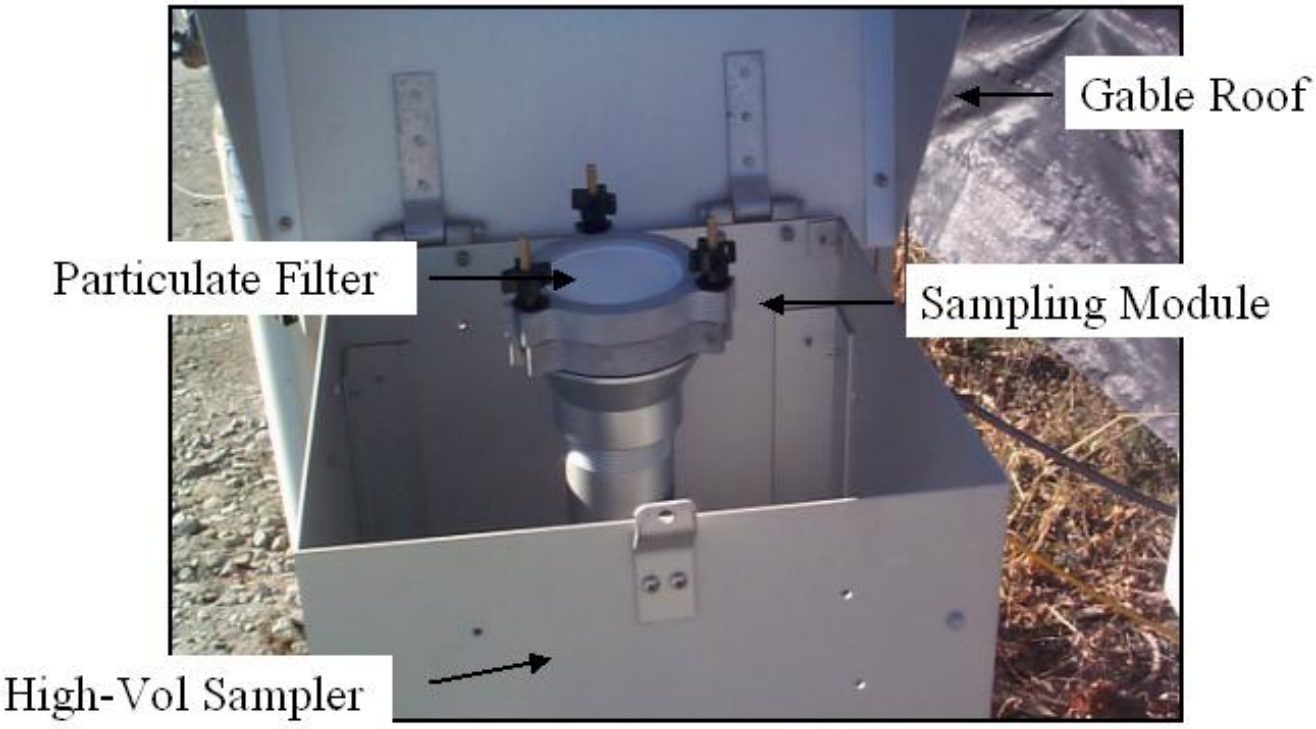


Figure 1. High-Volume Sampler & Sample Module

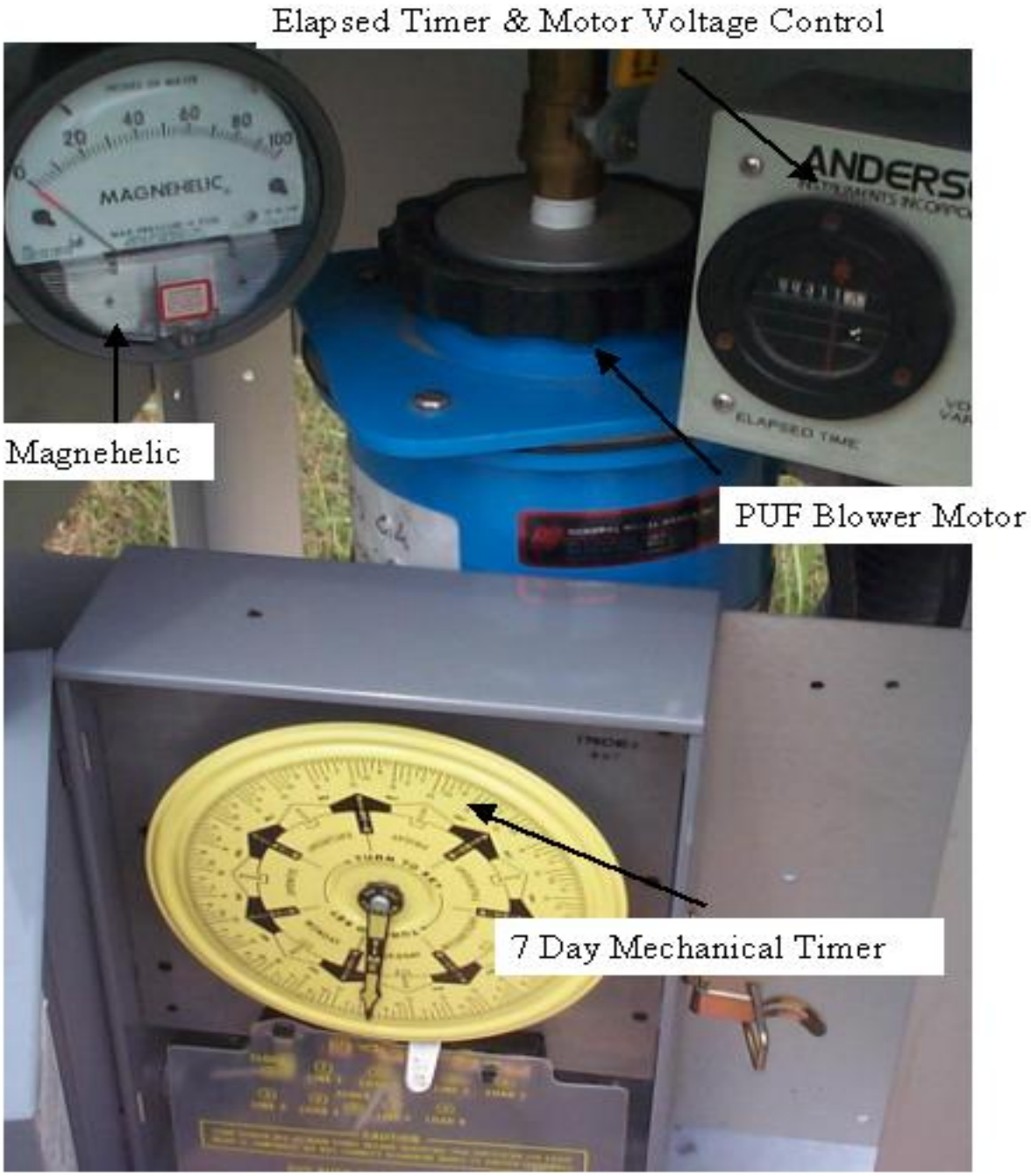


Figure 2. Internal View of High-Volume Sampler

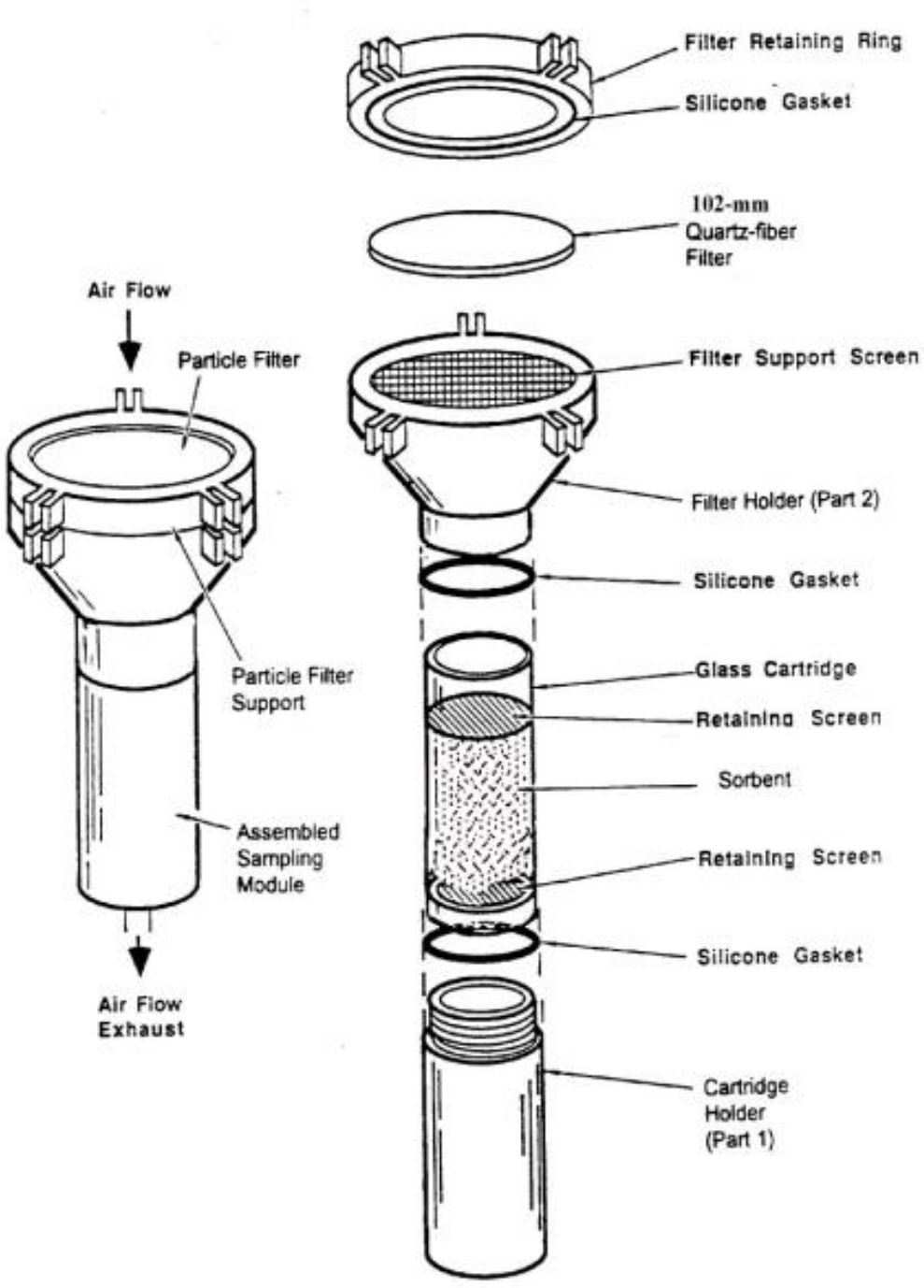


Figure 3: Sampling Module

PUF HIGH-VOLUME SAMPLER CALIBRATION

Site:		**Date:**	
Project No.:		**Time:**	
Sampler Serial No.:		**Technician:**	
Orifice Serial No.:		**Ambient Temperature (deg. C):**	
Orifice Cal. Date:		**Ambient Pressure (mm Hg):**	

Orifice Data:

Slope (m_s) _____ **Intercept (b_s):** _____ **Corr. Coef .'(r):** _____

Sampler Calibration

Orifice Manometer in. H_2O (delta H)	Sampler Magnehelic in. H_2O (I)
	80
	70
	60
	50
	40

Was Orifice Manometer Zeroed prior to Calibration? **Y / N**

Figure 4. Example Calibration Data Sheet

Network: _____ Site: _____ Serial #: **684** Station #: _____

Technician: _____ Date: **8/29/2005** OrificeS/N: **932** Orif. Cal. Date: **4-Aug-05**

Reason for Puff Sampler Calibration: ***New PS1*** , ~~*Motor/Brush Change*~~ , ~~*Quarterly Recal*~~

Amb. Temp, T1 (^{o}F)	**84.2**	Bar. Press., P1 (in Hg)	**29.8**
Amb. Temp, T1 (K)	302.0	Bar. Press., P1 (mmHg)	756.9

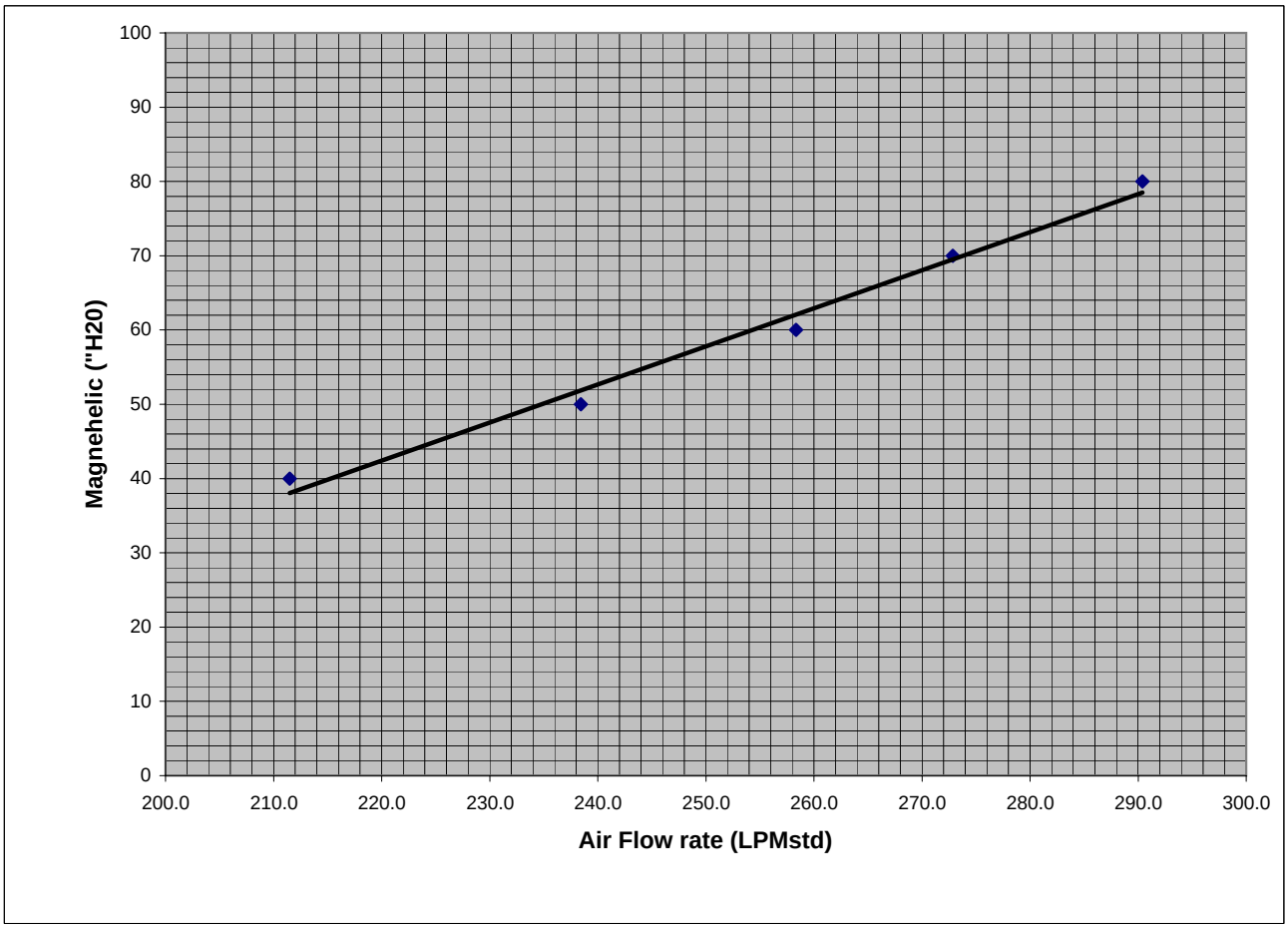
Orifice Data

Qstd (m_o) = **9.49592** Qstd (b_o) = **-0.02839** Qstd (r_o) = **0.99997**

ΔH	Q_{std}	I	I_c
7.60	290.395	**80**	8.87
6.70	272.841	**70**	8.29
6.00	258.356	**60**	7.68
5.10	238.426	**50**	7.01
4.00	211.495	**40**	6.27

I_c = sqrt[I x 0.392 x (P1/T1)] Q_{std} = {(1/m_o) x sqrt[ΔH x (P1/760) x (297.18/T1) - b_o]} x 1000

m_s = 0.033 b_s = -0.87400 r_s = 0.99724



Desired Flow Rate (lpm): 250 Sampler Setting: 57.8

Figure 5. Example Calibration Spreadsheet

TO-4A FIELD SAMPLING DATA SHEET

Site: _____ **Sampler Location:** _____
Project No.: _____ **Sampler Serial No.:** _____

Setup:		**Recovery:**	
Date:		**Date:**	
Time:		**Time:**	
Technician:		**Technician:**	
Sample ID:		**Sample ID:**	
Elapsed Timer:		**Elapsed Timer:**	
Magnehelic Reading:		**Magnehelic Reading:**	

(Note: Initial Magnehelic reading should be adjusted to the desired reading provided in the sampler calibration spreadsheet.)

Ave. Ambient Temp. (deg. C):	(obtain from site met. Station)	
Ave Ambient Pressure (mm HG):	(obtain from site met. Station)	
Ave. Magnehelic Reading:	(setup reading + Recovery Reading/2)	
Magnehelic RPD:	[setup-recovery/(setup+recovery/2)]*100	

(Note: IF RPD = >20%, A problem may exist, contact Field Team Leader for corrective action.)

INTERIM SAMPLING OBSERVATIONS

Time:		**Time:**	
Elapsed Timer:		**Elapsed Timer:**	
Magnehelic Reading:		**Magnehelic Reading:**	
Time:		**Time:**	
Elapsed Timer:		**Elapsed Timer:**	
Magnehelic Reading:		**Magnehelic Reading:**	
Time:		**Time:**	
Elapsed Timer:		**Elapsed Timer:**	
Magnehelic Reading:		**Magnehelic Reading:**	

Comments:

Figure 6. Example Field Data Sheet

APPENDIX 10
SOP FOR PCBS SAMPLING WITH LOW VOLUME SAMPLERS (EPA TO-10A)

Standard Operating Procedures

Sampling for Polychlorinated Biphenyl (PCB) Sampling by EPA Method TO-10A Using a Polyurethane Foam (PUF) Cartridge

Revision 0
December 2006

_____
Author

_____
Technical Reviewer

_____
Project Manager

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QA Officer

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1.0 PURPOSE OF SOP

This SOP was designed to describe the procedures used to sample for polychlorinated biphenyl Aroclors (PCBs) in ambient air using a Polyurethane foam (PUF) cartridge by EPA Method TO-10A.

2.0 SCOPE

This document describes a low volume PUF sampling procedure for PCBs in ambient air utilizing a SKC Leland Legacy Pump. The Legacy pump will pull ambient air through the PUF cartridge at a rate of 5 liters/minute for 24 hours. The air borne PCBs will be collected on the PUF that will be subsequently extracted in the laboratory and the extract analyzed for PCBs by a gas chromatograph equipped with an electron capture detector.

3.0 EQUIPMENT AND MATERIALS

3.1 Continuous-Flow Sampling Pump

The pump should provide a constant flow rate of 1 to 5 liters/minute. The SKC Leland Legacy pump will be used (see Figure 1). The Leland Legacy dual diaphragm sample pump is designed specifically to provide constant airflows from 5 to 15 L/min with minimum power requirements and low noise. The pump's internal flow sensor measures flow directly and acts as a secondary standard, constantly maintaining the set flow rate. The built-in sensors automatically correct flow for variations in temperature and atmospheric pressure.

3.2 Polyurethane Foam (PUF)

The PUF should be of the polyether type with a density of 0.0225g/cm^3. This type of foam is used for furniture upholstery and mattresses. The PUF is cut in cylinders that will fit into the sampling cartridge under slight compression (approximately 22-mm I.D. and 7.6-cm

long). The PUF must be solvent extracted and dried prior to use. The cleanliness of the PUF must be demonstrated prior to use. Pre-extracted PUF plugs and sampling cartridges may be purchased by SKC (Cat. No.226-92). These PUFs must be demonstrated clean prior to use.

3.3 Sampling Cartridge

The sampling cartridge should be a 20-mm (I.D.) by 10-cm long borosilicate glass tube drawn down to a 7-mm (O.D.) open connection for attachment to a pump using flexible tubing. These cartridges must be solvent rinsed and dried prior to loading the PUF. The analytical laboratory performing the PCB analysis will perform loading of the PUF into the cartridge (see Figure 1). The laboratory will provide loaded PUF cartridges sealed with plastic caps and contained in a clean glass jar.

3.4 Flexible Tubing

The flexible tubing should have an inside diameter such that the drawn down end of the PUF cartridge will snugly fit inside the tubing with out leaking. The tubing should also be able to fit over the pump connection. The tubing should be Tygon, or silicone in construction. The length of the tubing will be dictated by the sampling location.

3.5 Sampling Stand

The sampling stand should be able to stand on its own and allow the PUF cartridge to be positioned 1 to 2 meters above the ground. The sampling stand should also be able to provide the pump protection from rain and snow (see Figure 1).

3.6 Dry-Cell Calibrator

A dry cell calibrator certified NIST traceable to be used to set the pump flow rate and verify the sample flow rates. A Bios Primary Flow Calibrator will be used.

4.0 SAMPLER SITING

Actual sample locations will be described in the associated Remedial Action Monitoring (RAM) Quality Assurance Project Plan. At each sample location, the sampler should be in an unobstructed area at least 30 meters from any obstacle to air flow. The PUF cartridge intake should be positioned 1 to 2 meters above ground level. The PUF cartridge intake should be orientated either downward or horizontal. If a horizontal orientation is used, care must be taken so that the cartridge intake does not collect rain water during rain events.

5.0 EQUIPMENT OPERATION

In order to operate the Leland Legacy pump, it is necessary to set up the pump.

5.1 Pump Setup

Keypad Basics

* Scrolls through run time data and setup options
▲ Increases values such as flow rate
▼ Decreases values such as flow rate
[▲▼] When pressed simultaneously, displayed item is selected or entered
***▲▼ *** Security code that must be pressed in sequence to enter Setup.

Turning the Pump On/Off

- Press any button to turn on the power.
- Press [▲▼] to run the pump or to place a running pump in Hold.
- Manual Off: from Hold, press and hold *.
- Auto Off turns off the pump after 5 minutes in Hold.

Entering and Navigating Setup

Entering: Press [▲▼], then press the security code in sequence ***▲▼ *.** Setup should appear briefly on the LCD.

Navigating: Press * to scroll through parameters. Once the LCD shows End, parameters will repeat until the user exits Setup.

Exiting: Press * until End appears on the LCD. Press [▲▼]. The pump is now in Hold.

Setup Options

After entering Setup, go to:

1. Flow Set: Press ▲ or ▼ to increase or decrease to the desired pump flow rate. Pump will start running. Press * to move to the next parameter.
2. ADJ: After attaching calibrator to pump, press ▲ or ▼ to increase or decrease flow adjustment until desired flow reading is indicated on calibrator. Press * until End appears. Press [▲▼] to save new flow adjustment settings and exit Setup.
3. CALCh: Pressing [▲▼] initiates single-point calibration. Pressing ▲ seven times initiates a full calibration. (Note: Full calibration is done once a year or after maintenance.)
4. 12Hr/24Hr Clock and Delayed Start: Press ▲ or ▼ to move between standard (12 hr), military (24 hr) and Dela (delayed start). Press * to select.
5. Time of day: Press ▲ or ▼ to increase or decrease flashing hour. Press * to move from hours to minutes. Press ▲ or ▼ to increase or decrease flashing minutes. Press * to move to next parameter.
6. ST (Sampling Time): Allows the user to program a specific run time. Press ▲ or ▼ to increase or decrease the time in minutes. Press * to move to next parameter.
7. Temperature: Press ▲ or ▼ to toggle between Fahrenheit (F) and Celsius (C). Press * to move to next parameter.
8. Atmospheric Pressure: Press ▲ or ▼ to toggle between mercury (In), millibars (mb) and millimeters of mercury (mm). Press * to move to next parameter.
9. CLr: Press [▲▼] to clear accumulated run time and volume data to zero.

10. ESC: Press [▲▼] to exit Setup without saving new settings.
11. End: Press [▲▼] to save new settings and exit Setup.

Resetting Run Time Data

To reset accumulated volume and run time data to zero:

1. Press [▲▼], then press the security code in sequence ***▲▼ *.** Setup will display briefly.
2. Press * until Clr appears, then press [▲▼].
3. Press * until End appears, then press [▲▼] to exit Setup. The pump is now in Hold.

5.1.1 Setting the Sampling Time

Program the pump from the integral keypad or a PC using DataTrac software to sample from 1 to 99999 minutes.

1. Press [▲▼], then press the security code in sequence ***▲▼ *.** Setup will display briefly.
2. Repeatedly press * until ST L/min and a flashing time and Set appear on the display.
3. Set the sampling time by pressing ▲ or ▼ to increase or decrease it to the desired time in minutes. (NOTE: For this ambient air program, the desired sampling time is 24 hours or 1440 minutes.)
4. Press * repeatedly until End appears.
5. Press [▲▼] to save the new sampling time and exit Setup.

5.1.2 Setting the Pump Flow Rate

1. Press [▲▼], then press the security code in sequence ***▲▼ *.**
2. The flow rate and setup will flash on the LCD. Press ▲ to increase flow rate. Press ▼ to decrease flow rate. The pump will run while the flow is set. (NOTE: For this ambient air program, the desired flow rate is 5 liters per minute which will allow for collection of approximately 7.2 m^3 over a 24-hour period.)

3. Once the desired flow rate is displayed, press * until End appears. The pump will stop running.
4. Press [▲▼] to save the new flow rate and exit Setup.

6.0 PUMP CALIBRATION

A flow system must be audited following initial setup of the Leland Legacy Pump and prior to sampling and at the end of sampling, as defined by the project specific QAPP, during the sampling event.

6.1 Setting Verified Flow Rate Using a Primary Standard Calibrator

Verification of the flow rate is performed prior to the sampling period as follows:

Connect the pump inlet to a calibrator (i.e., primary source dry- cell calibrator) with representative media in-line.

1. Press [▲▼], then press the security code in sequence ***▲▼ *.** The flow rate and Set will flash.
2. Set the flow on the pump display by pressing ▲ or ▼ to increase or decrease flow to the desired rate.
3. Press *. Adj will appear.
4. If the calibrator reads a higher flow rate than the pump is set for, press ▼ until they are in agreement (within ±10%). If the calibrator a reads lower flow rate, press ▲ until they are in agreement (within ±10%). When pressing ▲ or ▼, the pump display will indicate the adjustment (or correction) made in L/min.
5. Press * until End appears.
6. Press [▲▼] to save the new flow rate and Adj and exit Setup. Reset the run time data.

6.2 Verifying Flow Rate Using a Primary Calibrator

1. Following steps 1 and 2 of Section 7.0, place the inlet to the dry calibrator to the intake of the PUF cartridge making a complete seal.
2. Read the flow rate from the calibrator and the flow rate from the pump. The two readings should be within ±5%. Record the flow rates and %D on the data sheet.
3. If agreement is not met, adjust pump flow rate as described in line 5 of Section 6.1. Press [▲▼] to save the new flow rate and Adj and exit Setup. Reset the run time data. Record the start time and adjusted pump flow rate.
4. At the completion of the sampling and prior to removal of the PUF cartridge, place the inlet to the dry calibrator to the intake of the PUF cartridge making a complete seal.
5. Read the flow rate from the calibrator and the flow rate from the pump. The two readings should be within ±5%. Record the flow rates and %D on the data sheet.
6. If agreement is not met, flag the sample volume as estimate due to a high difference in initial and final flow rate.

7.0 SAMPLING

Note: During handling of sample media, nitrile and/or cotton gloves will be used.

1. Following the setup and calibration procedures, remove plastic caps from pre-cleaned cartridge assembly and return to the jar for later use. Attach cartridge to the pump using the flexible tubing.
2. To begin sampling, press [▲▼] to run the pump. Record the start time (clock time) and pump flow rate.
3. Perform flow rate verification (section 6.2).
4. Sample for the time specified in the QAPP. (NOTE: For this ambient air program, the desired sampling time is 24 hours or 1440 minutes).
5. To stop sampling, press [▲▼] to place the pump in Hold. Record the stop time (clock time), sampling elapsed time (in minutes) (should be 1440 minutes), flow rate, and final volume.

6. When sampling is complete, pump data are retained in memory for recovery. Data can be viewed on the LCD by using the * button to scroll through it.
7. Perform flow rate calibration verification (Section 6.2).
8. Remove PUF cartridge from the pump and replace the plastic caps on the cartridge.
9. Put the cartridge back in its original sealed and labeled (as designated in the RAM QAPP) container.
10. Place sample in a temperature controlled (4°C ± 2°C) storage facility (refrigerator or cooler) until transport to an analytical laboratory.

Note: If flow drops by more than 5%, the pump goes into Hold and retains historical data. The flow fault icon flashes during flow fault. The pump will restart in 20 seconds and try to continue sampling. If the flow remains restricted, the pump returns to flow fault. Auto-restart is attempted every 20 seconds up to 10 times. Flow fault time is not added to the displayed run time or cumulative volume display.

8.0 SAMPLE VOLUME DETERMINATION

The SKC Leland Legacy pump displays the volume collected at the end of the sampling period. This data is collected as per item 5 of Section 7.0. The sample volume is measured in liters and must be divided by a factor of 1000 to convert the units from liters (L) to cubic meters (m^3). This sample volume will be used along with the analytical results to yield a PCB concentration.

9.0 SAMPLE SHIPMENT AND CHAIN OF CUSTODY

Prior to transferring the samples to the analytical laboratory, the samples must be packaged such that the samples will remain intact and at the proper temperature (4°C ± 2°C) during transport to the laboratory for proper sample integrity. Documentation of the transfer of sample custody from the sampler to the laboratory must also be performed for proper sample integrity.

9.1 Chain of Custody Form

Prior to sample transfer a chain of custody form must be completed. This form will either be supplied by the sampler or the analytical laboratory. Refer to the RAM QAPP for the chain of custody form. At a minimum, the following items must be completed for each sample:

- Project Name.
- Shipping Date.
- Sample Identification (as specified by the RAM QAPP and on the sample label).
- Date of Sample Collection.
- Sample Description (location, station #, etc.).
- Sample volume (m^3).
- Requested Analysis (PCBs).

When transferring the custody of the samples to the laboratory (or laboratory currier) sign and date/time the "Relinquished By:" section of the form and have the laboratory or currier sign and date/time the "Received By:" section. Keep a copy of each form for the project file.

9.2 Packing of Samples

The following procedure should be followed for packing of the samples for shipment.

1. Verify the sample ID against the chain of custody form.
2. Wrap the sample container in packing material (i.e. bubble wrap, bubble bags).
3. Place wrapped container into cooler which is lined with cushioning material.
4. Place bags of ice or blue ice on top and around the sample containers such that the sample temperature will be maintained.

5. Place a water filled vial labeled “Temperature blank” in among the samples to act as a representative sample. Upon receipt at the laboratory, the laboratory will measure the temperature of the water contained in this vial to determine if the temperature of the samples was maintained at 4°C ± 2°C.
6. Secure the cooler lid closed.

10.0 BATTERY OPERATION

Installing the Battery

1. Align connector of battery pack with connector of pump body.
2. Gently press battery pack into pump body until it is flush with the pump case. Insert and tighten three screws. Note: Make sure the longest of 3 screws is placed in the top screw hole.

Charging the Battery

1. Insert the plug on the Charging Unit into the battery-charging jack on top of the pump (underneath the protective cover).
2. Insert the plug on the Power Supply into the jack on the Charging Unit.
3. Slide the appropriate wall plug into the Power Supply and plug the Power Supply into a wall outlet.

Note: The battery will recharge in approximately 15 hours.

Removing and Replacing the Battery Pack

1. Turn off pump before removing battery. Removing the battery while in operation may corrupt pump history.
2. Position pump with belt clip facing upward.
3. Use a Philips head screwdriver to remove three screws on bottom half of pump.

4. Grasp and remove battery pack by pulling it up and away from pump body.
5. Align connector of new battery pack with connector of pump body.
6. Gently press battery pack into pump body until it is flush with the pump case. Insert and tighten three screws. Note: Make sure the longest of three screws is placed in the top screw hole.

11.0 PUMP MAINTENANCE

If pump maintenance is required, return the pump to the manufacturer for repair.

12.0 ADDITIONAL INFORMATION

A more detailed equipment manual is available from SKC and is located in the site office for any other questions about the Leland Pump.

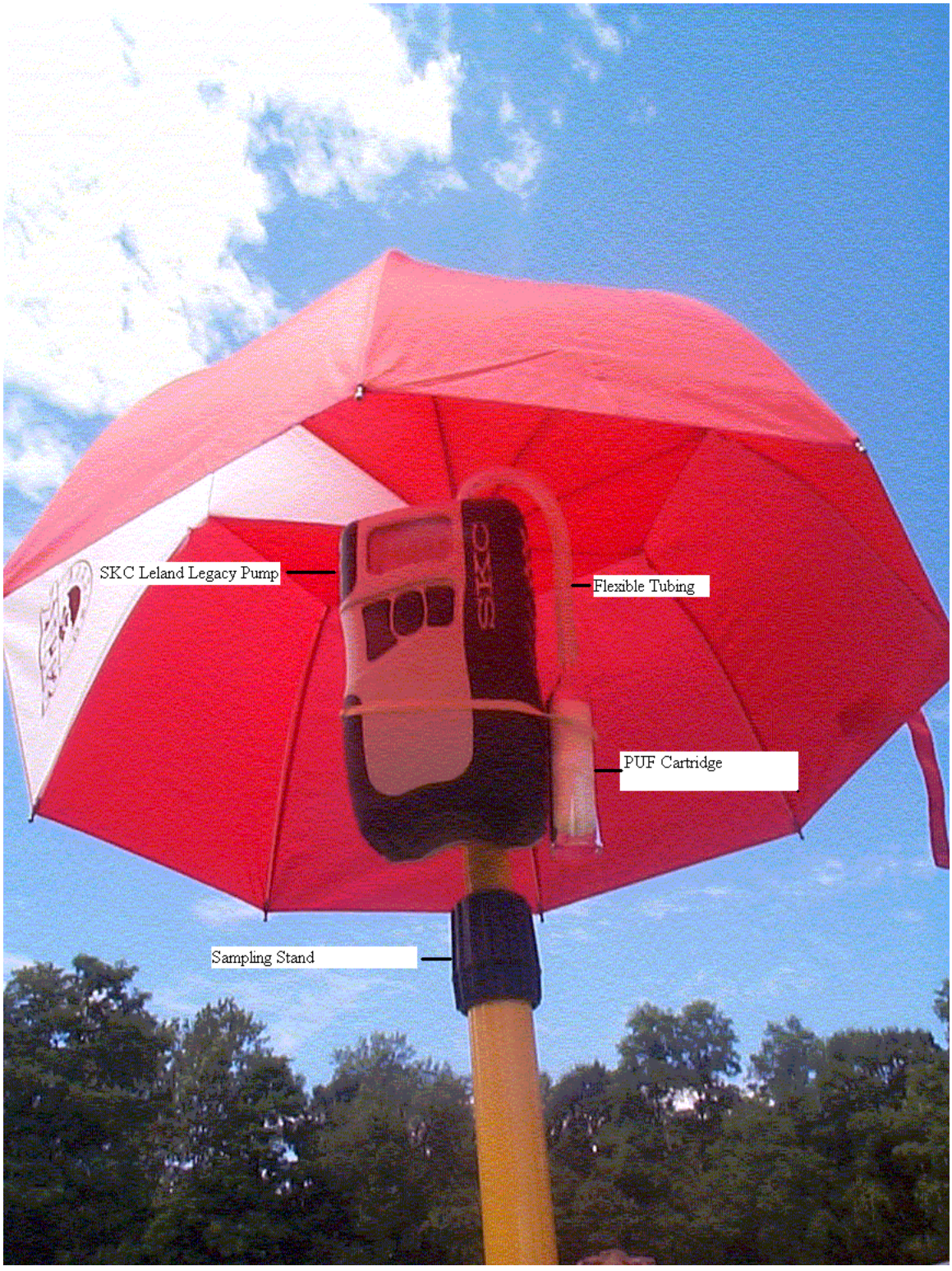

Figure 1. TO-10A Sampler Setup

APPENDIX 11
SOP FOR SAMPLING FOR VISUAL EMISSIONS

Standard Operating Procedures

Sampling for Visible Emissions

Revision 0
December 2006

_____
Author

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Technical Reviewer

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Project Manager

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1.0 PURPOSE AND OBJECTIVES

This SOP describes the procedures used to determine visible opacity of air emissions from applicable on-site sources in use at the GE Hudson remediation. Possible emission sources from this site include diesel engine emissions from equipment on the river (tug and push boats, dredging equipment on barges), on land (process facility heavy equipment, dump trucks, switching yard locomotive engine).

2.0 CERTIFICATION REQUIREMENTS – FIELD OBSERVERS

This document describes the sampling procedures to be used in the field by qualified observers, for determination of visible opacity in ambient air. A qualified observer is an individual who has met the requirements of Section 3.12.1 **Certification and Training of Observers**, from the ***Quality Assurance Handbook for Air Pollution Measurement Systems: Volume III. Stationary Source Specific Methods***, EPA-600/4-77-027b Feb. 1984, Section 3.12 *Method 9 – Visible Determination of the Opacity of Emissions from Stationary Sources*. **Only persons who have met the certification and training requirements identified in this Section should perform opacity measurements for this program.**

3.0 EQUIPMENT OPERATION

In order to observe visible emissions, the following equipment may be necessary if supporting meteorological data are not available for the observation period from the dedicated station in place at the processing facility.

3.1 Equipment

- Compass.
- Abney Level.
- Sling Psychrometer.

- Wind meter.
- Range Finder.
- Stop watch/timer.
- Visible Emission Observation (VEO) Forms.
- Camera.
- Hand-held GPS.

3.1.1 Compass

The compass is used to determine the direction of the emission point from the spot of where the observer stands and for determining the wind direction at the source.

1. Set the compass declination to the value corresponding to the appropriate geographical location.
2. Hold the compass base horizontal at all times.
3. Open the compass cover to about 45°, so that you can see the graduated bezel and long white index line the mirror.
4. Sight on the target using the “gun sight” on the edge of the cover.
5. Align the compass so that the black line on the mirror passes through the long index mark.
6. Once the compass needle and arrow are parallel, the compass base is level and the emission is in the “gun sight”, open the compass fully and read the bezel scale where it is aligned with the small index line adjacent to the mirror hinge and white triangle.
7. Record reading on data sheet (direction of source in relationship to observer).
8. Note the wind direction at the emission source and record the compass reading on the data sheet (this can be accomplished by noting the direction the plume slants or the direction leaves are blowing, etc.).

3.1.2 Abney Level

The abney level is used to determine the vertical viewing angle of the observer to the plume. Use the level as follows:

1. With the scale and bubble level upright, place the peephole eyepiece near your eye.
2. View the plume through the left side of the abney level view screen, and align the black cross hair with the observation point.
3. Rotate the bubble level until the mirror on the right side of the abney level view screen shows the reflection of the bubble with its center aligned with the cross hair.
4. Re-check that Steps 2 and 3 are carried out simultaneously.
5. Remove the abney level from your eye and read the scale for the angle of inclination. The angle is the value marked on the scale that aligns with the zero line marked on the pivot arm.

3.1.3 Sling Psychrometer

The sling psychrometer is used to determine the relative humidity (RH) during the observation. Relative humidity can be obtained from the on-site meteorological station (MET station) located at the processing facility. In the event that the relative humidity cannot be obtained from the MET station, follow the steps provided below to obtain the RH.

1. Open the psychrometer by pulling on each end.
2. Check that the wet-bulb wick is moist.
3. Hold the main body as a handle and spin the thermometers for approximately 90 seconds.
4. Stop their spin and quickly read the wet bulb thermometer value and then the dry bulb value.
5. Repeat Step 4 until two consecutive readings of the wet bulb and dry bulb scales do not vary from the previous values.

6. Slide the psychrometer halves back together so that the slide rule scales are visible on the side of the instrument.
7. Find the wet bulb value on the wet bulb scale and the dry bulb on the dry bulb scale.
8. Align the wet bulb with the dry bulb value. The arrow at the end of the inside scale will then be pointing at the correct relative humidity value.
9. Read and record the relative humidity on the field data sheet.

3.1.4 Wind meter

The hand held wind speed meter will provide the wind speed at the time of the observation when the wind speed cannot be obtained from the on-site MET station. To use the hand held wind meter follow the procedure presented below.

1. Hold the meter vertical with the wind blowing against the back of the unit.
2. Hold the middle of the unit so that the intake holes at the bottom rear are not covered.
3. Read the left hand low mph scale where the white ball in the center vertical tube aligns with the scale.
4. If the white ball goes to the top of the scale, cover the top of the red tube on the top of the meter with your finger.
5. Read the right hand high mph scale where the white ball aligns with the scale.
6. Because the wind speed fluctuates, the ball will range up and down the scale. Report the high and low values of the range on the field data sheet.

3.1.5 Hand-held GPS

The hand held GPS will be used to record the position of the observer and the piece of equipment being observed. The GPS will be operated in accordance with the manufacturers instructions. Coordinates will be recorded on the field data sheet.

4.0 PROCEDURE

The observer shall use the following procedures for visually determining the opacity of emissions.

4.1 Emission Source and Ambient Condition Data Gathering

Prior to making opacity measurements, the observer must document a description of the source being observed, the position of the observer relative to the source, and the ambient weather conditions the source is exposed to during the opacity measurement.

4.1.1 Emission Source Description

A description of the emission source must be made prior to performing the opacity measurement. The field data sheet (see Figure 1) includes fields that prompt the observer to provide the necessary information to describe the emission source. The completion of the data sheet is described in Section 4.3. Items to be recorded are:

- The vehicle or area of fugitive emission being observed.
- What the vehicle is doing (starting up, pushing barges, etc.) or the cause of the fugitive emission.
- The description of the emission point (can be a tail pipe or dust generated from a truck driving down a road, etc.).
- The height of the emission point relative to the ground/water surface. This can be an estimate of how high the vehicle exhaust plume or fugitive emission starts relative to the ground/water surface.

4.1.2 Position of Observer Relative to Source

A description of the position of the observer relative to the emission source must be made prior to performing the opacity measurement. The field data sheet includes fields that prompt the

observer to provide the necessary information to describe the emission source. The completion of the data sheet is described in Section 4.3. Items to be recorded are:

- Height of the emission source relative to the observer (how high is the vehicle exhaust pipe exit or the source of the fugitive emissions above the observers head). This height can be estimated by the observer.
- The distance the observer is from the source being observed. (This distance can be estimated or determined with a range finder).
- The position of the source relative to the observer. (This can be done using a compass).
- Whether the source is stationary or moving.
- Background behind emissions (clear sky, overcast, structures, vegetation, etc.)

4.1.3 Ambient Weather Conditions

The ambient weather conditions must be made prior to performing the opacity measurement. The field data sheet includes fields that prompt the observer to provide the necessary information to describe the emission source. The completion of the data sheet is described in Section 4.3. Items to be recorded are:

- Sky conditions (clear, cloudy, etc.).
- Wind Speed (obtain from MET station or hand held meter).
- Wind direction (obtain from MET station or compass).
- Temperature (obtain from MET station or other local weather station).
- Relative humidity (obtain from MET station or sling psychrometer).

4.2 Position

The observer will stand at a distance sufficient to provide a clear view of the emissions with the sun positioned within a 140° arch behind the observer. Also, the observer will position himself or herself in such that the line of sight is perpendicular to the source of opacity emissions. When

observing multiple locations, the observers' line of sight should not include more than one plume at a time.

4.3 Observations

Opacity observations shall be made at the point within the plume with the greatest opacity. The observer should not look continuously at the plume, since this can lead to eye fatigue, but instead should observe and evaluate the plume momentarily at 15-second intervals. Readings must be made to the nearest 5% opacity. Opacity will be determined as an average of 24 consecutive recorded observations. Equating actual in-field opacity observations to percent opacity measurements can only be performed by a trained observer who meets the certification requirements identified in Section 2.0

4.4 Field Record

The observer shall record the name of site, emission location, name, and date on the field data sheet (Figure 1). The time, distance to emission source, wind direction, wind speed, description of the sky conditions, and background are recorded on a field data sheet at the time opacity are started and completed.

The following are brief descriptions of the type of information that needs to be entered on the field data sheet.

1. Source Name – In this case it would be the site name.
2. Address –Physical location of site where observations are being made.
3. Process Equipment, Operating Mode – Brief description of process equipment and operating rate.
4. Describe Emission Point – Emission point location, diameter color for identification purposes.
5. Height Above Ground Level – Emission point height.
6. Height Relative to Observer – Indicate vertical position of observation relative to stack top.

7. Distance from Observer – Distance to emission point; estimate or determine by the range finder.
8. Direction from Observer – Direction to emission point; as determined using the compass.
9. Describe Emissions – Include plume behavior and other physical characteristics.
10. Emission Color – Gray, brown, white, red, black, etc.
11. Plume Type – Continuous, Fugitive, Intermittent.
12. Water Droplets Present – Determine by observation. (Note: Water droplet plumes are very white, opaque and dissipate rapidly)
13. If Water Droplet Plume – Attached (forms prior to exiting emission point) or detached (forms after exiting stack).
14. Point in Plume at Which Opacity was Determined – describe physical location in plume where readings were made.
15. Describe Background – Object that the plume is read against.
16. Background Color – Blue, white, green, etc.
17. Sky Conditions – Indicate cloud coverage by description (clear, scattered, overcast, etc.).
18. Wind speed – Obtain from on-site MET station or use wind meter to determine.
19. Wind Direction – Obtain from on-site MET station. Or use compass.
20. Ambient Temperature - °F or °C.
21. Relative Humidity – Obtain from on-site MET station or use the sling psychrometer when MET station not available.
22. Source Layout Sketch – Include wind direction, and other landmarks to identify location of emission point from observer location.
23. Draw North Arrow – Draw arrow using compass.
24. Sun Location Line – Point line of sight in direction of emission point, place pen upright on sun location line and mark location of sun when pen's shadow crosses the observers' position.
25. Comments – Any information not addressed else where on field data sheet.
26. Observation Date – Date observations conducted.
27. Start Time, Stop Time – Beginning and end times of observation period.

4.5 Data Reduction

Opacity shall be determined as an average of 24 consecutive observations recorded at 15-second intervals. For each set of 24 observations, calculate the average by summing the opacity of the 24 observations and dividing this sum by 24 (block average). Due to the mobility of the emission sources at this site, a single set of 24 observations will be sufficient for an opacity measurement of the emission sources at this site.

5.0 ADDITIONAL INFORMATION

Please refer to EPA 40 CFR 60, Method 9 for more information regarding visible emissions and ***Quality Assurance Handbook for Air Pollution Measurement Systems: Volume III. Stationary Source Specific Methods***, EPA-600/4-77-027b Feb. 1984, Section 3.12 *Method 9 – Visible Determination of the Opacity of Emissions from Stationary Sources*.

GE HUDSON REMEDIATION PROGRAM
Visible Emission Observation Form

TRC
Customer-Focused Solutions

SITE						Project Number				
ADDRESS			OBSERVATION DATE			START TIME			STOP TIME	
			SEC / MIN	0	15	30	45	SEC / MIN	0	15	30	45
CITY	STATE	ZIP	1					31				
PHONE	SOURCE ID NUMBER		2					32				
PROCESS EQUIPMENT	OPERATING MODE		3					33				
			4					34				
			5					35				
			6					36				
DESCRIBE EMISSION POINT			7					37				
START	STOP		8					38				
HEIGHT ABOVE GROUND LEVEL	HEIGHT RELATIVE TO OBSERVER		9					39				
START STOP	START STOP		10					40				
DISTANCE FROM OBSERVER	DIRECTION FROM OBSERVER		11					41				
START STOP	START STOP		12					42				
DESCRIBE EMISSIONS			13					43				
START	STOP		14					44				
EMISSION COLOR	PLUME TYPE: CONTINUOUS ☐		15					45				
START STOP	FUGITIVE ☐ INTERMITTENT ☐		16					46				
WATER DROPLETS PRESENT	IF WATER DROPLET PLUME		17					47				
NO ☐ YES ☐	ATTACHED ☐ DETACHED ☐		18					48				
POINT IN THE PLUME AT WHICH OPACITY WAS DETERMINED			19					49				
START	STOP		20					50				
DESCRIBE BACKGROUND			21					51				
START	STOP		22					52				
BACKGROUND COLOR	SKY CONDITIONS		23					53				
START STOP	START STOP		24					54				
WIND SPEED	WIND DIRECTION		25					55				
START STOP	START STOP		26					56				
AMBIENT TEMP		RH percent	27					57				
START STOP			28					58				
Source Layout Sketch	Draw North Arrow		29					59				
X Emission Point			30					60				
Sun Wind Plume and Stack			OBSERVER'S NAME (PRINT)									
140°			OBSERVER'S SIGNATURE					DATE				
Sun Location Line			ORGANIZATION									
COMMENTS			CERTIFIED BY					DATE				
			VERIFIED BY					DATE				

Figure 1

APPENDIX 12
SOP FOR ODOR (H_2S) MONITORING - TEDLAR® BAG SAMPLING/JEROME METER

Standard Operating Procedures

Performing Odor Sampling and Hydrogen Sulfide Analysis Using Tedlar Bag Collection and the Jerome Hydrogen Sulfide Analyzer

Revision 0
December 2006

Author

Technical Reviewer

Project Manager

QA Officer

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1.0 PURPOSE OF SOP

This SOP describes the procedures used to measure odor as hydrogen sulfide. The SOP details the collection of a one hour integrated sample of ambient air using a Tedlar bag and analysis of the sample using a Jerome Hydrogen Sulfide Analyzer. Alternatively, if the Jerome meter is in the immediate vicinity of the odor observation the analyzer can be used as a direct instrument without use of the Tedlar bag sampling technique.

2.0 EQUIPMENT DESCRIPTION

Ambient air is pumped into a Tedlar bag at a prescribed flow rate over an approximately one hour time period to yield an integrated ambient air sample. A SKC Universal Sample Pump (or equivalent technology), a constant flow air sampler, will be used to collect the one hour integrated ambient air sample. The ambient air sample will be attached to the Jerome Hydrogen Sulfide Analyzer (or equivalent technology) using flexible tubing for analysis. The Jerome Hydrogen Sulfide Analyzer is an ambient air analyzer with a range of 0.003 ppm (3 ppb) to 50 ppm (parts per million).

3.0 EQUIPMENT AND MATERIALS

3.1 Tedlar Bag

A 10 liter Tedlar bag (see Figure 1 for an example) with a non-metallic valve. The valves should be constructed of polypropylene or Teflon.

3.2 ¼-Inch Tygon Tubing

Flexible tubing to be used to connect the Tedlar bag to the SKC pump for collection of ambient air and\or connection of the Tedlar bag to the Jerome Hydrogen Sulfide Analyzer for analysis.

3.3 Continuous-Flow Sampling Pump

The pump must be capable of pulling ambient air at a flow rate of approximately 0.10 - 0.15 liters per minute (LPM) to obtain a total sample volume of 6 - 9 liters over a one-hour period. A SKC Universal Sample Pump (or equivalent technology) (see Figure 2), a constant flow air sampler will be used to collect the ambient air sample. The SKC Universal sample pump will be set to the low flow setting which will allow a 0.1 liter/minute flow rate. The sampler should be set to operate for a one-hour sampling period (see Section 4.2.4).

3.4 Hydrogen Sulfide Analyzer

The hydrogen sulfide analyzer must be able to measure hydrogen sulfide in ambient air at levels of 0.01 ppm (parts per million). The Jerome Hydrogen Sulfide Analyzer (Figure 3) is an ambient air analyzer with a range of 0.003 ppm to 50 ppm (parts per million). When sampling, an internal pump pulls ambient air over a gold film sensor for a precise period. The sensor absorbs the hydrogen sulfide and determines the amount absorbed and displays the measured concentration of hydrogen sulfide in ppm. The analyzer's microprocessor automatically re-zeroes the digital meter at the start of each sample cycle and freezes the meter reading until the next sample is taken, eliminating drift between samples.

3.5 Jerome Hydrogen Sulfide Analyzer Zero Air Filter

The Zero Air Filter removes mercury vapor, mercaptans, and hydrogen sulfide from the air sample. Readings with the filter installed should be near zero. The Zero Air Filter is used to equilibrate the unit to ambient air temperature to limit biases to measured values introduced by air warmer or cooler than the analyzer temperature. Also, the Zero Air Filter is used to identify contamination. If the readings do not approach near zero when installed, contamination may be present.

3.6 Dry-Cell Calibrator

A dry cell calibrator certified NIST traceable to be used to set the pump flow rate and verify the sample flow rates. A Bios Primary Flow Calibrator will be used.

3.7 Calibration Functional Test Module

The functional test module includes a permeation tube containing hydrogen sulfide. The module will produce a hydrogen sulfide gas at a concentration of 250 ppb (0.25 ppm) ± 20% that will be introduced into the Jerome analyzer as a calibration check.

4.0 SAMPLE COLLECTION

Odor sampling will be performed as a result of either on-site worker notifications of odors or odor complaints received from the public in the immediate vicinity of the remediation zone.

4.1 Sample Location Determination

Based on the information in the odor complaint, determine the possible source of the odor. Place Tedlar bags and sampling pumps in up-wind and down locations from the possible source. Use the on-site meteorological station located at the processing facility to determine the wind direction relative to the possible odor source.

4.2 SKC Universal Sample Pump Operation

Pump calibrations should be performed daily prior to commencement of remediation. In this manner they can be rapidly deployed from multiple locations as needed in response to odor events/observations.

4.2.1 Initial Setup

1. Ensure the pump is set for low flow: Remove the cap screw covering the regulator valve and turn the exposed screw **counter-clockwise** 4 or 5 turns. Replace the cap screw. The pump is now set for low flow.
2. Insert positive pressure attachment: Remove the cap screw covering the pump exhaust. Screw in the positive pressure adaptor. This adaptor will allow the pump to fill the Tedlar bag with ambient air.

4.2.2 Setting Flow Rate

1. Connect ¼ inch tygon tubing to the pump intake.
2. Start the pump using the on/off switch.
3. Connect the dry-cell calibrator to the intake end of the ¼ inch Tygon tubing. Adjust the flow using the flow adjust screw until the flowmeter reads the desired flow rate (see Section 4.3).
4. When the flow rate is set, press Flow and Battery Check to place the pump in Hold. Disconnect the calibrator.

4.2.3 Sampling

1. Following flow rate setting, open the Tedlar bag valve and connect the ¼ tygon tubing to the bag for sample collection.
2. While the LCD displays HOLD, start sampling by pressing Start/Hold. Record the start time. At the end of the sampling period, press Start/Hold and record the stop time. Verify the flow rate at the end of the sampling period (see Section 4.3).
3. At the end of the sampling period, close valve on the Tedlar bag and disconnect the Tygon tubing.
4. Transport sample to field office/laboratory for analysis.

4.2.4 Programming Delayed and Intermittent Sampling

1. To enter Delayed Start Mode: From Hold, press Set-up. Enter the number of minutes delay (up to 9999) before the sampling period begins by pressing Digit Select and Digit Set. Digit Select advances the flashing digit and digit set increases the value of the flashing digit.
2. To enter Sample Period Mode: Press Mode. Press Digit Select and Digit Set to enter the sampling time period in minutes. **Note:** The sample period is the total period in which sampling is performed and NOT the pump run time.
3. To enter Pump Period Mode: Press Mode. This is the actual running time of the pump. Use Digit Select and Digit Set to enter the pump run time.

Options during Sampling

1. Pause – Pause (shutdown) the pump by pressing Start/Hold. All timing data will freeze. To resume sampling, press Start/Hold; timing data will resume.
2. Flow or Battery Fault Shutdown – During restricted flow or low battery conditions, the sampler will shutdown. HOLD will display on the LCD and timing functions will pause. LO BATT or FLOW FAULT will display on the LCD. To restart from flow fault, correct the blockage and press Start/Hold. If LO BATT is displayed, recharge battery.
3. Display Times – Elapsed sampling period is continuously displayed on the LCD. Press and hold Pump Run Time to display pump run time. Press and hold Total Elapsed Time, to display total elapsed time, including delayed start time.

4.3 Sample Pump Calibration

Flow rates are checked twice a day (before and after sampling). If pumps are not used to collect a sample on any given day a single calibration prior to the start of remediation is satisfactory.

4.3.1 Pre-sample Calibration

1. Connect the pump inlet to a calibrator (i.e., primary source Dry-cell calibrator) with ¼ inch Tygon tubing.
2. If the calibrator reads a higher flow rate than the pump is set for, adjust the pump until they are in agreement (within ±20%). If the calibrator reads a lower flow rate, adjust the pump until they are in agreement (within ±20%).
3. Record the flow rate on the sample data sheet (Figure 4).

4.3.2 Post-Sample Calibration

1. Close the inlet valve to the Tedlar bag.
2. Connect the pump inlet to a calibrator (i.e., primary source Dry-cell calibrator) with ¼ inch Tygon tubing.
3. Measure and record the flow rate from the dry-cell calibrator. Calculate the flow rate percent difference (%D) from the initial flow rate from the final flow rate. If the %D is greater than 20%, flag the data as estimated due to a non-constant flow rate.

5.0 SAMPLE ANALYSIS

Tedlar bags containing ambient air samples will be brought to the on-site field trailer (or other suitable location) for hydrogen sulfide analysis using the Jerome Hydrogen Sulfide Analyzer. Tedlar bag samples will be analyzed for hydrogen sulfide within one hour from the completion of sample collection.

5.1 Jerome Hydrogen Sulfide Analyzer Operation

In order to operate the Jerome Hydrogen Sulfide Analyzer, it is necessary to understand the LCD codes on the analyzer.

5.2 LCD Codes

LCD Codes	Explanation
000	Ready to Sample
.000	No hydrogen sulfide reading
.8.8.8	Sensor saturated-regeneration needed
.H.H.H	Sensor regeneration in progress (.H.H.H flashes)
.L.L.L	Re-zero needed
.P.P.P	Power cord needed or low line power
.LO BAT	Recharge batteries
.E.E.E	Same as LO BAT, automatically shuts off
.HL	Very high concentration has been detected.
During Sampling	
.-	0-25% sensor saturation
.--	25-50% sensor saturation
.---	50-75% sensor saturation
-.---	75-100% sensor saturation
During Sampling, Survey Mode	
-	Survey Sampling (- sign flashes continuously)

5.3 Daily Operation

Before each day's use, perform the following steps to verify proper instrument operation:

1. Press the power ON button.
    a. The digital meter displays 000.
    b. Recharge or replace battery pack if LO BAT indicator remains on.
    c. Allow 1-minute warm up time for stabilization.
2. Use the Zero Air Filter to equilibrate the instrument to ambient air temperature.
    a. Install the Zero Air Filter in the analyzer's intake.
    b. Sample continuously until the reading is stabilized.
3. Perform sensor regeneration. (See Section 5.4)
4. 30 minutes after sensor regeneration is complete, zero the instrument (Section 5.4)
5. Press the SAMPLE button.
    a. During the sample cycle, the digital meter displays bars (-, --, or ---), to indicate the amount of sensor saturation.
6. At the end of sample cycle, read the digital meter.

a. The number shown on the digital meter is the hydrogen sulfide concentration in ppm.
b. This value remains on the display until the next sample is taken.
c. The digital meter automatically zeroes at the start of each sample.

7. At the end of the day, perform sensor regeneration. (See Section 5.4)

5.4 Sensor Regeneration

Sensor regeneration is needed to clear the sensor of any accumulated hydrogen sulfide. This procedure should be done:

- At the beginning of each day.
- During the day when the instrument becomes saturated.
- At the end of the day.

To perform the sensor regeneration, use the following steps:

1. Attach the power cord to the sensor and plug it into the AC power. This is required to thermally regenerate the sensor.
2. Press the power ON button.
3. Press the REGEN button. The digital meter flashes .H.H.H for the duration of the 10-minute cycle and displays .0.0.0 when the cycle is completed.
4. **DO NOT INTERRUPT CYCLE**
5. A minimum 30-minute wait after the sensor regeneration cycle is complete assures maximum sample accuracy. When the sensor regeneration is complete, press ZERO and adjust the ZERO ADJUST pot until 0 appears on the display. Install the zero air filter in the intake and take several samples or lock the instrument to survey mode (See Section 5.2). After approximately 1 minute, stop sampling and check the ZERO. Adjust to 0. Repeat sampling through the zero air filter until reading remains on 0.

5.5 Zero Adjust

1. To ensure that air entering the analyzer is clean, install the zero air filter in the instrument's intake and sample until the readings stabilize.
2. While pressing ZERO button, turn the ZERO ADJUST potentiometer using the trimmer tool until the digital meter reads 0.
    a. If the LCD reads H, turn the ZERO ADJUST counterclockwise.
    b. If the LCD reads L, turn the ZERO ADJUST clockwise.
3. Press the power OFF button and disconnect the power cord.
4. The analyzer is ready for sampling. (NOTE: The analyzer is intended for vapor use only. Moisture or liquids drawn into the instrument can damage the sensor and flow system).

5.6 Hydrogen Sulfide Measurement

5.6.1 Standard Operation Mode

The standard operation mode is used for optimum accuracy.

1. Press the power ON button.
    a. The LCD displays 000.
    b. Disregard the LCD's initial momentary readings.
    c. Recharge or replace the battery pack if the LO BAT indicator REMAINS ON.
2. Allow a 1-minute warm up before beginning the next step to ensure the analyzer's electronics have stabilized.
3. Connect ¼ inch Tygon tubing to the valve of the Tedlar bag and open the valve. Connect the other end of the ¼ inch Tygon tube to the inlet of the analyzer.
4. Press the SAMPLE button.
    a. During the sampling cycle, the bar shown on the LCD indicates the current percentage of sensor saturation.
    b. The length of the sample cycle depends on the concentration of hydrogen sulfide.

Range	Concentration	Response Time	Accuracy at Mid-Range
0	0.001 to 0.099 ppm	30 seconds	±0.003 ppm at 0.050 ppm
1	0.10 to 0.99 ppm	25 seconds	±0.03 ppm at 0.50 ppm
2	1.0 to 9.9 ppm	16 seconds	±0.3 ppm at 5.0 ppm
3	10 to 50 ppm	13 seconds	±2 ppm at 25 ppm

5. At the end of the sampling cycle, read the LCD.
    a. The number shown on the digital meter is the hydrogen sulfide concentration in ppm.
    b. As the instrument auto-ranges, the decimal point moves to the correct position to show the concentration.
    c. The value remains displayed until the next sample is taken. The digital meter will then automatically zero before displaying the next sample value.
    d. When elevated readings are detected:
        - Confirm the reading by taking an additional sample.
        - Install the zero air filter and verify that the readings reduce to zero or very near zero.
        - Remove the filter and sample the location again to verify that elevated readings do exist.
    e. When the sensor is completely saturated, the LCD displays .8.8.8 instead of a value. No further sampling is possible until the sensor regeneration is performed. (See section 4.3).
6. Repeat Steps 4 and 5 an additional two times to get three hydrogen sulfide results per Tedlar bag sample. Report the average of the three results for each sample location or bag sample.
7. Press the power OFF button when not in use.

5.6.2 Survey Mode

If direct measurement of the ambient air without prior Tedlar bag sample collection is required, the survey mode can be used. The survey mode takes samples every 3 to 20 seconds automatically. The length of time varies with the hydrogen sulfide concentration. After the survey mode is activated, the analyzer samples continuously.

1. Press the power ON button.
    a. The digital meter displays 000.
    b. Disregard the LCD's initial momentary readings.
    c. Recharge or replace the battery pack if the LO BAT indicator REMAINS ON.
2. Allow a 1-minute warm up before beginning the next step to ensure the analyzer's electronics have stabilized.
3. Lock the instrument in the survey mode.
    a. Hold the SAMPLE button down until the sensor status indicator bar begins flashing on the display.
    b. Press the ZERO button, then release the SAMPLE button.
    c. The pump should continue to run and display should update every survey cycle.
4. The instrument remains in survey mode until one of the following occurs:
    a. The sensor is saturated.
    b. A LO BAT (low battery) signal appears.
    c. An HL (high hydrogen sulfide level) is encountered.
    d. The instrument is turned off.
5. Press the power OFF button to end the survey mode. (NOTE: Approximately 100 samples at 0.5 ppm may be taken before the sensor saturates and regeneration is required.)

5.7 Calibration

The Jerome meter's gold film sensor should be calibrated approximately every year. This is a factory calibration and needs to be sent back to the manufacturer for calibration.

5.7.1 Calibration Check

The Jerome Hydrogen Sulfide Functional Test Module provides verification that the Jerome Hydrogen Sulfide Analyzer is within specifications. This test should be done to verify proper instrument operation when unexpected readings are obtained in normal sampling; as part of a weekly maintenance routine and to determine if analyzer calibration is necessary.

The Function Test Module includes a permeation tube containing hydrogen sulfide. When activated, the test module releases H_2S from the permeation tube at a specific, known concentration. The H_2S flows over the gold film sensor of the Jerome analyzer, which then measures the amount of exposure to the gas. The flow rate and temperature of the release is factory set to provide a concentration of approximately 0.250 ppm ± 20%. This is then compared to the reading on the Jerome analyzer. If the H_2S level shown on the analyzer's display falls within the expected range, the instrument is functioning properly. If the level is not in the expected range, it should be returned to the factory for calibration. The calibration check should be performed weekly when odor measurements are taken.

6.0 MAINTENANCE

6.1 SKC Universal Sample Pump

Maintenance on the Universal Sample SKC pump consists primarily of cleaning the filter/trap. The pump is fitted with a filter/trap inside an intake port housing. The filter should be visually checked to assure that it does not become clogged. If maintenance is necessary, the following procedures should be followed:

1. Clean dust and debris from around the filter housing.
2. Remove the four screws and the front filter housing.
3. Remove and discard the filter membrane and O-ring.
4. Clean the filter housing.
5. Insert a new filter membrane and O-ring.
6. Reattach the front filter housing.

6.2 Jerome Hydrogen Sulfide Analyzer

6.2.1 Flow System

The analyzer's flow system must be properly maintained. The systems' maintainable components are the intake filter (0.25 inch fritware), 2 scrubber filters and connecting tubing.

6.2.1.1 0.25 inch Fritware Filter

Replace the 0.25 inch fritware filter once each week or as needed.

1. Unscrew and remove the intake.
2. Push the old fritware filter disc out of the intake with trimmer tool.
3. Avoid touching the new fritware disc with fingers. Use tweezers to insert the new fritware.
4. Use the blunt end of the trimmer tool to seat the fritware disc firmly against the inner ledge of the intake.
5. Screw the intake back on the analyzer.

6.2.1.2 Internal Filters

Replace the internal filters after 6 months of use or as needed.

1. Press the power OFF button and unplug the power cord.
2. Remove the 2 side screws from the intake end of the instrument and open the case.
3. Carefully disconnect the Tygon tubing from both ends of the filters and discard the old filters.
4. Connect the new filters to the Tygon tubing, ensuring all straight hose barbs point toward the intake/pump corner of the case and elbow hose barbs point toward the sensor housing. Push the Tygon as far as it will go onto the filter fittings.
5. Push the filters into the mounting clips.

6. Remove any crimps or twists in the tubing and ensure that tubing connections are secure. If the tubing is loose, readings may not be accurate. Replace any tubing that has deteriorated due to heat and/or use.
7. Close the case and replace the screws.

Dispose of all filters in accordance with state and federal environmental regulations.

6.2.2 Changing the Fuse

If the instrument reads .P.P.P when the instrument is connected to AC power or when REGEN is pressed or if the battery will not charge the fuse may need to be replaced.

1. Locate the power receptacle on the rear of the instrument.
2. Insert a small screwdriver in the slot, located in the power receptacle, and gently slide the fuse compartment out.
3. If the fuse in the open-sided clip is open, remove and discard it.
4. Replace the discarded fuse with the spare fuse located in the slide-out spare fuse compartment.
5. Replace the fuse compartment in the power receptacle.

6.2.3 Battery Operation

Charging the Battery

1. Press the power OFF button.
2. Connect the AC power cord between the analyzer power receptacle and an AC power source without damaging the battery pack.

Note: The battery will recharge in approximately 14 hours.

Maintaining Maximum Battery Life

To maintain maximum battery life, follow the following steps:

1. At least once a month wait until LO BAT appears on the digital meter before recharging the battery pack.
2. Charge the battery pack when the LO BAT indicator comes on. Excessive discharge can damage the battery pack.
3. Before storing the analyzer verify the power is OFF.

Note: When the batteries fail to hold a charge they should be replaced. The battery life is approximately 1 year, depending on the number of charge and discharge cycles.

Replacing the Battery Pack

1. Press the power OFF button.
2. Unplug the power cord.
3. Remove the 2 side screws from the intake end of the instrument and open the case lid.
4. Disconnect the battery connector from the board.
5. Loosen the 2 captive screws holding the batter bracket and remove the bracket.
6. Remove the old battery pack and replace with a new battery pack.
7. Replace the battery bracket and tighten the captive screws.
8. Connect the new battery connector to the board.
9. Close the case and replace the 2 side screws.

7.0 ADDITIONAL INFORMATION

7.1 SKC Universal Pump

A more detailed equipment manual is available from SKC (www.skcinc.com) and is located in the site office for any other questions about the Universal Sample Pump.

7.2 Jerome Hydrogen Sulfide Analyzer

A more detailed equipment manual is available from Arizona Instruments LLC (www.azic.com) and is located in the site office for any other questions about the Jerome Hydrogen Sulfide Analyzer.

Figure 1. Example Tedlar Bag

Figure 2. SKC Universal Pump.

Figure 3. Jerome Hydrogen Sulfide Analyzer.

ODOR SAMPLING DATA SHEET

Site:		**Sampler Location**	
Project No.:		**Sampler Serial No.:**	
SETUP:		**RECOVERY:**	
Date:		**Date:**	
Technician:		**Technician:**	
Sample ID:		**Sample ID:**	
Start Time:		**Stop Time:**	
Flow Rate (LPM):		**Flow Rate (LPM):**	

SAMPLE COLLECTION CALCULATIONS

Flow Rate RPD (%)		((setup-recovery)/((setup + recovery)/2) * 100)
Ave. Flow Rate (LPM)		((setup + recovery)/2)
Sample Time (min)		(stop time – start time)
Sample Vol. (L)		(ave. flow rate (LPM) * sample time (min))

SAMPLE ANALYSIS

Analyzer Serial No.: _____

Measurement No.:	**H_2S Conc. (PPM)**
1	
2	
3	
Ave:	

Figure 4. Sample Data Sheet.

APPENDIX 13
SOP FOR CONTINUOUS FLOW MONITORING (INCLUDES CONTINUOUS FLOW MONITORING OF DISCHARGE FROM PROCESSING FACILITY)

ARCADIS

Standard Operating Procedure: Continuous Flow Monitoring

I. Scope and Application

This Standard Operating Procedure (SOP) applies to the measurement of flow rate of the processing facility discharge, during Phase 1 of the Hudson River remedial action. An

electromagnetic flow meter will be used to measure the flow rate, which will be measured on a continuous basis.

II. Personnel Qualifications

Field sampling personnel will have current health and safety training, including 40-hour Occupational Safety and Health Administration (OSHA) Hazardous Waste Operations (HAZWOPER) training and an annual refresher course, site supervisor training, and site-specific training, as needed. In addition, Arcadis field sampling personnel will be versed in the relevant SOPs and possess the skills and experience necessary to successfully complete the desired fieldwork.

III. Equipment List

The following materials, as required, will be available during field measurement of flow rate:

- Health and safety equipment, as required by the site Health and Safety Plan (HASP; Parsons 2008)
- Sparling TigermagEP™ Model FM656 Obstructionless Electromagnetic Flowmeter
- Appropriate power supply
- Appropriate forms and field book

IV. Cautions

Follow health and safety procedures outlined in the site HASP (Parsons 2008).

V. Health and Safety Considerations

Follow health and safety procedures outlined in the site HASP (Parsons 2008).

VI. Procedure for Measuring Flow

The electromagnetic flow meter will be installed, and the flow measured, according to the manufacturer's instructions (Attachment 1).

VII. Calibration and Maintenance

The electromagnetic flow meter will be calibrated and maintained, to the extent necessary, following the manufacturer's instructions (Attachment 1). Information will be recorded in the field notebook.

VIII. Waste Management

Waste generated during flow monitoring will be placed in labeled 55-gallon drums onsite.

IX. Data Recording and Management

The electromagnetic flow meter will be equipped with a transmitter. Instantaneous and totalized flow data may be accessed locally at the transmitter by the operator. The transmitter will also be equipped with an analog output connection from where the flow data will be sent to and recorded by the Water Treatment Plant control system computer. The average, maximum, and total flow will be recorded on the Processing Facility Discharge Monitoring Reporting Form (Figure 2-19) on a weekly basis for the previous week.

X. Quality Assurance

Not applicable.

XI. References

Parsons, 2008. Phase 1 Remedial Action Health and Safety Plan, Hudson River PCBs Superfund Site. Prepared for General Electric Company, Albany, NY. August 2008.

Attachment 1

Flow Meter Operation & Maintenance Manual

TIGERMAG EP™

INSTALLATION OPERATION & MAINTENANCE MANUAL

Issue Date: March 2002

SPARLING

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cont'd.

1.0 General

1.1 Measuring System

The Sparling TigermagEP™ Model FM-626, FM627, FM-656 and FM-657 flowmeters are obstructionless devices for monitoring the volumetric flow of conductive liquids in full closed pipes.

The flowmeter consists of a sensor (wafer or flanged) with a nonmagnetic liner, sensing electrodes and a measuring transmitter.

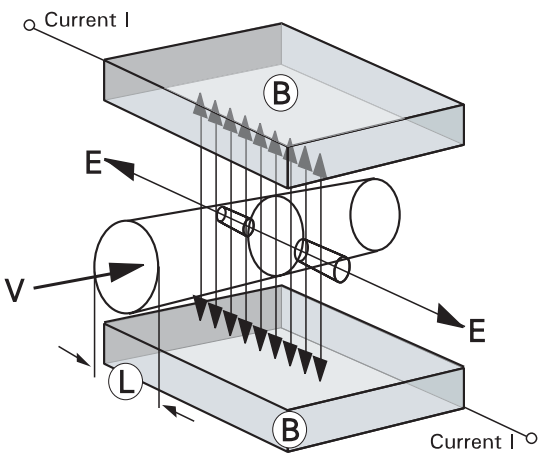
1.2 Operating Principle

Operation is based on Faraday's Law of Magnetic Induction. An electrically conductive liquid flowing through a magnetic field induces a voltage which is perpendicular to this field and to the direction of the flow. This voltage is proportional to the average flow velocity. See Figure 1.1.

The mathematical formula describing Faraday's law reads:

$E = B \times L \times V$

E = Induced voltage
B = Magnetic field intensity (flux density)
L = Distance between the electrodes (pipe diameter)
V = Average flow velocity of liquid



Measuring Principle
Figure 1.1

1.3 Application to Magnetic Flow Measurement

In a magnetic flowmeter the liquid acts as a moving conductor as it flows through the pipe. The induced voltage (E) in the liquid is measured by two sensing electrodes mounted opposite each other in the meter sensing head.

The length of the conductor is equal to the distance between sensing electrodes and also the internal diameter (D) of the pipe. The flux density is proportional to the coil current (I), times a constant (k). The above formula can be restated as follows:

$E = I \times k \times D \times V$

$$V = \frac{\text{flow}}{\text{cross sectional area}} = \frac{Q}{A}$$

$$E = \frac{Q \times I \times 4 \times k}{D^2}$$

Note that if I is held constant, E is proportional to Q or *the induced voltage is directly proportional to the average flow rate* (V).

1.4 Interference

1.4.1 Electrochemical Interference

The signal voltage is measured by two electrodes. Galvanic elements form on the surface areas between the ion-conducting liquid and the metal electrodes. The polarization voltages which result are dependent on temperature, pressure, and the chemical composition of the electrodes and liquid. These are direct voltages which cannot be predicted and which can be different at each electrode. The signal voltage must be separated from the interference direct voltage. Proper grounding eliminates these unpredictable voltages from interfering with the signal voltage.

1.4.2 Induction Interference (Quadrature)

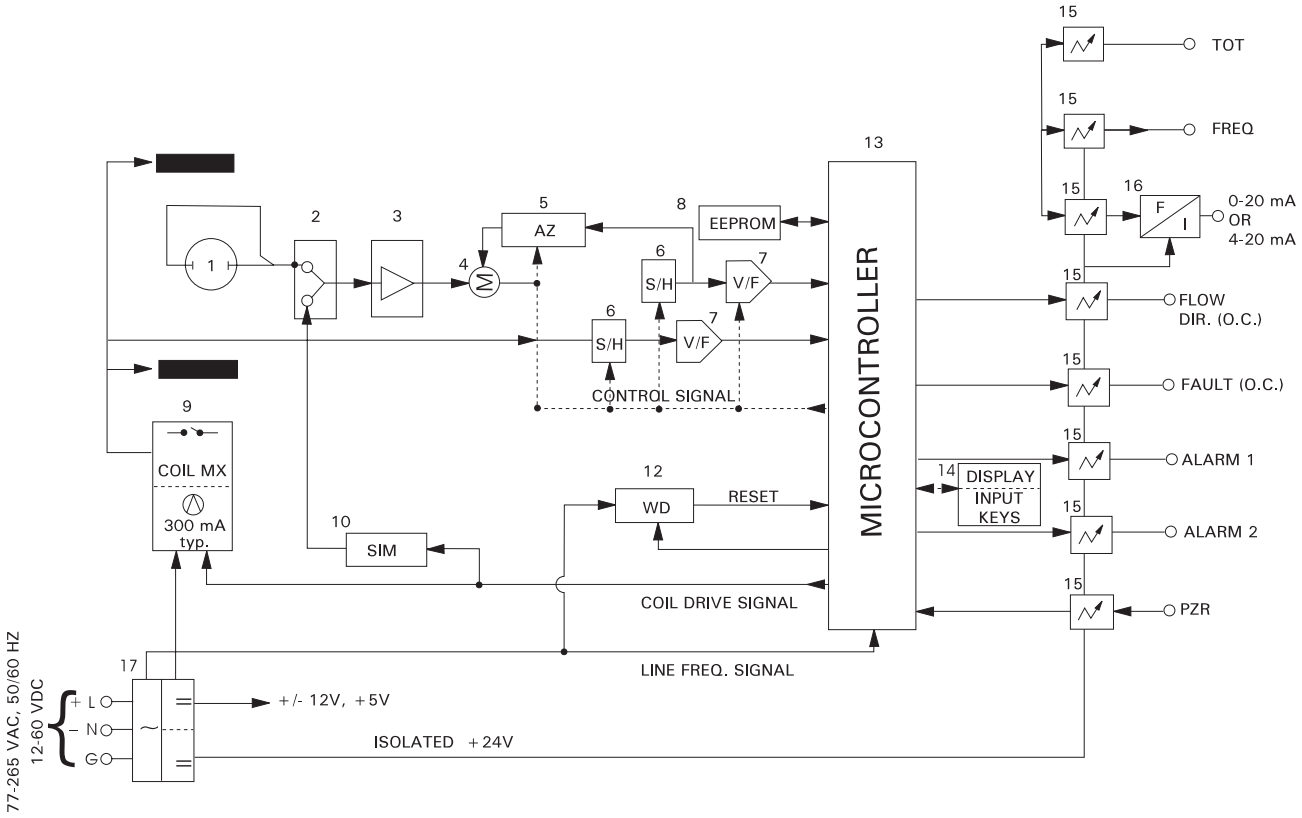
Electrode cables connect the electrodes with the meter electronics. Because these cables must run within the magnetic field, a voltage is induced which is proportional to the rate of change of the magnetic field strength. The meter design minimizes the length of conductor within the magnetic field in order to keep the value of this interference as low as possible.

1.4.3 Other Interference Voltages

Pipes and the liquids within them are often used as a conductor for electrical grounding. This creates a voltage potential between electrodes which can be high relative to the signal voltage. Proper grounding of the flowmeter to the liquid is necessary to achieve correct meter operation. Grounding rings should be installed if the flowing medium has a voltage potential, if piping is nonconductive (plastic or lined) or if conductivity is below 20 micromhos/cm. See Section 3.8 – Grounding.

1.5 System Operation

The Sparling TigermagEP™ uses the autozeroing, bipolar, pulsed-DC measuring technique. The circuitry (Fig. 1.2) energizes the coil with 300 mA typical current at a frequency of up to 100 Hz. The signal generated at the electrodes is measured near the end of each measuring cycle to eliminate the capacitive effects of coatings. The Hi-Z ($10^{12}\,\Omega$) input impedance eliminates the resistive effects of electrode coatings. The field current alternates to a positive and negative state and the two measured signals are averaged to eliminate the effect of a zero offset—this is the auto-zeroing feature.



1. Measuring Sensor
2. Electrode Cable PCB
3. Input Amplifier
4. Summing Point
5. Autozero Circuit
6. Sample and Hold
7. Voltage to Frequency Converter
8. Nonvolatile E²PROM (constants)
9. Coil Current Multiplexer
10. Built-in Simulator
11. Adjustable Empty Pipe Detection (in software)
12. Watchdog Timer
13. Microcontroller
14. LCD Display with Hall-Effect Switches
15. Optocouplers
16. Frequency to Current Converter
17. Power Supply Section

Block Diagram
Figure 1.2

1.6 Construction

1.6.1 Sensor

The **FM626** is a wafer style meter. It is available with either a ceramic or optional *Tefzel*® liner. The *Tefzel*® liner is rotamolded onto a stainless steel sensor tube. Both liners are press-fit into a carbon steel housing. The **FM627** is a wafer style meter. The flow sensor housing is made of steel with a polyurethane liner. Sensor coils are completely encapsulated in polyurethane. The **FM656** flow sensor is a welded fabrication of 304 stainless steel, fitted with two carbon steel flanges. The flow sensor contains a nonconductive liner of ceramic, polyurethane, *Tefzel*®, hard rubber, soft rubber, or neoprene. The **FM657** flow sensor housing is made of steel with a polyurethane liner. Sensor coils are completely encapsulated in polyurethane. All TigermagEP™ meters are rugged, waterproof assemblies capable of handling a wide range of highly corrosive and abrasive liquids.

Fused platinum electrodes, standard on ceramic meters from 0.1" to 2", require no O-rings, eliminating the possibility of leaking. Platinum is suitable for nearly all conductive liquids. The electrodes in all other liners are self-sealing.

All internal cavities of the FM-626 sensor housing are filled with a high temperature silicone potting compound to prevent the possibility of moisture damage and to avoid the possibility of collection of explosive gases.

▼ WHEN PROPERLY CONNECTED WITH LIQUID-TIGHT CONDUIT, THE FM626 AND FM627 REMOTE FLOW SENSOR WILL WITHSTAND ACCIDENTAL SUBMERGENCE. (SEE FIG. 3.16 ON PAGE 25).

1.6.2 Integral Transmitter

The transmitter is mounted on the meter body and housed in a NEMA-4X and NEMA-7 enclosure that is approved by CSA and Factory Mutual. The power and signal electrical connections are made in a separate section of the housing which is isolated from the electronics.

1.6.3 Remote Transmitter

The transmitter is housed in a NEMA-4X enclosure some distance away from the meter body.

Remote mounting is recommended where pipe vibration is excessive or when flooding is possible.

Remote mounting ***for the FM626 and FM656 is REQUIRED*** when high process temperatures exist at high ambient temperatures (above 212° F/100° C). The FM627 and FM657 should not be installed where process temperatures will exceed 180° F.

The optional remote mounting kit includes interconnecting cable between the sensor and transmitter enclosure. The standard interconnecting cable length is 15 feet. Shorter or longer cables should be specified when ordered from the factory. The cable may be shortened in the field.

CAUTION

DO NOT MAKE CONNECTIONS WHILE POWER IS APPLIED.

Disconnect Power Before Proceeding

1.7 Specifications

Power Requirements	See Nameplate
Fuses	Slo-Blo (12-60 Vdc) ..... 2.0 amp Slo-Blo (77-265 Vac) ..... 1.0 amp Spare fuse provided on connector PCB.
Wire Size	Power ..... 16 AWG; 14 AWG Max Signal ..... 18 AWG
Ground Cable	Third wire ground of power cable
Accuracy (Frequency Output)	0.1" - 0.5" 0.5% of span (1-3 fps) 0.25% of span (≤ 50% of span) (3-33 fps) 0.5% of flow rate (≥ 50% of span) (3-33 fps) 1.0" - 48.0" 0.25% of span (≤ 50% of span) (1-3 fps) 0.5% of flow rate (≥ 50% of span) (1-3 fps) 0.1% of span (≤ 20% of span) (3-33 fps) 0.5% of flow rate (≥ 20% of span) (3-33 fps)
Reference Conditions	25° C, 6 fps full scale. Temperature effect, 0.025% Full Scale/°C. Accuracy statement based on digital outputs
Repeatability	Within ±0.1% full scale
Power Consumption	Less than 20 VA
Output Signals	Simultaneous isolated analog and digital (all referenced to the same isolated ground) Analog: 0 to 20 or 4-20 mAdc into 800 ohms max. Digital: Scaled pulse and frequency a. Scaled, 24 Vdc pulse with 12.5/25/50/100 ms on-time, 0-60 Hz max into 150 ohm impedance min. b. Scaled frequency. 15 Vdc square wave, 50/50 duty cycle, 0-1000 Hz max into 1000 ohms min. c. Fault, with open collector d. All open collectors are rated (100mA at 30 Vdc) e. RS232 Communication
Fault	Open collector. Active on self test failure, empty pipe and during programming, low/no coil drive and failure of external totalizer to keep up with the flow (registration too small).
Input Signal	Positive zero return (PZR). Connect to remote dry contact to drive analog and digital outputs to zero when an empty pipe condition can occur.
Minimum Conductivity	5 micromhos/cm
Flow Direction	Open collector (rating: 100 mA at 30 Vdc). Active in reverse flow.
Two Flow Alarms	Open collector. Relay option available in remote mounting only.

1.7 Specifications Cont'd.

Full Scale Velocity Ranges 0-3 to 0-33 fps (0-1 to 0-10 mps)

Ambient Temp Limits -20° to 140°F (-30° to 60 °C) (Display may darken above 158 °F)

Process Temp

Integral Mount
Hard rubber, Soft rubber, Neoprene, Polyurethane ..... -40 - 180°F
Tefzel®, Ceramic: ..... -40 - 212° F

Remote Mount (opt)
Hard rubber, Soft rubber, Neoprene, Polyurethane ..... -40 - 180° F
Tefzel® (to 300 psi), Ceramic: ..... -40 - 266° F

High Temp Coils (opt)
Tefzel® (to 100 psi): ..... -40 - 300° F
Ceramic: ..... -40 - 420° F

Temperatures above 212°F (100° C) require mounting the electronics in a remote location (max. distance 15 feet at liquid conductivity of 5 micro-mhos and min. velocity of 1 fps).

Storage Temp Limits -20° to 140° F (-30° to 60° C)

Construction

Metering Tube ..... Model 626 – Steel, epoxy coated
Model 656 – 0.5"-4" Steel, epoxy coated
Model 656 - 6" - 72" 304 SS welded, epoxy coated
Model 627 - 1" - 8" Cast Ductile Iron, epoxy coated
Model 657 - 2" - 48" Fabricated Steel, epoxy coated

Flanges Carbon steel ANSI compatible

Lining ..... Model 626 – Aluminum Oxide 99.5% or *Tefzel*®
Model 656 – Polyurethane, Aluminum Oxide 99.5%
Tefzel®, Hard Rubber, Soft Rubber, Neoprene
Model 627 & 657 – Polyurethane

Electrodes ..... 316 SS. Others as required

Integral Housing (XMTR) ..... Cast Aluminum, Hi-build Epoxy Coated
Remote Housing (XMTR) ..... Fiberglass

Protection rating
Integral NEMA-4X, NEMA-7
Remote NEMA-4X

Electrical rating
Remote Mount - General Purpose
Integral Mount - Hazardous Locations
FM Approved* for Class I, Division 1, Groups B, C, D;
Class II Groups E, F, G
CE Approved (pending)
CSA Approved* for Class 1, Division 2, Groups A, B, C, D

*FM and CSA applies to integrally mounted transmitters up to 150 psi only.

1.8 Interchangeability

The TigermagEP™ transmitter is designed to be used with any **FM626, FM627, FM656** or **FM657** sensor. Electronics are completely interchangeable. Meter identification (tube ID, Serial Number, K, Offset, etc.) is stored on an E^2PROM chip independent of transmitter electronics. This provides universal compatibility between all Tigermag EP electronics modules, eliminating the need for reprogramming when switching modules. **FM656** (0.5"- 4"), **FM627** (1"-4") and **FM657** (2"-4") sizes have the same face-to-face dimensions as **FM626** wafer-style meters (0.5"- 4"). See Figure 1.3

1.9 Flow Rates, Dimensions & Weight

On meters smaller than 1" accuracy is ±1% of rate

Table 1 – Nominal Flow Rates (Full Scale GPM)

Nominal Meter Size		626 (Ceramic/Tefzel)**			626 (Sanitary)			627 (Poly)			626, 656, 657 (others)		
		±.5%	Min	Max	±.5%	Min	Max	±.5%	Min	Max	±.5%	Min	Max
Inches	mm	1 fps	3 fps	33 fps	1 fps	3 fps	33 fps	1 fps	3 fps	33 fps	1 fps	3 fps	33 fps
*0.1	2.5	0.04	0.1	1.3	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
*0.25	6	0.22	0.6	7.2	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
*0.5	12	0.50	1.5	16	N/A	N/A	N/A	N/A	N/A	N/A	0.6	1.7	18
1.0	25	1.62	4	53	1.3	4	42	1.6	4.8	53	2	6	66
1.5	40	4	13	145	3.7	11	120	N/A	N/A	N/A	5	15	174
2.0	50	7	21	231	7.2	22	239	7	21	231	9	27	303
2.5	65	N/A	N/A	N/A	12	36	398	N/A	N/A	N/A	N/A	N/A	N/A
3.0	80	N/A	N/A	N/A	18	54	598	20	60	660	20	60	664
4.0	100	N/A	N/A	N/A	33	99	1088	35	105	1155	35	107	1182
6.0	150	N/A	N/A	N/A	N/A	N/A	N/A	88	264	2910	85	254	2800
8.0	200	N/A	N/A	N/A	N/A	N/A	N/A	147	441	4851	145	436	4800
10.0	250	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	236	709	7800
12.0	300	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	333	1000	11000
14.0	350	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	409	1227	13500
16.0	400	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	545	1636	18000
18.0	450	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	667	2000	22000
20.0	500	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	879	2636	29000
24.0	600	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	1273	3818	42000
30.0	750	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	1909	5727	63000
36.0	900	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	2925	8775	96525
42.0	1050	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	4040	12120	133320
48.0	1200	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	5322	15966	175626
54.0	1350	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	7144	21433	235800
60.0	1500	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	8500	25500	280500
66.0	1650	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	10300	31000	341000
72.0	1800	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	12700	38100	419100

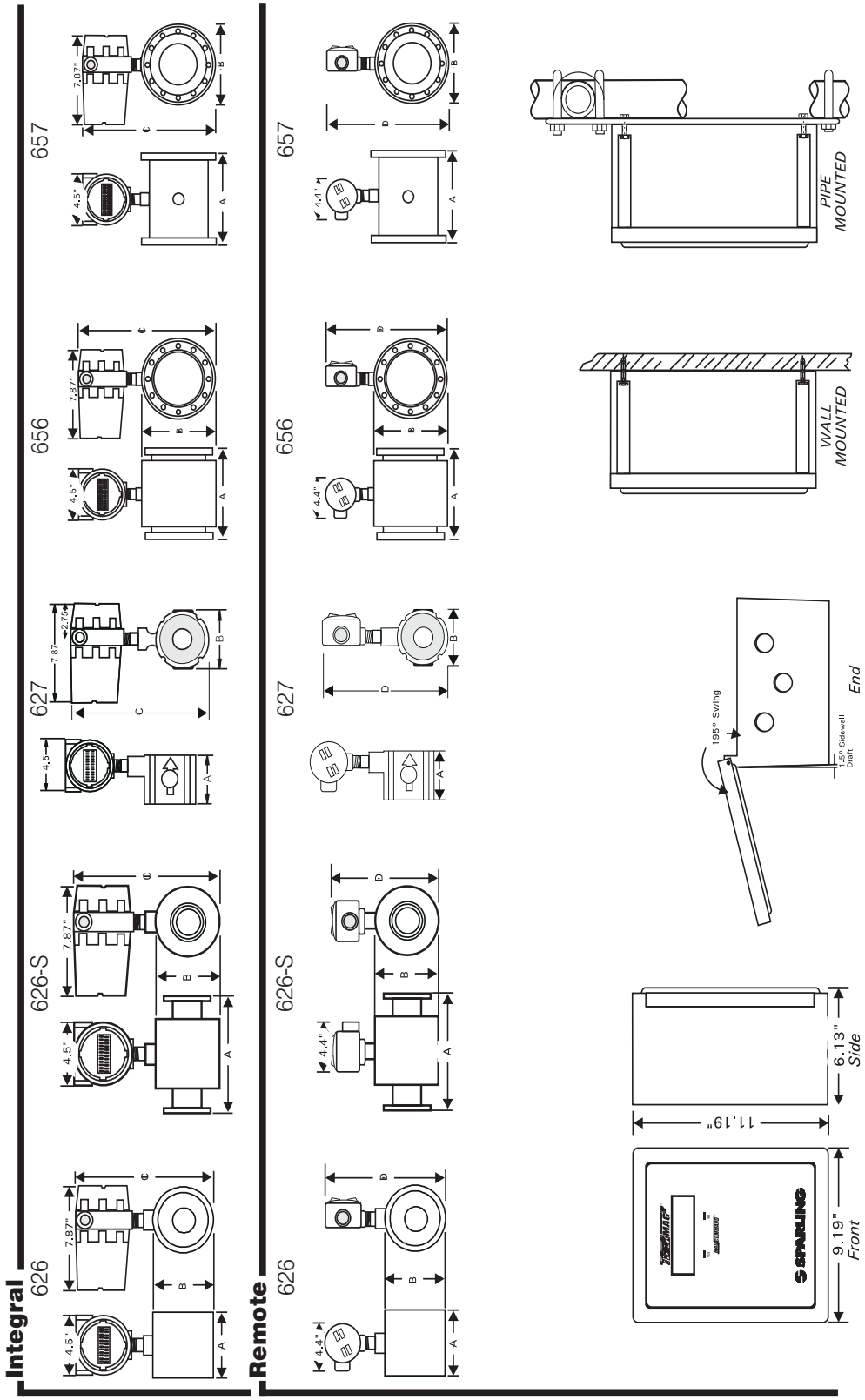
**Ceramic liners are slightly smaller than Tefzel. Flow rates for Tefzel lined meters from .5" to 2" ID's are slightly higher than shown in Table 1 (above). Refer to PDS-626 for actual numbers.

Table 2 – Weight

Nominal Meter Size		626		627		656		657	
inches	mm	lbs	kg	lbs	kg	lbs	kg	lbs	kg
0.1	2.5	15	7	N/A	N/A	N/A	N/A	N/A	N/A
0.25	6	15	7	N/A	N/A	N/A	N/A	N/A	N/A
0.5	12	15	7	N/A	N/A	18	8	N/A	N/A
1.0	25	15	7	15	7	20	9	N/A	N/A
1.5	40	20	9	N/A	N/A	26	12	N/A	N/A
2.0	50	20	9	20	9	30	14	30	14
2.5	65	20	9	N/A	N/A	N/A	N/A	N/A	N/A
3.0	80	30	14	30	14	48	22	48	22
4.0	100	35	16	35	16	55	25	55	25
6.0	150	N/A	N/A	46	21	75	34	75	34
8.0	200	N/A	N/A	49	22	105	77	105	77
10.0	250	N/A	N/A	N/A	N/A	155	86	155	86
12.0	300	N/A	N/A	N/A	N/A	235	117	235	117
14.0	350	N/A	N/A	N/A	N/A	365	140	365	140
16.0	400	N/A	N/A	N/A	N/A	460	182	460	182
18.0	450	N/A	N/A	N/A	N/A	555	209	555	209
20.0	500	N/A	N/A	N/A	N/A	625	250	625	250
24.0	600	N/A	N/A	N/A	N/A	860	336	860	336
30.0	750	N/A	N/A	N/A	N/A	1325	432	1325	432
36.0	900	N/A	N/A	N/A	N/A	1800	648	1800	648
42.0	1050	N/A	N/A	N/A	N/A	2280	818	2280	818
48.0	1200	N/A	N/A	N/A	N/A	3500	977	3500	977

1.9

Flow Rates, Dimensions & Weight
cont'd.



Dimensions
Figure 1.3

Table 3 – Dimensions

Nominal Meter Size		Dimensions (Inches)																		
		A			B					C					D				
Inches	mm	*All	626-S	627	626	626-S	627	656	657	626	626-S	627	656	657	626	626-S	627	656	657
0.1	2.5	4.00	N/A	N/A	2.31	N/A	N/A	N/A	N/A	8.75	N/A	N/A	N/A	N/A	8.50	N/A	N/A	N/A	N/A
0.25	6	4.00	N/A	N/A	2.31	N/A	N/A	N/A	N/A	8.75	N/A	N/A	N/A	N/A	8.50	N/A	N/A	N/A	N/A
0.5	12	4.00	N/A	N/A	2.31	N/A	N/A	3.50	N/A	8.75	N/A	N/A	9.50	N/A	8.50	N/A	N/A	9.25	N/A
1.0	25	4.00	4.12	4.00	2.92	2.375	2.92	4.25	N/A	9.38	9.125	10.2	10.19	N/A	9.13	7.88	9.9	9.94	N/A
1.5	40	4.00	4.12	N/A	3.62	3.50	N/A	5.00	N/A	10.00	10.25	N/A	10.88	N/A	9.75	9.00	N/A	10.63	N/A
2.0	50	4.00	4.12	4.00	4.12	3.50	4.25	6.00	6.00	10.63	10.25	11.8	11.69	11.25	10.38	9.00	11.5	11.44	11.00
2.5	65	N/A	4.12	N/A	N/A	4.00	N/A	N/A	N/A	N/A	10.75	N/A	N/A	N/A	N/A	9.50	N/A	N/A	N/A
3.0	80	6.00	8.00	6.00	5.70	4.50	5.40	7.50	7.50	11.75	11.25	13.4	13.00	13.00	11.50	10.00	13.1	12.75	12.75
4.0	100	6.00	8.00	6.00	6.60	6.625	6.60	9.00	9.00	13.00	13.375	14.9	14.38	14.38	12.75	12.12	14.6	14.13	14.13
6.0	150	13.38	N/A	8.00	N/A	N/A	9.00	11.00	11.00	N/A	N/A	17.3	17.00	16.25	N/A	N/A	17.0	16.75	16.00
8.0	200	13.38	N/A	8.00	N/A	N/A	10.70	13.50	13.50	N/A	N/A	19.4	19.40	18.50	N/A	N/A	19.1	19.15	18.25
10.0	250	18.15	N/A	N/A	N/A	N/A	N/A	16.00	16.00	N/A	N/A	N/A	22.56	20.75	N/A	N/A	N/A	22.31	20.50
12.0	300	19.40	N/A	N/A	N/A	N/A	N/A	19.00	19.00	N/A	N/A	N/A	25.00	23.25	N/A	N/A	N/A	24.75	23.00
14.0	350	21.38	N/A	N/A	N/A	N/A	N/A	21.00	21.00	N/A	N/A	N/A	26.67	25.25	N/A	N/A	N/A	26.42	25.00
16.0	400	23.38	N/A	N/A	N/A	N/A	N/A	23.50	23.50	N/A	N/A	N/A	28.97	27.50	N/A	N/A	N/A	28.72	27.25
18.0	450	27.25	N/A	N/A	N/A	N/A	N/A	25.00	25.00	N/A	N/A	N/A	31.14	29.25	N/A	N/A	N/A	30.89	29.00
20.0	500	27.63	N/A	N/A	N/A	N/A	N/A	27.50	27.50	N/A	N/A	N/A	33.39	31.50	N/A	N/A	N/A	33.14	31.25
24.0	600	32.75	N/A	N/A	N/A	N/A	N/A	32.00	32.00	N/A	N/A	N/A	37.44	35.75	N/A	N/A	N/A	37.19	35.50
30.0	750	43.50	N/A	N/A	N/A	N/A	N/A	38.75	38.75	N/A	N/A	N/A	43.72	42.13	N/A	N/A	N/A	43.47	41.88
36.0	900	47.75	N/A	N/A	N/A	N/A	N/A	46.00	46.00	N/A	N/A	N/A	50.20	48.75	N/A	N/A	N/A	49.95	48.50
42.0	1050	51.75	N/A	N/A	N/A	N/A	N/A	53.00	53.00	N/A	N/A	N/A	56.90	55.25	N/A	N/A	N/A	56.65	55.00
48.0	1200	51.75	N/A	N/A	N/A	N/A	N/A	59.50	59.50	N/A	N/A	N/A	63.05	61.50	N/A	N/A	N/A	62.80	61.25
54.0	1350	53.50	N/A	N/A	N/A	N/A	N/A	66.25	N/A	N/A	N/A	N/A	69.88	N/A	N/A	N/A	N/A	69.63	N/A
60.0	1500	65.50	N/A	N/A	N/A	N/A	N/A	73.00	N/A	N/A	N/A	N/A	76.75	N/A	N/A	N/A	N/A	76.50	N/A
66.0	1650	65.50	N/A	N/A	N/A	N/A	N/A	80.00	N/A	N/A	N/A	N/A	83.75	N/A	N/A	N/A	N/A	83.50	N/A
72.0	1800	72.75	N/A	N/A	N/A	N/A	N/A	86.50	N/A	N/A	N/A	N/A	90.00	N/A	N/A	N/A	NA	89.75	N/A

Note 1: Dimensions and chart values for 150 lb. flanges (ANSI template).
Note 2: Allow 1/4" for 0.5 to 6" meters and 1/2" for 8" and larger meters for grounding rings and gaskets.
Note 3: "C" & "D" Dimensions ±0.125"

2.0 Pre-Installation

2.1 Receiving and Inspection

When the equipment is received, the outside of the package should be inspected for damage. If any damage or shortage is found, notation to that effect should be made on the carrier's delivery receipt.

Visually inspect the sensor and transmitter for damage from rough handling or faulty packaging. If concealed damage is discovered, notify the delivering carrier at once and request an inspection. Confirm telephone conversations in writing. If inspection is not made, prepare an affidavit stating that you notified the transportation company and that they failed to inspect. Save containers and packaging material.

It is essential that the carrier be notified within 15 days from the date of delivery in order to be in a position to present your claim. Make your claim promptly.

Unpacking and handling of TigermagEP™ Magnetic Flowmeters should be consistent with the procedures used to handle field instruments.

2.2 Storage

This equipment should be stored in a clean, dry environment. Do not store outside in an unprotected area. Observe the storage temperature requirements. Unpowered storage should not exceed two years.

2.3 Return of Equipment

Obtain an **RGA (Returned Goods Authorization)** number from the factory prior to returning any materials. The RGA number should be marked on the outside of the package. Failure to obtain authorization will unnecessarily delay any work to be performed at the factory.

CAUTION

When meter is returned to our factory, a statement MUST be attached indicating the liquid that was flowing through the meter, the concentration of the liquid and that the meter has been decontaminated and flushed clean.

WE WILL NOT HANDLE THE RETURNED EQUIPMENT UNLESS THIS STATEMENT ACCOMPANIES THE METER.

This procedure is in accordance with the Toxic Substance Control Act 7.

3.0 Installation

3.1 Application Considerations

The TigermagEP™ can be used to accurately measure the volumetric flow rate of liquids having a conductivity of at least 5 micromhos/cm.

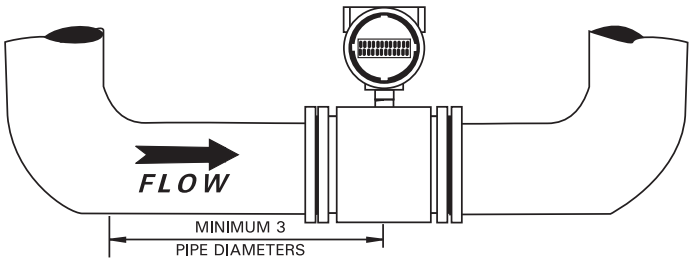
The presence of entrained air or gases in the process liquid will not prevent meter operation, but will produce a positive (+) error equal to the % by volume gas entrainment.

▼ FULL SCALE FLOW RATES SHOULD BE SELECTED ABOVE 3 FEET PER SECOND (1 METER PER SECOND) FOR BEST ACCURACY.

3.2 Site Selection

Select a pipe location which will always be full of liquid. The equipment should be located where the flowmeter will be accessible for adjustment. Provide a minimum of 18" clearance to the electronics enclosure.

The meter may be located in any position from vertical to horizontal. Flow may be in either direction through the meter. Vertical installation with the liquid flowing upwards, minimizes the possibility of slurry separation and assures a full pipe condition.



Full Pipe Required
Figure 3.1

Horizontal installation requires that the sensing electrodes be positioned in the horizontal plane. See Figure 3.7.

Provide at least three pipe diameters of straight piping approach between an upstream elbow and the midpoint of the meter. In small meters this can be achieved within the meter itself. More straight approach should be provided after valves or multiple elbows. Provide at least 10 diameters after expanders or laterals which are of smaller diameter than the line size.

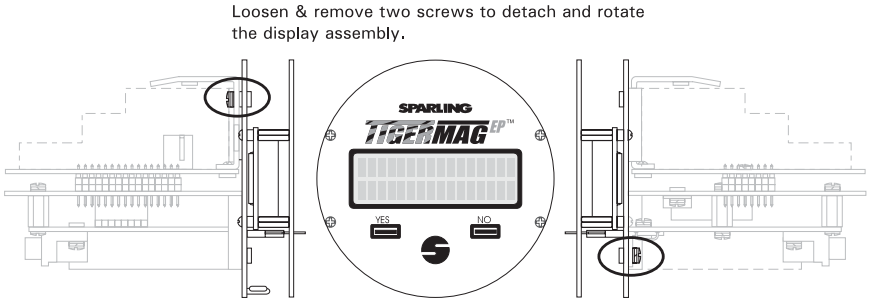
3.3

Rotating the Transmitter Display

The Sparling TigermagEP's modular display is designed to allow you to rotate the display in four different orientations. The display assembly can be rotated, at 90° intervals, by removing the two screws circled in Figure 3.2 below, for ease of reading the display.

The display features long lasting LCD numerals. The display may darken if ambient temperatures exceed its temperature rating of -4° to +158° F. Darkening usually occurs when the electronics are installed in direct sunlight. To avoid this problem install a sun shield when the flowmeter is in direct sunlight.

The display assembly can be replaced in the field without replacing the entire electronics, by following the same procedures as utilized for rotating the display.



Removing the Rotatable Display
Figure 3.2

3.4 Removable Electrodes (optional)

The line must be depressurized and drained in order to check and replace the removable electrodes.

3.4.1 How the Design Works

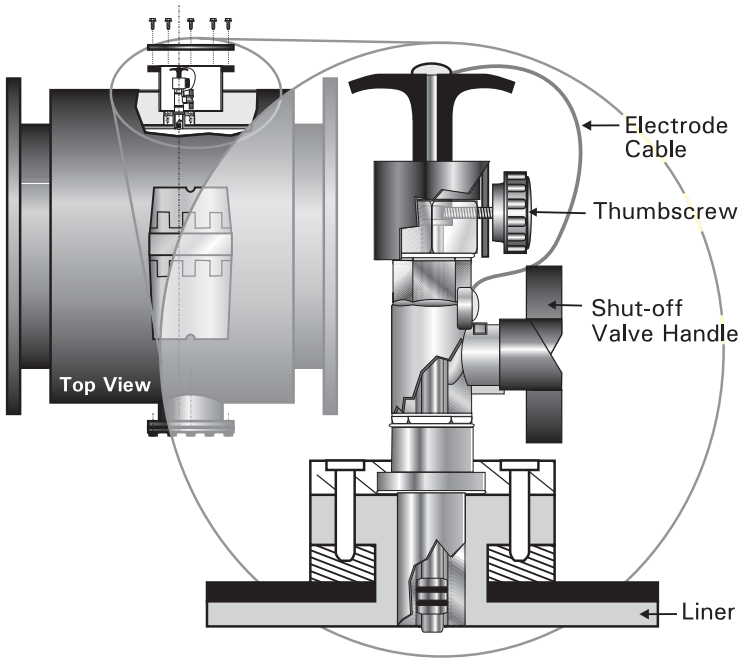
This design utilizes electrodes which are installed through accessible ports provided on the sensor body. Electrodes are sealed using two o-rings. One o-ring acts as a primary seal while the other is a backup seal. This redundant sealing approach provides positive sealing.

To withdraw the electrodes, process line has to be depressurized and drained. The outer cover must be removed by unscrewing cap bolts using an 11/32 nut driver to allow access to the electrode cavity. Remove cables from electrodes by removing nuts and lock washers. Using a 3/4" socket, unscrew and remove the electrode assembly.

3.4.2 The Need for Replacement

Sparling's flowmeter design utilizes High Impedance circuitry (Hi-Z) which is not affected by coating buildup on the electrodes. Replacement of the electrode only becomes necessary when physical damage due to erosion or corrosion has occurred.

3.5 Hot-Tap Removable Electrodes (optional)



Hot-Tap Removable Electrode
Figure 3.4

Sparling's optional hot-tap removable electrode design allows the inspection or replacement of electrodes without stopping the flow or depressurizing the line. The electrode assembly is sealed with multiple o-rings to maintain isolation from the pressurized medium. During removal of the electrode, a stainless steel ball valve is closed to keep the process fluid from leaking out while the electrodes are inspected or cleaned. The electrode housing, wired as a backup electrode, functions as a redundant electrode assembly providing the flow signal to the electronics. In other words, even when the electrode is withdrawn, the flowmeter keeps on providing important flow information.

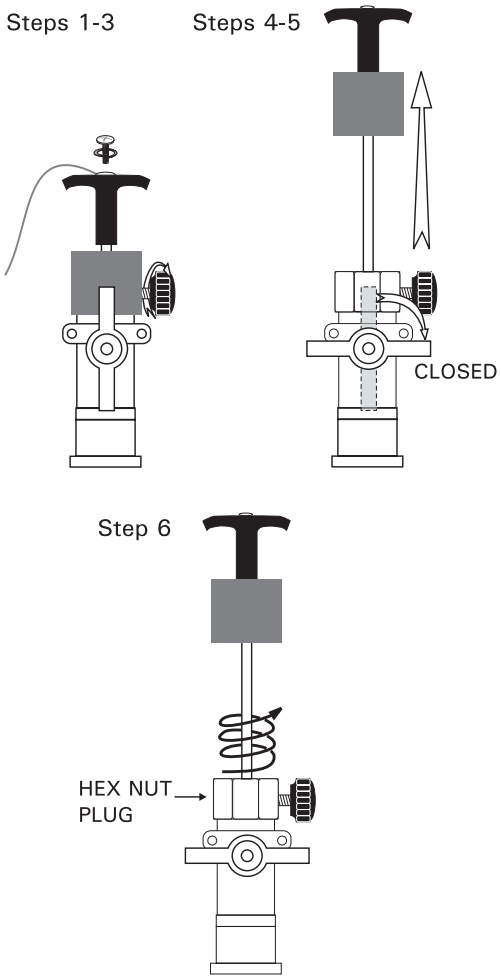
3.5 Hot-Tap Removable Electrodes (cont'd)

3.5.1 Electrode Removal

1. Use a cross recessed (phillips) screwdriver to remove the screw and lock washer from the handle.
2. Gently remove the electrode cable (orange wire) and place aside.
3. Secure cable then loosen the side knob.
4. Using the handle on the electrode head, pull electrode straight to the point that the valve can be closed.
5. Close the ball valve clockwise.
6. Unscrew the hex plug from the valve counterclockwise and remove the electrode assembly.

3.5.2 Electrode Installation

1. Install hex plug clockwise. Seal tight into closed valve assembly.
2. Open ball valve counterclockwise.
3. Push electrode assembly in, aligning the slot in the cover with the screw, until firmly seated.
4. Tighten the side knob.
5. Place electrode cables on handle.
6. Install the lock washer and screw, tighten.
7. Replace gasket, cover, cover screws and tighten securely.



Removing the Electrode
Figure 3.5

CAUTION

- **Avoid scratching or damaging the withdrawn electrode.**
- **Ball valve must be closed before the hex-head electrode assembly is unscrewed and removed.**
- **Electrode hex-head assembly must be replaced and secured tightly before opening the ball valve and reinserting the electrode.**

3.5.3 When to Replace

Sparling's flowmeter design utilizes High Impedance circuitry (Hi-Z) which is not affected by coating buildup on the electrodes. Replacement of the electrode only becomes necessary when physical damage due to erosion or corrosion has occurred.

3.6 Pipe Connections

MODELS FM626 & FM627 FLANGELESS (WAFER) SENSOR

The flangeless sensor is installed between two process pipe flanges. The sensor contains a nonconductive polyurethane, ceramic or *Tefzel*® liner. The integrity of this liner must be maintained for the flowmeter to function. **CARE SHOULD BE TAKEN DURING INSTALLATION TO INSURE THAT THIS LINER IS NOT DAMAGED.** Depending upon meter size, four (4) or eight (8) steel bolts are required for installation of the FM626 & FM627. These bolts are used to install the meter between existing flanges. See Table 4. Gaskets are required between the meter and the pipe flanges and between grounding rings and the mating surfaces.

Install the two bolts at the bottom of the meter. Place the meter temporarily between the flanges to confirm correct positioning. The meter should rest directly on the bolts. Remove the meter.

▼ REINSTALL THE METER TAKING CARE TO KEEP THE GASKET CENTERED. INSTALL ALL BOLTS AND TURN FINGER TIGHT. COMPLETE INSTALLATION WITH TORQUE WRENCH. IT IS IMPORTANT THAT THE BOLTS BE TIGHTENED ALTERNATELY SO THAT EXCESSIVE FORCE IS NOT APPLIED TO A CONCENTRATED POINT. SEE FIGURE 3.6. DO NOT EXCEED THE TORQUE LIMITS IN TABLE 6.

MODELS FM656 & FM657 FLANGED SENSORS

The flanged sensor is installed between two process pipe flanges. The sensing head tube interior is covered with an electrically nonconductive liner which overlaps the flange seal surfaces. The integrity of this liner must be maintained for the flowmeter to function. **CARE SHOULD BE TAKEN DURING INSTALLATION TO INSURE THAT THIS LINER IS NOT DAMAGED. FLANGE GASKETS MUST BE USED.**

Gasket material should be selected which is compatible with the piping and process conditions. Table 4 contains typical satisfactory gasket materials. Do not use spiral wound metal gaskets as they may cause liner damage.

Table 4 – Gasket Material

LINER MATERIAL	GASKET MATERIAL
Ceramic	*Teflon*®
Tefzel®	*Teflon*® Coated Asbestos
Hard or Soft Rubber	Asbestos Neoprene Rubber
Neoprene	Asbestos Neoprene Rubber
Polyurethane	Asbestos Neoprene Rubber
FM627 Polyurethane	Armstrong Syntheseal

▼ THE GASKETS, METER FLANGES, AND MATING PIPE FLANGES SHOULD BE DUSTED WITH GASKET TALC PRIOR TO INSTALLATION TO PREVENT DAMAGE TO THE LINER SHOULD IT BE NECESSARY TO REMOVE THE METER FROM THE LINE. DO NOT USE GRAPHITE TO DUST THE GASKET. A CONDUCTIVE FILM WILL COAT THE METER INTERIOR AND CAUSE A MALFUNCTION.

DO NOT EXCEED THE TORQUE LIMITS IN TABLE 6.

3.7

Special Mounting Bolts & Gaskets

Sparling provides carbon steel mounting hardware with wafer meter sizes 0.1"to 4", On flanged meters, *special* mounting bolts are provided for meter sizes 0.5", 1.5" and 3" only. Gaskets are provided for ceramic sensors only.

Optional 304SS mounting bolts for these sizes are available at extra cost.

Table 5 – Meter I.D.

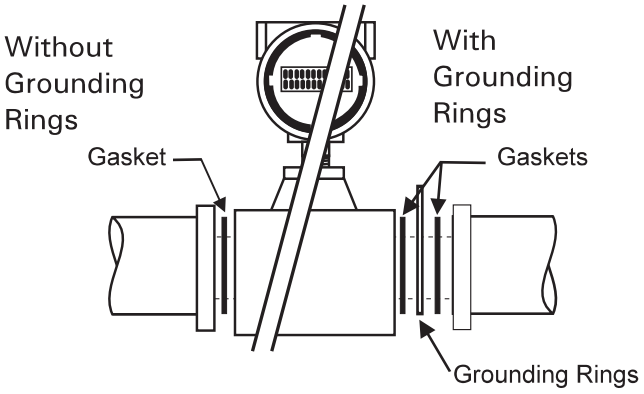
Nominal I.D.	Actual I.D.			
	Ceramic		Other	
in	in	mm	in	mm
0.10	0.125	3.17	N/A	N/A
0.25	0.302	7.67	N/A	N/A
0.50	0.452	11.48	0.48	12.24
1.0	0.812	20.62	0.91	23.09
1.5	1.34	34.04	1.47	37.34
2.0	1.69	42.93	1.94	49.20
2.5	N/A	N/A	2.24	56.90
3.0	N/A	N/A	2.87	72.85
4.0	N/A	N/A	3.83	97.18
6.0	N/A	N/A	6.00	152.40
8.0	N/A	N/A	7.75	196.85
10.0	N/A	N/A	10.00	254.00
12.0	N/A	N/A	12.00	304.80
14.0	N/A	N/A	13.00	330.20
16.0	N/A	N/A	15.00	381.00
18.0	N/A	N/A	17.00	431.80
20.0	N/A	N/A	19.00	482.60
24.0	N/A	N/A	22.90	581.66
30.0	N/A	N/A	29.00	736.60
36.0	N/A	N/A	34.60	878.84
42.0	N/A	N/A	40.60	1031.24
48.0	N/A	N/A	46.60	1183.64
54.0	N/A	N/A	52.50	1333.50
60.0	N/A	N/A	58.50	1485.90
66.0	N/A	N/A	64.50	1638.30
72.0	N/A	N/A	70.25	1790.70

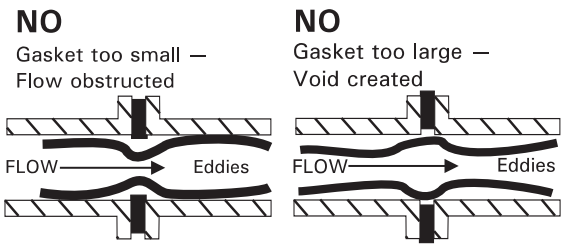
Table 6 – Torque, Flange & Bolt Specifications

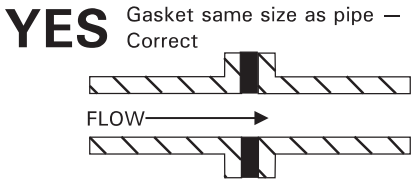
Nom. Meter Size(in)	Maximum Torque		ANSI / AWWA Flange & Bolt Specs						DIN Flange & Bolt Specs					
	ft-lbs	kg-m	Mating Flange	Pressure Rating	OD Inch	Bolt Circle	Hole Dia	Bolt Size	Mating Flange	Pressure Rating	OD mm	Bolt Circle	Hole Dia	Bolt Size
0.1	17	2.3	0.5	150	3-1/2	2-3/8	4 @ 5/8	7/16-14 x 6-3/4	15	10	95	65	4 @ 14	M10 X 170
	17	2.3	0.5	300	3-3/4	2-5/8	4 @ 5/8	1/2-13 x 6-3/4	15	25	95	65	4 @ 14	M12 X 170
	17		0.5	600	3-3/4	2-5/8	4 @ 5/8	1/2-13 x 6-3/4						
0.25	17	2.3	0.5	150	3-1/2	2-3/8	4 @ 5/8	7/16-14 x 6-3/4	15	10	95	65	4 @ 14	M10 X 170
	17	2.3	0.5	300	3-3/4	2-5/8	4 @ 5/8	1/2-13 x 6-3/4	15	25	95	65	4 @ 14	M12 X 170
	17		0.5	600	3-3/4	2-5/8	4 @ 5/8	1/2-13 x 6-3/4						
0.5	17	2.3	0.5	150	3-1/2	2-3/8	4 @ 5/8	7/16-14 x 6-3/4	15	10	95	65	4 @ 14	M10 X 170
	17	2.3	0.5	300	3-3/4	2-5/8	4 @ 5/8	1/2-13 x 6-3/4	15	25	95	65	4 @ 14	M12 X 170
	17		0.5	600	3-3/4	2-5/8	4 @ 5/8	1/2-13 x 6-3/4						
1.0	17	2.3	1	150	4-1/2	3-1/8	4 @ 5/8	7/16-14 x 6-3/4	25	10	115	85	4 @ 14	M12 X 170
	17	2.3	1	300	4-7/8	3-1/2	4 @ 3/4	5/8-11 x 7-1/2	25	25	115	85	4 @ 14	M12 X 170
	17		1	600	4-7/8	3-1/2	4 @ 3/4	5/8-11 x 7-1/2						
1.5	17	2.3	1.5	150	5	3-7/8	4 @ 5/8	1/2-13 x 6-3/4	40	10	150	110	4 @ 18	M16 X 190
	17	2.3	1.5	300	6-1/8	4-1/2	4 @ 7/8	3/4-10 x 7-1/2	40	25	150	110	4 @ 18	M16 X 190
	17		1.5	600	6-1/8	4-1/2	4 @ 7/8	3/4-10 x 7-1/2						
2.0	17	2.3	2	150	6	4-3/4	4 @ 3/4	5/8-11 x 7-1/2	50	10	165	125	4 @ 18	M16 X 190
	17	2.3	2	300	6-1/2	5	8 @ 3/4	5/8-11 x 7-1/2	50	25	165	125	4 @ 18	M16 X 190
	17		2	600	6-1/2	5	8 @ 3/4	5/8-11 x 7-1/2						
3.0	24	3.3	3	150	7-1/2	6	4 @ 3/4	5/8-11 x 9-1/2	80	10	200	160	8 @ 18	M16 X 240
	24	3.3	3	300	8-1/4	6-5/8	8 @ 7/8	3/4-10 x 10-1/2	80	25	200	160	8 @ 18	M16 X 240
4.0	30	4	4	150	9	7-1/2	8 @ 3/4	5/8-11 x 9-1/2	100	10	220	180	8 @ 18	M12 X 240
	30	4	4	300	10	7-7/8	8 @ 7/8	3/4-10 x 10-1/2	100	25	235	190	8 @ 22	M20 X 260
6.0	92	12.7	All specifications per Customer requirements and in compliance with recognized standards such as: ANSI / AWWA/ DIN											
8.0	133	18.4												
10.0	70	9.7												
12.0	83	11.5												
14.0	100	13.8												
16.0	110	15.2												
18.0	110	15.2												
20.0	115	15.9												
24.0	135	18.7												
30.0	140	19.4												
36.0	140	19.4												
42.0	140	19.4												
48.0	140	19.4												
54.0 & 60.0	140	19.4												
66.0 & 72.0	140	19.4												

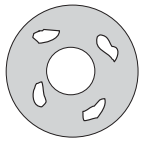
FM626/ FM627 (Wafer Style)

Gasket Installation

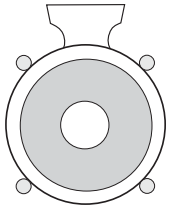




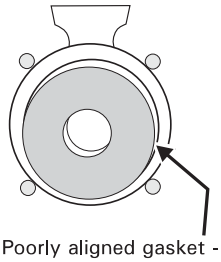




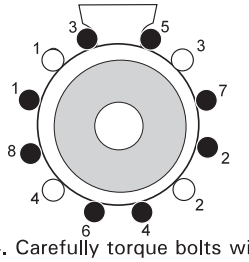
1. Apply silicone grease or other viscous fixative to gasket for temporary positioning



2. Fit gaskets, checking to ensure it is perfectly centered



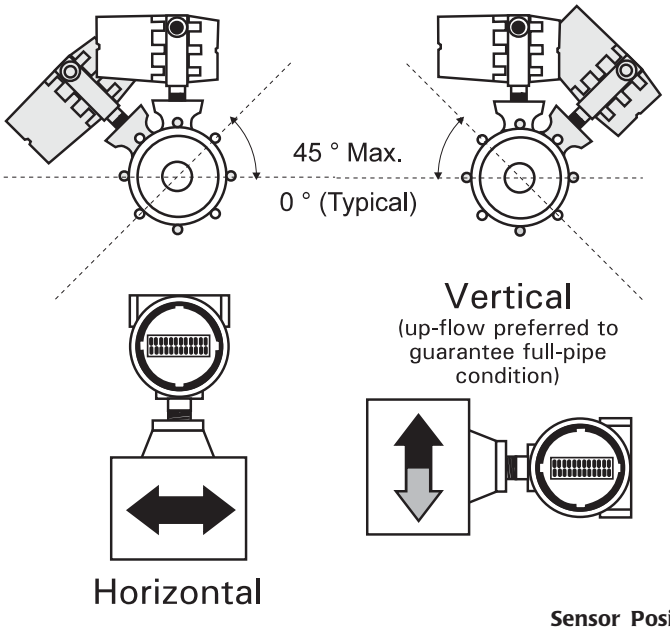
3. Poorly aligned gasket - can cause catastrophic leaks and flow errors



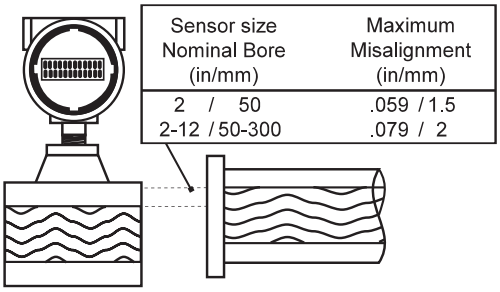
4. Carefully torque bolts with Bolt torque sequence above
   - ○ 4 Bolt Pattern
   - ● 8 Bolt Pattern See Table 4

Gasket Installation
Figure 3.6

Sensor Position



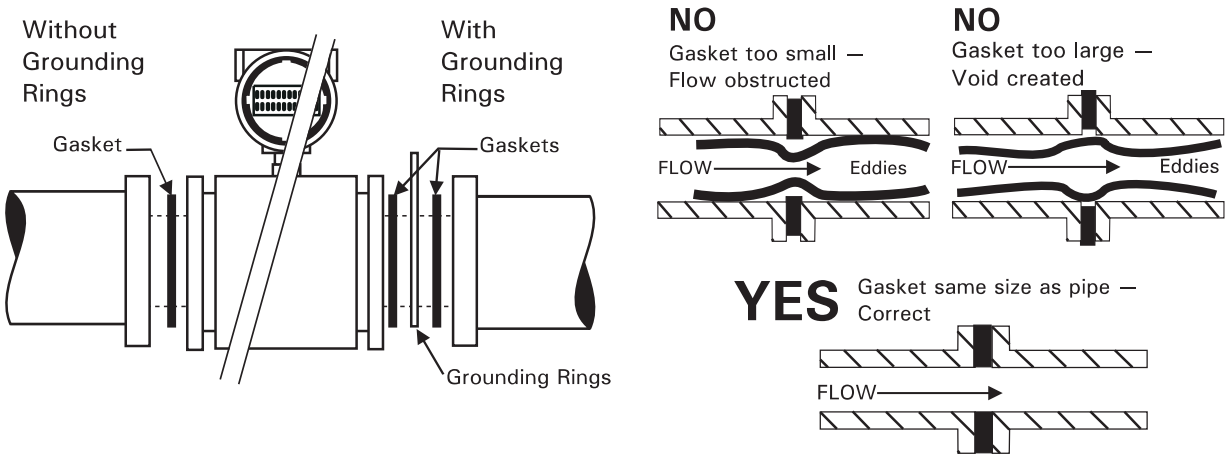
Sensor Alignment

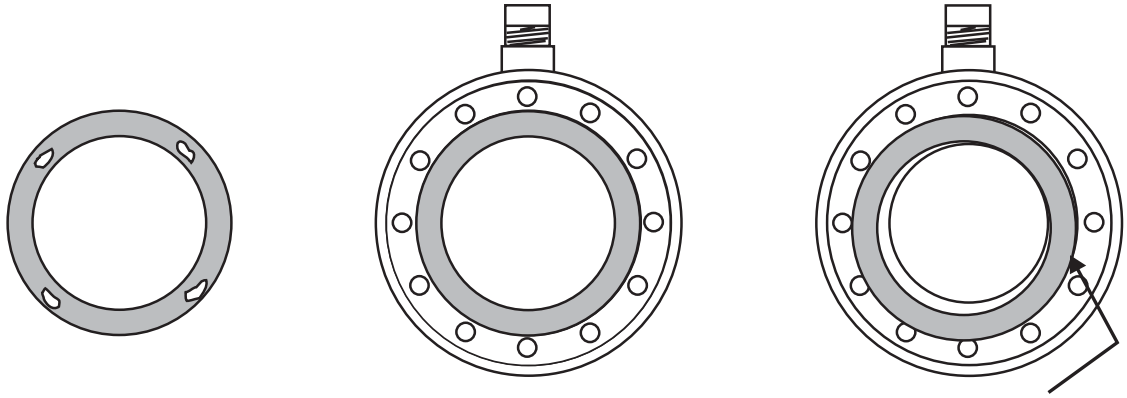


Sensor size Nominal Bore (in/mm)	Maximum Misalignment (in/mm)
2 / 50	.059 / 1.5
2-12 / 50-300	.079 / 2

Sensor Position
Figure 3.7

FM656 / FM657 (Flanged)
Gasket Installation

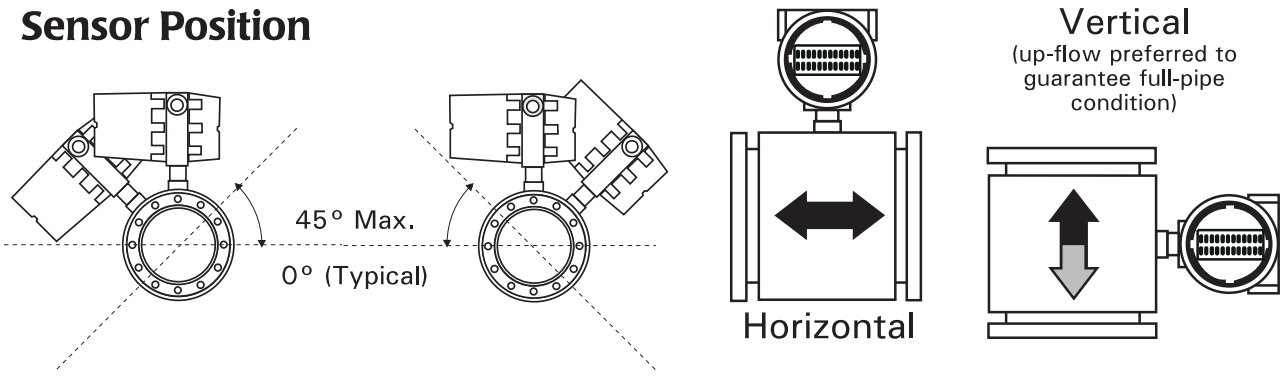




1. Apply silicone grease or other viscous fixative to gasket for temporary positioning
2. Fit gaskets, checking to ensure it is perfectly centered
3. Poorly aligned gasket - can cause catastrophic leaks and flow errors

Gasket Installation
Figure 3.8

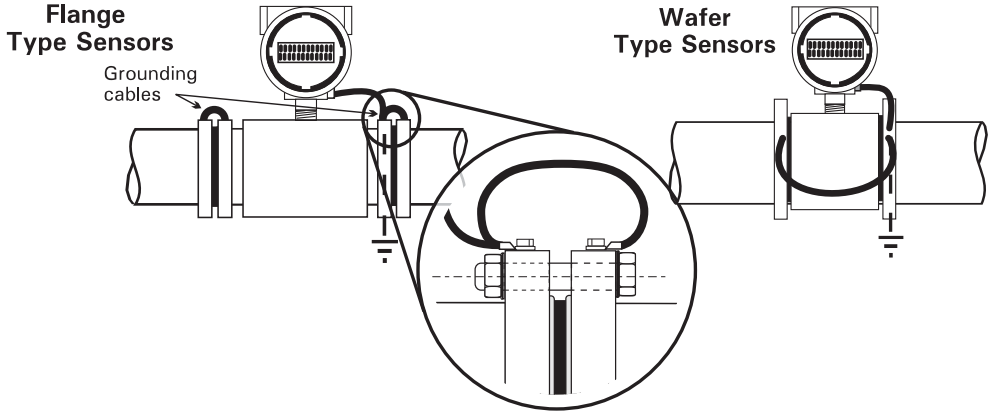
Sensor Position



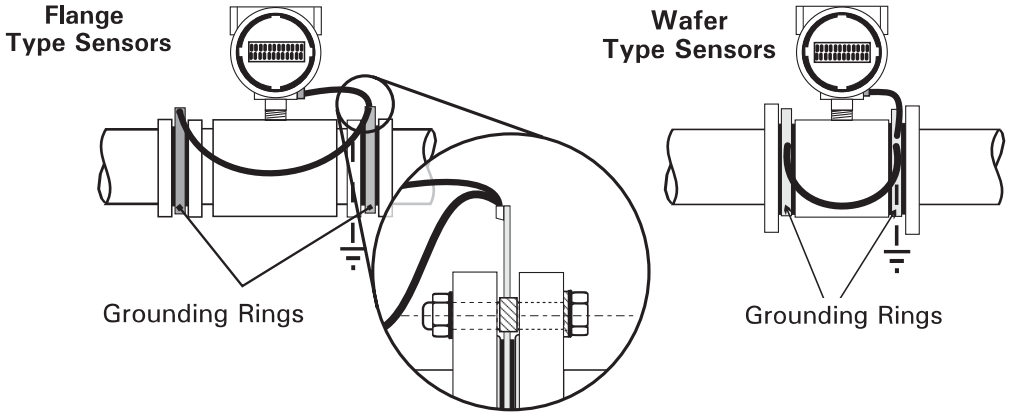
Sensor Position
Figure 3.9

3.8 Grounding

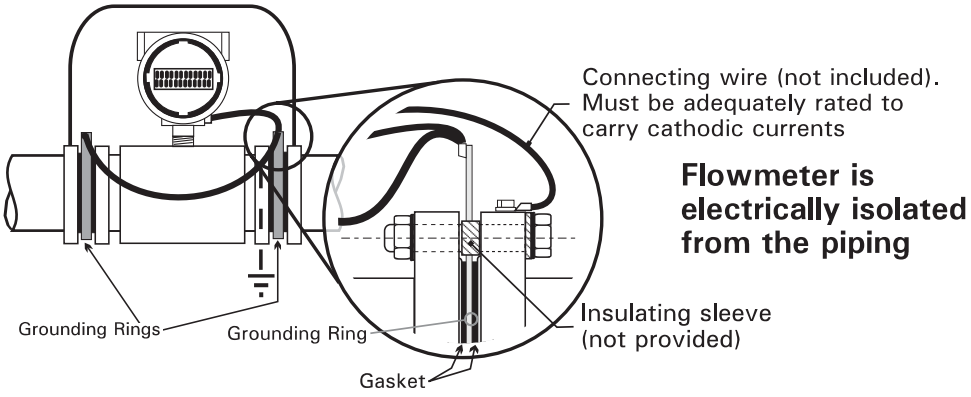
Mounting in Unlined Metal Pipelines



Mounting in Plastic or Lined Pipeline, or where Conductivity < 20 micromhos/cm



Mounting in Pipes with Cathodic Protection



Grounding
Figure 3.10

3.8 Grounding Cont'd.

DC and AC voltages can be transmitted through conductive fluids which can lead to magnetic flow meter instrument errors. Adequate grounding between the liquid and the instrument is essential to ensure correct flow measurement. Magnetic flow meters should always be grounded at four places: 1) Flowmeter tube, 2) Transmitter, 3) Receiving instrument, 4) the fluid.

▼ **EXTERNAL GROUNDING RINGS SHOULD BE INSTALLED ON ANY METER WHERE THERE IS LINED OR NONCONDUCTIVE PIPE OR CONDUCTIVITY IS LESS THAN 20 MICROMHOS/CM. SEE FIGURE 3.10.**

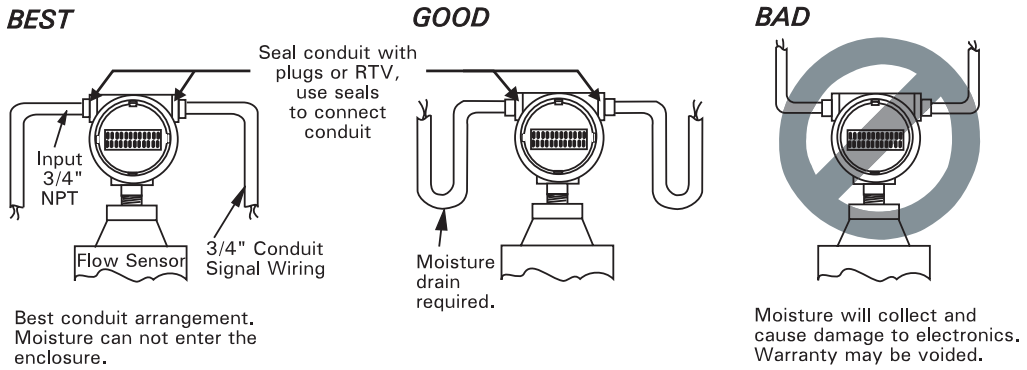
The grounding rings are in continuous contact with the process liquid providing a direct means for grounding electrical noise in the liquid. The electrical noise potential in the process liquid is at a similar level to the electrical ground plane to which the AC power supply ground is connected. This grounding method stabilizes the electrical field within the sensor measuring section permitting accurate flow detection. Grounding resistance must be less than 20 ohms.

▼ **CONTACT OUR TECHNICAL SUPPORT GROUP IF PROCESS LIQUID NEEDS TO BE MAINTAINED AT A POTENTIAL ABOVE OR OTHER THAN GROUND.**

3.9 Electrical Connections

Unscrew the small blind cover of the electronics enclosure to gain access to the I/O PCB. Separate 3/4" NPT conduit entrances are provided for power and signal wiring. Conduit connections should follow good practice and should be routed from below the meter. If conduit cannot be routed from below, provide moisture traps and seals to prevent moisture from entering the meter enclosure. See Figure 3.11. **Be sure to tighten conduit connections.**

Watertight conduit, NEMA-6P fittings and seals are required to maintain the moisture-free integrity of all enclosures and electronics in the system. Entry of moisture may void Sparling's warranty. All fittings must conform to NEMA-6P Classifications.

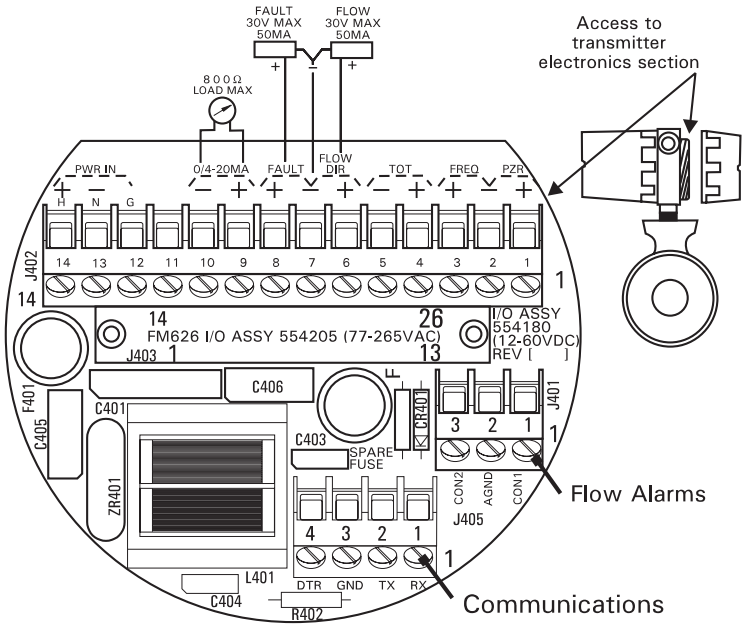


Conduit Connections
Figure 3.11

3.9

Electrical Connections

cont'd.



Electrical Connections I/O PCB
Figure 3.12

CONNECTING POWER LEADS

A connection diagram is located in the cover of the connection section and in Figure 3.12.

Connect power leads to terminal block J402, terminals 14 (H), 13 (N), and 12 (G). Be sure to connect a good ground to terminal 12.

The TigermagEP series is equipped with a switching power supply (standard) which accommodates power sources of 77-265 Vac 50/60 Hz. An optional 12-60 Vdc power supply is available. No adjustments or jumpers are required.

CAUTION

Disconnect power before proceeding.
Do not make connections while power is applied.

See next page for output connections.

3.9 Electrical Connections Cont'd.

CAUTIONS REGARDING CONNECTING 4-20mA OUTPUT

CAUTION

The TigermagEP provides voltage to drive the 4-20mA output to your device. Only 4-20mA devices without external power supplies may be connected to the TigermagEP.

If devices with external power supplies are connected to the 4-20mA output terminals, it will blow the power supply and void your warranty.

CONNECTING OUTPUTS

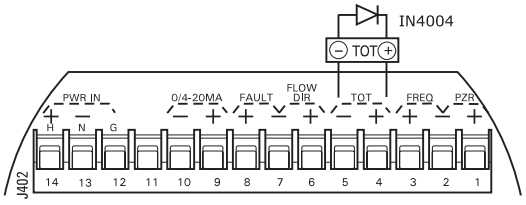
Determine which of the outputs (4-20 mA, fault, flow direction, pulse or frequency) are to be used. Connectors for available outputs are also located on terminal block J402.

After you have determined what outputs are required you need to verify that the external load on the outputs is within the limits specified. Calculate the external load by summing the input resistance, including all interconnecting cable. Signal cable of 18-22 gauge is normally adequate.

External load limits	Analog output	800 Ω max. impedance
	Pulse output	150 Ω min. impedance
	Frequency	1000 Ω min. impedance

Connect the required outputs as shown in Figure 3.12. When driving inductive loads, install 1N4004 diodes across the load as shown in Figure 3.13. If required, connect the Positive Zero Return (PZR) input. Note that meter outputs are forced to zero when terminals 1 and 2 (Terminal J402) are connected together through normally closed relay contacts.

All outputs are floating and use the same isolated ground. If more than one output is used simultaneously, only one of the common legs can be grounded. If both are grounded, a ground loop will occur causing erroneous signals. ***Do not ground any part of current loop if another output is already ready.***



Connecting Diode When Driving Inductive Loads
Figure 3.13

CAUTION

Only one load may have a leg strapped to ground unless the loads are isolated from each other.

3.10

Remote Mounted Transmitter

Figure 3.14
Tigermag EP NEMA-4X Enclosure
Remote Display

Remote mounting of the electronics is required when process temperatures exceed 212°F(100° C), when pipe vibration is excessive or when flooding is possible. Remote mounting should be used when high process temperatures exist at high ambient temperatures.

A bracket for wall or pipe mounting is furnished as part of the optional remote mounting kit. Interconnecting cable is supplied between the sensor and transmitter enclosure. Also supplied is a sensor mounted NEMA-7 rated junction box and a transmitter-mounted junction box in which coil and electrode connections are made.

The standard interconnecting cable length is 15 feet. Shorter or longer cables should be ordered from the factory. The cable may be shortened in the field. DO **NOT** SPLICE CABLE IN THE FIELD.

When installing provide moisture traps and seals to prevent moisture from entering the meter enclosure. See Figure 3.15. *Be sure to tighten conduit connections.*

WATERTIGHT CONDUIT, NEMA-6P FITTINGS AND SEALS ARE REQUIRED TO MAINTAIN THE MOISTURE-FREE INTEGRITY OF ALL ENCLOSURES AND ELECTRONICS IN THE SYSTEM. ENTRY OF MOISTURE MAY VOID SPARLING'S WARRANTY.

ALL FITTINGS MUST CONFORM TO NEMA-6P CLASSIFICATIONS.

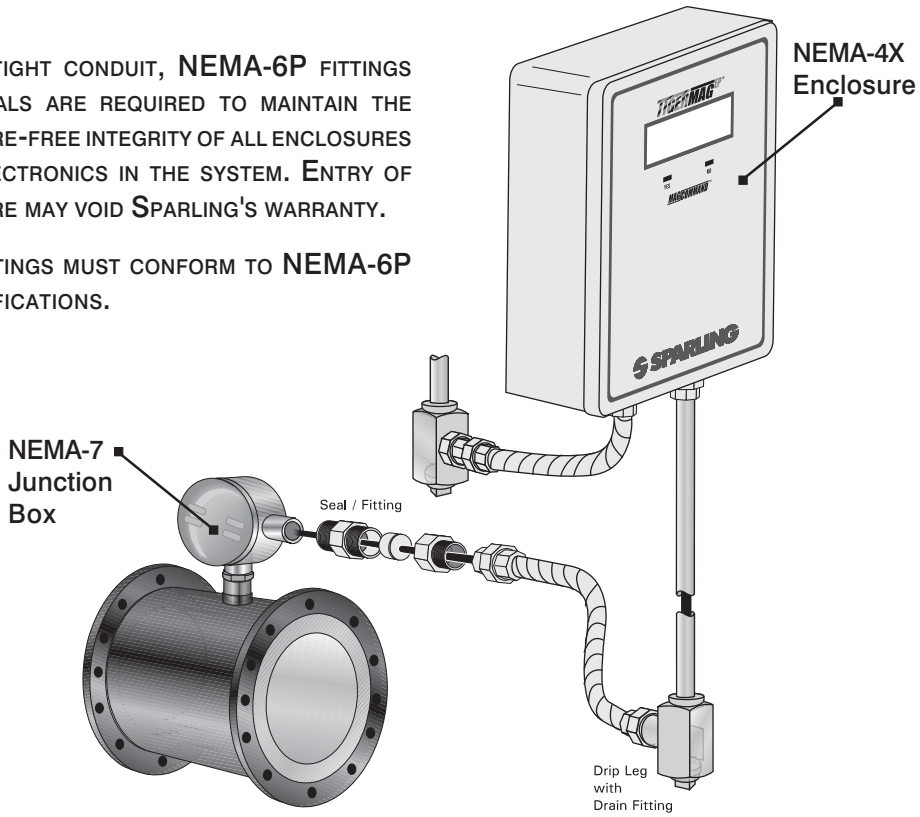


Figure 3.15
Tigermag EP Remote Conduit Connections

3.10

Remote Mounted Transmitter

cont'd.

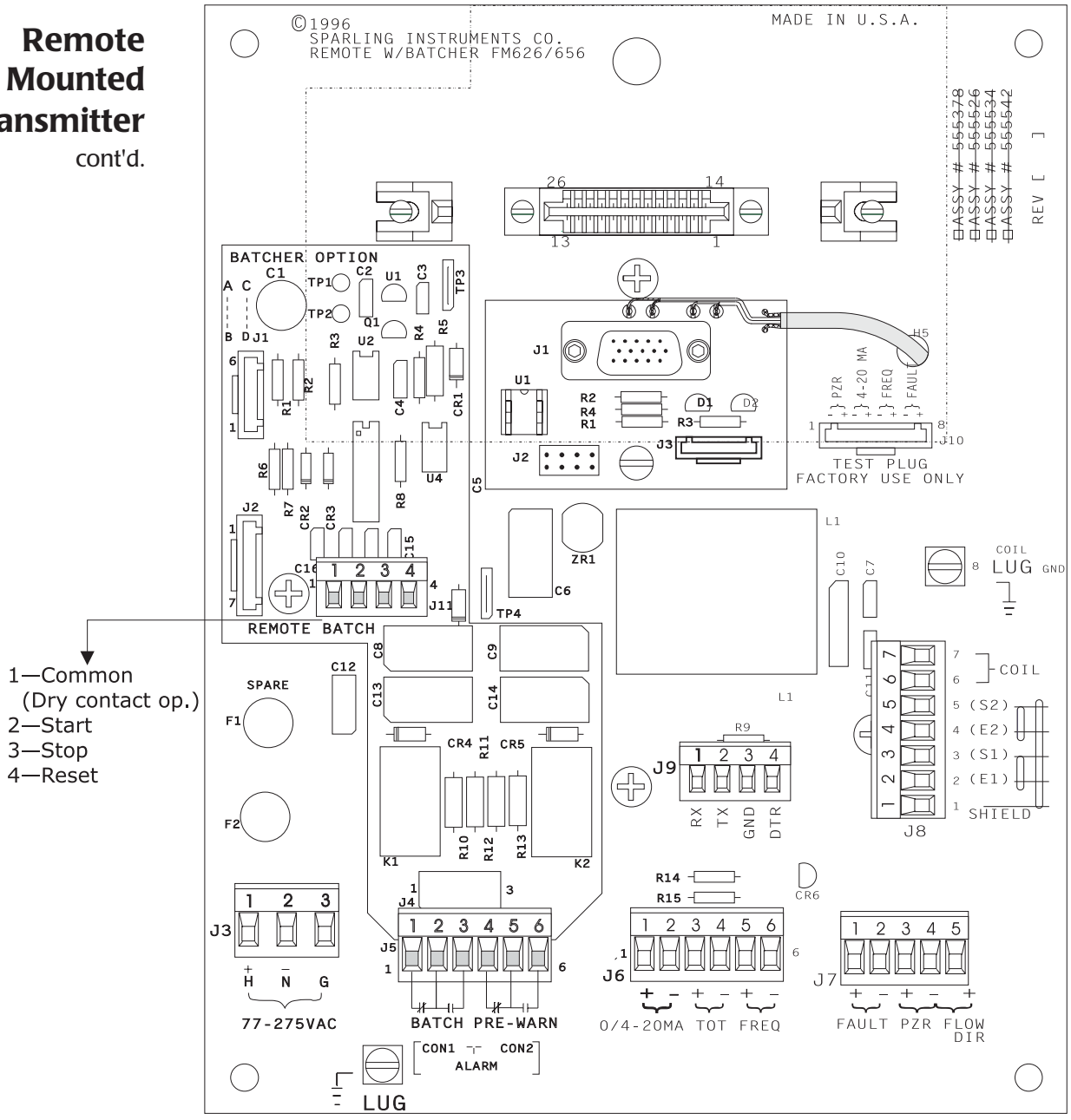


Figure 3.16
Tigermag EP Standard Motherboard

CAUTION

Disconnect power before proceeding. Do not make connections while power is applied.

3.10 Remote Mounted Transmitter cont'd.

Open the NEMA-4X enclosure to gain access to the motherboard. Separate 3/4" NPT conduit entrances are provided for power and signal wiring at the bottom of the enclosure. Connect the required outputs as shown in Figure 3.17.

CONNECTING POWER LEADS

Connect power leads to Connector J1, terminals 1 (H) and 2 (N). Be sure to connect a good ground to terminal 3 (G).

The TigermagEP series is equipped with a switching power supply (standard) which accommodates power sources of 77-265 Vac 50/60 Hz. An optional 12-60 Vdc power supply is available. No adjustments or jumpers are required.

CAUTION

Disconnect power before proceeding. Do not make connections while power is applied.

CONNECTING OUTPUTS

Connectors for available outputs are on connectors J6 & J7 See Figure 3.16. After you have determined what outputs are required you need to verify that the external load on the outputs are within the limits specified. Calculate the external load by summing the input resistance, including all interconnecting cable. Signal cable of 18-22 gauge is normally adequate.

External load limits	Analog output	800 Ω max. impedance
	Pulse output	150 Ω min. impedance
	Frequency	1000 Ω min. impedance

All outputs are floating and use the same isolated ground. If more than one output is used simultaneously, only one of the common legs can be grounded. If both are grounded, a ground loop will occur causing erroneous signals. ***Do not ground any part of current loop if another output is already ready.***

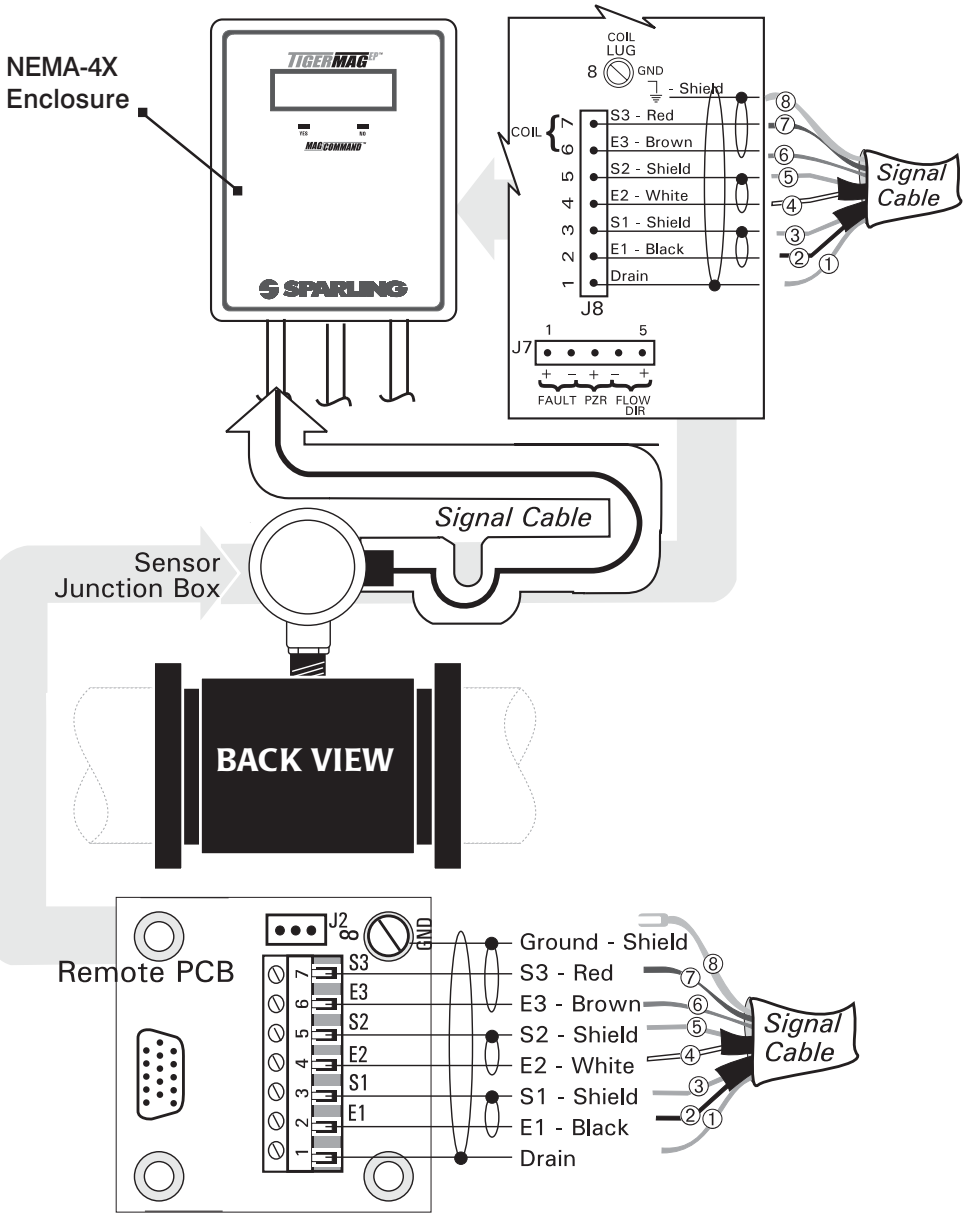
CAUTION

Only one load may have a leg strapped to ground unless the loads are isolated from each other.

3.10

Remote Mounted Transmitter

Cont'd.



Remote Mounted Transmitter
Figure 3.17

SIGNAL CONNECTIONS

Signal connections are made on the motherboard at connector J8, terminals 1 through 7 and ground (8) to lug. Similar connections are made in the remote junction box on the Remote PCB. Connect terminals 1 through 7 and ground (8) as shown using the special cable provided.

CAUTION

Disconnect power before proceeding. Do not make connections while power is applied.

3.11 Lightening & Transient Protection

Sparling's magnetic flowmeters utilize micro-processor based circuitry and are protected from noisy AC power, however power line transients generated by inductive motors, power line regulators and power load switching, commonly known as brown-outs, can cause memory loss, erroneous readout, blown semi-conductors and integrated circuits. These problems can be eliminated by using proper AC power transient suppressors.

It is also recommended that whenever the equipment is subjected to lightening, or high voltage transients, lightning supressors be used to protect the flowmeters.

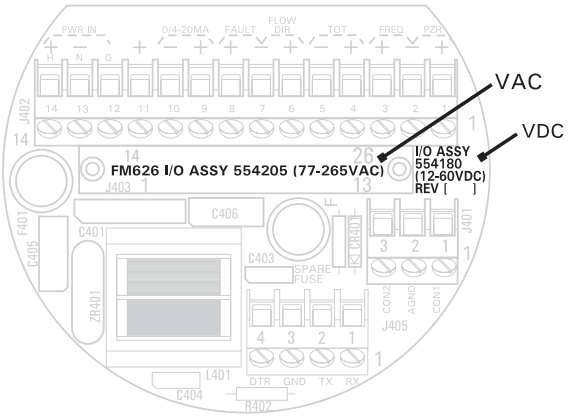
If you require assistance in proper selection of transient or lightening supressors, please contact Sparling.

4.0 Start-Up

4.1 Start-Up Procedure

Prior to applying power, the following checks should be made:

a) Check the flowmeter nameplate to insure that the power supply voltage is correct.
b) Verify that all electrical connections are correct. See Figures 3.12 and 3.17. The power supply voltage rating will be marked on the I/O PCB See Figure 4.1.
c) Check the polarity of external loads connected to the outputs.
d) Check to see that the two hall effect switches on the front of the transmitter are in place with the **dark side** of the switch **facing up** towards the LCD display. Do not remove these switches unless authorized by factory personnel. If you suspect that one of the hall effect switches is defective, contact the factory.



Power Supply Voltage Ratings
Figure 4.1

5.0 Calibration

5.1 Calibration

All flowmeters are calibrated before leaving the factory. No field recalibration is required. The 4 and 20 mA current level may be checked if desired by following the procedure in **Appendix I DIAGNOSTICS**. The meter can be used as a current calibrator to **check connected equipment.** See Appendix 1, para. 2.3.3.

6.0 Maintenance

No routine maintenance is required.

7.0 Troubleshooting

The following sections describe field tests and bench tests that can be performed on Sparling's magnetic flow meters.

7.1 General

Each flowmeter is rigorously tested during production. The final test stage is a wet flow calibration in a Sparling precision primary flow laboratory traceable to the National Institute of Standards and Technology (NIST).

Before troubleshooting, carefully verify the operating conditions of the meter:

1. Verify the interconnecting wiring by using a local milliammeter connected to the current output with no other load connected.
2. Verify that the sensor is completely filled with liquid. An empty or partially full sensor will continue to send an erratic flow signal even with no flow.
3. Verify that any flow test comparison is valid before assuming that the meter is in error.
4. If in doubt, verify the conductivity of the liquid to see that it exceeds 5 micromhos/cm.

7.2 Trouble-shooting Chart

The following trouble shooting chart should assist in correcting meter malfunction. For additional assistance, contact Technical Support (800)800-FLOW, (626)444-0571 in California.

WARNING

a) "WARNING - EXPLOSION HAZARD - SUBSTITUTION OF COMPONENTS MAY IMPAIR SUITABILITY FOR CLASS 1, DIVISION 2";

"AVERTISSEMENT - RISQUE D'EXPLOSION- LA SUBSTITUTION DE COMPOSANTS PEUT RENDRE CE MATERIEL INACCEPTABLE POUR LES EMPLACEMENTS DE CLASSE 1, DIVISION 2".

b) "THIS EQUIPMENT IS SUITABLE FOR USE IN CLASS 1, DIVISION 2, GROUPS (AS APPLICABLE) OR NONHAZARDOUS LOCATIONS ONLY".

Troubleshooting Chart

SYMPTOM	POSSIBLE CAUSE AND CURE
1. Erratic Reading (Output Wandering)	1. A. Installation a. Is sensor properly grounded? A good liquid ground is required. b. Empty pipe? Pipe must be full of liquid. c. Air in pipe? De-aerate d. Chemical being injected upstream of flowmeter? Change the chemical dosage downstream of the flowmeter. B. Electrical a. Variable Frequency Drive? Need additional filtering and improved grounding. b. Marginal Connection (particularly for remote units)? Rewire to insure good contacts. C. Moisture intrusion? Use leak tight fittings and keep the covers tight.
2. Inaccurate Reading	2. A. Run simulator test (47000/K) - Appendix 1, Section 2.3.6. B. Coil drive blown? Electronic module has to be returned to factory for repair C. Conductive coating? Clean sensor.
3. Output Incorrect (Pulse & Analog)	3. A. Disconnect wires and check circuit output with DVM. Reprogram current output. If program is OK, there is a sensor failure, return to factory. B. For pulse output need oscilloscope. If there is flow no pulse output, there is a sensor failure, return to factory.
4. Analog Output Zero	4. A. No external power required, unit is not loop powered. If external voltage was connected, electronics are damaged and should be returned to factory for repair.
5. Display Readings Locked	5. A. Program errors? Cycle the power off and on, then reprogram if necessary.
6. Meter Reads Zero	6. Did it ever work? A. Blown coil drive? Return for repair B. Not properly wired (remote units)? Rewire correctly C. Conductive coating? Clean sensor.
7. Blank Display	7. A. Blown fuse? Replace Fuse B. Power supply damage? Return for repair.
8. Display is turning black around edges	8. Temperature is too high inside the enclosure. Relocate the meter or shield against the heat source. Continuing to power the meter in this condition will permanently damage the display.
9. Display is difficult to read	9. Improve the lighting conditions if ambient light is dim. Remove large cover and adjust the pot directly above the display for best contrast while viewing from the intended viewing angle.

If the above steps fail to correct the problem, try different flow rates and disconnecting loads temporarily and see if the problem persists. Perform simulator check and call the factory. **Please have the following information available when you call:**

- Meter serial number; G, I, Z values from "SHOW METER DATA?".
- Description of the problem. (Display, current output, totalizer/frequency, all of the above.)
- When does the symptom occur or repeat?
- What are the flow rates, the orientation of the meter in the pipeline, environmental conditions, output loads on the meter, pipe material and grounding technique?
- How did you verify the discrepancy?

Contact Technical Support 800/800-FLOW (in California 626/444-0571) for additional assistance.

7.3 Electronics Self Test

Using the **MAG-COMMAND**™ magnetized screwdriver, enter programming mode by holding the magnet to the **"NO"** switch for five seconds. See **Appendix 1** for detailed instructions. Answer **"NO"** to all prompts until the DIAGNOSTICS menu appears. Answer YES to the DIAGNOSTICS menu. Follow the menu instructions. See Appendix 1, Section 2.3.

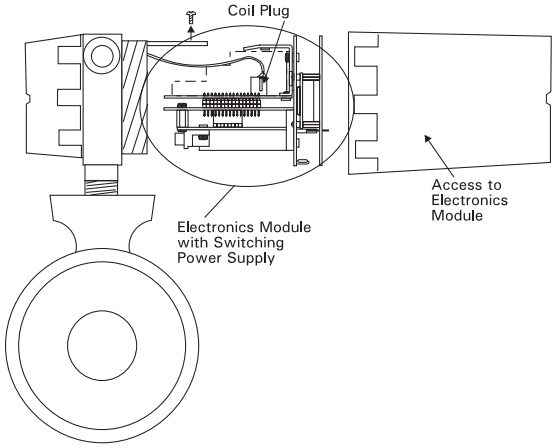
7.4 Electronics Module Replacement

To remove the electronics module, first unscrew the larger enclosure cover and remove the screw fastening the module bracket. Now unplug the coil cable converter. See Figures 7.1 and 7.2.

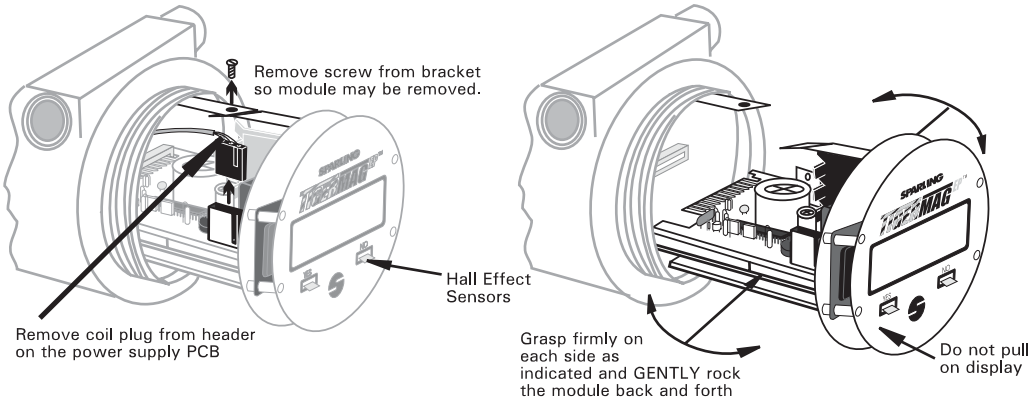
Grasp the module at each side and pull firmly while rocking the boards gently from side to side. Do not pull the module out by the display. See Figure 7.2.

WARNING

Do not remove Electronics Module while power is applied. Disconnect Power before proceeding.



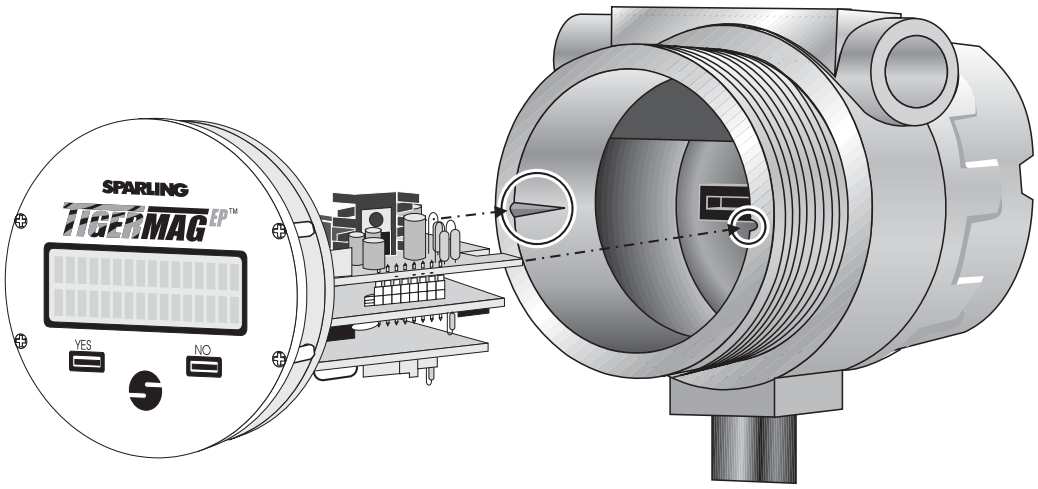
Access to Electronics
Figure 7.1



Removing the Electronics Module
Figure 7.2

▼ METER ELECTRONICS ARE CONTAINED IN A PLUG IN MODULE. THIS MODULE CONTAINS NO USER SERVICEABLE PARTS.

7.4 Electronics Module Replacement Cont'd.

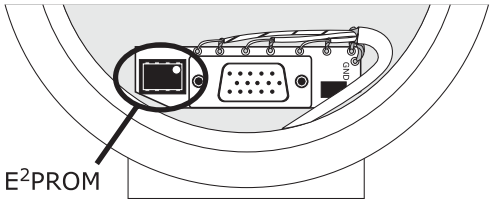


Aligning Electronics Module with Card Guides
Figure 7.3

When reinstalling the electronics module, observe the connector located in the base of the electronics enclosure. Line up the electronics module with housing card guides and the connector. See Figure 7.3. Plug in the replacement module. Plug in coil connector. **Be certain the plug wires are routed properly and will not interfere with the housing cover. Don't forget to replace the screw that fastens the module to the bracket. See Figure 7.2**

Apply power and observe display. Now, reprogram any values which were modified from factory preset levels. To obtain factory settings, look at calibration record shipped with meter. If sensor E^2PROM chip is damaged or has lost its data, call factory with the meter serial number and request another copy of the E^2PROM chip programmed with factory constants.

To replace the E^2PROM chip, you must remove the coil plug and the module. (See Figures 7.1 and 7.2). The E^2PROM is on the Coil PCB in the rear of the electronics enclosure. **Note the directional dot on the chip**. The new chip must be placed in this orientation. Gently remove the old chip and place the new factory-programmed chip in its' place.



Replacing the E^2PROM Chip
Figure 7.4

7.5 Sensor Testing

The sensor consists of a measuring section with electrodes and coils in a steel enclosure. The following paragraphs describe field tests that can be performed by the instrument technician. Defective sensors should be returned to the factory for repair. **OBTAIN A RETURNED GOODS AUTHORIZATION (RGA) PRIOR TO RETURNING MATERIALS TO PREVENT DELAYS.**

7.6 Coil Continuity Testing

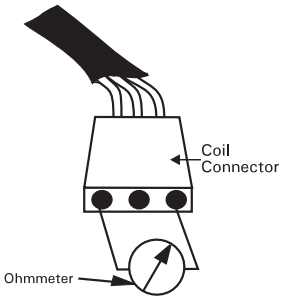
WARNING

Disconnect power before proceeding. Do not make or break coil connection while power is applied.

Unplug coil cable plug. Using a short 22 gauge (or appropriate) test lead, connect ohmmeter between coil wires and measure resistance. See Figure 7.5.

▼ COIL RESISTANCE SHOULD MEASURE 110 OHMS ±10% AT ROOM TEMPERATURE. HOT COILS MAY READ AS HIGH AS 150 OHMS.

If the coil resistance is too high or low (including open and short circuits) the sensor must be returned to the factory for inspection and/or repair.



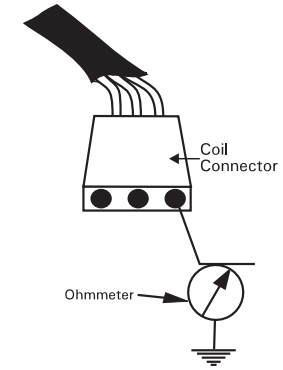
Coil Resistance Testing
Figure 7.5

7.7 Coil Insulation Test

Required test equipment: Insulation tester 10^{12} ohm.

Disconnect power and signal cables. Disconnect coil connector, Figure 7.6. Connect insulation tester between coil wire and housing ground. Test the insulation at 500 Vdc. A reading below 10,000 meg ohms indicates moisture in the sensor. The sensor must be returned to the factory for inspection and/or repair.

Connect insulation tester between coil wire and housing ground. Test the insulation at 500 Vdc. A reading below 10,000 meg ohms indicates moisture in the sensor. The sensor must be returned to the factory for inspection and/or repair.



Coil Insulation Test
Figure 7.6

7.8 Electrode Circuit Insulation Test

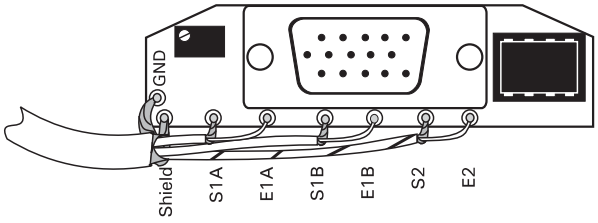
Unplug coil and remove module from electronic enclosure.

▼ SENSOR MUST BE EMPTY AND DRY.

Connect insulation tester three ways (see Figure 7.7.):

1. Between top post labeled E1A and S1A (shield)
2. Between center post labeled E1B and S1B (shield).
3. Between bottom post labeled E2 and S2 (shield).

Any leakage or fault indication indicates that the sensor should be returned to the factory for inspection and repair.



Electrode Circuit Insulation Test
Figure 7.7

8.0 Replacement Parts List

Description ***Part Number***

1. Electronics Modules
   - Integral Mount
     - 77 - 265 Vac 555584
     - 12 - 60 Vdc 555930
   - Remote NEMA 4X Mount
     - 77-265 Vac 555865
     - 12 - 60 Vdc 556409
   - Remote NEMA 4X Mount with Batcher
     - 77-265 Vac 555857
     - 12 - 60 Vdc 556417

2. I/O PCB
   - 12-60 Vdc 554180
   - 77-265 Vac 554205

3. Fuses
   - Slo-Blo, (12-60 Vdc) 2.0 amp 148743
   - Slo-Blo (77-265 Vac) 1.0 amp 148446

4. Kit, remote mount for NEMA 7 Integral Transmitter 902579-019
   Assembly includes:
   a) Mounting bracket with U-bolt
   b) Cable grip
   c) Sensor junction box (two with Remote PCB)
   d) 15 ft. cable assembly
   e) Tee mounting stand-off

5. Kit, remote mount for NEMA 4X Fiberglass Enclosure with larger display 555724
   Includes:
   a) Hardware Kit
   b) Display board
   c) Remote PCB (Motherboard)
   d) Fiberglass enclosure
   e) Lexan label

   Mounting bracket with U-bolt (optional) 555732

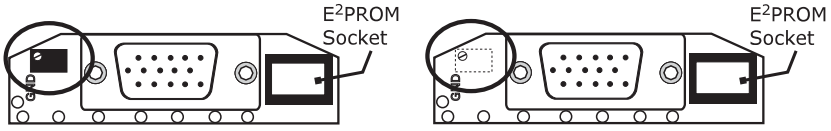
6. Cable PCB (Integral or Remote) 554239

POT on Board Front

Factory Supplied on Integral Mount Meter

POT on Board Reverse

Factory Supplied on Remote Mount Meter



Integral Remote

Do not adjust POTS. Do not attempt to alter board.
Both boards are functionally identical & interchangeable.

6. Replacement remote mount cable 150721
7. Grounding rings ..... Contact Factory

Your TigermagEP™ can be fitted with an optional digital communication capability utilizing HART® protocol. In order to operate this feature, you must have a Sparling model KP602 transmitter interface. Consult factory for more details. HART® is a registered trademark of Rosemount Inc.

Teflon® is a registered trademark of duPont

A.1 Appendix 1– Programming Firmware Ver. 1.0

1.1 General

The 16 character 2 line alphanumeric display is located directly above two magnetically operated Hall effect switches. The left switch is labeled **"YES"** and the right switch is labeled **"NO". THESE SWITCHES ARE THE ONLY CONTROLS REQUIRED TO SELECT AND CHANGE PARAMETERS ON THE TigermagEP. DO NOT ADJUST POTS.**

The TigermagEP is configured to the user's installation (programmed) using the **MAG-COMMAND** magnetic probe furnished with each meter. It can also be programmed with any high strength magnet. See Figure A1.1. Either switch is activated through the glass window in the housing by momentarily holding the **MAG-COMMAND** probe close to the switch.

IT IS NOT NECESSARY TO OPEN THE ELECTRONICS COMPARTMENT IN ORDER TO CHANGE PROGRAM SETTINGS.

Refer to Figure A 1.2 to determine how to get to each section of the program.
Alphanumeric data is required for the password and to enter or change constants.

1.2 Entering Data

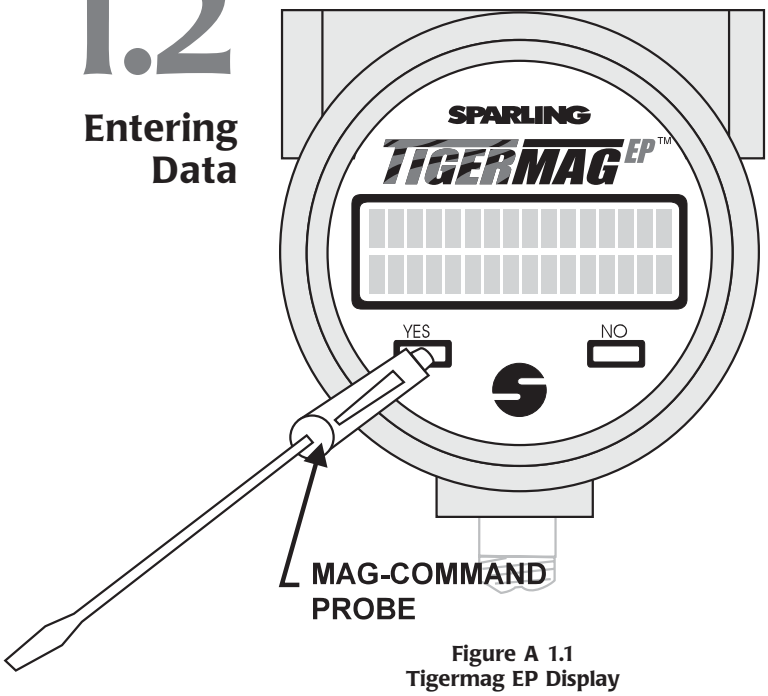


Figure A 1.1
Tigermag EP Display

When data is required, the cursor will be positioned under the first character. A **"NO"** answer will cause the next valid character to be displayed in turn. A **"YES"** answer accepts the displayed character or digit and moves the cursor to the next position. After answering **"YES"** to the last character, you will be prompted with the entire data just entered. Answer **"NO"** if you wish to change. Answer **"YES"** when it is correct.

1.3 Batching Modes

If your TigermagEP is equipped with the optional batching function, answer **"YES"** while the meter is in normal operation mode to display batching information. For detail, see Appendix 2, Batch Programming.

1.4 Show Meter Data

Hold the **MAG-COMMAND** probe next to the **"NO"** switch for approximately 5 seconds. The meter will respond:

SHOW METER DATA?

a) Answer **"YES"** and the meter will display the model number, firmware version, serial number, tag number, K factor (pulses/gallon) liner and electrode material. The last three values, G, I, & Z, are useful when calling factory technical assistance when troubleshooting the meter. As each data line is displayed a **"YES"** answer will display the next item. *A 'NO' answer at any item (or lack of response for 12 seconds) will return the meter to the operating display.*

b) A failure to answer this prompt within a few seconds will automatically bring the PASSWORD menu. See Section 1.5.

c) Answer **"NO"** and the PASSWORD prompt appears. A failure to enter a correct password will return the meter to operation.

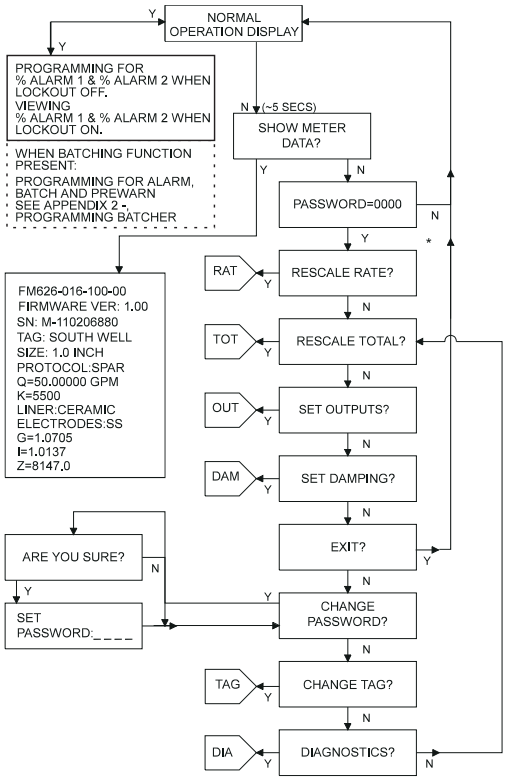


Figure A 1.2
Main Program

1.5 Password Entry

PASSWORD=0000

To go beyond this point, a valid password is required. **Every meter is shipped with the default password "0001"**. Any user with a valid password can change the password.

▼ Default Password "0001"

The meter password is entered by responding to each digit of the password with a **"YES"** or **"NO"**. A **"YES"** moves the cursor under the next digit to the right. A **"NO"** scrolls to the next higher value for the underlined digit and then back to 0 again. A 12 second time limit applies to each digit selection, i.e., a lack of response advances the cursor to the next position. Upon entry of a valid password, the meter enters a program mode and activates the fault output to signal remotely that programming is taking place.

1.6 Rescale Rate

RESCALE RATE?

A **"YES"** answer enters the Rescale Rate loop. A **"NO"** answer continues to the next menu item.

A menu is presented to select the engineering units in which rate is displayed and scaled. By answering **"NO"** each menu selection is presented in turn. A **"YES"** selection chooses the unit displayed and moves on to the next item.

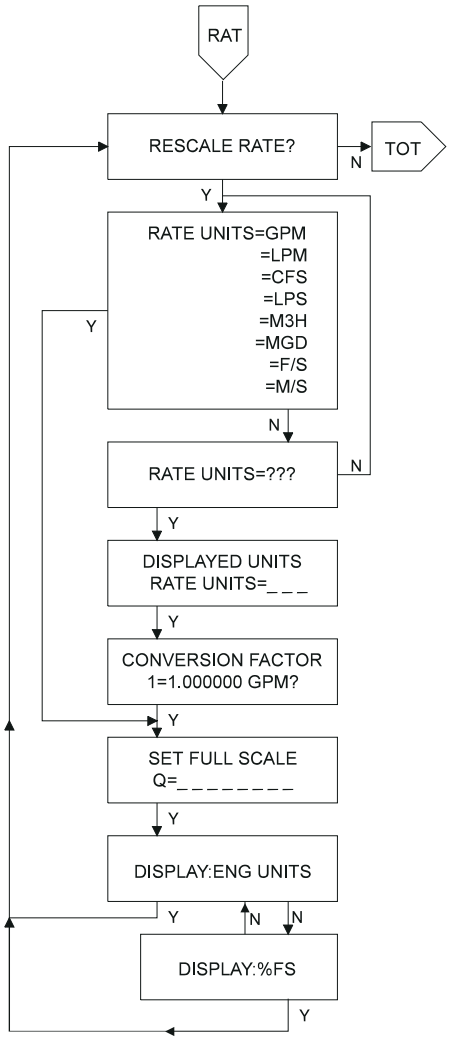


Figure A 1.3
Rescale Rate Flowchart

1.6.1 Select Rate Units

RATE UNITS=GPM

An answer of **"YES"** will display the rate in "GPM". Otherwise answer **"NO"**. A **"NO"** answer will display the other predefined choices in turn, i.e., liters/min., cu. ft./sec., liters/sec., cubic meters/hour, million gallons/day, ft./sec, meters/sec. and ???. Answer **"YES"** to the predefined rate units or to "???". A **"NO"** to each item brings you back to the beginning of the loop. *A **"YES"** answer is required to one of the selections to leave the loop.*

Select one of the presented units of measure by answering **"YES"** and skip to Sec. 1.6.2. If no appropriate choice is displayed, select "???" and define your own units in 1.6.1a.

1.6.1a User Defined Rate Units

RATE UNITS=AAA

Note the cursor under the first A. Select the three alphabetic or numeric characters which you want displayed for your selected rate units by answering **"NO"** until the correct character is displayed in the current cursor position. A **"YES"** answer then accepts that character and moves the cursor one position to the right. A **"YES"** to the last character brings the conversion factor menu.

1.6.1b Conversion Factor

1=1.200000 GPM?

The conversion factor is defined as U.S. GPM/user unit. Enter the number of GPM which is equal to 1 of your selected units.

Example: To set the conversion factor for gallons per hour, enter the number of gallons per minute which is equal to 1 gallon per hour. One gallon per minute is equal to 0.016666 gallons per hour (1 ÷ 60). In this case, enter 0.0166666.

1.6 Rescale Rate Cont'd.

1.6.2 Set Full Scale

The full scale flow rate defines only the flow rate at which the current output is set to 20 mA and at which the frequency output is set to 1000 Hz. **It does not affect the display or the accuracy of the frequency or pulse output.**

Q=5.000000 GPH?

In the case above, entering 5.0 GPH here will set the current output to 20 milliamps and the frequency to 1000 Hz when the fluid flow reaches 5.0 GPH. Full scale flow is selected in the units defined in 1.6.1 above. Thus, if "GPH" were defined, full scale would be defined in GPH not GPM. By answering **"YES"** or **"NO"** to each digit, it is possible to enter the full scale flow rate. A full scale below 3 FPS or above 35 FPS will receive a warning of "OUT OF RANGE LOW" or "OUT OF RANGE HIGH". Unit is still functional, but is operating out of recommended range.

1.6.3 Select Rate as Percent of Full Scale

DISPLAY:RATE UNITS

A **"YES"** answer will display flow in engineering units as defined in 1.6.2 **"NO"** displays rate as a percentage of full scale. Either choice will affect only the format of the display and nothing else.

1.7 Rescale Total

If your TigermagEP is equipped with the optional remote batcher, refer to Appendix 2.

RESCALE TOTAL?

A **"YES"** answer enters the Rescale Total loop. A **"NO"** answer continues to the next menu item.

1.7.0 Lockout

LOCKOUT: ON

LOCKOUT: OFF

LOCKOUT: OFF allows you to reprogram the high and low flow alarms when the **"YES"** key is activated while in normal operating mode. No password is required.

LOCKOUT: ON will only allow the viewing of high and low flow alarms while in normal operating mode. To reprogram these values you will need to enter the MagCommand Rescale Total menu which requires a password.

After choice is made select **"YES"** to continue.

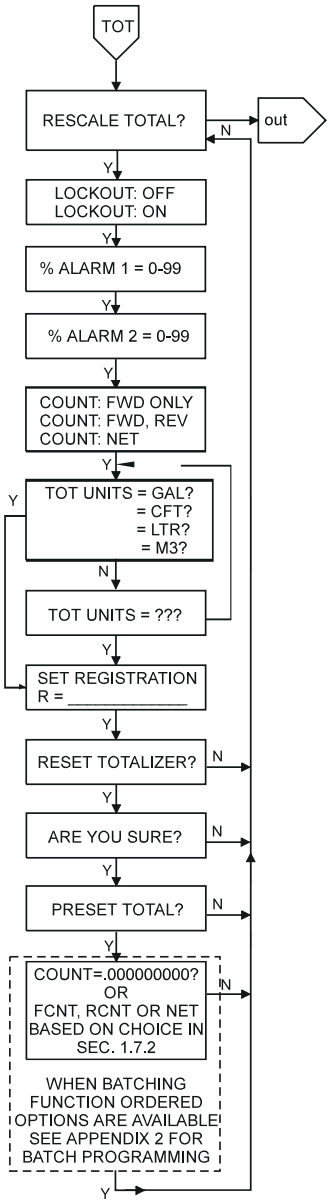


Figure A1.4
Rescale Total Flow

1.7 Rescale Total Cont'd.

1.7.1 Alarms

% ALARM 1 = 0-99

% ALARM 2 = 0-99

Using MagCommand, you can set these alarm contacts to activate when flow rate exceeds the set value in percent of full scale desired, from 0 through 99%. These contacts enable you to activate alarms, small relays, equipment, etc. at a preset percentage of full scale. Most commonly used as high and low flow alarms (through complementary contacts of externally supplied relays), these can be set to warn you of conditions outside your process parameters.

1.7.2 Count Direction

The internal totalizer can be programmed to totalize in the forward direction, to totalize separately for forward and reverse or provide you with net flow.

COUNT:FWD ONLY

Answer **"YES"** to count in the forward direction *only* (shown in the "operate" mode as "COUNT=")

COUNT:FWD,REV

Answer **"YES"** to have separate internal counters for forward and reverse flow (displayed as "F CNT=" and "R CNT=" respectively).

COUNT:NET

Answer **"YES"** to count net flow *only.*

1.7.3 Select Total Units

A menu is presented to select the engineering units in which totalization or frequency is displayed and scaled. By answering **"NO"** each menu selection is presented in turn. A **"YES"** selects the unit displayed and moves on to the next item.

TOT UNITS=GAL

Answer **"NO"** to view the available predefined totalization units. Select **"YES"** to the preferred engineering units for totalization. One of the options will be ???. This permits the definition of any desired units. A **"YES"** must be selected to one of the options to exit this loop.

1.7.3a User Defined Totalizer Units

TOT UNITS = AAA

Select the desired three (3) character abbreviation as in 1.6.1a on the previous page.

1.7.3b Conversion Factor

1=1.2500000 GAL?

Enter the number of U.S. gallons which is equivalent to 1 of your selected units.

For example, the conversion factor from U.S. Gallons to Imperial Gallons is 1.25 because there are 1.25 U.S. Gallons to each 1 Imperial Gallon.

1.7 Rescale Total Cont'd.

1.7.4 Set Registration

R=100.000 GAL?

Enter the number of your engineering units of totalization which is equivalent to one count of the internal totalizer and external "TOT" output. This is normally an even number such as 0.1, 1, 10, 100, etc. In the above case 100 gallons will produce one totalizer pulse.

1.7.5 Reset Totalizer

Allows you to zero or reset the starting number on the totalizer.

RESET TOTALIZER?

Answer **"YES"** to advance, **"NO"** to return to RESCALE TOTAL?

ARE YOU SURE?

Answer **"YES"** to perform the reset of totalizer(s), **"NO"** to return to RESCALE TOTAL? (This is your last chance to abort before you lose your present value of totalizer(s).)

PRESET TOTAL?

Answer **"YES"** to be able to initialize the new nonzero beginning total, **"NO"** to return to RESCALE TOTAL? with totalizer(s) already reset to zero in the last step.

COUNT=.000000000?

Enter new beginning total. If counting FWD, REV or NET were selected earlier (1.7.2) then FCNT and RCNT can be preset to their starting values.

1.8 Set Outputs

SET OUTPUTS?

A **"YES"** answer enters the Set Outputs loop. A **"NO"** answer continues to the next menu item.

OUTPUT:4-20 MA

This permits the selection of 4-20 or 0-20 mA dc outputs. Answer **"YES"** to the output desired. Most North American installations will use 4-20.

1.8.1 Select Pulse Width

ONTIME:12.5

This selects the totalizer output of 0-60 Hz 12.5/25/50/100 ms, 24 Vdc. The choice is based on the external device requirement as well as your values of Q (Sect. 1.6.2) and R so that pulses don't run together at the maximum flow. The frequency output of 0-1000 Hz, 50/50 duty cycle is always available (Section 1.6.2). See Figure 3.12, Electrical Connections.

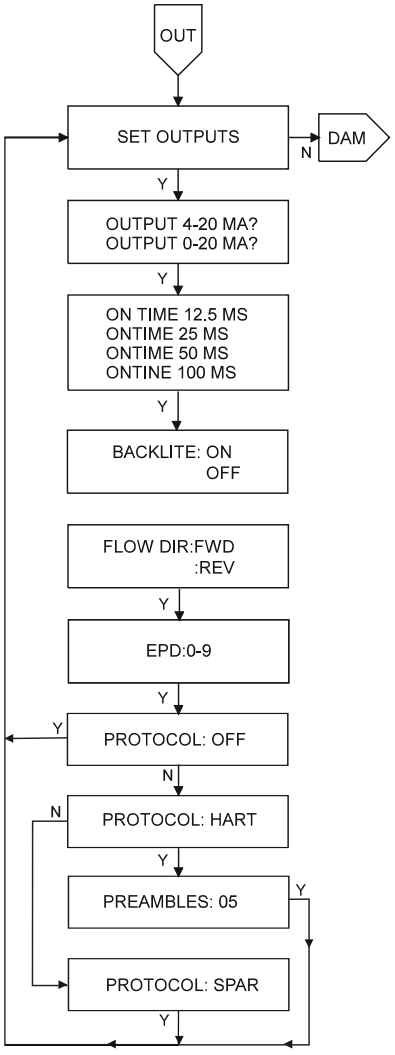


Figure A 1.5
Set Outputs Flow Chart

1.8 Set Outputs Cont'd.

1.8.2 Backlight

BACKLITE:ON

BACKLITE:OFF

This allows you to turn the display backlight on or off. **"NO"** toggles between the choices. **"YES"** selects and advances.

1.8.3 Set Flow Direction

FLOW DIR: FWD

FLOW DIR: REV

This allows the user to reverse the **normal flow direction.** The default flow direction is from left to right as you face the display. *If flow is in the opposite direction a minus sign (-) will appear in the display, the flow direction output will be active and the internal totalizer will be inhibited in the count forward direction.* Apart from that, the meter will operate properly in either direction. Both pulse and analog outputs will operate in both directions. Answer **"NO"** to reverse the normal flow direction.

1.8.4 Empty Pipe Detection

It allows the user to set the EPD control between 0 (=off) and 9 as part of "SET OUTPUTS?" menu. Numerically, this represents the approximate delay in seconds before the activation of EPD state (outputs driven to zero, totalizer on hold, message "OUTPUT INHIBITED" on display). Note EPD setting functions like a "volume" control, with "0" serving as an "EPD-off" click and "1" thru "9" enabling various levels of detection. Typical setting may be between 3 and 6, the lower the number, the higher the possibility of "false" detection of a single air bubble. Factory setting is "0" (off).

1.8.5 Protocol

Selects between "SPAR"-Sparling MagCommand and "OFF"-no programming interface. "HART" will also appear if meter has been equipped with the optional HART interface and will allow you to set the number of HART's preambles in a message.

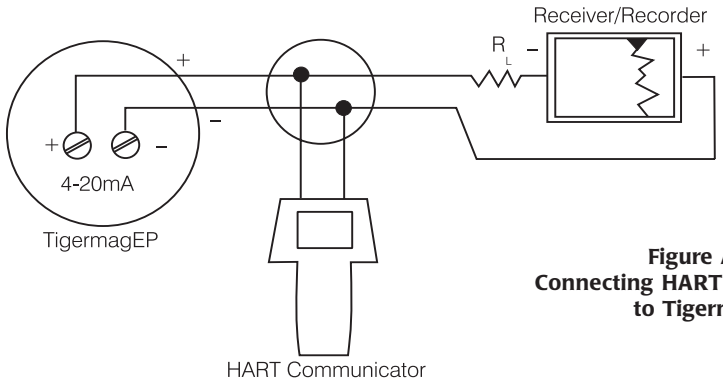


Figure A 1.6
Connecting HART Communicator to TigermagEP

NOTE: For the HART Communicator to function properly, a minimum of 250 ohms resistance RL must be present in the loop. The HART Communicator does not measure loop current directly.

WARNING

Explosions can result in death or serious injury. Before connecting the HART Communicator in an explosive atmosphere, make sure the instruments in the loop are installed in accordance with intrinsically safe or non-incendive field wiring practices.

1.9 Damping Adjustments

SET DAMPING?

Display and current output are damped *independently.* Answer **"YES"** to enter this loop.

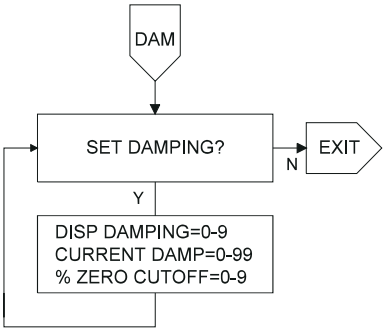


Figure A 1.7
Set Damping Flow Chart

1.9.1 Display Damping

DISP DAMPING - 5

A **"NO"** answer scrolls from 0 (no damping) through 9 (maximum damping). Answer **"YES"** to the desired degree of display damping. Some experimentation may be necessary to obtain optimum results.

1.9.2 Current Damping

CURRENT DAMP=15

Current damping may be selected from 0-99 seconds. This corresponds approximately to the number of seconds to respond 90% of the way to a step change in input.

1.9.3 Low Flow Cutoff

% ZERO CUTOFF=2

This is the minimum flow rate below which meter outputs are forced to zero. The number entered corresponds to the selected percentage of full scale as set for "Q" in Section 1.6.2. Choices range from 0 (low flow cutoff disabled) through 9%.

2.0 Exit Programming

EXIT?

A **"YES"** answer stores the changes which have been made and returns the meter to operation. A **"NO"** goes to the next menu item.

2.1 Change Password

CHANGE PASSWORD?

ARE YOU SURE?

Answer **"NO"** to return to CHANGE PASSWORD. Answer **"NO"** again to continue to the next item.

A **"YES"** answer permits changing the password by scrolling through the four available digits. Be sure to record the new password.

▼ FAILURE TO REENTER THE NEW PASSWORD WILL RESULT IN NOT BEING ABLE TO REPROGRAM AT A LATER DATE.

2.2 Change Tag

CHANGE TAG?

Answer **"YES"** to change the tag. Default is "SPAR".

TAG=_ _ _ _ _ _ _ _ _ _ _ _

A **"NO"** answer scrolls through your character choices. Answer **"YES"** to skip to next letter. When you have finished the tag name, **"YES"** will bring you back to the "CHANGE TAG" menu. **"NO"** will advance to "DIAGNOSTICS", **"YES"** will enter the TAG loop again.

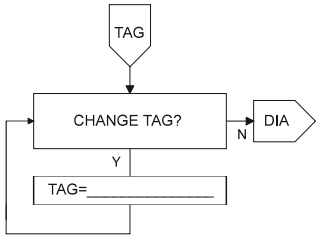


Figure A 1.8
Change Tag

2.3 Diagnostics

DIAGNOSTICS?

Answer **"YES"** to enter the diagnostics loop. A **"NO"** answer returns to the RESCALE RATE menu.

WARNING

It is NOT recommended that diagnostics be performed unless malfunction is suspected. Refer to the trouble-shooting section for coil and electrode tests which can be performed.

Warning—the meter totalizers and flow rate will cease to be updated while you are in this loop. Outputs will be affected by some tests as well as totalizer count. Use Caution.

2.3.1A Check HART Transmission

This option is only available if your meter is equipped with HART® communications. Toggle between MARK and SPACE by selecting **"NO"**. Enter next box by selecting **"YES".**

2.3.1B Check Coil Current

STOP COIL DRIVE?

Answer **"YES"**

COIL=HIGH

Note the value on the second line of the display. To test low coil, enter **"NO"**

COIL=LOW

Again, note its value. Both values should match closely. The typical coil current should range around 1/4 to 1/3 amp. Coil currents are affected by temperature. Unit is operating correctly unless currents don't match and are widely out of this range. To test high coil again, enter **"NO"**. To end this test, enter **"YES"**.

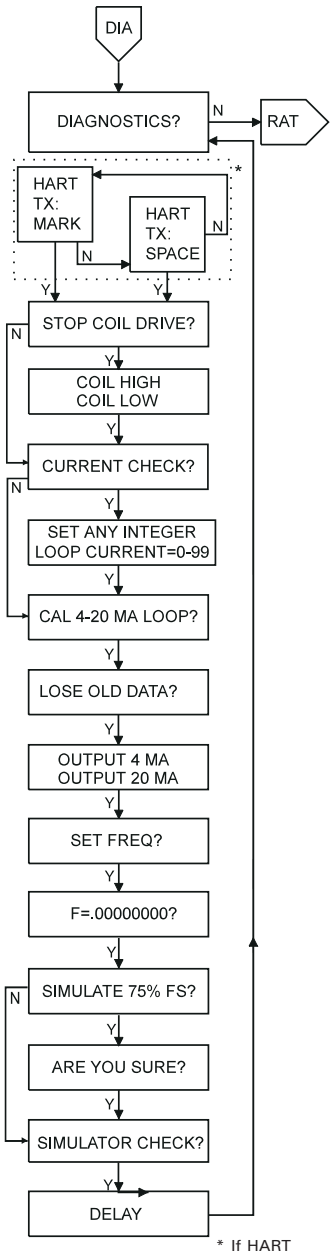


Figure A 1.9
Diagnostics Flow

2.3 Diagnostics Cont'd.

2.3.2 Check Current Loop

LOOP CURRENT=04

By answering **"NO"** the loop current can be scrolled by 1 mA increments, from 4 mA up to 20 mA and then back to 4. Answer **"NO"** to step to the next desired value. Answering **"YES"** at any time will exit the loop. Check the 4 mA and 20 mA positions with a digital milliammeter. Each should be accurate within ±0.02 mA (no damping is used).

The current output can also be used to test other equipment in the current loop such as recorders and controllers.

2.3.3 Calibrate 4-20 mA Loop

CAL 4-20mA LOOP?

Answer **"YES"** to enter the calibrate mode. You must leave your recently calibrated milliammeter connected in series with the 4-20 loop at this time.

LOSE OLD DATA?

Answer **"YES"** to continue, **"NO"** will exit leaving calibration unchanged. This is your last chance to abort if your setup is not ready.

OUTPUT: 4mA?

Answer **"YES"** if your meter reads 4.00 mA. **"NO"** will allow you to calibrate current for zero flow.

I= 4.0000000?

Enter in the actual reading value from your digital milliammeter to calibrate zero flow. Answer **"YES"** to continue.

OUTPUT: 20mA?

Answer **"YES"** if your meter reads 20.00 mA. **"NO"** will allow you to calibrate current for full scale.

I= 20.000000?

Enter in the actual reading value from your digital milliammeter to calibrate full scale. Answer **"YES"** to continue.

2.3.4 Set Frequency

Set frequency can be used to verify or set the frequency received by other devices to insure compatibility.

SET FREQ?

Select **"YES"** to enter the set frequency mode, select **"NO"** to continue.

F = .000000000

Enter desired frequency in the 1-1250 Hz range to appear as the frequency output or select **"YES"** to zero value and end this test.

2.3 Diagnostics Cont'd.

2.3.5 Simulate 75% FS

This step will drive all outputs to 75% of full scale rate including the display.

CAUTION

This test will alter the totalizer counts. On exit from this test, reset or preset totalizers to their proper value.

Enter **"YES"** to get last chance to abort "ARE YOU SURE?" Enter **"YES"** only if you wish to continue at which point the meter will begin simulated 75% of its full scale (as signified by the letter "S" in the third from the last position on the top line of display (just before "12" for alarms - See figure A 2.0). To end, reenter diagnostics and reply **"NO"** to either "SIMULATE 75% FS?" or "ARE YOU SURE?" that follows.

2.3.6 Simulator Check

Simulator Check is used to verify that electronics are working satisfactorily by comparing actual values to the factory preset values. Testing is done internally.

SIMULATOR CHECK?

Select **"YES"** to enter the simulator check mode, select **"NO"** to continue.

PLEASE WAIT

"PLEASE WAIT" is displayed while electronics self-check.

SELF TEST PASSED

The electronics are working satisfactorily.

SELF TEST FAILED

The electronics are not working satisfactorily. Replace electronics module. The second line of the display will show a 47000/K value as GPM. Obtain K from meter record and calculate 47,000/K to check for match.

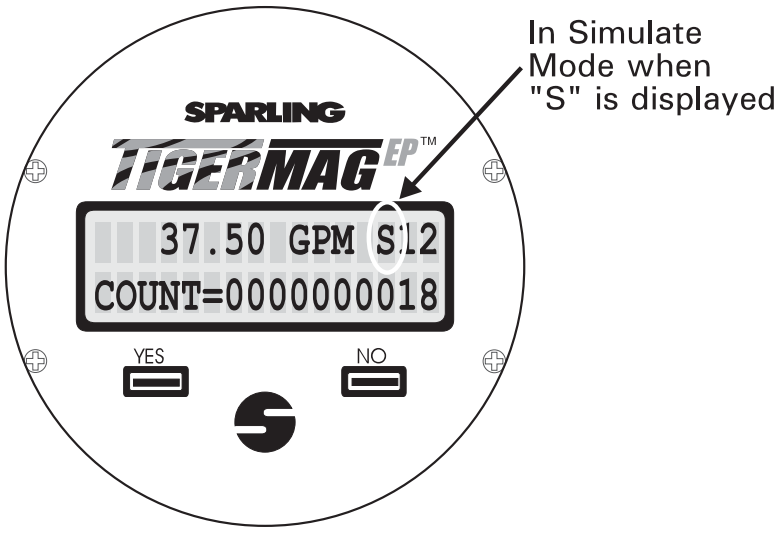


Figure A2.0
Simulate Mode

A.2 Appendix 2

Batch Programming & Operation - Firmware Ver. 1.0

This section of the manual covers only the batching function. For programming of other loops not associated with the batching function, see Appendix 1.

1.1 General

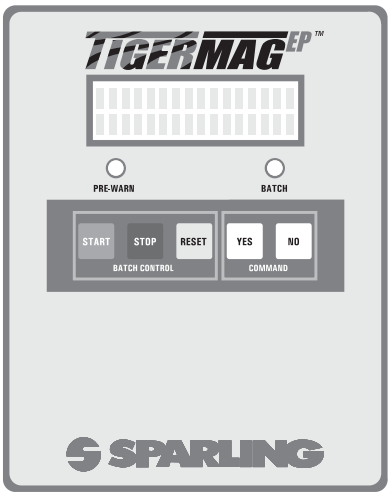


Figure A 2.1
Enclosure for TigermagEP with Batching

The TigermagEP Batcher utilizes a touch pad for programming both meter and batch operations. The **"YES"** and **"NO"** buttons are the only controls required to select and change parameters on the TigermagEP. Nothing else is required for programming the meter with MagCommand.

IT IS NOT NECESSARY TO OPEN THE ELECTRONICS COMPARTMENT IN ORDER TO CHANGE PROGRAM SETTINGS.

1.2 Programming

The batching mode is activated in the Rescale Total menu. Refer to Figure A1.2 to determine how to reach this section.

RESCALE TOTAL?

"YES" to enter the Rescale Total menu.

1.2.0 Lockout

LOCKOUT: ON
LOCKOUT: OFF

LOCKOUT: OFF allows you to reprogram batch size and prewarn levels while in normal operating mode. No password is required.

LOCKOUT: ON will only allow you to view batch size and prewarn levels while in normal operating mode. To reprogram these values you will need to enter the **MAG-COMMAND** Rescale Total menu which requires a password.

After choice is made select **"YES"** to continue.

1.3 Rescale Total

1.3.1 Batch On/Off

BATCH: ON

BATCH: OFF

"NO" toggles between 'Batch On' and 'Batch Off'.

BATCH: ON

1) gives you access to TigermagEP's batching functions while in normal operation mode
2) disables Alarms 1 and 2.
3) batch size and prewarn levels become accessible for viewing or reprogramming while in normal operation mode.

BATCH: OFF

1) turns off the TigermagEP's batching functions.
2) allows access to TigermagEP's Alarm 1 and Alarm 2
3) % Alarm 1 and % Alarm 2 become accessible for viewing or reprogramming while in normal operation mode.

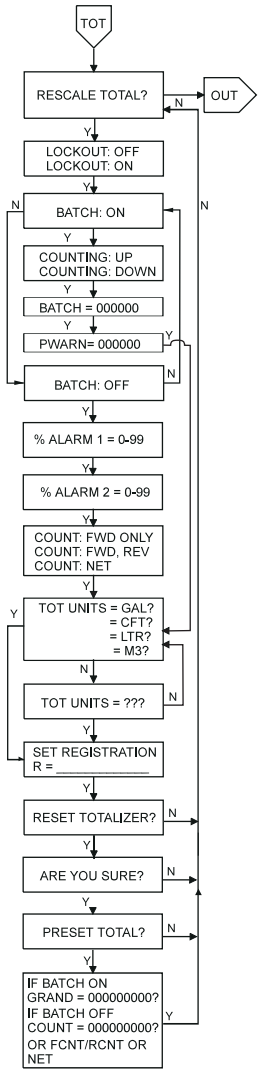


Figure A 2.2
Rescale Rate - Batcher

1.3.2 Alarms

% ALARM 1 = 0-99

% ALARM 2 = 0-99

Using MagCommand, you can set these alarm contacts to activate at any percent of full scale desired, from 0 through 99%. These contacts enable you to activate alarms, equipment, etc. at a preset percentage of full scale. Most commonly used as high and low flow alarms, these can be set to alert you that process parameters may be out of range.

Alarms 1 & 2 are only available when batch mode is turned off (BATCH: OFF). Alarm 1 and Alarm 2 can be set to activate at the percentage of full scale specified here. After setting, **"YES"** accepts selection of Alarm 1 and advances to Alarm 2. When lockout status is on (LOCKOUT: ON) you will be able to view % Alarm 1 and % Alarm 2 values from normal operation mode. When lockout status is off (LOCKOUT: OFF) you will be able to change the values of % Alarm 1 and % Alarm 2.

1.3.3 Count Direction

The internal totalizer can be programmed to totalize in the forward direction, to totalize separately for forward and reverse or provide you with net flow.

COUNT:FWD ONLY

Answer **"YES"** to count in the forward direction ***only*** (shown in the "operate" mode as "COUNT=")

COUNT:FWD,REV

Answer **"YES"** to have separate internal counters for forward and reverse flow (displayed as "F CNT=" and "R CNT=" respectively).

COUNT:NET

Answer **"YES"** to count net flow ***only***.

1.3 Rescale Total Cont'd.

1.3.4 Select Total Units

A menu is presented to select the engineering units in which totalization or frequency is displayed and scaled. By answering **"NO"** each menu selection is presented in turn. A **"YES"** selects the unit displayed and moves on to the next item.

TOT UNITS=GAL

Answer **"NO"** to view the available predefined totalization units. S**elect "YES"** to the preferred engineering units for totalization. One of the options will be ???. This permits the definition of any desired units. A **"YES"** must be selected to one of the options to exit this loop.

1.3.5a User Defined Totalizer Units

TOT UNITS = AAA

Select the desired 3 character abbreviation as in 1.6.1a on the previous page.

1.3.5b Conversion Factor

1=1.2500000 GAL?

Enter the number of U.S. gallons which is equivalent to 1 of your selected units.

For example, the conversion factor from U.S. Gallons to Imperial Gallons is 1.25 because there are 1.25 U.S. Gallons to each 1 Imperial Gallon.

RESCALE TOTAL

A **"YES"** answer enters the Rescale Total loop. A **"NO"** answer continues to the next menu item. See Section 1.7.5 for details.

RESET TOTALIZER?

A **"NO"** answer ends this loop.

If batch is on (BATCH: ON) display will read:

GRAND = 000000000?

Enter

If batch is off (BATCH: OFF) display will read:

COUNT = 000000000?

1.4 Description of Operation

1.4.1 Description of Operation

This option, if available, can be either enabled (BATCH: ON) or disabled (BATCH: OFF) in users menu of "RESCALE TOTAL?" When enabled, the batch menu offers the choice of display direction of counting (up or down) and the limits of the prewarn (relay #2) and the batch (relay #1). The status of the relays will be displayed on line 1 (last two places) as digits 1 and/or 2 whenever the corresponding relay coil gets energized. Line 2 will show GRAND total, batch size, and the status of the batch.

Once the programming is in place, the cycle starts when RESET is pushed. The display line 2 will stop toggling between GRAND and BATCH and show 'BATCH=xxxxxx PZR' indicating that PZR input has reset the 626 for the next batch. Pushing START activates both relays (shown in line 1 and changes 'PZR' to 'RUN' as the batch starts counting off. Reaching PREWARN level drops out relay #2 and 'PRE' replaces 'RUN' in line 2. At the end of the batch, relay #2 drops out and line 2 reverts to toggling between Grand and 'BATCH=XXXXXX HLD' as the batching is on hold until RESET starts it again. To abort batch in progress, push STOP. This overrides relays ON command dropping them out (note line 1 will report them as ON). The flow and the count off will stop, at which point one can resume this batch by pushing START or abort it via RESET for another batch (note however that GRAND will include any flow that went into the batch prior to pushing STOP).

A.3 Appendix 3 – Communications

1.1 RS232 Sparling Protocol

Wiring (3-wire cable less than 50 ft.)

Connect as follows:

PC "COM" Port 25 pin		626 J405 on I/O PCB (Integral) 626 J9 (Remote - Motherbd)
2-TX	to	1-RX
3-RX	to	2-TX
7-GND	to	3-GND
4-RTS to 5-CTS	to	4 - No Connection

PC "COM" Port 9 pin		626 J405 on I/O PCB 626 J9 (Remote - Motherbd)
2-RX	to	2-TX
3-TX	to	1-RX
5-GND	to	3-GND
7-RTS to 8-CTS	to	4 - No Connection

Set up the PC communications software (DOS, Windows 3.x, Windows 95)) as follows:

Example: Hyper Terminal
1200 baud
8 data bits
1 stop bit
Odd Parity
(Flow control = none)

Conversation:

Control-Q (11 hex) starts it (626 will reply; PZR/PGM on the PC screen),
Control-U (15 hex) ends it (626 - no reply, its display - back to run mode).
Menu follows MagCommand.
Keyboard exceptions (for compatibility with existing programmers):
(Space Bar) steps over existing characters
(Backspace) clears characters
(Enter) or "Y" key serves as "yes", anything else as "no".

Burst mode
Control-S (13 hex) starts it.
The 626 will continuously copy its 2-line display to RS232 line.
Press and hold Control-U to end it.

Problems checklist:
- Check wiring
- Check PC setup
- Verify that 626 in its "SHOW METER DATA?" menu (or user's "SET OUTPUTS?) has PROTOCOL: SPAR and not PROTOCOL: OFF nor PROTOCOL: HART.

1.2 RS-485

RS-485 (one-on-one only, no multidrop, less than 4000 ft.)
On digital PCB, U105 should be removed and U108 installed.

Wire and use as RS232

Line 485		626 (J405 on I/O PCB)
(+) or A	to	2-TX (also line load)
(1) or B	to	1-RX (also line load)
Shield	to	3-GND

Problems checklist:

- See Section 1.1, RS232
- Line must terminate in its characteristic impedance at BOTH ends, e.g. for 24 AWG twisted pair install terminating 120 ohm resister between 1 & 2 of J405 as well as across the other end. See Figure 3.12.

Sparling Instruments, Inc.
4097 N. Temple City Blvd. • El Monte, California 91731 • Ph (626) 444-0571 • Fax (626) 452-0723
Website: http://www.sparlinginstruments.com • E-mail: sales@sparlinginstruments.com

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APPENDIX 14
SOP FOR GRAB SAMPLING (INCLUDES DISCHARGE GRAB SAMPLING FROM PROCESSING FACILITY FOR MONTHLY PH SAMPLES AND TWICE WEEKLY SAMPLES FOR OTHER PARAMETERS)

Standard Operating Procedure: Collection of Grab Samples from Facility Discharge

I. Scope and Application

This Standard Operating Procedure (SOP) applies to the collection of processing facility discharge grab samples, via a tap in the discharge line, for various required analyses, and pH and dissolved oxygen (DO) measurements during Phase 1 of the Hudson River remedial action. Grab samples of the discharge from the dredged sediment dewatering facilities will be collected weekly (except pH). The parameters that will be monitored weekly are listed below:

- Total suspended solids
- Total organic carbon
- Cadmium, total
- Chromium, total
- Copper, total
- Lead, total
- Mercury, total
- DO

One grab sample will be collected monthly (during one of the weekly events) to measure pH in the discharge.

The pH will be measured with a Hanna HI 991301 meter, or equivalent, and DO will be measured with a YSI 55 meter, or equivalent.

II. Personnel Qualifications

Field personnel, trained in grab sampling procedures, will collect the grab samples. All field personnel are required to take a 40-hour Occupational Safety and Health Administration (OSHA) Hazardous Waste Operations (HAZWOPER) training course and annual refresher courses, and participate in a medical monitoring program prior to engaging in any field collection activities as required in 29 CFR 1910.120. ARCADIS field sampling personnel will be versed in the relevant SOPs and possess the skills and

experience necessary to successfully complete the desired field work. Additionally, field personnel will be under the direct supervision of qualified professionals who are experienced in performing the tasks required for sample collection.

III. Equipment List

Equipment needed to collect processing facility discharge grab samples includes:

- Health and safety equipment, as required by the site Health and Safety Plan (HASP; Parsons 2008)
- pH and DO meters
- Glass sample container
- Standard solutions for calibration
- Extra batteries for the pH and DO meters
- Disposable non-talc gloves
- Wind suit
- Pre-preserved sample containers
- Plastic (polyethylene) resealable food storage bags
- Polyethylene wrap
- Distilled water

- Dedicated, clean cooler with ice
- Field notebook and forms
- Chain of custody forms

- Labels for sample containers
- Permanent marker

IV. Cautions

Potential sources of trace metals contamination during sampling include metallic or metal-containing sampling equipment, containers, personal protective equipment (PPE), reagent water, and improperly cleaned and stored equipment. If laboratory analyses indicate that processing facility discharge water contains substances that interfere in the determination of metals, additional sample volume will be collected in the event following such determination to allow the laboratory to identify and address interference problems.

Sample containers should be packed on ice and stored in a cool, shaded place to maintain a sample temperature of approximately 4□C, if possible. Ice must be double-bagged to prevent leaks. Sample containers should be stored inside sealable plastic bags to prevent interference from external sources should a container break during transit.

V. Health and Safety Considerations

Health and safety considerations are addressed in the site Health and Safety Plan (HASP; Parsons 2008).

VI. Procedures for Collecting Grab Samples for Inorganic Analysis, Except Mercury

The procedure for collecting the grab samples for inorganic analysis, except mercury, is described below:

1. Complete project and sample location information on the Processing Facility Discharge Form (Figure 2-19).

2. Put on a new pair of disposable gloves.

3. Fill appropriate sample container from the grab sample tap in discharge line.

4. Affix a label to each sample container and record the following information (in accordance with Appendix 28) on the label: date and time of sample retrieval, sample identification, and analysis method/parameter. Note: the sample identification is "Processing Facility Discharge."

5. Seal each sample container in a resealable plastic bag; label the bags with date, time, and sample identification; and place the bags in the cooler with ice.

6. Repeat Steps 2 through 5 as necessary to collect a volume sufficient to fill all of the required sample containers.

7. Complete the chain of custody form in accordance with Section 10.1 of the main text.

VII. Procedure for Collecting Samples for Mercury Analysis

The procedures for collecting samples for mercury analysis are outlined in Method 1669: Sampling Ambient Water for Trace Metals at EPA Water Quality Criteria Levels (EPA 1996), which is included as Attachment 1. The key procedures are described below:

1. Upon arrival at the sampling site, one member of the two-person sampling team is designated as "dirty hands"; the second member is designated as "clean hands." All operations involving contact with the sample bottle are handled by the individual designated as "clean hands." "Dirty hands" is responsible for opening the sample tap, operating any machinery, and for all other activities that do not involve direct contact with the sample.

2. An unlined, long-sleeved wind suit consisting of pants and jacket and constructed of nylon or other synthetic fiber is worn when sampling for mercury to prevent mercury adsorbed onto cotton or other clothing from contaminating samples.

   The wind suit is washed by itself or with other wind suits only in a home or commercial washing machine and dried in a clothes dryer. The clothes dryer must

   be thoroughly vacuumed, including the lint filter, to remove all traces of lint before drying. After drying, the wind suit is folded and stored in a clean polyethylene bag for shipment to the sample site.

3. The following steps detail sample collection:

   a. The sampling team puts on gloves (and wind suits, if applicable).

   b. "Clean hands" positions the fluoropolymer sample bottle beneath the sample tap.

   c. "Dirty hands" operates sample tap so that an appropriate sample volume is achieved.

   d. "Clean hands" seals the fluoropolymer bottle.

   e. Documentation – After each sample is collected, the sample number is documented in the sampling log, and any unusual observations concerning the sample and the sampling are documented.

4. Preservation must be performed in the glove bag or in a designated clean area, with gloved hands, as rapidly as possible to preclude particulates from contaminating the sample. It is advisable to set up a work area that contains a "clean" cooler to store clean equipment, a "dirty" cooler to store "dirty" equipment, and a third cooler to store samples for shipment to the laboratory.

VIII. Procedure for Collecting Samples for Field Parameters

The procedure for collecting the grab samples for measurement of field parameters is described below.

1. Complete Processing Facility Discharge Reporting Form (Figure 2-14).

2. Put on a new pair of disposable gloves.

3. Open sample tap and fill glass jar with adequate sample volume.

4. Measure pH and DO. Two readings will be made and the average will be recorded in the field notebook and on the form.

The meters will be operated following the manufacturer's instructions (Attachment 2).

IX. Calibration and Maintenance

Calibration information will be recorded in the field notebook and calibration and maintenance logs (Attachment 3). Prior to use, the meters will be calibrated following the manufacturer's instructions (Attachment 2).

Maintenance of the pH and DO meters will be done according to the manufacturer's instructions. Maintenance information will be recorded in the field notebook and calibration and maintenance logs. A replacement meter and probes will be available onsite or ready for overnight shipment, as necessary. Batteries will be replaced on a regular basis. The meters will be stored in the protective casing when not in use, and will be sent back to the manufacturer for service when needed.

X. Waste Management

Waste generated during collection of the grab samples, such as gloves and other expendables, will be placed in labeled 55-gallon drums onsite.

XI. Data Recording and Management

he Processing Facility Discharge Monitoring Form (Figure 2-19) will be completed.

XII. Quality Assurance

Quality assurance/quality control (QA/QC) procedures are defined in Section 10.2 of this document, and include collecting field QA/QC samples. Field QA/QC samples to be

collected are equipment blanks, field duplicates, and matrix spike samples. Matrix spike samples and field duplicates will be prepared by filling additional appropriately marked containers.

XIII. References

EPA, 1996. Method 1669: Sampling Ambient Water for Trace Metals at EPA Water Quality Criteria Levels. EPA Office of Water, Washington, D.C. July 1996.

Parsons, 2008. Phase 1 Remedial Action Health and Safety Plan, Hudson River PCBs Site. Prepared for General Electric Company, Albany, NY. August 2008.

Attachment 1

Sampling Ambient Water for Trace Metals at EPA Water Quality Criteria Levels

Method 1669

Sampling Ambient Water for Trace Metals at EPA Water Quality Criteria Levels

July 1996

U.S. Environmental Protection Agency
Office of Water
Engineering and Analysis Division (4303)
401 M Street S.W.
Washington, D.C. 20460

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Disclaimer

This sampling method has been reviewed and approved for publication by the Analytical Methods Staff within the Engineering and Analysis Division of the U.S. Environmental Protection Agency. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

Further Information

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Introduction

This sampling method was designed to support water quality monitoring programs authorized under the Clean Water Act. Section 304(a) of the Clean Water Act requires EPA to publish water quality criteria that reflect the latest scientific knowledge concerning the physical fate (e.g., concentration and dispersal) of pollutants, the effects of pollutants on ecological and human health, and the effect of pollutants on biological community diversity, productivity, and stability.

Section 303 of the Clean Water Act requires states to set a water quality standard for each body of water within its boundaries. A state water quality standard consists of a designated use or uses of a waterbody or a segment of a waterbody, the water quality criteria that are necessary to protect the designated use or uses, and an antidegradation policy. These water quality standards serve two purposes: (1) they establish the water quality goals for a specific waterbody, and (2) they are the basis for establishing water quality-based treatment controls and strategies beyond the technology-based controls required by Sections 301(b) and 306 of the Clean Water Act.

In defining water quality standards, the state may use narrative criteria, numeric criteria, or both. However, the 1987 amendments to the Clean Water Act required states to adopt numeric criteria for toxic pollutants (designated in Section 307(a) of the Act) based on EPA Section 304(a) criteria or other scientific data, when the discharge or presence of those toxic pollutants could reasonably be expected to interfere with designated uses.

In some cases, these water quality criteria are as much as 280 times lower than those achievable using existing EPA methods and required to support technology-based permits. Therefore, this sampling method, and the analytical methods referenced in Table 1 of this document, were developed by EPA to specifically address state needs for measuring toxic metals at water quality criteria levels, when such measurements are necessary to protect designated uses in state water quality standards. The latest criteria published by EPA are those listed in the National Toxics Rule (57 *FR* 60848) and the Stay of Federal Water Quality Criteria for Metals (60 *FR* 22228). These rules include water quality criteria for 13 metals, and it is these criteria on which this sampling method and the referenced analytical methods are based.

In developing these methods, EPA found that one of the greatest difficulties in measuring pollutants at these levels was precluding sample contamination during collection, transport, and analysis. The degree of difficulty, however, is highly dependent on the metal and site-specific conditions. This method, therefore, is designed to provide the level of protection necessary to preclude contamination in nearly all situations. It is also designed to provide the procedures necessary to produce reliable results at the lowest possible water quality criteria published by EPA. In recognition of the variety of situations to which this method may be applied, and in recognition of continuing technological advances, the method is performance-based. Alternative procedures may be used, so long as those procedures are demonstrated to yield reliable results.

Requests for additional copies of this method should be directed to:

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11029 Kenwood Road
Cincinnati, OH 45242
513/489–8190

Note: This document is intended as guidance only. Use of the terms "must," "may," and "should" are included to mean that EPA believes that these procedures must, may, or should be followed in order to produce the desired results when using this guidance. In addition, the guidance is intended to be performance-based, in that the use of less stringent procedures may be used so long as neither samples nor blanks are contaminated when following those modified procedures. Because the only way to measure the performance of the modified procedures is through the collection and analysis of uncontaminated blank samples in accordance with this guidance and the referenced methods, it is highly recommended that any modifications be thoroughly evaluated and demonstrated to be effective before field samples are collected.

Method 1669

Sampling Ambient Water for Determination of Metals at EPA Water Quality Criteria Levels

1.0 Scope and Application

1.1 This method is for the collection and filtration of ambient water samples for subsequent determination of total and dissolved metals at the levels listed in Table 1. It is designed to support the implementation of water quality monitoring and permitting programs administered under the Clean Water Act.

1.2 This method is applicable to the metals listed below and other metals, metals species, and elements amenable to determination at trace levels.

Analyte	Symbol	Chemical Abstract Services Registry Number (CASRN)
Antimony	(Sb)	7440-36-0
Arsenic	(As)	7440-38-2
Cadmium	(Cd)	7440-43-9
Chromium (III)	Cr^{+3}	16065-83-1
Chromium (VI)	Cr^{+6}	18540-29-9
Copper	(Cu)	7440-50-8
Lead	(Pb)	7439-92-1
Mercury	(Hg)	7439-97-6
Nickel	(Ni)	7440-02-0
Selenium	(Se)	7782-49-2
Silver	(Ag)	7440-22-4
Thallium	(Tl)	7440-28-0
Zinc	(Zn)	7440-66-6

1.3 This method is accompanied by the 1600 series methods listed in Table 1. These methods include the sample handling, analysis, and quality control procedures necessary for reliable determination of trace metals in aqueous samples.

1.4 This method is not intended for determination of metals at concentrations normally found in treated and untreated discharges from industrial facilities. Existing regulations (40 *CFR* Parts 400-500) typically limit concentrations in industrial discharges to the mid to high part-per-billion (ppb) range, whereas ambient metals concentrations are normally in the low part-per-trillion (ppt) to low ppb range. This guidance is therefore directed at the collection of samples to be measured at or near the levels listed in Table 1. Actual concentration ranges to which this guidance is applicable will be dependent on the sample matrix, dilution levels, and other laboratory operating conditions.

1.5 The ease of contaminating ambient water samples with the metal(s) of interest and interfering substances cannot be overemphasized. This method includes sampling techniques that should maximize the ability of the sampling team to collect samples reliably and eliminate sample contamination. These techniques are given in Section 8.0 and are based on findings of researchers performing trace metals analyses (References 1-9).

1.6 Clean and Ultraclean—The terms "clean" and "ultraclean" have been used in other Agency guidance to describe the techniques needed to reduce or eliminate contamination in trace metals determinations. These terms are not used in this sampling method due to a lack of exact definitions. However, the information provided in this method is consistent with summary guidance on clean and ultraclean techniques (Reference 10).

1.7 This sampling method follows the EPA Environmental Methods Management Council's "Format for Method Documentation" (Reference 11).

1.8 Method 1669 is "performance-based"; i.e., an alternate sampling procedure or technique may be used, so long as neither samples nor blanks are contaminated when following the alternate procedures. Because the only way to measure the performance of the alternate procedures is through the collection and analysis of uncontaminated blank samples in accordance with this guidance and the methods referenced in Table 1, it is highly recommended that any modifications be thoroughly evaluated and demonstrated to be effective before field samples are collected. Section 9.2 provides additional details on the tests and documentation required to support equivalent performance.

1.9 For dissolved metal determinations, samples must be filtered through a 0.45 µm capsule filter at the field site. The filtering procedures are described in this method. The filtered samples may be preserved in the field or transported to the laboratory for preservation. Procedures for field preservation are detailed in this sampling method; procedures for laboratory preservation are provided in the methods referenced in Table 1. Preservation requirements are summarized in Table 2.

1.10 The procedures in this method are for use only by personnel thoroughly trained in the collection of samples for determination of metals at ambient water quality control levels.

2.0 Summary of Method

2.1 Before samples are collected, all sampling equipment and sample containers are cleaned in a laboratory or cleaning facility using detergent, mineral acids, and reagent water as described in the methods referenced in Table 1. The laboratory or cleaning facility is responsible for generating an acceptable equipment blank to demonstrate that the sampling equipment and containers are free from trace metals contamination before they are shipped to the field sampling team. An acceptable blank is one that is free from contamination below the minimum level (ML) specified in the referenced analytical method (Section 9.3).

2.2 After cleaning, sample containers are filled with weak acid solution, individually double-bagged, and shipped to the sampling site. All sampling equipment is also bagged for storage or shipment.

NOTE: *EPA has found that, in some cases, it may be possible to empty the weak acid solution from the bottle immediately prior to transport to the field site. In this case, the bottle should be refilled with reagent water (Section 7.1).*

2.3 The laboratory or cleaning facility must prepare a large carboy or other appropriate clean container filled with reagent water (Section 7.1) for use with collection of field blanks during sampling activities. The reagent-water-filled container should be shipped to the field site and handled as all other sample containers and sampling equipment. At least one field blank should be processed per site, or one per every ten samples, whichever is more frequent (Section 9.4). If samples are to be collected for determination of trivalent chromium, the sampling team processes additional QC aliquots are processed as described in Section 9.6.

2.4 Upon arrival at the sampling site, one member of the two-person sampling team is designated as "dirty hands"; the second member is designated as "clean hands." All operations involving contact with the sample bottle and transfer of the sample from the sample collection device to the sample bottle are handled by the individual designated as "clean hands." "Dirty hands" is responsible for preparation of the sampler (except the sample container itself), operation of any machinery, and for all other activities that do not involve direct contact with the sample.

2.5 All sampling equipment and sample containers used for metals determinations at or near the levels listed in Table 1 must be nonmetallic and free from any material that may contain metals.

2.6 Sampling personnel are required to wear clean, nontalc gloves at all times when handling sampling equipment and sample containers.

2.7 In addition to processing field blanks at each site, a field duplicate must be collected at each sampling site, or one field duplicate per every 10 samples, whichever is more frequent (Section 9.5). Section 9.0 gives a complete description of quality control requirements.

2.8 Sampling

2.8.1 Whenever possible, samples are collected facing upstream and upwind to minimize introduction of contamination.

2.8.2 Samples may be collected while working from a boat or while on land.

2.8.3 Surface samples are collected using a grab sampling technique. The principle of the grab technique is to fill a sample bottle by rapid immersion in water and capping to minimize exposure to airborne particulate matter.

2.8.4 Subsurface samples are collected by suction of the sample into an immersed sample bottle or by pumping the sample to the surface.

2.9 Samples for dissolved metals are filtered through a 0.45 µm capsule filter at the field site. After filtering, the samples are double-bagged and iced immediately. Sample containers are shipped to the analytical laboratory. The sampling equipment is shipped to the laboratory or cleaning facility for recleaning.

2.10 Acid preservation of samples is performed in the field or in the laboratory. Field preservation is necessary for determinations of trivalent chromium. It has also been shown that field preservation can increase sample holding times for hexavalent chromium to 30 days; therefore it is recommended that preservation of samples for hexavalent chromium be performed in the field. For other metals, however, the sampling team may prefer to utilize laboratory preservation of samples to expedite field operations and to minimize the potential for sample contamination.

2.11 Sampling activities must be documented through paper or computerized sample tracking systems.

3.0 Definitions

3.1 Apparatus—Throughout this method, the sample containers, sampling devices, instrumentation, and all other materials and devices used in sample collection, sample processing, and sample analysis activities will be referred to collectively as the Apparatus.

3.2 Definitions of other terms are given in the Glossary (Section 15.0) at the end of this method.

4.0 Contamination and Interferences

4.1 Contamination Problems in Trace Metals Analysis

4.1.1 Preventing ambient water samples from becoming contaminated during the sampling and analytical process is the greatest challenge faced in trace metals determinations. In recent years, it has been shown that much of the historical trace metals data collected in ambient water are erroneously high because the concentrations reflect contamination from sampling and analysis rather than ambient levels (Reference 12). Therefore, it is imperative that extreme care be taken to avoid contamination when collecting and analyzing ambient water samples for trace metals.

4.1.2 There are numerous routes by which samples may become contaminated. Potential sources of trace metals contamination during sampling include metallic or metal-containing sampling equipment, containers, labware (e.g. talc gloves that contain high levels of zinc), reagents, and deionized water; improperly cleaned and stored equipment, labware, and reagents; and atmospheric inputs such as dirt and dust from automobile exhaust, cigarette smoke, nearby roads, bridges, wires, and poles. Even human contact can be a source of trace metals contamination. For example, it has been demonstrated that dental work (e.g., mercury amalgam fillings) in the mouths of laboratory personnel can contaminate samples that are directly exposed to exhalation (Reference 3).

4.2 Contamination Control

4.2.1 Philosophy—The philosophy behind contamination control is to ensure that any object or substance that contacts the sample is nonmetallic and free from any material that may contain metals of concern.

4.2.1.1 The integrity of the results produced cannot be compromised by contamination of samples. Requirements and suggestions for controlling sample contamination are given in this sampling method and in the analytical methods referenced in Table 1.

4.2.1.2 Substances in a sample or in the surrounding environment cannot be allowed to contaminate the Apparatus used to collect samples for trace metals measurements. Requirements and suggestions for protecting the Apparatus are given in this sampling method and in the methods referenced in Table 1.

4.2.1.3 While contamination control is essential, personnel health and safety remain the highest priority. Requirements and suggestions for personnel safety are given in Section 5 of this sampling method and in the methods referenced in Table 1.

4.2.2 Avoiding contamination—The best way to control contamination is to completely avoid exposure of the sample and Apparatus to contamination in the first place. Avoiding exposure means performing operations in an area known to be free from contamination. Two of the most important factors in avoiding/reducing sample contamination are (1) an awareness of potential sources of contamination and (2) strict attention to work being performed. Therefore, it is imperative that the procedures described in this method be carried out by well

trained, experienced personnel. Documentation of training should be kept on file and readily available for review.

4.2.2.1 Minimize exposure—The Apparatus that will contact samples or blanks should only be opened or exposed in a clean room, clean bench, glove box, or clean plastic bag, so that exposure to atmospheric inputs is minimized. When not being used, the Apparatus should be covered with clean plastic wrap, stored in the clean bench or in a plastic box or glove box, or bagged in clean, colorless zip-type bags. Minimizing the time between cleaning and use will also reduce contamination.

4.2.2.2 Wear gloves—Sampling personnel must wear clean, nontalc gloves (Section 6.7) during all operations involving handling of the Apparatus, samples, and blanks. Only clean gloves may touch the Apparatus. If another object or substance is touched, the glove(s) must be changed before again handling the Apparatus. If it is even suspected that gloves have become contaminated, work must be halted, the contaminated gloves removed, and a new pair of clean gloves put on. Wearing multiple layers of clean gloves will allow the old pair to be quickly stripped with minimal disruption to the work activity.

4.2.2.3 Use metal-free Apparatus—All Apparatus used for metals determinations at the levels listed in Table 1 must be nonmetallic and free of material that may contain metals. When it is not possible to obtain equipment that is completely free of the metal(s) of interest, the sample should not come into direct contact with the equipment.

4.2.2.3.1 Construction materials—Only the following materials should come in contact with samples: fluoropolymer (FEP, PTFE), conventional or linear polyethylene, polycarbonate, polysulfone, polypropylene, or ultrapure quartz. PTFE is less desirable than FEP because the sintered material in PTFE may contain contaminants and is susceptible to serious memory effects (Reference 6). Fluoropolymer or glass containers should be used for samples that will be analyzed for mercury because mercury vapors can diffuse in or out of other materials, resulting either in contamination or low-biased results (Reference 3). Metal must not be used under any circumstance. Regardless of construction, all materials that will directly or indirectly contact the sample must be cleaned using the procedures described in the referenced analytical methods (see Table 1) and must be known to be clean and metal-free before proceeding.

4.2.2.3.2 The following materials have been found to contain trace metals and must not be used to hold liquids that come in contact with the sample or must not contact the sample, unless these materials have been shown to be free of the metals of interest at the desired level: Pyrex, Kimax, methacrylate, polyvinylchloride, nylon, and Vycor (Reference 6). In addition, highly colored plastics, paper cap liners, pigments used to mark increments on plastics, and rubber all contain trace levels of metals and must be avoided (Reference 13).

4.2.2.3.3 Serialization—Serial numbers should be indelibly marked or etched on each piece of Apparatus so that contamination can be traced, and logbooks should be maintained to track the sample from the container through the sampling process to shipment to the laboratory. Chain-of-custody procedures may also be used if warranted so that contamination can be traced to particular handling procedures or lab personnel.

4.2.2.3.4 The Apparatus should be clean when the sampling team receives it. If there are any indications that the Apparatus is not clean (e.g., a ripped storage bag), an assessment of the likelihood of contamination must be made. Sampling must not proceed if it is possible that the Apparatus is contaminated. If the Apparatus is contaminated, it must be returned to the laboratory or cleaning facility for proper cleaning before any sampling activity resumes.

4.2.2.3.5 Details for recleaning the Apparatus between collection of individual samples are provided in Section 10.0.

4.2.2.4 Avoid sources of contamination—Avoid contamination by being aware of potential sources and routes of contamination.

4.2.2.4.1 Contamination by carryover—Contamination may occur when a sample containing low concentrations of metals is processed immediately after a sample containing relatively high concentrations of these metals. At sites where more than one sample will be collected, the sample known or expected to contain the lowest concentration of metals should be collected first with the sample containing the highest levels collected last (Section 8.1.4). This will help minimize carryover of metals from high- concentration samples to low- concentration samples. If the sampling team does not have prior knowledge of the waterbody, or when necessary, the sample collection system should be rinsed with dilute acid and reagent water between samples and followed by collection of a field blank (Section 10.3).

4.2.2.4.2 Contamination by samples—Significant contamination of the Apparatus may result when untreated effluents, in-process waters, landfill leachates, and other samples containing mid- to high-level concentrations of inorganic substances are processed. As stated in Section 1.0, this sampling method is not intended for application to these samples, and samples containing high concentrations of metals must not be collected, processed, or shipped at the same time as samples being collected for trace metals determinations.

4.2.2.4.3 Contamination by indirect contact—Apparatus that may not directly contact samples may still be a source of contamination. For example, clean tubing placed in a dirty plastic bag may pick up contamination from the bag and subsequently transfer the contamination to the sample. Therefore, it is imperative that every

piece of the Apparatus that is directly or indirectly used in the collection of ambient water samples be cleaned as specified in the analytical method(s) referenced in Table 1.

4.2.2.4.4 Contamination by airborne particulate matter—Less obvious substances capable of contaminating samples include airborne particles. Samples may be contaminated by airborne dust, dirt, particulate matter, or vapors from automobile exhaust; cigarette smoke; nearby corroded or rusted bridges, pipes, poles, or wires; nearby roads; and even human breath (Section 4.1.2). Whenever possible, the sampling activity should occur as far as possible from sources of airborne contamination (Section 8.1.3). Areas where nearby soil is bare and subject to wind erosion should be avoided.

4.3 Interferences—Interferences resulting from samples will vary considerably from source to source, depending on the diversity of the site being sampled. If a sample is suspected of containing substances that may interfere in the determination of trace metals, sufficient sample should be collected to allow the laboratory to identify and overcome interference problems.

5.0 Safety

5.1 The toxicity or carcinogenicity of the chemicals used in this method has not been precisely determined; however, these chemicals should be treated as a potential health hazard. Exposure should be reduced to the lowest possible level. Sampling teams are responsible for maintaining a current awareness file of OSHA regulations for the safe handling of the chemicals specified in this method. A reference file of Material Safety Data Sheets should also be made available to all personnel involved in sampling. It is also suggested that the organization responsible perform personal hygiene monitoring of each sampling team member who uses this method and that the results of this monitoring be made available to the member.

5.2 Operating in and around waterbodies carries the inherent risk of drowning. Life jackets must be worn when operating from a boat, when sampling in more than a few feet of water, or when sampling in swift currents.

5.3 Collecting samples in cold weather, especially around cold water bodies, carries the risk of hypothermia, and collecting samples in extremely hot and humid weather carries the risk of dehydration and heat stroke. Sampling team members should wear adequate clothing for protection in cold weather and should carry an adequate supply of water or other liquids for protection against dehydration in hot weather.

6.0 Apparatus and Materials

NOTE: *Brand names, suppliers, and part numbers are for illustration only and no endorsement is implied. Equivalent performance may be achieved using apparatus and materials other than those specified here. Meeting the performance requirements of this method is the responsibility of the sampling team and laboratory.*

6.1 All sampling equipment and sample containers must be precleaned in a laboratory or cleaning facility, as described in the methods referenced in Table 1, before they are shipped to the field site.

Performance criteria for equipment cleaning is described in the referenced methods. To minimize difficulties in sampling, the equipment should be packaged and arranged to minimize field preparation.

6.2 Materials such as gloves (Section 6.7), storage bags (Section 6.8), and plastic wrap (Section 6.9), may be used new without additional cleaning unless the results of the equipment blank pinpoint any of these materials as a source of contamination. In this case, either a different supplier must be obtained or the materials must be cleaned.

6.3 Sample Bottles—Fluoropolymer (FEP, PTFE), conventional or linear polyethylene, polycarbonate, or polypropylene; 500 mL or 1 L with lids. If mercury is a target analyte, fluoropolymer or glass bottles should be used. Refer to the methods referenced in Table 1 for bottle cleaning procedures.

6.3.1 Cleaned sample bottles should be filled with 0.1% HCl (v/v). In some cases, it may be possible to empty the weak acid solution from the sample bottle immediately prior to transport to the field site. In this case, the bottle should be refilled with reagent water (Section 7.1).

6.3.2 Whenever possible, sampling devices should be cleaned and prepared for field use in a class 100 clean room. Preparation of the devices in the field should be done within the glove bag (Section 6.6). Regardless of design, sampling devices must be constructed of nonmetallic material (Section 4.2.2.3.1) and free from material that contains metals. Fluoropolymer or other material shown not to adsorb or contribute mercury must be used if mercury is a target analyte; otherwise, polyethylene, polycarbonate, or polypropylene are acceptable. Commercially available sampling devices may be used provided that any metallic or metal-containing parts are replaced with parts constructed of nonmetallic material.

6.4 Surface Sampling Devices—Surface samples are collected using a grab sampling technique. Samples may be collected manually by direct submersion of the bottle into the water or by using a grab sampling device. Examples of grab samplers are shown in Figures 1 and 2 and may be used at sites where depth profiling is neither practical nor necessary.

6.4.1 The grab sampler in Figure 1 consists of a heavy fluoropolymer collar fastened to the end of a 2-m-long polyethylene pole, which serves to remove the sampling personnel from the immediate vicinity of the sampling point. The collar holds the sample bottle. A fluoropolymer closing mechanism, threaded onto the bottle, enables the sampler to open and close the bottle under water, thereby avoiding surface microlayer contamination (Reference 14). Polyethylene, polycarbonate, and polypropylene are also acceptable construction materials unless mercury is a target analyte. Assembly of the cleaned sampling device is as follows (refer to Figure 1):

6.4.1.1 Thread the pull cord (with the closing mechanism attached) through the guides and secure the pull ring with a simple knot. Screw a sample bottle onto the closing device and insert the bottle into the collar. Cock the closing plate so that the plate is pushed away from the operator.

6.4.1.2 The cleaned and assembled sampling device should be stored in a double layer of large, clean zip-type polyethylene bags or wrapped in two layers of clean polyethylene wrap if it will not be used immediately.

6.4.2 An alternate grab sampler design is shown in Figure 2. This grab sampler is used for discrete water samples and is constructed so that a capped clean bottle can be submerged, the cap

removed, sample collected, and bottle recapped at a selected depth. This device eliminates sample contact with conventional samplers (e.g., Niskin bottles), thereby reducing the risk of extraneous contamination. Because a fresh bottle is used for each sample, carryover from previous samples is eliminated (Reference 15).

6.5 Subsurface Sampling Devices—Subsurface sample collection may be appropriate in lakes and sluggish deep river environments or where depth profiling is determined to be necessary. Subsurface samples are collected by pumping the sample into a sample bottle. Examples of subsurface collection systems include the jar system device shown in Figure 3 and described in Section 6.5.1 or the continuous-flow apparatus shown in Figure 4 and described in Section 6.5.2.

6.5.1 Jar sampler (Reference 14)—The jar sampler (Figure 3) is comprised of a heavy fluoropolymer 1-L jar with a fluoropolymer lid equipped with two 1/4 in. fluoropolymer fittings. Sample enters the jar through a short length of fluoropolymer tubing inserted into one fitting. Sample is pulled into the jar by pumping on fluoropolymer tubing attached to the other fitting. A thick fluoropolymer plate supports the jar and provides attachment points for a fluoropolymer safety line and fluoropolymer torpedo counterweight.

6.5.1.1 Advantages of the jar sampler for depth sampling are (1) all wetted surfaces are fluoropolymer and can be rigorously cleaned; (2) the sample is collected into a sample jar from which the sample is readily recovered, and the jar can be easily recleaned; (3) the suction device (a peristaltic or rotary vacuum pump, Section 6.15) is located in the boat, isolated from the sampling jar; (4) the sampling jar can be continuously flushed with sample, at sampling depth, to equilibrate the system; and (5) the sample does not travel through long lengths of tubing that are more difficult to clean and keep clean (Reference 14). In addition, the device is designed to eliminate atmospheric contact with the sample during collection.

6.5.1.2 To assemble the cleaned jar sampler, screw the torpedo weight onto the machined bolt attached to the support plate of the jar sampler. Attach a section of the 1/4 in. o.d. tubing to the jar by inserting the tubing into the fitting on the lid and pushing down into the jar until approximately 8 cm from the bottom. Tighten the fitting nut securely. Attach the solid safety line to the jar sampler using a bowline knot to the loop affixed to the support plate.

6.5.1.3 For the tubing connecting the pump to the sampler, tubing lengths of up to 12 m have been used successfully (Reference 14).

6.5.2 Continuous-flow sampler (References 16-17)—This sampling system, shown in Figure 4, consists of a peristaltic or submersible pump and one or more lengths of precleaned fluoropolymer or styrene/ethylene/butylene/ silicone (SEBS) tubing. A filter is added to the sampling train when sampling for dissolved metals.

6.5.2.1 Advantages of this sampling system include (1) all wetted surfaces are fluoropolymer or SEBS and can be readily cleaned; (2) the suction device is located in the boat, isolated from the sample bottle; (3) the sample does not travel through long lengths of tubing that are difficult to clean and keep clean; and (4) in-line filtration is possible, minimizing field handling requirements for dissolved metals samples.

6.5.2.2 The sampling team assembles the system in the field as described in Section 8.2.8. System components include an optional polyethylene pole to remove sampling personnel from the immediate vicinity of the sampling point and the pump, tubing, filter, and filter holder listed in Sections 6.14 and 6.15.

6.6 Field-Portable Glove Bag—I2R, Model R-37-37H (nontalc), or equivalent. Alternately, a portable glove box may be constructed with a nonmetallic (PVC pipe or other suitable material) frame and a frame cover made of an inexpensive, disposable, nonmetallic material (e.g., a thin-walled polyethylene bag) (Reference 7).

6.7 Gloves—Clean, nontalc polyethylene, latex, vinyl, or PVC; various lengths. Shoulder-length gloves are needed if samples are to be collected by direct submersion of the sample bottle into the water or when sampling for mercury.

6.7.1 Gloves, shoulder-length polyethylene—Associated Bag Co., Milwaukee, WI, 66-3-301, or equivalent.

6.7.2 Gloves, PVC—Fisher Scientific Part No. 11-394-100B, or equivalent.

6.8 Storage Bags—Clean, zip-type, nonvented, colorless polyethylene (various sizes).

6.9 Plastic Wrap—Clean, colorless polyethylene.

6.10 Cooler—Clean, nonmetallic, with white interior for shipping samples.

6.11 Ice or Chemical Refrigerant Packs—To keep samples chilled in the cooler during shipment.

6.12 Wind Suit—Pamida, or equivalent.

NOTE: *This equipment is necessary only for collection of metals, such as mercury, that are known to have elevated atmospheric concentrations.*

6.12.1 An unlined, long-sleeved wind suit consisting of pants and jacket and constructed of nylon or other synthetic fiber is worn when sampling for mercury to prevent mercury adsorbed onto cotton or other clothing materials from contaminating samples.

6.12.2 Washing and drying—The wind suit is washed by itself or with other wind suits only in a home or commercial washing machine and dried in a clothes dryer. The clothes dryer must be thoroughly vacuumed, including the lint filter, to remove all traces of lint before drying. After drying, the wind suit is folded and stored in a clean polyethylene bag for shipment to the sample site.

6.13 Boat

6.13.1 For most situations (e.g., most metals under most conditions), the use of an existing, available boat is acceptable. A flat-bottom, Boston Whaler-type boat is preferred because sampling materials can be stored with reduced chance of tipping.

6.13.1.1 Immediately before use, the boat should be washed with water from the sampling site away from any sampling points to remove any dust or dirt accumulation.

6.13.1.2 Samples should be collected upstream of boat movement.

6.13.2 For mercury, and for situations in which the presence of contaminants cannot otherwise be controlled below detectable levels, the following equipment and precautions may be necessary:

6.13.2.1 A metal-free (e.g., fiberglass) boat, along with wooden or fiberglass oars. Gasoline- or diesel-fueled boat motors should be avoided when possible because the exhaust can be a source of contamination. If the body of water is large enough to require use of a boat motor, the engine should be shut off at a distance far enough from the sampling point to avoid contamination, and the sampling team should manually propel the boat to the sampling point. Samples should be collected upstream of boat movement.

6.13.2.2 Before first use, the boat should be cleaned and stored in an area that minimizes exposure to dust and atmospheric particles. For example, cleaned boats should not be stored in an area that would allow exposure to automobile exhaust or industrial pollution.

6.13.2.3 The boat should be frequently visually inspected for possible contamination.

6.13.2.4 After sampling, the boat should be returned to the laboratory or cleaning facility, cleaned as necessary, and stored away from any sources of contamination until next use.

6.14 Filtration Apparatus—Required when collecting samples for dissolved metals determinations.

6.14.1 Filter—0.45 µm, 15 mm diameter or larger, tortuous-path capsule filters (Reference 18), Gelman Supor 12175, or equivalent.

6.14.2 Filter holder—For mounting filter to the gunwale of the boat. Rod or pipe made from plastic material and mounted with plastic clamps.

NOTE: *A filter holder may not be required if one or a few samples are to be collected. For these cases, it may only be necessary to attach the filter to the outlet of the tubing connected to the pump.*

6.15 Pump and Pump Apparatus—Required for use with the jar sampling system (Section 6.5.1) or the continuous-flow system (Section 6.5.2). Peristaltic pump; 115 V a.c., 12 V d.c., internal battery, variable-speed, single-head, Cole-Parmer, portable, "Masterflex L/S," Catalog No. H-07570-10 drive with Quick Load pump head, Catalog No. H-07021-24, or equivalent.

NOTE: *Equivalent pumps may include rotary vacuum, submersible, or other pumps free from metals and suitable to meet the site-specific depth sampling needs.*

6.15.1 Cleaning—Peristaltic pump modules do not require cleaning. However, nearly all peristaltic pumps contain a metal head and metal controls. Touching the head or controls necessitates

changing of gloves before touching the Apparatus. If a submersible pump is used, a large volume of sample should be pumped to clean the stainless steel shaft (hidden behind the impeller) that comes in contact with the sample. Pumps with metal impellers should not be used.

6.15.2 Tubing—For use with peristaltic pump. SEBS resin, approximately 3/8 in. i.d. by approximately 3 ft, Cole-Parmer size 18, Cat. No. G-06464-18, or approximately 1/4 in. i.d., Cole-Parmer size 17, Catalog No. G-06464-17, or equivalent. Tubing is cleaned by soaking in 5-10% HCl solution for 8-24 hours, rinsing with reagent water in a clean bench in a clean room, and drying in the clean bench by purging with mercury-free air or nitrogen. After drying, the tubing is double-bagged in clear polyethylene bags, serialized with a unique number, and stored until use.

6.15.3 Tubing—For connection to peristaltic pump tubing. Fluoropolymer, 3/8 or 1/4 in. o.d., in lengths as required to reach the point of sampling. If sampling will be at some depth from the end of a boom extended from a boat, sufficient tubing to extend to the end of the boom and to the depth will be required. Cleaning of the fluoropolymer can be the same as cleaning the tubing for the rotary vacuum pump (Section 6.15.1.2). If necessary, more aggressive cleaning (e.g., concentrated nitric acid) may be used.

6.15.4 Batteries to operate submersible pump—12 V, 2.6 amp, gel cell, YUASA NP2.6-12, or equivalent. A 2 amp fuse connected at the positive battery terminal is strongly recommended to prevent short circuits from overheating the battery. A 12 V, lead-acid automobile or marine battery may be more suitable for extensive pumping.

6.15.5 Tubing connectors—Appropriately sized PVC, clear polyethylene, or fluoropolymer "barbed" straight connectors cleaned as the tubing above. Used to connect multiple lengths of tubing.

6.16 Carboy—For collection and storage of dilute waste acids used to store bottles.

6.17 Apparatus—For field preservation of aliquots for trivalent chromium determinations.

6.17.1 Fluoropolymer forceps—1 L fluoropolymer jar, and 30 mL fluoropolymer vials with screw-caps (one vial per sample and blank). It is recommended that 1 mL of ultrapure nitric acid (Section 7.3) be added to each vial prior to transport to the field to simplify field handling activities (See Section 8.4.4.6).

6.17.2 Filters—0.4 µm, 47 mm polycarbonate Nuclepore (or equivalent). Filters are cleaned as follows. Fill a 1 L fluoropolymer jar approximately two-thirds full with 1 N nitric acid. Using fluoropolymer forceps, place individual filters in the fluoropolymer jar. Allow the filters to soak for 48 hours. Discard the acid, and rinse five times with reagent water. Fill the jar with reagent water, and soak the filters for 24 hours. Remove the filters when ready for use, and using fluoropolymer forceps, place them on the filter apparatus (Section 6.17.3).

6.17.3 Vacuum filtration apparatus—Millipore 47 mm size, or equivalent, vacuum pump and power source (and extension cords, if necessary) to operate the pump.

6.17.4 Eppendorf auto pipet and colorless pipet tips (100-1000 µL)

6.17.5 Wrist-action shaker—Burrel or equivalent.

6.17.6 Fluoropolymer wash bottles—One filled with reagent water (Section 7.1) and one filled with high- purity 10% HCl (Section 7.4.4), for use in rinsing forceps and pipet tips.

7.0 Reagents and Standards

7.1 Reagent Water—Water in which the analytes of interest and potentially interfering substances are not detected at the Method Detection Limit (MDL) of the analytical method used for analysis of samples. Prepared by distillation, deionization, reverse osmosis, anodic/cathodic stripping voltammetry, or other techniques that remove the metal(s) and potential interferent(s). A large carboy or other appropriate container filled with reagent water must be available for the collection of field blanks.

7.2 Nitric Acid—Dilute, trace-metal grade, shipped with sampling kit for cleaning equipment between samples.

7.3 Sodium Hydroxide—Concentrated, 50% solution for use when field-preserving samples for hexavalent chromium determinations (Section 8.4.5).

7.4 Reagents—For field-processing aliquots for trivalent chromium determinations

7.4.1 Nitric Acid, Ultrapure—For use when field-preserving samples for trivalent chromium determinations (Sections 6.17 and 8.4.4).

7.4.2 Ammonium Iron (II) Sulfate Solution (0.01M)—Used to prepare the chromium (III) extraction solution (Section 7.4.3) necessary for field preservation of samples for trivalent chromium (Section 8.4.4). Prepare the ammonium iron (II) sulfate solution by adding 3.92 g ammonium iron (II) sulfate (ultrapure grade) to a 1 L volumetric flask. Bring to volume with reagent water. Store in a clean polyethylene bottle.

7.4.3 Chromium (III) extraction solution—For use when field-preserving samples for trivalent chromium determinations (Section 8.4.4). Prepare this solution by adding 100 mL of ammonium iron (II) sulfate solution (Section 7.4.2) to a 125 mL polyethylene bottle. Adjust pH to 8 with approximately 2 mL of ammonium hydroxide solution. Cap and shake on a wrist-action shaker for 24 hours. This iron (III) hydroxide solution is stable for 30 days.

7.4.4 Hydrochloric acid—High-purity, 10% solution, shipped with sampling kit in fluoropolymer wash bottles for cleaning trivalent chromium sample preservation equipment between samples.

7.4.5 Chromium stock standard solution (1000 µg/mL)—Prepared by adding 3.1 g anhydrous chromium chloride to a 1 L flask and diluting to volume with 1% hydrochloric acid. Store in polyethylene bottle. A commercially available standard solution may be substituted.

7.4.6 Standard chromium spike solution (1000 µg/L)—Used to spike sample aliquots for matrix spike/matrix spike duplicate (MS/MSD) analysis and to prepare ongoing precision and recovery standards. Prepared by spiking 1 mL of the chromium stock standard solution (Section 7.4.5) into a 1 L flask. Dilute to volume with 1% HCl. Store in a polyethylene bottle.

7.4.7 Ongoing precision and recovery (OPR) standard (25 µg/L)—Prepared by spiking 2.5 mL of the standard chromium spike solution (Section 7.4.6) into a 100 mL flask. Dilute to volume with 1% HCl. One OPR is required for every 10 samples.

8.0 Sample Collection, Filtration, and Handling

8.1 Site Selection

8.1.1 Selection of a representative site for surface water sampling is based on many factors including: study objectives, water use, point source discharges, non-point source discharges, tributaries, changes in stream characteristics, types of stream bed, stream depth, turbulence, and the presence of structures (bridges, dams, etc.). When collecting samples to determine ambient levels of trace metals, the presence of potential sources of metal contamination are of extreme importance in site selection.

8.1.2 Ideally, the selected sampling site will exhibit a high degree of cross-sectional homogeneity. It may be possible to use previously collected data to identify locations for samples that are well mixed or are vertically or horizontally stratified. Since mixing is principally governed by turbulence and water velocity, the selection of a site immediately downstream of a riffle area will ensure good vertical mixing. Horizontal mixing occurs in constrictions in the channel. In the absence of turbulent areas, the selection of a site that is clear of immediate point sources, such as industrial effluents, is preferred for the collection of ambient water samples (Reference 19).

8.1.3 To minimize contamination from trace metals in the atmosphere, ambient water samples should be collected from sites that are as far as possible (e.g., at least several hundred feet) from any metal supports, bridges, wires or poles. Similarly, samples should be collected as far as possible from regularly or heavily traveled roads. If it is not possible to avoid collection near roadways, it is advisable to study traffic patterns and plan sampling events during lowest traffic flow (Reference 7).

8.1.4 The sampling activity should be planned to collect samples known or suspected to contain the lowest concentrations of trace metals first, finishing with the samples known or suspected to contain the highest concentrations. For example, if samples are collected from a flowing river or stream near an industrial or municipal discharge, the upstream sample should be collected first, the downstream sample collected second, and the sample nearest the discharge collected last. If the concentrations of pollutants is not known and cannot be estimated, it is necessary to use precleaned sampling equipment at each sampling location.

8.2 Sample Collection Procedure—Before collecting ambient water samples, consideration should be given to the type of sample to be collected, the amount of sample needed, and the devices to be used (grab, surface, or subsurface samplers). Sufficient sample volume should be collected to allow for necessary quality control analyses, such as matrix spike/matrix spike duplicate analyses.

8.2.1 Four sampling procedures are described:

8.2.1.1 Section 8.2.5 describes a procedure for collecting samples directly into the sample container. This procedure is the simplest and provides the least potential for contamination because it requires the least amount of equipment and handling.

8.2.1.2 Section 8.2.6 describes a procedure for using a grab sampling device to collect samples.

8.2.1.3 Section 8.2.7 describes a procedure for depth sampling with a jar sampler. The size of sample container used is dependent on the amount of sample needed by the analytical laboratory.

8.2.1.4 Section 8.2.8 describes a procedure for continuous-flow sampling using a submersible or peristaltic pump.

8.2.2 The sampling team should ideally approach the site from down current and downwind to prevent contamination of the sample by particles sloughing off the boat or equipment. If it is not possible to approach from both, the site should be approached from down current if sampling from a boat or approached from downwind if sampling on foot. When sampling from a boat, the bow of the boat should be oriented into the current (the boat will be pointed upstream). All sampling activity should occur from the bow.

If the samples are being collected from a boat, it is recommended that the sampling team create a stable workstation by arranging the cooler or shipping container as a work table on the upwind side of the boat, covering this worktable and the upwind gunnel with plastic wrap or a plastic tablecloth, and draping the wrap or cloth over the gunnel. If necessary, duct tape is used to hold the wrap or cloth in place.

8.2.3 All operations involving contact with the sample bottle and with transfer of the sample from the sample collection device to the sample bottle (if the sample is not directly collected in the bottle) are handled by the individual designated as "clean hands." "Dirty hands" is responsible for all activities that do not involve direct contact with the sample.

Although the duties of "clean hands" and "dirty hands" would appear to be a logical separation of responsibilities, in fact, the completion of the entire protocol may require a good deal of coordination and practice. For example, "dirty hands" must open the box or cooler containing the sample bottle and unzip the outer bag; clean hands must reach into the outer bag, open the inner bag, remove the bottle, collect the sample, replace the bottle lid, put the bottle back into the inner bag, and zip the inner bag. "Dirty hands" must close the outer bag and place it in a cooler.

To minimize unnecessary confusion, it is recommended that a third team member be available to complete the necessary sample documentation (e.g., to document sampling location, time, sample number, etc). Otherwise, "dirty hands" must perform the sample documentation activity (Reference 7).

8.2.4 Extreme care must be taken during all sampling operations to minimize exposure of the sample to human, atmospheric, and other sources of contamination. Care must be taken to avoid breathing directly on the sample, and whenever possible, the sample bottle should be opened, filled, and closed while submerged.

8.2.5 Manual collection of surface samples directly into the sample bottle.

8.2.5.1 At the site, all sampling personnel must put on clean gloves (Section 6.7) before commencing sample collection activity, with "clean hands" donning shoulder-length gloves. If samples are to be analyzed for mercury, the sampling team must also put their precleaned wind suits on at this time. Note that "clean hands" should put on the

shoulder-length polyethylene gloves (Section 6.7.1) and both "clean hands" and "dirty hands" should put on the PVC gloves (Section 6.7.2).

8.2.5.2 "Dirty hands" must open the cooler or storage container, remove the double-bagged sample bottle from storage, and unzip the outer bag.

8.2.5.3 Next, "clean hands" opens the inside bag containing the sample bottle, removes the bottle, and reseals the inside bag. "Dirty hands" then reseals the outer bag.

8.2.5.4 "Clean hands" unscrews the cap and, while holding the cap upside down, discards the dilute acid solution from the bottle into a carboy for wastes (Section 6.16) or discards the reagent water directly into the water body.

8.2.5.5 "Clean hands" then submerges the sample bottle, and allows the bottle to partially fill with sample. "Clean hands" screws the cap on the bottle, shakes the bottle several times, and empties the rinsate away from the site. After two more rinsings, "clean hands" holds the bottle under water and allows bottle to fill with sample. After the bottle has filled (i.e., when no more bubbles appear), and while the bottle is still inverted so that the mouth of the bottle is underwater, "clean hands" replaces the cap of the bottle. In this way, the sample has never contacted the air.

8.2.5.6 Once the bottle lid has been replaced, "dirty hands" reopens the outer plastic bag, and "clean hands" opens the inside bag, places the bottle inside it, and zips the inner bag.

8.2.5.7 "Dirty hands" zips the outer bag.

8.2.5.8 Documentation—After each sample is collected, the sample number is documented in the sampling log, and any unusual observations concerning the sample and the sampling are documented.

8.2.5.9 If the sample is to be analyzed for dissolved metals, it is filtered in accordance with the procedure described in Section 8.3.

8.2.6 Sample collection with grab sampling device—The following steps detail sample collection using the grab sampling device shown in Figure 1 and described in Section 6.4.1. The procedure is indicative of the "clean hands/dirty hands" technique that must be used with alternative grab sampling devices such as that shown in Figure 2 and described in Section 6.4.2.

8.2.6.1 The sampling team puts on gloves (and wind suits, if applicable). Ideally, a sample bottle will have been preattached to the sampling device in the class 100 clean room at the laboratory. If it is necessary to attach a bottle to the device in the field, "clean hands" performs this operation, described in Section 6.4.2, inside the field-portable glove bag (Section 6.6).

8.2.6.2 "Dirty hands" removes the sampling device from its storage container and opens the outer polyethylene bag.

8.2.6.3 "Clean hands" opens the inside polyethylene bag and removes the sampling device.

8.2.6.4 "Clean hands" changes gloves.

8.2.6.5 "Dirty hands" submerges the sampling device to the desired depth and pulls the fluoropolymer pull cord to bring the seal plate into the middle position so that water can enter the bottle.

8.2.6.6 When the bottle is full (i.e., when no more bubbles appear), "dirty hands" pulls the fluoropolymer cord to the final stop position to seal off the sample and removes the sampling device from the water.

8.2.6.7 "Dirty hands" returns the sampling device to its large inner plastic bag, "clean hands" pulls the bottle out of the collar, unscrews the bottle from the sealing device, and caps the bottle. "Clean hands" and "dirty hands" then return the bottle to its double-bagged storage as described in Sections 8.2.5.6 through 8.2.5.7.

8.2.6.8 Closing mechanism—"Clean hands" removes the closing mechanism from the body of the grab sampler, rinses the device with reagent water (Section 7.1), places it inside a new clean plastic bag, zips the bag, and places the bag inside an outer bag held by "dirty hands." "Dirty hands" zips the outer bag and places the double-bagged closing mechanism in the equipment storage box.

8.2.6.9 Sampling device—"Clean hands" seals the large inside bag containing the collar, pole, and cord and places the bag into a large outer bag held by "dirty hands." "Dirty hands" seals the outside bag and places the double-bagged sampling device into the equipment storage box.

8.2.6.10 Documentation—After each sample is collected, the sample number is documented in the sampling log, and any unusual observations concerning the sample and the sampling are documented.

8.2.6.11 If the sample is to be analyzed for dissolved metals, it is filtered in accordance with the procedures described in Section 8.3.

8.2.7 Depth sampling using a jar sampling device (Figure 3 and Section 6.5.1)

8.2.7.1 The sampling team puts on gloves (and wind suits, if applicable) and handles bottles as with manual collection (Sections 8.2.5.1 through 8.2.5.4 and 8.2.5.6 through 8.2.5.7).

8.2.7.2 "Dirty hands" removes the jar sampling device from its storage container and opens the outer polyethylene bag.

8.2.7.3 "Clean hands" opens the inside polyethylene bag and removes the jar sampling apparatus. Ideally, the sampling device will have been preassembled in a class 100 clean room at the laboratory. If, however, it is necessary to assemble the device in the field, "clean hands" must perform this operation, described in Section 6.5.2, inside a field-portable glove bag (Section 6.6).

8.2.7.4 While "dirty hands" is holding the jar sampling apparatus, "clean hands" connects the pump to the to the 1/4 in. o.d. flush line.

8.2.7.5 "Dirty hands" lowers the weighted sampler to the desired depth.

8.2.7.6 "Dirty hands" turns on the pump allowing a large volume (>2 L) of water to pass through the system.

8.2.7.7 After stopping the pump, "dirty hands" pulls up the line, tubing, and device and places them into either a field-portable glove bag or a large, clean plastic bag as they emerge.

8.2.7.8 Both "clean hands" and "dirty hands" change gloves.

8.2.7.9 Using the technique described in Sections 8.2.5.2 through 8.2.5.4, the sampling team removes a sample bottle from storage, and "clean hands" places the bottle into the glove bag.

8.2.7.10 "Clean hands" tips the sampling jar and dispenses the sample through the short length of fluoropolymer tubing into the sample bottle.

8.2.7.11 Once the bottle is filled, "clean hands" replaces the cap of the bottle, returns the bottle to the inside polyethylene bag, and zips the bag. "Clean hands" returns the zipped bag to the outside polyethylene bag held by "dirty hands."

8.2.7.12 "Dirty hands" zips the outside bag. If the sample is to be analyzed for dissolved metals, it is filtered as described in Section 8.3.

8.2.7.13 Documentation—After each sample is collected, the sample number is documented in the sampling log, and any unusual observations concerning the sample and the sampling are documented.

8.2.8 Continuous-flow sampling (Figure 4 and Section 6.5.2)—The continuous-flow sampling system uses peristaltic pump (Section 6.15) to pump sample to the boat or to shore through the SEBS-resin or PTFE tubing.

8.2.8.1 Before putting on wind suits or gloves, the sampling team removes the bags containing the pump (Section 6.15), SEBS-resin tubing (Section 6.15.2), batteries (Section 6.15.4), gloves (Section 6.7), plastic wrap (Section 6.9), wind suits (Section 6.12), and, if samples are to be filtered, the filtration apparatus (Section 6.14) from the coolers or storage containers in which they are packed.

8.2.8.2 "Clean hands" and "dirty hands" put on the wind suits and PVC gloves (Section 6.7.2).

8.2.8.3 "Dirty hands" removes the pump from its storage bag, and opens the bag containing the SEBS-resin tubing.

8.2.8.4 "Clean hands" installs the tubing while "dirty hands" holds the pump. "Clean hands" immerses the inlet end of the tubing in the sample stream.

8.2.8.5 Both "clean hands" and "dirty hands" change gloves. "Clean hands" also puts on shoulder length polyethylene gloves (Section 6.7.1).

8.2.8.6 "Dirty hands" turns the pump on and allows the pump to run for 5-10 minutes or longer to purge the pump and tubing.

8.2.8.7 If the sample is to be filtered, "clean hands" installs the filter at the end of the tubing, and "dirty hands" sets up the filter holder on the gunwale as shown in Figure 4.

NOTE: *The filtration apparatus is not attached until immediately before sampling to prevent buildup of particulates from clogging the filter.*

8.2.8.8 The sample is collected by rinsing the sample bottle and cap three times and collecting the sample from the flowing stream.

8.2.8.9 Documentation—After each sample is collected, the sample number is documented in the sampling log, and any unusual observations concerning the sample and the sampling are documented.

8.3 Sample Filtration—The filtration procedure described below is used for samples collected using the manual (Section 8.2.5), grab (Section 8.2.6), or jar (Section 8.2.7) collection systems (Reference 7). In-line filtration using the continuous-flow approach is described in Section 8.2.8.7. Because of the risk of contamination, it is recommended that samples for mercury be shipped unfiltered by overnight courier and filtered when received at the laboratory.

8.3.1 Set up the filtration system inside the glove bag, using the shortest piece of pump tubing as is practicable. Place the peristaltic pump immediately outside of the glove bag and poke a small hole in the glove bag for passage of the tubing. Also, attach a short length of tubing to the outlet of the capsule filter.

8.3.2 "Clean hands" removes the water sample from the inner storage bag using the technique described in Sections 8.2.5.2 through 8.2.5.4 and places the sample inside the glove bag. "Clean hands" also places two clean empty sample bottles, a bottle containing reagent water, and a bottle for waste in the glove bag.

8.3.3 "Clean hands" removes the lid of the reagent water bottle and places the end of the pump tubing in the bottle.

8.3.4 "Dirty hands" starts the pump and passes approximately 200 mL of reagent water through the tubing and filter into the waste bottle. "Clean hands" then moves the outlet tubing to a clean bottle and collects the remaining reagent water as a blank. "Dirty hands" stops the pump.

8.3.5 "Clean hands" removes the lid of the sample bottle and places the intake end of the tubing in the bottle.

8.3.6 "Dirty hands" starts the pump and passes approximately 50 mL through the tubing and filter into the remaining clean sample bottle and then stops the pump. "Clean hands" uses the filtrate to rinse the bottle, discards the waste sample, and returns the outlet tube to the sample bottle.

8.3.7 "Dirty hands" starts the pump and the remaining sample is processed through the filter and collected in the sample bottle. If preservation is required, the sample is acidified at this point (Section 8.4).

8.3.8 "Clean hands" replaces the lid on the bottle, returns the bottle to the inside bag, and zips the bag. "Clean hands" then places the zipped bag into the outer bag held by "dirty hands."

8.3.9 "Dirty hands" zips the outer bag, and places the double-bagged sample bottle into a clean, ice-filled cooler for immediate shipment to the laboratory.

NOTE: *It is not advisable to reclean and reuse filters. The difficulty and risk associated with failing to properly clean these devices far outweighs the cost of purchasing a new filter.*

8.4 Preservation

8.4.1 Field preservation is not necessary for dissolved metals, except for trivalent and hexavalent chromium, provided that the sample is preserved in the laboratory and allowed to stand for at least two days to allow the metals adsorbed to the container walls to redissolve. Field preservation is advised for hexavalent chromium in order to provide sample stability for up to 30 days. Mercury samples should be shipped by overnight courier and preserved when received at the laboratory.

8.4.2 If field preservation is required, preservation must be performed in the glove bag or in a designated clean area, with gloved hands, as rapidly as possible to preclude particulates from contaminating the sample. For preservation of trivalent chromium, the glove bag or designated clean area must be large enough to accommodate the vacuum filtration apparatus (Section 6.17.3), and an area should be available for setting up the wrist-action shaker (Section 6.17.5). It is also advisable to set up a work area that contains a "clean" cooler for storage of clean equipment, a "dirty" cooler for storage of "dirty" equipment, and a third cooler to store samples for shipment to the laboratory.

8.4.3 Preservation of aliquots for metals other than trivalent and hexavalent chromium—Using a disposable, precleaned, plastic pipet, add 5 mL of a 10% solution of ultrapure nitric acid in reagent water per liter of sample. This will be sufficient to preserve a neutral sample to pH <2.

8.4.4 Preservation of aliquots for trivalent chromium (References 8-9).

8.4.4.1 Decant 100 mL of the sample into a clean polyethylene bottle.

8.4.4.2 Clean an Eppendorf pipet by pipeting 1 mL of 10% HCl (Section (7.4.4) followed by 1 mL of reagent water into an acid waste container. Use the rinsed pipet to add 1 mL of chromium (III) extraction solution (Section 7.4.3) to each sample and blank.

8.4.4.3 Cap each bottle tightly, place in a clean polyethylene bag, and shake on a wrist action shaker (Section 6.17.5) for one hour.

8.4.4.4 Vacuum-filter the precipitate through a 0.4 µm pretreated filter membrane (Section 6.17.2), using fluoropolymer forceps (Section 6.17.1) to handle the membrane, and a 47 mm vacuum filtration apparatus with a precleaned filter holder (Section 6.17.3). After all sample has filtered, rinse the inside of the filter holder with approximately 15 mL of reagent water.

8.4.4.5 Using the fluoropolymer forceps, fold the membrane in half and then in quarters, taking care to avoid touching the side containing the filtrate to any surface. (Folding is done while the membrane is sitting on the filter holder and allows easy placement of the membrane into the sample vial). Transfer the filter to a 30 mL fluoropolymer vial. If the fluoropolymer vial was not pre-equipped with the ultrapure nitric acid (Section 7.4.1), rinse the pipet by drawing and discharging 1 mL of 10% HCl followed by 1 mL of reagent water into a waste container, and add 1 mL of ultrapure nitric acid to the sample vial.

8.4.4.6 Cap the vial and double-bag it for shipment to the laboratory.

8.4.4.7 Repeat Steps 8.4.4.4-8.4.4.6 for each sample, rinsing the fluoropolymer forceps and the pipet with 10% high-purity HCl followed by reagent water between samples.

8.4.5 Preservation of aliquots for hexavalent chromium (Reference 20).

8.4.5.1 Decant 125 mL of sample into a clean polyethylene bottle.

8.4.5.2 Prepare an Eppendorf pipet by pipeting 1 mL of 10% HCl (Section 7.4.4) followed by 1 mL of reagent water into an acid waste container. Use the rinsed pipet to add 1 mL NaOH to each 125 mL sample and blank aliquot.

8.4.5.3 Cap the vial(s) and double-bag for shipment to the laboratory.

9.0 Quality Assurance/Quality Control

9.1 The sampling team shall employ a strict quality assurance/ quality control (QA/QC) program. The minimum requirements of this program include the collection of equipment blanks, field blanks, and field replicates. It is also desirable to include blind QC samples as part of the program. If samples will be processed for trivalent chromium determinations, the sampling team shall also prepare method blank, OPR, and MS/MSD samples as described in Section 9.6.

9.2 The sampling team is permitted to modify the sampling techniques described in this method to improve performance or reduce sampling costs, provided that reliable analyses of samples are obtained and that samples and blanks are not contaminated. Each time a modification is made to the procedures, the sampling team is required to demonstrate that the modification does not result in contamination of field and equipment blanks. The requirements for modification are given in Sections 9.3 and 9.4. Because the acceptability of a modification is based on the results obtained with the modification, the sampling team must work with an analytical laboratory capable of making trace metals determinations to demonstrate equivalence.

9.3 Equipment Blanks

9.3.1 Before using any sampling equipment at a given site, the laboratory or equipment cleaning contractor is required to generate equipment blanks to demonstrate that the equipment is free from contamination. Two types of equipment blanks are required: bottle blanks and sampling equipment blanks.

9.3.2 Equipment blanks must be run on all equipment that will be used in the field. If, for example, samples are to be collected using both a grab sampling device and the jar sampling device,

then an equipment blank must be run on both pieces of equipment.

9.3.3 Equipment blanks are generated in the laboratory or at the equipment cleaning contractor's facility by processing reagent water through the equipment using the same procedures that are used in the field (Section 8.0). Therefore, the "clean hands/dirty hands" technique used during field sampling should be followed when preparing equipment blanks at the laboratory or cleaning facility. In addition, training programs must require must require sampling personnel to collect a clean equipment blank before performing on-site field activities.

9.3.4 Detailed procedures for collecting equipment blanks are given in the analytical methods referenced in Table 1.

9.3.5 The equipment blank must be analyzed using the procedures detailed in the referenced analytical method (see Table 1). If any metal(s) of interest or any potentially interfering substance is detected in the equipment blank at the minimum level specified in the referenced method, the source of contamination/interference must be identified and removed. The equipment must be demonstrated to be free from the metal(s) of interest before the equipment may be used in the field.

9.4 Field Blank

9.4.1 To demonstrate that sample contamination has not occurred during field sampling and sample processing, at least one field blank must be generated for every 10 samples that are collected at a given site. Field blanks are collected before sample collection.

9.4.2 Field blanks are generated by filling a large carboy or other appropriate container with reagent water (Section 7.1) in the laboratory, transporting the filled container to the sampling site, processing the water through each of the sample processing steps and equipment (e.g., tubing, sampling devices, filters, etc.) that will be used in the field, collecting the field blank in one of the sample bottles, and shipping the bottle to the laboratory for analysis in accordance with the method(s) referenced in Table 1. For example, manual grab sampler field blanks are collected by directly submerging a sample bottle into the water, filling the bottle, and capping. Subsurface sampler field blanks are collected by immersing the tubing into the water and pumping water into a sample container.

9.4.3 Filter the field blanks using the procedures described in Section 8.3.

9.4.4 If it is necessary to acid clean the sampling equipment between samples (Section 10.0), a field blank should be collected after the cleaning procedures but before the next sample is collected.

9.4.5 If trivalent chromium aliquots are processed, a separate field blank must be collected and processed through the sample preparation steps given in Sections 8.4.4.1 through 8.4.4.6.

9.5 Field Duplicate

9.5.1 To assess the precision of the field sampling and analytical processes, at least one field duplicate sample must be collected for every 10 samples that are collected at a given site.

9.5.2 The field duplicate is collected either by splitting a larger volume into two aliquots in the glove box, by using a sampler with dual inlets that allows simultaneous collection of two samples,

or by collecting two samples in rapid succession.

9.5.3 Field duplicates for dissolved metals determinations must be processed using the procedures in Section 8.3. Field duplicates for trivalent chromium must be processed through the sample preparation steps given in Sections 8.4.4.1 through 8.4.4.6.

9.6 Additional QC for Collection of Trivalent Chromium Aliquots

9.6.1 Method blank—The sampling team must prepare one method blank for every ten or fewer field samples. Each method blank is prepared using the steps in Sections 8.4.4.1 through 8.4.4.6 on a 100 mL aliquot of reagent water (Section 7.1). Do not use the procedures in Section 8.3 to process the method blank through the 0.45 µm filter (Section 6.14.1), even if samples are being collected for dissolved metals determinations.

9.6.2 Ongoing precision and recovery (OPR)—The sampling team must prepare one OPR for every ten or fewer field samples. The OPR is prepared using the steps in Sections 8.4.4.1 through 8.4.4.6 on the OPR standard (Section 7.4.7). Do not use the procedures in Section 8.3 to process the OPR through the 0.45 µm filter (Section 6.14.1), even if samples are being collected for dissolved metals determinations.

9.6.3 MS/MSD—The sampling team must prepare one MS and one MSD for every ten or fewer field samples.

9.6.3.1 If, through historical data, the background concentration of the sample can be estimated, the MS and MSD samples should be spiked at a level of one to five times the background concentration.

9.6.3.2 For samples in which the background concentration is unknown, the MS and MSD samples should be spiked at a concentration of 25 µg/L.

9.6.3.3 Prepare the matrix spike sample by spiking a 100-mL aliquot of sample with 2.5 mL of the standard chromium spike solution (Section 7.4.6), and processing the MS through the steps in Sections 8.4.4.1 through 8.4.4.6.

9.6.3.4 Prepare the matrix spike duplicate sample by spiking a second 100-mL aliquot of the same sample with 2.5 mL of the standard chromium spike solution, and processing the MSD through the steps in Sections 8.4.4.1 through 8.4.4.6.

9.6.3.5 If field samples are collected for dissolved metals determinations, it is necessary to process an MS and an MSD through the 0.45 µm filter as described in Section 8.3.

10.0 Recleaning the Apparatus Between Samples

10.1 Sampling activity should be planned so that samples known or suspected to contain the lowest concentrations of trace metals are collected first with the samples known or suspected to contain the highest concentrations of trace metals collected last. In this manner, cleaning of the sampling equipment between samples in unnecessary. If it is not possible to plan sampling activity in this manner, dedicated sampling equipment should be provided for each sampling event.

10.2 If samples are collected from adjacent sites (e.g., immediately upstream or downstream), rinsing of the sampling Apparatus with water that is to be sampled should be sufficient.

10.3 If it is necessary to cross a gradient (i.e., going from a high-concentration sample to a low-concentration sample), such as might occur when collecting at a second site, the following procedure may be used to clean the sampling equipment between samples:

10.3.1 In the glove bag, and using the "clean hands/dirty hands" procedure in Section 8.2.5, process the dilute nitric acid solution (Section 7.2) through the Apparatus.

10.3.2 Dump the spent dilute acid in the waste carboy or in the waterbody away from the sampling point.

10.3.3 Process 1 L of reagent water through the Apparatus to rinse the equipment and discard the spent water.

10.3.4 Collect a field blank as described in Section 9.4.

10.3.5 Rinse the Apparatus with copious amounts of the ambient water sample and proceed with sample collection.

10.4 Procedures for recleaning trivalent chromium preservation equipment between samples are described in Section 8.4.4.

11.0 Method Performance

Samples were collected in the Great Lakes during September–October 1994 using the procedures in this sampling method.

12.0 Pollution Prevention

12.1 The only materials used in this method that could be considered pollutants are the acids used in the cleaning of the Apparatus, the boat, and related materials. These acids are used in dilute solutions in small amounts and pose little threat to the environment when managed properly.

12.2 Cleaning solutions containing acids should be prepared in volumes consistent with use to minimize the disposal of excessive volumes of acid.

12.3 To the extent possible, the Apparatus used to collect samples should be cleaned and reused to minimize the generation of solid waste.

13.0 Waste Management

13.1 It is the sampling team's responsibility to comply with all federal, state, and local regulations governing waste management, particularly the discharge regulations, hazardous waste identification rules, and land disposal restrictions; and to protect the air, water, and land by minimizing and controlling all releases from field operations.

13.2 For further information on waste management, consult *The Waste Management Manual for Laboratory Personnel* and *Less is Better—Laboratory Chemical Management for Waste Reduction,*

available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th Street NW, Washington, DC 20036.

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15.0 Glossary of Definitions and Purposes

These definitions and purposes are specific to this sampling method but have been conformed to common usage as much as possible.

15.1 Ambient Water—Waters in the natural environment (e.g., rivers, lakes, streams, and other receiving waters), as opposed to effluent discharges.

15.2 Apparatus—The sample container and other containers, filters, filter holders, labware, tubing, pipets, and other materials and devices used for sample collection or sample preparation, and that will contact samples, blanks, or analytical standards.

15.3 Equipment Blank—An aliquot of reagent water that is subjected in the laboratory to all aspects of sample collection and analysis, including contact with all sampling devices and apparatus. The purpose of the equipment blank is to determine if the sampling devices and apparatus for sample collection have been adequately cleaned before they are shipped to the field site. An acceptable equipment blank must be achieved before the sampling devices and Apparatus are used for sample collection.

15.4 Field Blank—An aliquot of reagent water that is placed in a sample container in the laboratory, shipped to the field, and treated as a sample in all respects, including contact with the sampling devices and exposure to sampling site conditions, filtration, storage, preservation, and all analytical procedures. The purpose of the field blank is to determine whether the field or sample transporting procedures and environments have contaminated the sample.

15.5 Field Duplicates (FD1 and FD2)—Two identical aliquots of a sample collected in separate sample bottles at the same time and place under identical circumstances using a duel inlet sampler or by splitting a larger aliquot and treated exactly the same throughout field and laboratory procedures. Analyses of FD1 and FD2 give a measure of the precision associated with sample collection, preservation, and storage, as well as with laboratory procedures.

15.6 Matrix Spike (MS) and Matrix Spike Duplicate (MSD)—Aliquots of an environmental sample to which known quantities of the analytes are added in the laboratory. The MS and MSD are analyzed exactly like a sample. Their purpose is to quantify the bias and precision caused by the sample matrix. The background concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the MS and MSD corrected for background concentrations.

15.7 May—This action, activity, or procedural step is optional.

15.8 May Not—This action, activity, or procedural step is prohibited.

15.9 Minimum Level (ML)—The lowest level at which the entire analytical system gives a recognizable signal and acceptable calibration point (Reference 21).

15.10 Must—This action, activity, or procedural step is required.

15.11 Reagent Water—Water demonstrated to be free from the metal(s) of interest and potentially interfering substances at the MDL for that metal in the referenced method or additional method.

15.12 Should—This action, activity, or procedural step is suggested but not required.

15.13 Trace-Metal Grade—Reagents that have been demonstrated to be free from the metal(s) of interest at the method detection limit (MDL) of the analytical method to be used for determination of this metal(s).

The term "trace-metal grade" has been used in place of "reagent grade" or "reagent" because acids and other materials labeled "reagent grade" have been shown to contain concentrations of metals that will interfere in the determination of trace metals at levels listed in Table 1.

TABLE 1. ANALYTICAL METHODS, METALS, AND CONCENTRATION LEVELS APPLICABLE TO METHOD 1669

Method	Technique	Metal	MDL (µg/L) [1]	ML (µg/L) [2]
1631	Oxidation/Purge & Trap/CVAFS	Mercury	0.0002	0.0005
1632	Hydride AA	Arsenic	0.003	0.01
1636	Ion Chromatography	Hexavalent Chromium	0.23	0.5
1637	CC/STGFAA	Cadmium	0.0075	0.02
		Lead	0.036	0.1
1638	ICP/MS	Antimony	0.0097	0.02
		Cadmium	0.013	0.1
		Copper	0.087	0.2
		Lead	0.015	0.05
		Nickel	0.33	1
		Selenium	0.45	1
		Silver	0.029	0.1
		Thallium	0.0079	0.02
		Zinc	0.14	0.5
1639	STGFAA	Antimony	1.9	5
		Cadmium	0.023	0.05
		Trivalent Chromium	0.10	0.2
		Nickel	0.65	2
		Selenium	0.83	2
		Zinc	0.14	0.5
1640	CC/ICP/MS	Cadmium	0.0024	0.01
		Copper	0.024	0.1
		Lead	0.0081	0.02
		Nickel	0.029	0.1

[1] Method Detection Limit as determined by 40 *CFR* Part 136, Appendix B.

[2] Minimum Level (ML) calculated by multiplying laboratory-determined MDL by 3.18 and rounding result to nearest multiple of 1, 2, 5, 10, 20, 50, etc., in accordance with procedures used by EAD and described in the EPA *Draft National Guidance for the Permitting, Monitoring, and Enforcement of Water Quality-Based Effluent Limitations Set Below Analytical Detection/Quantitation Levels*, March 22, 1994.

TABLE 2. ANALYTES, PRESERVATION REQUIREMENTS, AND CONTAINERS

Metal	Preservation Requirements	Acceptable Containers
Antimony Arsenic Cadmium Copper Lead Nickel Selenium Silver Thallium Zinc	Add 5 mL of 10% $HN0_3$ to 1-L sample; preserve on-site or immediately upon laboratory receipt.	500 mL or 1 L fluoropolymer, conventional or linear polyethylene, polycarbonate, or polypropylene containers with lid
Chromium (III)	Add 1 mL chromium (III) extraction solution to 100 mL aliquot, vacuum filter through 0.4 µm membrane, add 1 mL 10% $HN0_3$; preserve on-site immediately after collection.	500 mL or 1 L fluoropolymer, conventional or linear polyethylene, polycarbonate, or polypropylene containers with lid
Chromium (IV)	Add 50% NaOH; preserve immediately after sample collection.	500 mL or 1 L fluoropolymer, conventional or linear polyethylene, polycarbonate, or polypropylene containers with lid
Mercury	Total: Add 0.5% high-purity HCl or 0.5% BrCl to pH < 2; Total & Methyl: Add 0.5% high-purity HCL; preserve on-site or immediately upon laboratory receipt	Fluoropolymer or borosilicate glass bottles with fluoropolymer or fluoropolymer-lined caps

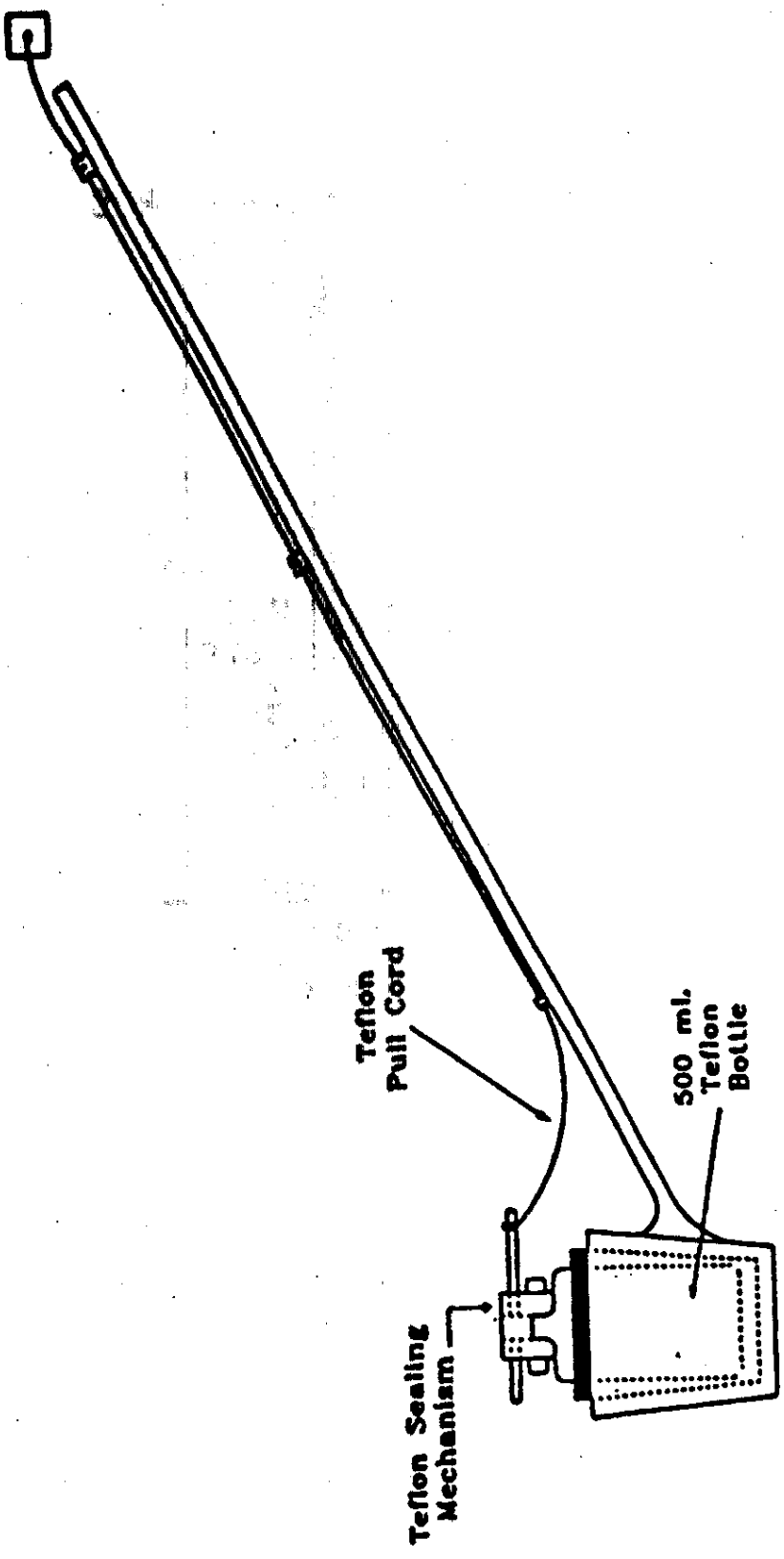


Figure 1 - Grab Sampling Device

Figure 2 - Grab Sampling Device

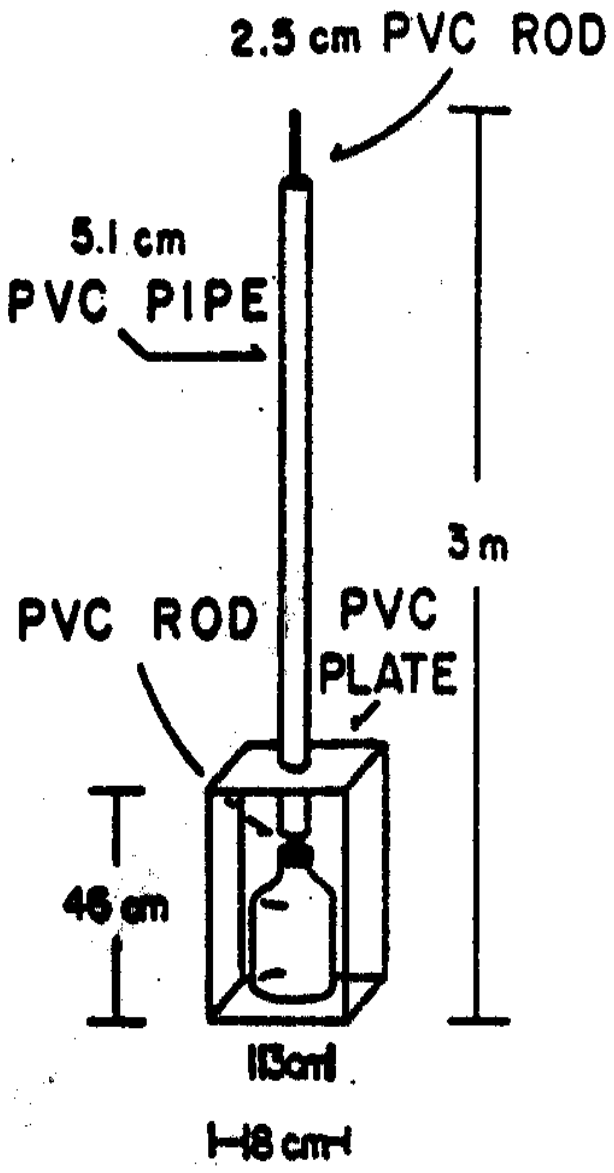


Figure 3 - Jar Sampling Device

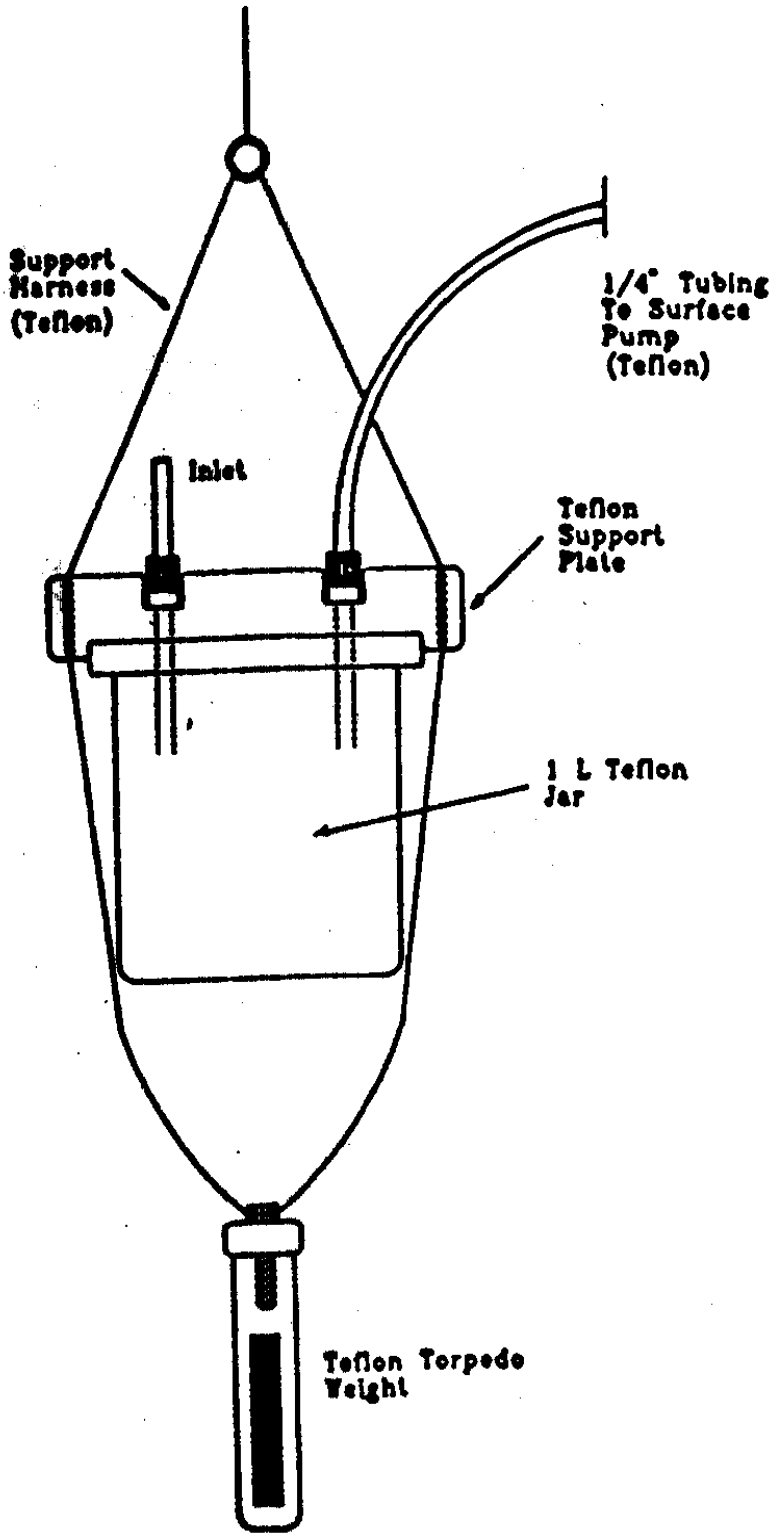
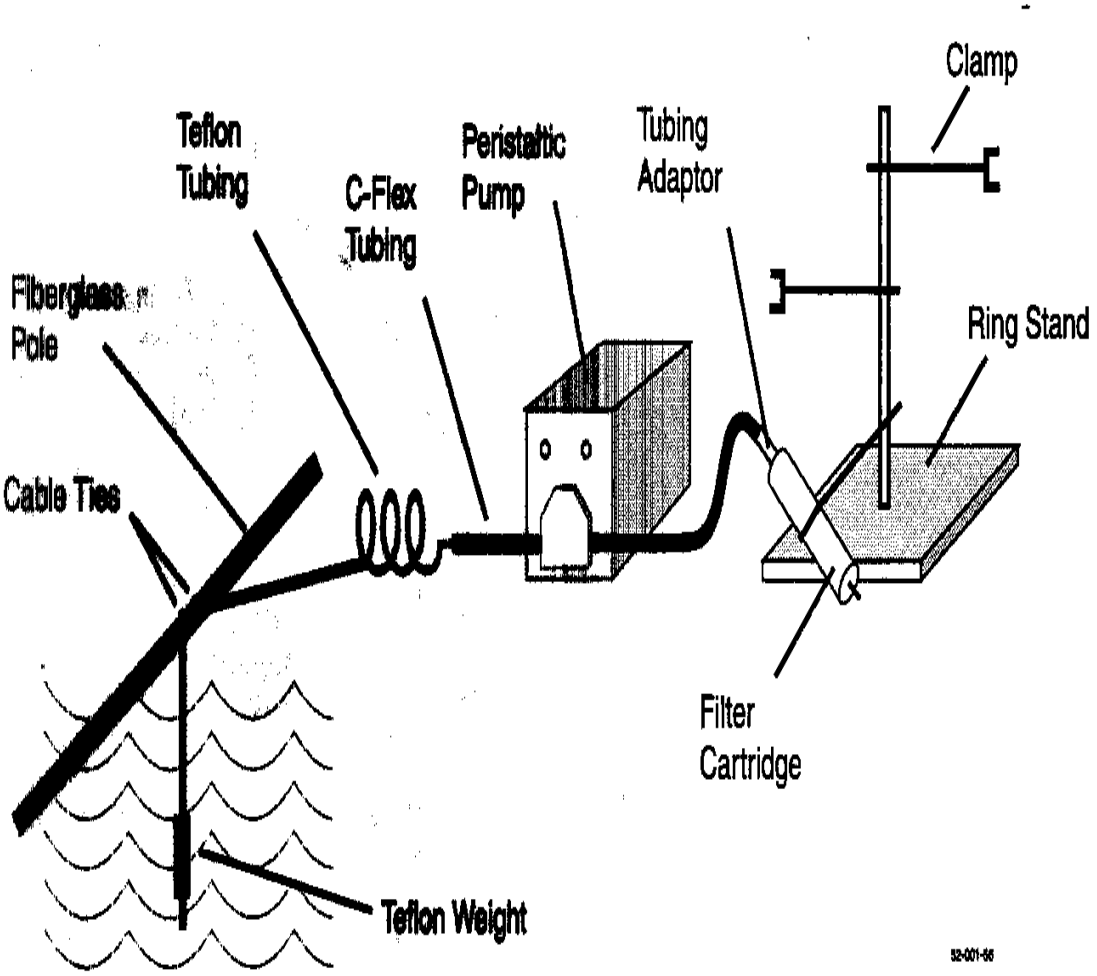


Figure 4 - Sample Pumping System



Attachment 2

Manufacturer's Instructions – pH and Dissolved Oxygen Meters

Use the SET/HOLD button to change the temperature unit, and then press the MODE button three times, until the meter returns to normal measurement mode.

To reset to the default calibration

To clear a previous calibration, press the MODE button after entering the calibration mode. The lower LCD will display ESC for 1 second and the meter will return to normal measurement mode. The “CAL” symbol on the LCD will disappear. The meter will be reset to the default calibration.

Battery replacement

The meter displays the remaining battery percentage every time it is turned on. When the battery level is below 5%, the symbol on the bottom left of the LCD lights up to indicate a low battery condition. If the battery level is so low as to cause erroneous reading, the Battery Error Prevention System (BEPS) will automatically turn the meter off.

To change the batteries, remove the 4 screws located on the back of the meter. Once the back has been removed, carefully replace the 4 AAA batteries located in the compartment while paying attention to their polarity. Replace the back, making sure that the gasket is properly seated in place, and tighten the screws.

Calibration solutions

HI 77400P	pH 4.01 & 7.01 (20 mL, 5 pcs each)
HI 770710P	pH 7.01 & 10.01 (20 mL, 5 pcs each)
HI 70004P	pH 4.01 calibration solution (20 mL, 25 pcs)
HI 70006P	pH 6.86 calibration solution (20 mL, 25 pcs)
HI 70007P	pH 7.01 calibration solution (20 mL, 25 pcs)
HI 70009P	pH 9.18 calibration solution (20 mL, 25 pcs)
HI 70010P	pH 10.01 calibration solution (20 mL, 25 pcs)
HI 70030P	12.88 mS/cm @25°C (20 mL, 25 pcs)
HI 70038P	6.44 ppt (g/L) @25°C (20 mL, 25 pcs)

Other accessories

HI 710007	Protective rubber boot

HI 991301 is in compliance with the CE directives.

HANNA instruments

IS991301R3 02/02

HI 991301 Instruction Manual

Portable pH/EC/TDS/Temperature Meter

SPECIFICATIONS

Range	***pH***	0.00 to 14.00
	EC	0.00 to 20.00 mS/cm
	TDS	0.00 to 10.00 ppt
	Temperature	0.0 to 60.0°C or 32.0 to 140.0°F
Resolution	***pH***	0.01pH
	EC	0.01 mS/cm
	TDS	0.01 ppt
	Temperature	0.1°C or 0.1°F
Accuracy (@20°C/68°F)	***pH***	±0.01pH
	EC/TDS	±2% F.S.
	Temperature	±0.5°C or ±1°F
Typical EMC Deviation	***pH***	±0.03pH
	EC/TDS	±2% F.S.
	Temperature	±0.5°C or ±1°F
Temperature Compensation	***pH***	Automatic
	EC/TDS	ß=0.0 to 2.4%/°C
pH Calibration		1 or 2 point with auto-buffer recognition 4.01/7.01/10.01 pH or 4.01/6.86/9.18 pH
EC/TDS Calibration		Automatic (25°C/77°F) 1 point at: 12.88 mS/cm, 6.44 ppt (0.5 conv.) 9.02 ppt (0.7 conv.)
Conductivity to TDS Conversion Factor		0.45 to 1.00 (CONV)
***Probe* HI 1288**		pH/EC/TDS/temp. probe (included)
Battery Type/Life		4 x 1.5V AAA with BEPS / 500 hours
Environment		0 to 50°C (32 to 122°F); RH 100%
Dimensions		143x80x38mm (5.6x3.2x1.5”)

OPERATIONAL GUIDE

To connect the probe

Connect the **HI 1288** probe to the DIN socket on the top of the meter by aligning the pins and pushing in the plug. Tighten the nut to ensure a good connection. Remove the protective cap from the **HI 1288** probe before taking any measurement.

To turn the meter on and to check battery status

Press and hold the ON/OFF/MODE button for 2 seconds. All the used segments on the LCD will be visible for a few seconds, followed by a percent indication of the remaining battery life. Eg. % 100 BATT.

To select the measurement unit (pH or EC or TDS)

Press the SET/HOLD button while in normal measurement mode. The meter will display pH or EC or TDS.Temperature will always be displayed on the bottom. Eg. pH 5.73 22.5 °C.

To freeze the display

Press and hold the SET/HOLD button for 2 seconds until HOLD appears on the secondary display. Eg. pH 5.73 hold. Press any button to return to normal mode.

To turn the meter off

Press the ON/OFF/MODE button while in normal measurement mode. OFF will appear on the lower part of display. Release the button.

pH MEASUREMENTS & CALIBRATION

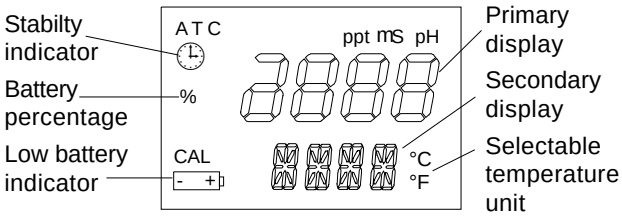
- Before taking any measurement make sure the meter has been calibrated.
- If the probe has been left dry, soak in a storage or pH 7 solution at least for one hour to reactivate it.
- Select the pH mode with the SET/HOLD button.
- Submerge the probe in the sample to be tested while stirring it gently. Wait until the ◷ stability symbol on the top left of the LCD disappears.
- The pH value automatically compensated for temperature is shown on the primary LCD while the secondary LCD shows the temperature of the sample.
- If measurements are taken in different samples successively, rinse the probe tip thoroughly to eliminate cross-contamination; and after cleaning, rinse the probe tip with some of the sample to be measured.

Calibration buffer set

- While in pH measurement mode, press and hold the MODE button until TEMP and the current temperature unit are displayed on the lower LCD. Eg. TEMP °C.
- Press the MODE button again to show the current buffer set: pH 7.01 BUFF (for 4.01/7.01/10.01) or pH 6.86 BUFF (for 4.01/6.86/9.18).
- Press the SET/HOLD button to change the buffer set.
- Press the MODE button to return to normal pH measurement mode.

pH calibration

- While in pH measurement mode, press and hold the MODE button until CAL is displayed on the lower LCD.
- Release the button. The LCD will display pH 7.01 USE or pH 6.86 USE (if you have selected the NIST buffer set).
- For a *single point pH calibration*, place the probe in any buffer from the selected buffer set (eg. pH 4.01 or pH 7.01 or pH 10.01). The meter will automatically recognize the buffer value.
  If using pH 7.01 (or 6.86 from the NIST buffer set), after recognition of the buffer press the MODE button to return to the pH measurement mode.
- For a *two point pH calibration*, place the probe in pH 7.01 (or 6.86, if you have selected the NIST buffer set). The meter will recognize the buffer value and then display pH 4.01 USE.



Place the probe in the second buffer (pH 4.01 or 10.01, or, if using NIST, pH 4.01 or 9.18). When the second buffer is recognized, the LCD will display OK for 1 second and the meter will return to normal measurement mode.

EC/TDS MEASUREMENTS & CALIBRATION

- Place the probe in the sample to be tested. Use plastic beakers or containers to minimize any electromagnetic interference.
- Select either EC or TDS mode with the SET/HOLD button.
- Tap the probe lightly on the bottom of the container to remove air bubbles that may be trapped inside the tip.
- Wait for a few minutes for the temperature sensor to reach thermal equilibirium (i.e. until the ¹ stability symbol on the top left of the LCD disappears).
- The meter will show the EC/TDS value automatically compensated for temperature and the temperature of the sample.

To change the EC/TDS conversion factor (CONV) and the EC/TDS temperature compensation (BETA)

- While in EC/TDS measurement mode, press and hold the MODE button until TEMP and the current temperature unit are displayed on the lower LCD. Eg. TEMP °C.
- Press the MODE button again to show the current conversion factor. Eg. 0.50 CONV.
- Press the SET/HOLD button to change the conversion factor.
- Press the MODE button to show the current temperature compensation ß. Eg. 2.1 BETA.
- Press the SET/HOLD button to change the temperature compensation ß.
- Press the MODE button return to normal operation.

EC calibration

- While in the EC measurement mode, press and hold the MODE button until CAL is displayed on the lower LCD.
- Release the button and immerse the probe in **HI7030** calibration solution (mS 12.88 USE).
- Once the calibration has been automatically performed, the LCD will display OK for 1 second and return to normal measurement mode.
- Since there is a known relationship between the EC and TDS reading, it is not necessary to calibrate the meter in TDS. If the EC/TDS conversion factor is either 0.5 or 0.7, the meter will allow a direct calibration in ppm by using the Hanna calibration solutions listed below.

TO CHANGE THE TEMPERATURE UNIT (FROM °C TO °F)

Press and hold the MODE button until TEMP and the current temperature unit are displayed on the secondary LCD. Eg. TEMP °C.

YSI Model 55 Handheld Dissolved Oxygen System

Service Manual

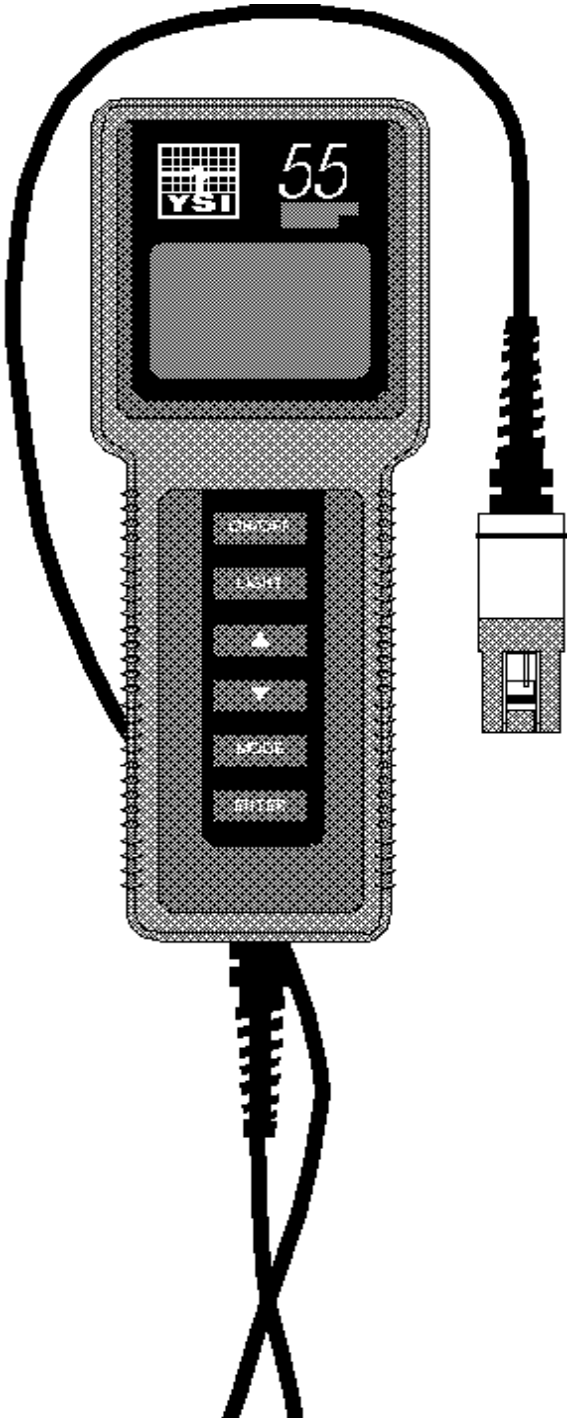


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Table of Contents

Service Philosophy

The YSI Model 55 is sold as a complete dissolved oxygen measuring system including an attached probe and either a 12 or 25 foot cable. Most service issues which occur in dissolved oxygen systems are caused by improper maintenance of the probe or cable. For this reason, troubleshooting efforts should be initially directed at determining the condition and function of the probe and cable.

In the event that a service problem is isolated to the meter itself, YSI recommends the replacement of the entire defective sub-assembly rather than individual components. All replacement systems are available through YSI; see section entitled *Warranty & Repair* for details.

Specifications

Operating Environment

Medium: fresh, sea, or polluted water
Temperature: -5 to +45°C
Depth: 0 to 12 or 0 to 25 feet (depending on cable length)

Storage Temperature: -10 to +50°C

Material: ABS, Stainless Steel, Acrylic, and other materials.

Dimensions:

Height:	.5 inches	(24.13 cm)
Thickness:	2.2 inches	(49.53 cm)
Width:	.5 inches max.	(8.89 cm)
Weight:	1.7 pounds	(3.74 kg)

Power: 9 VDC - 6 AA-size Alkaline Batteries (included)
Approximately 100 hours operation from each new set of batteries

Water Tightness: Meets or exceeds IP65 standards

Extensive testing of the YSI Model 55 suggests the following typical performance:

Temperature

Sensor Type:	Thermistor
Range:	-5 to +45°C
Accuracy:	± 0.4°C
Resolution:	0.1°C

Dissolved Oxygen % Saturation

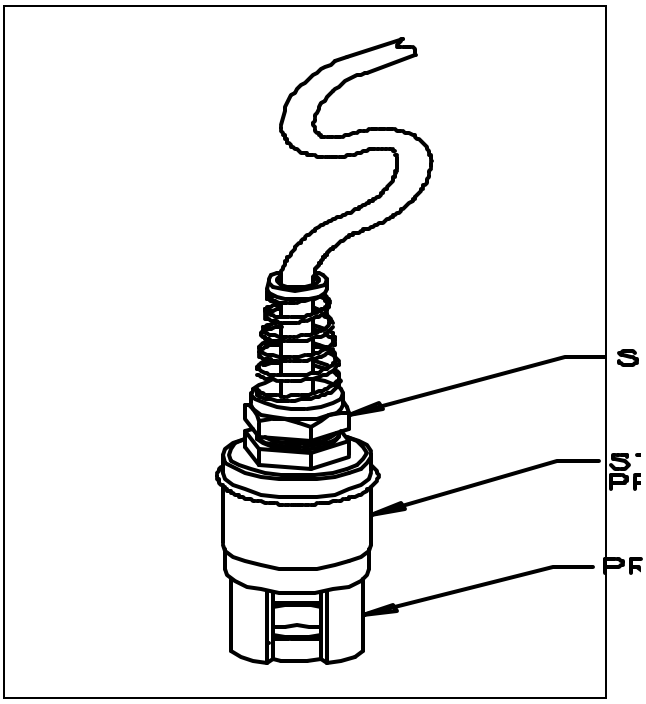
Sensor Type:	Membrane covered polarographic
Range:	0 to 200 % air saturation
Accuracy:	± 2 % air saturation
Resolution:	0.1 % air saturation

Dissolved Oxygen mg/L

Sensor Type:	Calculated from % air saturation, temperature and salinity.
Range:	0 to 20 mg/L
Accuracy:	± 0.3 mg/L
Resolution:	0.01 mg/L

Principles of Operation

The sensor consists of an acrylic body with a circular gold cathode embedded in the end. Inside the gold ring there is a small chamber containing a porous silver anode. In operation, this chamber is filled with a solution of KCl electrolyte containing a small amount of surfactant to improve wetting action.



A thin permeable membrane, stretched over the sensor, isolates the electrodes from the environment, while allowing gases to enter. When a polarizing voltage is applied to the sensor electrodes, oxygen which has passed through the membrane reacts at the cathode causing a current to flow.

The membrane passes oxygen at a rate proportional to the pressure difference across it. Since oxygen is rapidly consumed at the cathode, it can be assumed that the oxygen pressure under the membrane is zero. Hence, the force causing the oxygen to diffuse through the membrane is proportional to the partial pressure of oxygen outside the membrane. As the oxygen partial pressure varies, so does the oxygen diffusion through the membrane. This causes the probe current to change proportionally.

It is important to recognize that oxygen dissolved in the sample is consumed during the test. It is therefore essential that the sample be continuously stirred at the sensor tip. If stagnation occurs, your readings will be artificially low. Stirring may be accomplished by mechanically moving the sample around the probe tip, or by rapidly moving the probe through the sample. The rate of stirring should be at least 1 foot per second.

Probe Operation & Maintenance

1. Membrane life depends on usage. Membranes will last a long time if installed properly and treated with care. Erratic readings are a result of loose, wrinkled, damaged, or fouled membranes, or from large (more than 1/8" diameter) bubbles in the electrolyte reservoir. If erratic readings or evidence of membrane damage occurs, you should replace the membrane and the KCl solution. The average replacement interval is two to four weeks.

2. If the membrane is coated with oxygen consuming (e.g. bacteria) or oxygen evolving organisms (e.g. algae), erroneous readings may occur.

3. Avoid any environment which contains substances that may attack the probe materials. Some of these substances are concentrated acids, caustics, and strong solvents. The probe materials that come in contact with the sample include FEP Teflon, acrylic plastic, EPR rubber, stainless steel, epoxy, polyetherimide and the polyurethane cable covering.

4. For correct probe operation, the gold cathode must always be bright. If it is tarnished (which can result from contact with certain gases), or plated with silver (which can result from extended use with a loose or wrinkled membrane), the gold surface must be restored. To restore the cathode you may either return the instrument to the factory, or clean it using the YSI Model 5680 Probe Reconditioning Kit. Never use chemicals or abrasives not supplied with this kit.

5. It is also possible for the silver anode to become contaminated, which will prevent successful calibration and/or operation. To clean the anode, remove the O-ring and membrane and soak the probe overnight in 3% ammonium hydroxide. Next, rinse the sensor tip and KCl reservoir with deionized water, add new KCl solution, and install a new membrane and O-ring. Turn the instrument on and allow the system to stabilize for at least 30 minutes. The same anode cleaning procedure can be done using a 14% solution of ammonium hydroxide and soak the sensor tip for 3-5 minutes. If, after several hours of stabilization time, you are still unable to calibrate or operate the probe, return the YSI Model 55 system to an authorized service center for service.

   NOTE: Soaking the anode in this fashion can, over time, errode the silver so that the probe is no longer functional. It is important, therefore, that the probe not be soaked longer than specified above.

6. If the sensor O-ring is worn or loose, replace it with the appropriate O-ring provided in the YSI Model 5945 O-ring Pack. It is recomended that the O-ring be replaced at least 4 times a year regardless of its physical appearance.

Calibration

Before You Calibrate

Before you calibrate the YSI Model 55, be certain that the probe is properly filled with KCl solution and has a new membrane and O-ring.

To accurately calibrate the YSI Model 55, you will need to know the following information:

1. The approximate altitude of the region in which you plan to take your dissolved oxygen measurements.

2. The approximate salinity of the water you will be analyzing. Fresh water has a salinity of approximately zero. Sea water has a salinity of approximately 35 parts per thousand (PPT). If you are not certain what the salinity of the sample water is, use a YSI Salinity-Conductivity-Temperature meter to determine it.

The Calibration Process

1. Ensure that the sponge inside the instrument's calibration chamber is wet. Insert the probe into the calibration chamber.

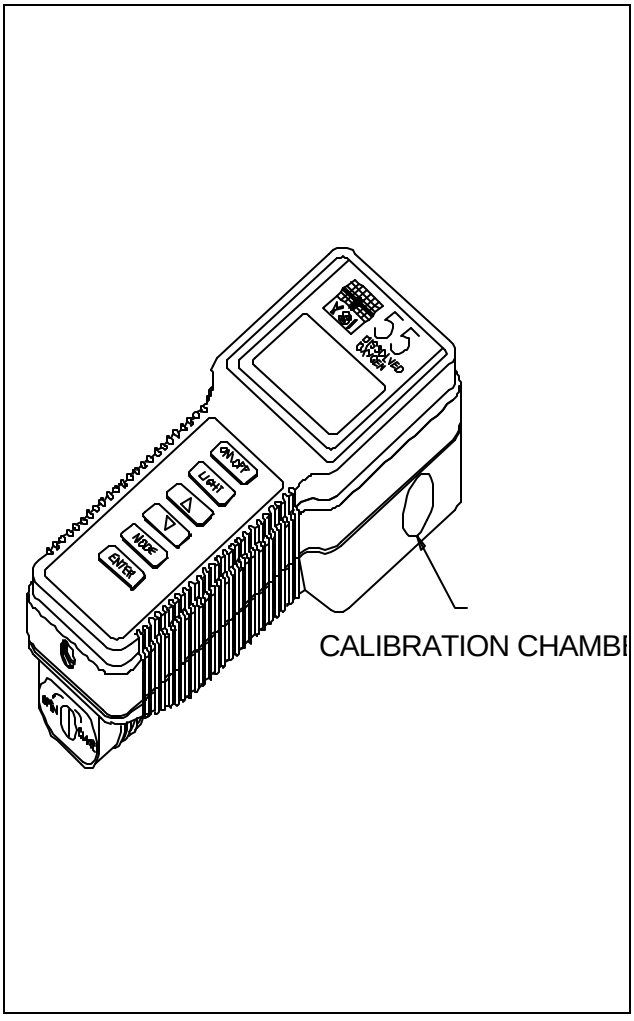
2. Turn the instrument on by pressing the **ON/OFF** button on the front of the instrument. Wait for the dissolved oxygen and temperature readings to stabilize (usually 15 to 30 minuites is required).

   Note: It is normal for error messages to appear momentarily at power up.

3. Use two fingers to press and release the two ▲ ▼ keys at the same time.

4. The LCD will prompt you to enter the local altitude in hundreds of feet. Use the arrow keys to increase or decrease the altitude.

   Example: Entering the number 12 here indicates 1200 feet.



When the proper altitude appears on the LCD, press the **ENTER** key once to view the calibration value in the lower right of the LCD; and a second time to move to the salinity compensation procedure.

5. The LCD will prompt you to enter the approximate salinity of the water you are about to analyze. You can enter any number from 0 to 40 parts per thousand (PPT) of salinity. Use the arrow keys to increase or decrease the salinity compensation. When the correct salinity appears on the LCD, press the **ENTER** key.

Operation

Once the calibration process is complete, the only keys which will remain operational are the **MODE** key, the **LIGHT** key, and the **ON/OFF** key. You can move back and forth from reading dissolved oxygen in the mg/L mode or the % air saturation mode by pressing the **MODE** key. If you are working in a dark area or have difficulty reading the LCD, press and hold the **LIGHT** key to activate the back-light of the YSI Model 55. The **ON/OFF** key turns the instrument on or off.

NOTE: Each time the YSI Model 55 has been turned off, it may be necessary to re-calibrate before taking measurements. All calibrations should be completed at a temperature which is as close as possible to the sample temperature. Dissolved Oxygen readings are only as good as the calibration.

Troubleshooting

SYMPTOM	POSSIBLE CAUSE	ACTION
1. Instrument will not turn on	A. Low battery voltage B. Keypad is defective C. Main board is defective	A. Replace batteries B. Replace keypad C. Troubleshoot or replace board
2. Instrument will not calibrate	A. Membrane is fouled or damaged B. Probe anode is fouled or dark C. Probe cathode is tarnished D. Probe is defective	A. Replace membrane & KCl B. Clean anode C. Clean cathode D. Replace probe
3. Instrument "locks up", keypad is non-functional	A. Instrument has rec'd a shock B. Batteries are low or damaged C. Main board is defective	A & B. Remove battery lid, wait 15 seconds for reset, replace lid. B. Replace batteries C. Troubleshoot or replace main board
4. Instrument readings are inaccurate or irratic	A. Cal altitude/salinity are incorrect B. Probe not in 100% O_2 saturated air during Cal procedure C. Probe didn't stabilize long enough before calibration D. Probe electrodes fouled or tarnished	A. Recalibrate w/correct value B. Moisten sponge & place in Cal chamber w/ probe & Recal C. Recalibrate after 15-30 minutes warm-up time D. Clean probe electrodes or replace probe
5. LCD displays "LO BAT"	A. Batteries are low or damaged	A. Replace batteries
6. LCD displays message "ER 0"	A. Instrument's self-test detects improper probe voltage during calibration.	A1. Clean probe electrodes and retry A2. Replace probe A3. Replace main board
7. LCD displays message "ER 1"	A. Instrument's self-test detects a variance in RAM	A1. Remove battery lid, wait 15 seconds for reset, replace lid. A2. Replace main board
8. LCD displays message "ER 2"	A. Instrument's self-test detects a variance in ROM checksum	A1. Remove battery lid, wait 15 seconds for reset, replace lid. A2. Replace main board
9. LCD displays message "ER 3"	A. Instrument's self-test detects a system malfunction or component failure	A1. Remove battery lid, wait 15 seconds for reset, replace lid. A2. Replace main board
10. LCD displays message "ER 4"	A. Sample O_2 concentration is more than 20mg/l. B. High probe output current	A. Recalibrate using correct altitude and salinity compensation B1. Service probe electrodes and retry B2. Replace probe assembly
11. LCD displays message "ER 5"	A. Sample O_2 concentration is below -0.5 mg/l. B. Low probe output current	A. Recalibrate using correct altitude and salinity compensation B1. Service probe electrodes and retry B2. Replace probe assembly
12. LCD displays message "ER 6"	A. Sample saturation is greater than 200% B. High probe current	A. Recalibrate using correct altitude and salinity compensation B1. Service probe electrodes and retry B2. Replace probe assembly
13. LCD displays message "ER 7"	A. Sample saturation is less than -3.0%. B. Low probe output current	A. Recalibrate using correct altitude and salinity compensation B1. Service probe electrodes and retry B2. Replace probe assembly
14. LCD displays message "ER 8"	A. Sample temperature is more than	A. Reduce the sample temperature

SYMPTOM	POSSIBLE CAUSE	ACTION
	+46°C. B. Probe thermistor defective	B. Replace probe assembly
15. LCD displays message "ER 9"	A. Sample temperature is less than -5°C. B. Probe thermistor defective	A. Increase sample temperature B. Replace probe assembly

Disassembly Procedures

Refer to the Assembly drawing on the next page before attempting to disassemble the meter case. Follow these steps to disassemble the meter case:

STEP 1 -- Place the instrument face down on a flat cloth-covered surface. Use a phillips screw driver to completely remove the screw located at the bottom of the hand strap.

STEP 2 -- Using a standard screwdriver or a small coin, loosen the battery lid screw and remove the battery lid and all six AA-size batteries.

STEP 3 -- With the instrument face down on the flat, cloth-covered surface, place two fingers into the battery chamber and your other hand over the cable strain-relief. Pull straight up on the battery chamber to seperate the case halves. Unplug the power connector from the PC Board.

> **NOTE:** Because the Model 55 is water tight, the case halves will be relatively difficult to separate.

STEP 4 -- The main PC Board is held in place by a single phillips screw located in the center of the board. Remove the screw, and gently pull the PC Board away from the front case.

> **NOTE:** The leads on the cable which connect to the main PC Board are quite short. Be careful not to damage the terminal connectors when you pull the PC Board away from the front case.

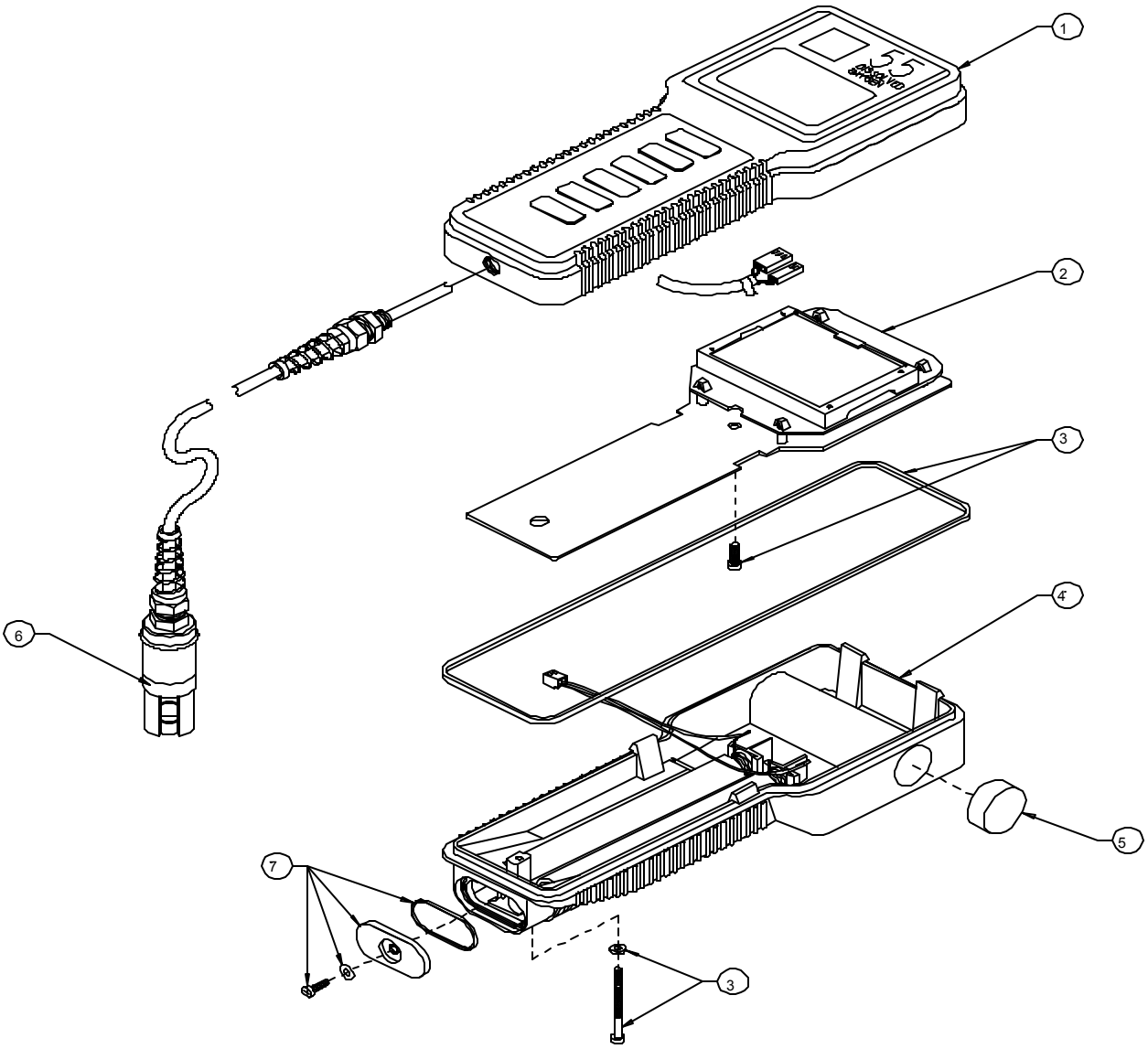
STEP 5 -- Carefully slide the probe cable terminal connector out of its mating connector. Make note of the wire color configuration so that the connectors can be correctly re-installed later.

STEP 6 -- To separate the probe cable from the front case, unscrew the outer portion of the strain relief (that portion which does not make contact with the front case). Slide the spiral portion of the strain relief down the cable toward the probe. Next, unscrew the remaining portion of the strain relief from the front case.

STEP 7 -- To separate the LCD from the main PC Board, squeeze the four plastic off-set spacers and slide the LCD PC board away from the main board one corner at a time. Next, remove the four small phillips screws from the back of the LCD and remove the LCD from its clear plastic frame.

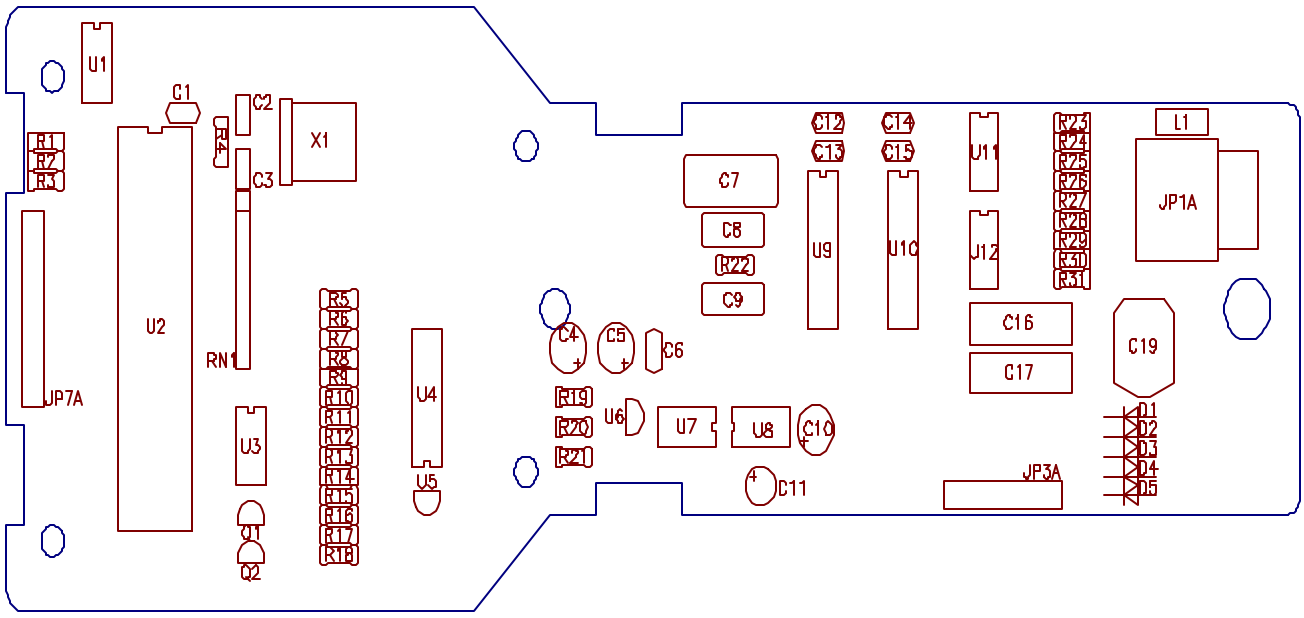
STEP 8 -- To remove the keypad from the front case, use a small phillips screwdriver to remove the screws from the keypad's metal backplate; then lift the keypad away from the front case.

Assembly Drawing

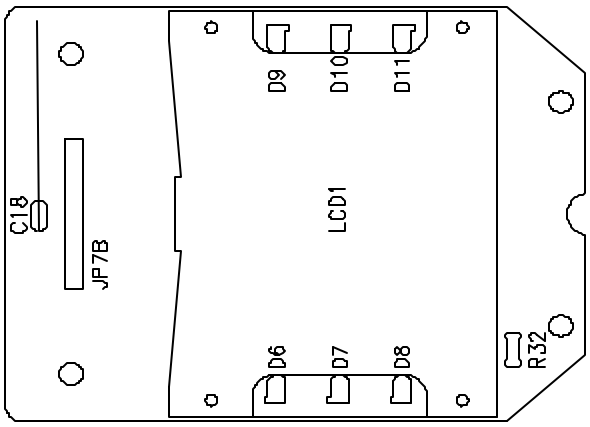


Bubble Number	Item Number	Description
1	055201	Front Cover Assembly W/Keypad
2	055203	Main Board Assembly W/055212 Display
3	055204	Case Hardware Kit
4	055202	Rear Cover Assembly
5	055219	Sponge
6	055205	Probe Assembly, 12 Foot
6	055206	Probe Assembly, 25 Foot
7	055210	Battery Hardware Kit

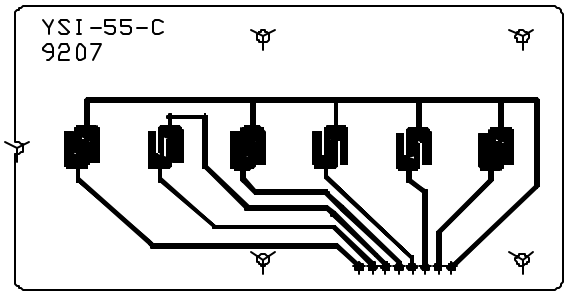
Board Assemblies



(PCB-A) Main Board



(PCB-B)Display Board



(PCB-C)Keypad Board

Test Procedures

System Test

The Model 55 and it's probe can be easily tested using the **YSI 16423 Test Box**. If a test box isn't available, the following quick test can be used to verify the system's operation.

1. If necessary, service the probe's electrodes. Follow the instructions on page 5.
2. Install a fresh membrane and KCl solution. Place the probe in its calibration chamber.
3. Turn the system on and allow it to stabilize for 30 minutes.
4. Calibrate the system as described in the **Calibration** section of this manual.
5. With the probe in the calibration chamber, check the displayed reading for stability. Erratic or drifting readings indicate a possible problem. See the **Troubleshooting** section for help.
6. Place the probe in a zero oxygen environment. The display should decrease rapidly and reach 0 ±2% in 7 minutes or less.

   A zero oxygen environment can be obtain by taking a reading in pure nitrogen gas, in a sodium sulfite solution, or in a BOD bottle filled with 350 mL of distilled water in which 3 to 7 grams of active dry yeast has been dissolved and allowed to consume the oxygen (about 5 minutes).

Probe Test

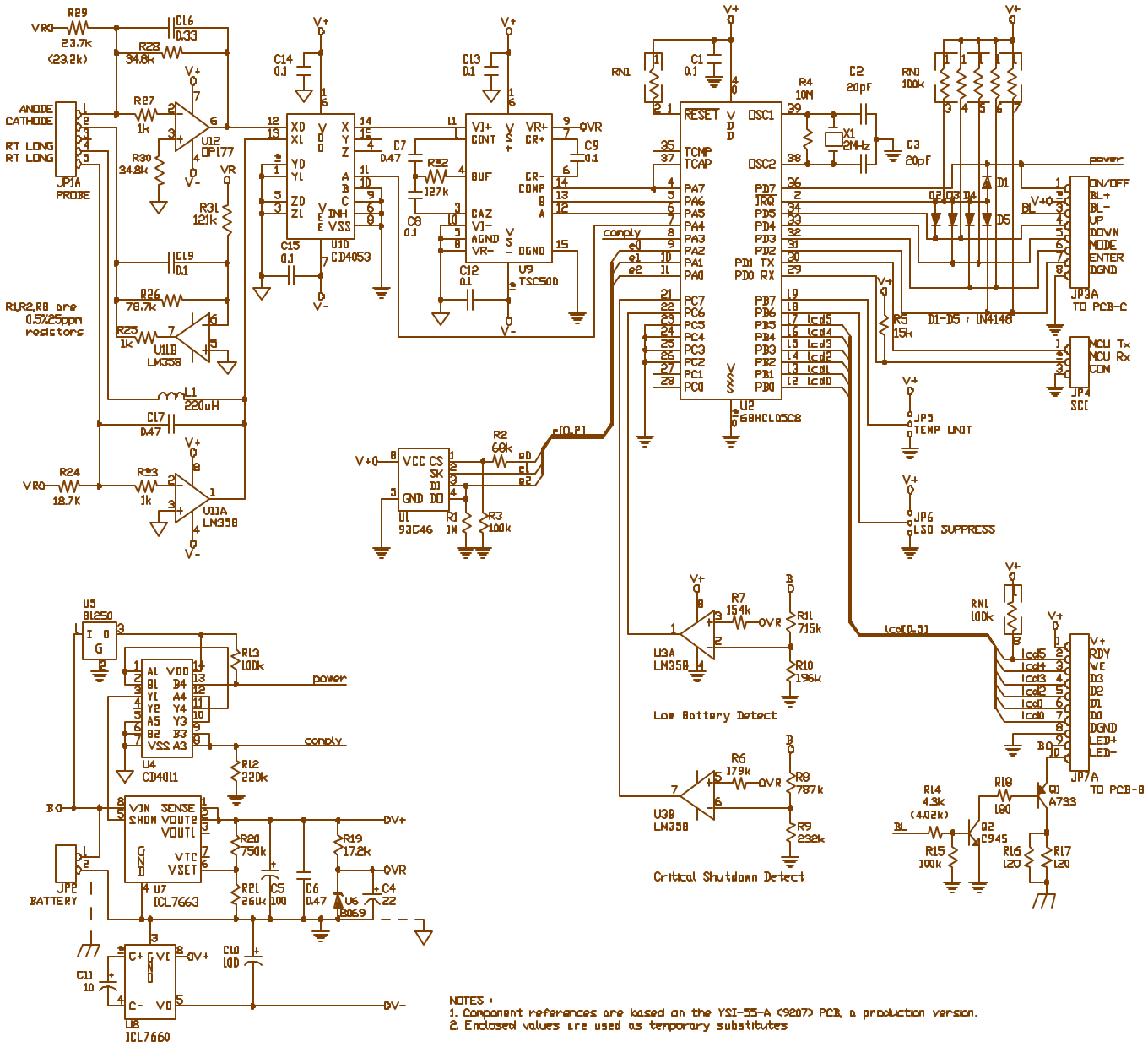
The probe thermistor can be tested by measuring its resistance in a temperature controlled bath and comparing the reading to the chart below. With the probe disconnected from the instrument, connect a precision ohm meter to the **Red** and **Black** probe wires. **All readings are ± 10 ohms**.

Bath temperature Degrees Celsius	**Resistance in Ohms**	**Bath temperature Degrees Celsius**	**Resistance in Ohms**
5	5721.11	25	2253.30
10	4484.22	30	1815.32
15	3540.50	35	1471.56
20	2815.03	40	1200.00

Electrical leakage between the sensor electrodes and/or the thermistors can cause system failures. Before using the test below, remove the probe's membrane and rinse the electrodes with distilled water. Then, thoroughly dry the sensor end, inside and outside, with compressed air or a soft towel before testing.

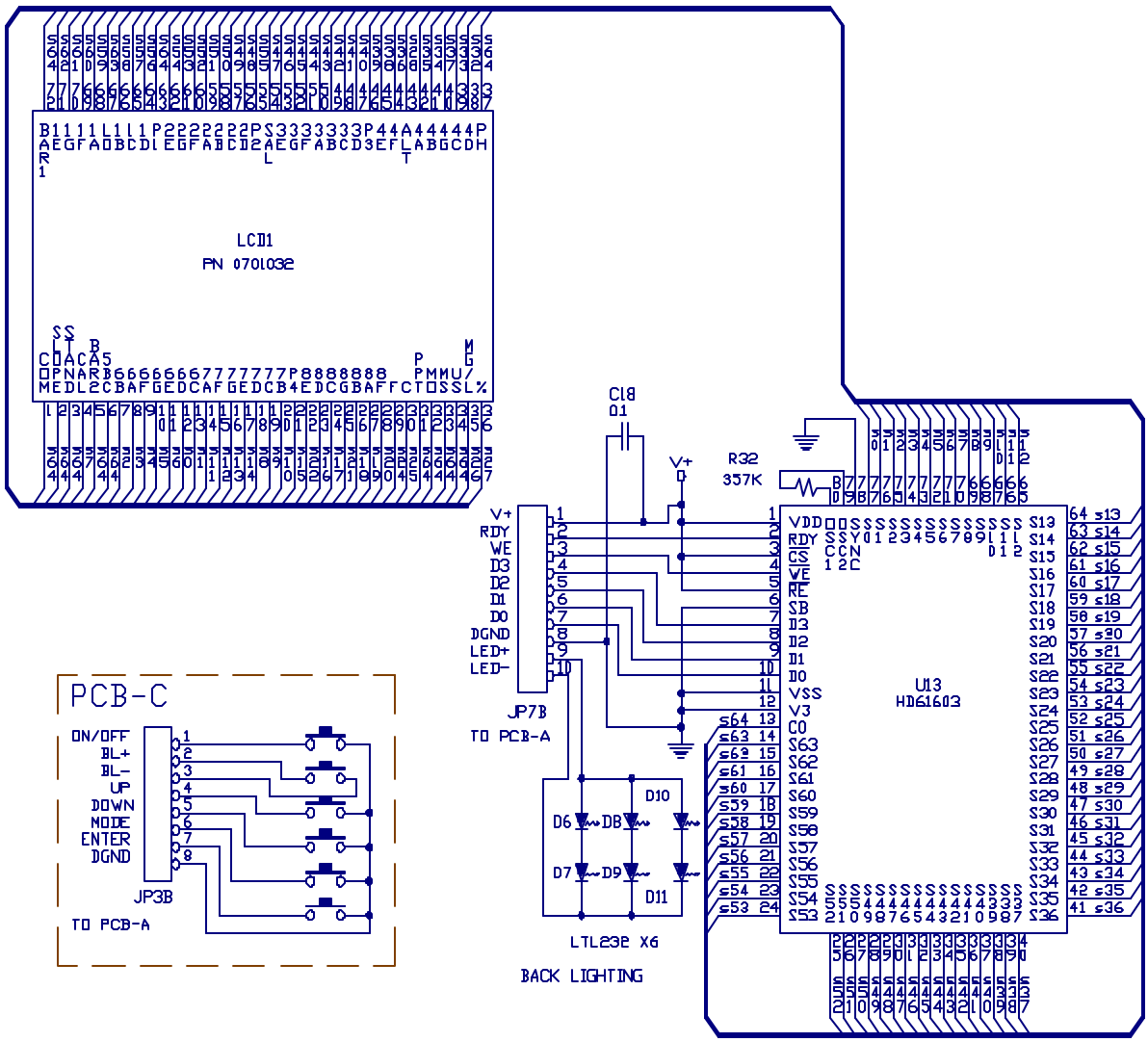
Ohm Meter Lead #1	**Ohm Meter Lead #2**	**Resistance Reading**
Green (silver anode)	White (gold cathode)	200 meg ohm or greater
Green (silver anode)	Red (thermistor)	200 meg ohm or greater
White (gold cathode)	Red (thermistor)	200 meg ohm or greater
Green, White, Red	Thermistor Tube	200 meg ohm or greater
Green, White, Red	Stainless steel probe body	200 meg ohm or greater

Circuit Diagram



Board-A

Circuit Diagram



Boards B & C

Parts List

Circuit Symbol	Description	YSI Order #
PCB-A & PCB-B	MAIN BOARD W/DISPLAY	055203
PCB-A	MAIN BOARD ASSEMBLY	055211
R1	RES,1M,5%,1/4W	
R2	RES,68K,5%,1/4W	
R3,R13,R15	RES,100K,5%,1/4W	
R4	RES,10M,5%,1/4W	
R5	RES,15K,5%,1/4W	
R6	RES,180K,1%,1/4W	
R7	RES,154K,1%,1/4W	
R8	RES,787K,1%,1/4W	
R9	RES,232K,1%,1/4W	
R10	RES,196K,1%,1/4W	
R11	RES,715K,1%,1/4W	
R12	RES,220K,5%,1/4W	
R14	RES,4.02K,1%,1/4W	
R16,R17	RES,120,5%,1/4W	
R18	RES,180,5%,1/4W	
R19	RES,17.2K,1%,1/4W	
R20	RES,750K,1%,1/4W	
R21	RES,261K,1%,1/4W	
R22	RES,127K,1%,1/4W	
R23,R25,R27	RES,1K,1%,1/4W	
R24	RES,18.7K,1%,1/4W	
R26	RES,78.7K,1%,1/4W	
R28,R30	RES,34.8K,1%,1/4W	
R29	RES,23.2K,1%,1/4W	
R31	RES,121K,1%,1/4W	
RN1	RES SIP,100K	
L1	COIL,220uH,10%,1/2W	
C1,C12,C13,C14,C15	CAPR,.1uF	
C2,C3	CAPR,CER,20pF	
C4	CAPR,ELE,22uF,16V	
C5,C10	CAPR,ELE,100uF,16V,105OC	
C7	CAPR,FILM,.47uF,5%,50V	
C8,C9,C19	CAPR,FILM,.1uF,100V	
C11	CAPR,ELE,10uF,25V	
C16	CAPR,FILM,.33uF,50V	
C17	CAPR,FILM,.47uF,100V	
D1,D2,D3,D4,D5	DIODE,1N4148A	

Circuit Symbol	Description	YSI Order #
X1	CRYSTAL,2.000MHz	
Q1	TRSTR,A733P118C	
Q2	TRSTR,M945	
U1	IC,EXCL,XLS93C46P	
U2	IC,MOTR,MC68HC705C8S	
U3,U11	IC,NATL,LM358N	
U4	IC,TOSH,TC4011B	
U5	IC,S81250HG9485	
U6	IC,HARR,DC8069J027	
U7	IC,HARR,7663SACPA	
U8	IC,TLDN,TSC7660CPA	
U9	IC,TLDN,TSC500CPE	
U10	IC,NATL,CD4053BCN	
U12	IC,PMI,OP177GP	
PCB-B	DISPLAY BOARD ASSEMBLY	055212
R32	RES,357K,1%,1/4W	
D6,D7,D8,D9,D10,D11	LED,GREEN	
U13	IC,HD61603	
LCD1	LCD DISPLAY (P/N 0701032)	055214
	LCD HOLDER (P/N 1701150)	
	ZEBRA CONNECTOR	055215
PCB-C	KEYPAD BOARD ASSEMBLY	055213
	KEYPAD (P/N 0801081)	055216
CASE COMPONENTS	SPRING TERMINAL,BATTERY	055217
	FRONT COVER ASSEMBLY	055201
	REAR COVER ASSEMBLY	055202
	** CASE HARDWARE KIT	055204
	## BATTERY HARDWARE KIT	055210
PROBE ASSEMBLIES	WITH 12 FOOT CABLE	055205
	WITH 25 FOOT CABLE	055206

NOTE:

** Case hardware kit includes:
- 1 Case gasket,custom
- 1 PCB screw,self-threaded,BT,#4
- 1 Case screw,metric,M3x1.5x42.5mm,custom
- 1 Case screw o-ring

Battery hardware kit includes:
- 1 Battery cover,molded
- 1 Battery screw,stainless,custom
- 1 Battery cover gasket,custom

Only parts with YSI order numbers are available from YSI.

Warranty And Repair

The YSI Model 55 Handheld Dissolved Oxygen Meter is warranted for two years from date of purchase, against defects in materials and workmanship, exclusive of batteries. YSI Model 55 dissolved oxygen probes and cables are warranted for one year from date of purchase, against defects in material and workmanship.

YSI products should be serviced by YSI Authorized Service Centers. Service by non-authorized technicians will void the manufacturer's warranty.

If you are experiencing difficulty with any YSI product, during or after the warranty period, contact the YSI dealer from whom you purchased the product, the YSI European Service Center or the YSI Technical Support Department. If a YSI product is returned for service during the warranty period, please supply proof of purchase.

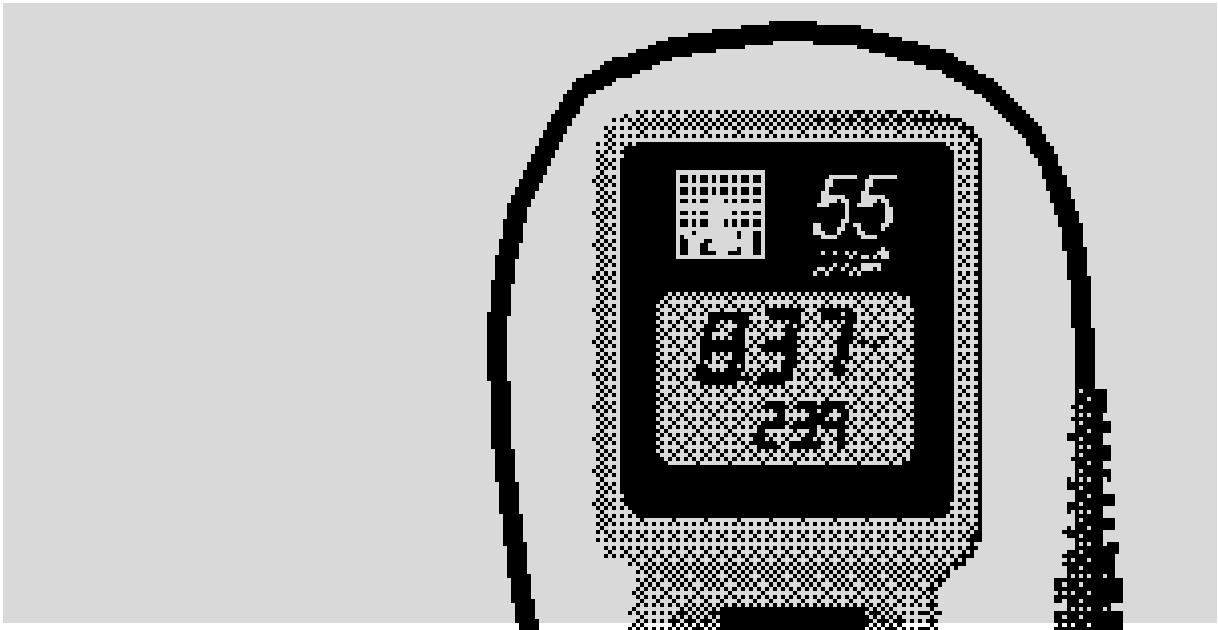
YSI Incorporated
Repair Center
1725 Brannum Lane
Yellow Springs, OH 45387

Phone 937 767-7241
800 765-4974
Fax 937 767-9353

YSI European Service Center
Lynchford House
Lynchford Lane
Farnborough, Hampshire
GU14 GLT, England

Phone 44 252 514711
Fax 44 252 511855

YSI incorporated



YSI Model 55

Handheld Dissolved Oxygen and Temperature System

Operations Manual

Table of Contents

1. General Description

The YSI Model 55 Handheld Dissolved Oxygen System is a rugged, micro-processor based, digital meter with an attached YSI dissolved oxygen probe.

The YSI Model 55 is designed for field use and is available with cable lengths of 12, 25 or 50 feet. The body of the probe has been manufactured with stainless steel to add rugged durability and sinking weight. The large Liquid Crystal Display (LCD) is easy to read and is equipped with a back-light for use in dark or poorly lighted areas.

The Model 55's micro-processor allows the system to be easily calibrated with the press of a few keys. Additionally, the micro-processor performs a self-diagnostic routine each time the instrument is turned on. The self-diagnostic routine provides you with useful information about the function of the instrument circuitry and the quality of the readings you obtain. For a list of these diagnostic features, see chapter *7 Troubleshooting*.

The system simultaneously displays temperature in ^{o}C and dissolved oxygen in either mg/L (milligrams per liter) or % air saturation. The system requires only a single calibration regardless of which dissolved oxygen display you use. You can switch back and forth from % air saturation to mg/L with a single push of the **MODE** key.

A calibration chamber is built into the instrument. A small sponge in the chamber can be moistened to provide a water saturated air environment which is ideal for air calibration. This chamber is also designed for transporting and storing the probe. When the probe is stored in the chamber, the moist environment will prolong effective membrane performance and probe life.

The instrument is powered by six AA-size alkaline batteries. A new set of alkaline batteries will provide approximately 100 hours of continuous operation. When batteries need to be replaced, the LCD will display a **"LO BAT"** message.

The YSI Model 55 instrument case is splash resistant. You can operate your Model 55 in a steady rain without damage to the instrument.

2. Specifications

Probe Operating Environment

Medium: fresh, sea, or polluted water
Temperature: -5 to +45°C
Depth: 0 to 12, 0 to 25 or 0 to 50 feet (depending on cable length)

Meter Ambient Operating/Storage Temperature: -10 to +50°C

Material: ABS, Stainless Steel, Acrylic, and other materials.

Dimensions:

Height: 9.5 inches		(24.13 cm)
Thickness:	2.2 inches	(5.6 cm)
Width:	3.5 inches max.	(8.89 cm)
Weight:	1.7 pounds	(0.77 kg)

Power: 9 VDC - 6 AA-size Alkaline Batteries (included)

Approximately 100 hours operation from each new set of batteries

Water Tightness: Meets or exceeds IP65 standards

Extensive testing of the YSI Model 55 suggests the following typical performance:

Temperature

Sensor Type ..... Thermistor
Range ..... -5 to +45°C
Accuracy ..... ± 0.2°C
Resolution ..... 0.1°C

Dissolved Oxygen % Saturation

Sensor Type ..... Membrane covered polarographic
Range ..... 0 to 200 % air saturation
Accuracy ..... ± 2 % air saturation
Resolution ..... 0.1 % air saturation

Dissolved Oxygen mg/L

Sensor Type ..... Calculated from % air saturation, temperature and salinity.
Range ..... 0 to 20 mg/L
Accuracy ..... ± 0.3 mg/L
Resolution ..... 0.01 mg/L

3. Preparing The Meter

3.1. Unpacking

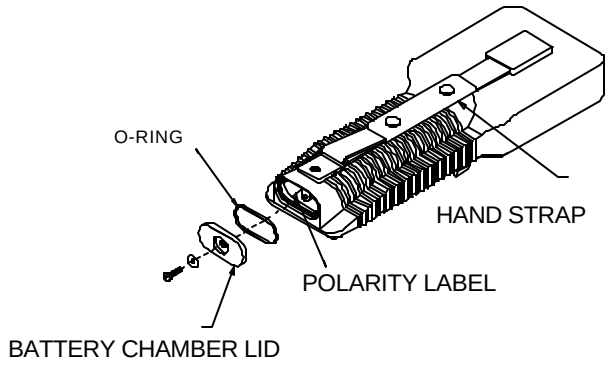
When you unpack your new YSI Model 55 Handheld Dissolved Oxygen System for the first time, check the packing list to make sure you have received everything you should have. If there is anything missing or damaged, call the dealer from whom you purchased the Model 55. If you do not know which of our authorized dealers sold the system to you, call YSI Customer Service at 800-765-4974 or 937-767-7241, and we'll be happy to help you.

3.2. Warranty Card

Before you do anything else, please complete the Warranty Card and return it to YSI. This will record your purchase of this quality instrument in our computer system. Once your purchase is recorded, you will receive prompt, efficient service in the event any part of your YSI Model 55 should ever need repair.

3.3. Batteries

There are a few things you must do to prepare your YSI Model 55 for use. First, locate the six AA-size alkaline batteries which were included. Use a screwdriver or a small coin to remove the thumbscrew on the bottom of the instrument. This thumbscrew holds the battery-chamber cover in place. The battery-chamber cover is marked with the words "OPEN" and "CLOSE."



NOTE: On some models, the battery cover thumbscrew may be unscrewed by hand (a screwdriver may not be required).

There is a small label inside each of the two battery-chamber sleeves. These labels illustrate the correct way to install the batteries into each sleeve of the battery-chamber.

NOTE: It is very important that the batteries be installed ONLY as illustrated. The instrument will not function if the batteries are installed incorrectly.

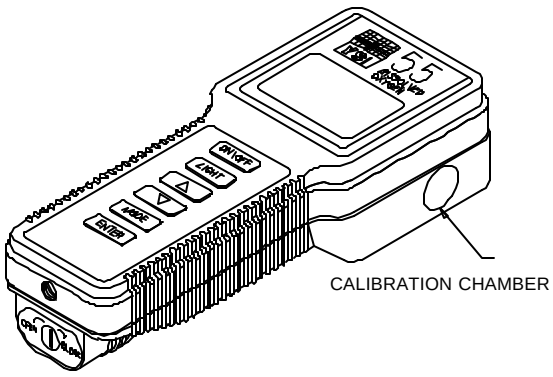
Turn the instrument on by pressing and releasing the **ON/OFF** button on the front of the instrument. The instrument will activate all segments of the display for a few seconds, which will be followed by a self test procedure which will last for several more seconds. During this power on self test sequence, the instrument's microprocessor is verifying that the instrument is working. If the instrument were to detect a problem, a **continuous** error message would be displayed. If the instrument does not operate, consult chapter *7 Troubleshooting*.

NOTE: The information on the display will be meaningless since the probe has not yet been prepared.

You may also want to take the instrument into a dark room and, with the instrument ON, hold down the **LIGHT** key. The instrument back-light should illuminate the LCD so that the display can be easily read.

3.4. Calibration/Storage Chamber

The Model 55 has a convenient calibration/storage chamber built into the instrument's side. This chamber provides an ideal storage area for the probe during transport and extended non-use. If you look into the chamber, you should notice a small round sponge in the bottom. Carefully put 3 to 6 drops of clean water into the sponge. Turn the instrument over and allow any excess water to drain out of the chamber. The wet sponge creates a 100% water saturated air environment for the probe which is ideal for dissolved oxygen calibration.



3.5. Hand Strap

The hand strap is designed to allow comfortable operation of the Model 55 with minimum effort. If the hand strap is adjusted correctly, it is unlikely that the instrument will be easily dropped or bumped from your hand.

To adjust the hand strap on the back of the meter, unsnap the leather cover and pull the two Velcro strips apart. Place your hand between the meter and the strap and adjust the strap length so that your hand is snugly held in place. Press the two Velcro strips back together and snap the leather cover back into place.

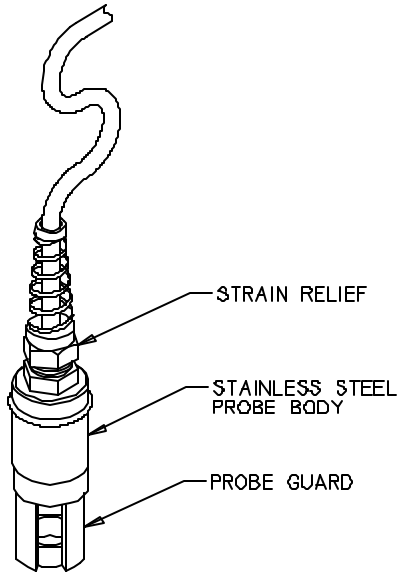
3.6. The Meter Case

The meter case is sealed at the factory and is not intended to be opened, except by authorized service technicians. **Do not attempt to separate the two halves of the meter case as this may damage the instrument, break the water-proof seal, and may void the manufacturer's warranty.**

4. Preparing The Probe

4.1. Description

The YSI Model 55 dissolved oxygen probe is a non-detachable, polarographic sensor designed specifically for the YSI Model 55 Handheld Dissolved Oxygen System. Probe cables are available in lengths of 12, 25 or 50 feet.



4.2. Choosing The Right Membrane

The YSI Model 5775 Standard Membrane Kit is supplied with the YSI Model 55. This kit contains thirty 1 mil (.001") membranes and a bottle of KCl solution. YSI recommends the 5775 membranes for most applications.

For special conditions, a 0.5 mil (.0005") membrane is available. Order YSI Model 5776 High Sensitivity Membrane Kit. This half-thickness membrane improves measurement time at low temperatures and helps suppress background current at very low dissolved oxygen levels. When data is routinely collected at sample temperatures below 15°C and at dissolved oxygen levels below 20% air saturation, the low signal current resulting from the use of the standard membranes tends to magnify the probe's inherent constant background signal. Using the high sensitivity membranes in this situation will decrease the percentage of error due to the probe's background current.

For long-term monitoring situations ONLY, a half-sensitivity, double-thickness, 2 mil (.002") membrane is available. For these applications, order the YSI Model 5685 Membrane Kit, which includes membranes and electrolyte.

4.3. Probe Preparation

The YSI Model 55 probe is shipped dry. **Before using the Model 55, the protective membrane on the probe tip must be removed, the probe must be filled with KCl solution and a new membrane must be installed.** Follow the instructions below to install the KCl solution and membrane.

To prepare for installation of a new membrane on your YSI Model 55 dissolved oxygen probe:

1. Unscrew the probe sensor guard.
2. Remove the old O-ring and membrane.
3. Thoroughly rinse the sensor tip and KCl reservoir with distilled water.
4. Prepare the electrolyte according to the directions on the KCl solution bottle.

4.4. Membrane Installation

A. Secure a membrane between your thumb and the probe body. Add electrolyte to the probe until a large meniscus completely covers the gold cathode.

   NOTE: Handle the membrane material with care, touching it at the ends only.

B. With the thumb and forefinger of your other hand, grasp the free end of the membrane.

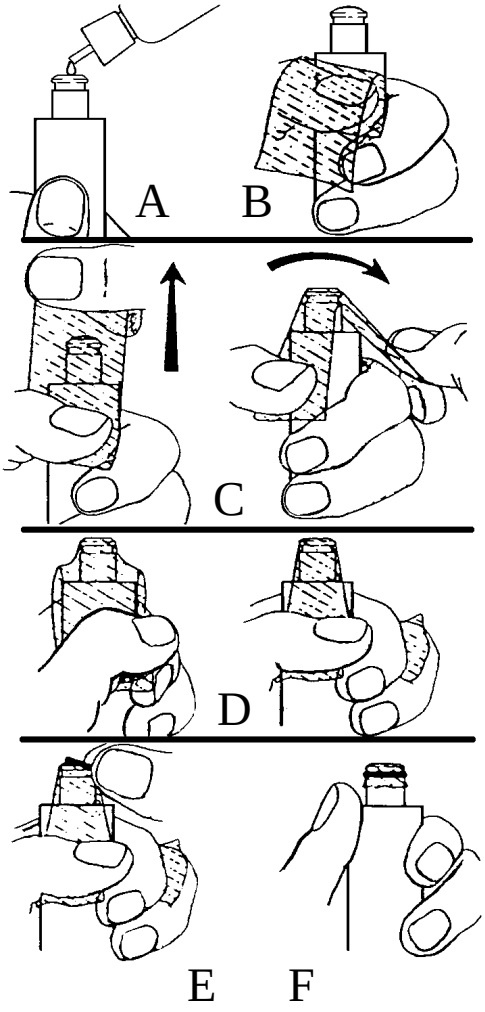
C. With a continuous motion, stretch the membrane up, over, and down the other side of the sensor. Stretching forms the membrane to the contour of the sensor tip.

D. Secure the end of the membrane under your forefinger while continuing to hold the probe.

E. Roll the O-ring over the end of the probe, being careful not to touch the membrane surface. There should be no wrinkles in the membrane or trapped air bubbles under the membrane. Some wrinkles may be removed by lightly tugging on the edges of the membrane beyond the O-ring.

F. Trim off excess membrane with scissors or a sharp knife. Check that the stainless steel temperature sensor is not covered by excess membrane.

G. Shake off excess KCl. Rinse the stainless steel thoroughly with distilled water to prevent corrosion. Reinstall the sensor guard. The sensor should be kept in a humid environment (such as the calibration chamber) between measurements and when not in use.



4.5. Probe Operation and Precautions

1. Membrane life depends on usage. Membranes will last a long time if installed properly and treated with care. Erratic readings are a result of loose, wrinkled, damaged, or fouled membranes, or from large (more than 1/8" diameter) bubbles in the electrolyte reservoir. If erratic readings or evidence of membrane damage occurs, you should replace the membrane and the KCl solution. The average replacement interval is two to four weeks.
2. If the membrane is coated with oxygen consuming (e.g. bacteria) or oxygen evolving organisms (e.g. algae), erroneous readings may occur.
3. Chlorine, sulfur dioxide, nitric oxide, and nitrous oxide can affect readings by behaving like oxygen at the probe. If you suspect erroneous readings, it may be necessary to determine if these gases are the cause.
4. Avoid any environment which contains substances that may attack the probe materials. Some of these substances are concentrated acids, caustics, and strong solvents. The probe materials that come in contact with the sample include FEP Teflon, acrylic plastic, EPR rubber, stainless steel, epoxy, polyetherimide and the polyurethane cable covering.
5. For correct probe operation, the gold cathode must always be bright. If it is tarnished (which can result from contact with certain gases), or plated with silver (which can result from extended use with a loose or wrinkled membrane), the gold surface must be restored. To restore the cathode, you may either return the instrument to the factory or clean it using the YSI Model 5680 Probe Reconditioning Kit. Never use chemicals or abrasives not supplied with this kit.
6. It is also possible for the silver anode to become contaminated, which will prevent successful calibration. To clean the anode, remove the O-ring and membrane and soak the probe overnight in 3% ammonium hydroxide. Next, rinse the sensor tip and KCl reservoir with deionized water, add new KCl solution, and install a new membrane and O-ring. Turn the instrument on and allow the system to stabilize for at least 30 minutes. If, after several hours, you are still unable to calibrate, return the YSI Model 55 system to an authorized service center for service.
7. If the sensor O-ring is worn or loose, replace it with the appropriate O-ring provided in the YSI Model 5945 O-ring Pack.
8. To keep the electrolyte from drying out, store the probe in the calibration/storage chamber with the wet sponge.

5. Calibration

Dissolved oxygen calibration must be done in an environment with a known oxygen content. Since the amount of oxygen in the atmosphere is known, it makes an excellent environment for calibration (at 100% relative humidity). The calibration/storage chamber contains a moist sponge to create a 100% water saturated air environment.

5.1. Before You Calibrate

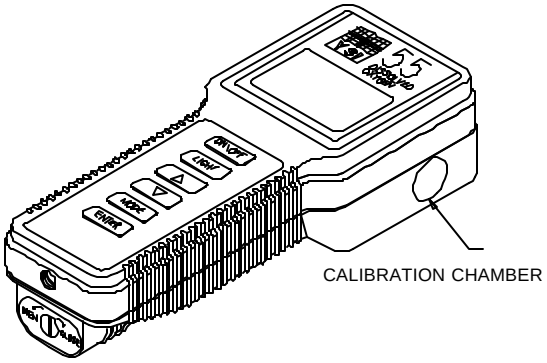
Before you calibrate the YSI Model 55, complete the procedures discussed in the *Preparing the Meter* and *Preparing the Probe* chapters of this manual.

To accurately calibrate the YSI Model 55, you will need to know the following information:

- The approximate altitude of the region in which you are located.
- The approximate salinity of the water you will be analyzing. Fresh water has a salinity of approximately zero. Sea water has a salinity of approximately 35 parts per thousand (ppt). If you are not certain what the salinity of the sample water is, use a YSI Model 30 Salinity-Conductivity-Temperature meter to determine it.

5.2. The Calibration Process

1. Ensure that the sponge inside the instrument's calibration chamber is wet. Insert the probe into the calibration chamber.
2. Turn the instrument on by pressing the **ON/OFF** button on the front of the instrument. Wait for the dissolved oxygen and temperature readings to stabilize (usually 15 minutes is required after turning the instrument on).



3. To enter the calibration menu, use two fingers to press and release both the **UP ARROW** and **DOWN ARROW** keys at the same time.
4. The LCD will prompt you to enter the local altitude in hundreds of feet. Use the arrow keys to increase or decrease the altitude.

   EXAMPLE: Entering the number 12 here indicates 1200 feet.

5. When the proper altitude appears on the LCD, press the **ENTER** key. The Model 55 should now display **CAL** in the lower left of the display, the calibration value should be displayed in the lower right of the display and the current DO reading (before calibration) should be on the main display.
6. Make sure that the DO reading (large display) is stable, then press the **ENTER** button. The LCD will prompt you to enter the approximate salinity of the water you are about to analyze. You can enter any number from 0 to 40 parts per thousand (PPT) of salinity. Use the arrow keys to increase or decrease the salinity setting. When the correct salinity appears on the LCD (zero for fresh water), press the **ENTER** key. The instrument will return to normal operation.

Once the calibration process is complete, the only keys which will remain operational are the **MODE** key, the **LIGHT** key and the **ON/OFF** key. You can move back and forth from reading dissolved oxygen in the mg/L mode or the % air saturation mode by pressing the **MODE** key. If you are working in a dark area and have difficulty reading the LCD, press and hold the **LIGHT** key to activate the back-light of the YSI Model 55. The **ON/OFF** key turns the instrument on or off.

For best results:

- Each time the Model 55 is turned off, re-calibrate before taking measurements.
- Calibrate at a temperature within ±10°C of the sample temperature.

6. Principles Of Operation

The sensor consists of an acrylic body with a circular gold cathode embedded in the end. Inside the gold ring there is a small chamber containing a porous silver anode. In operation, this chamber is filled with a solution of KCl electrolyte containing a small amount of surfactant to improve wetting action.

A thin permeable membrane, stretched over the sensor, isolates the electrodes from the environment, while allowing gases to enter. When a polarizing voltage is applied to the sensor electrodes, oxygen which has passed through the membrane reacts at the cathode causing a current to flow.

The membrane passes oxygen at a rate proportional to the pressure difference across it. Since oxygen is rapidly consumed at the cathode, it can be assumed that the oxygen pressure inside the membrane is zero. Hence, the force causing the oxygen to diffuse through the membrane is proportional to the partial pressure of oxygen outside the membrane. As the oxygen partial pressure varies, so does the oxygen diffusion through the membrane. This causes the probe current to change proportionally.

It is important to recognize that oxygen dissolved in the sample is consumed during the test. It is therefore essential that the sample be continuously stirred at the sensor tip. If stagnation occurs, your readings will be artificially low. Stirring may be accomplished by mechanically moving the sample around the probe tip, or by rapidly moving the probe through the sample. The rate of stirring should be at least 1 foot per second.

6.1. Discussion Of Measurement Errors

There are three basic types of dissolved oxygen errors. Type 1 errors are related to limitations of instrument design and tolerances of instrument components. These are primarily the meter linearity and the resistor tolerances. Type 2 errors are due to basic probe accuracy tolerances, mainly background signal, probe linearity, and variations in membrane temperature coefficient. Type 3 errors are related to the operator's ability to determine the conditions at the time of calibration. If calibration is performed against more accurately known conditions, type 3 errors are appropriately reduced.

Type 1 Errors

A. Meter linearity error: ±1% of full scale reading, or ±0.15 mg/L

B. Component and circuitry error: ±0.05 mg/L

Type 2 Errors

A. DO errors caused by temperature compensation for measurements at ±10°C from calibration temperature: ±1% (0.08 mg/L at 25°C)

DO errors caused by temperature measurement errors: A maximum ±0.2°C temperature error is equal to ±0.5% (0.04mg/L at 25°C).

Type 3 Errors

A. Altitude:

Operator Error: A 1000 foot error in altitude (when calibrating) is equal to an error of approximately 3.6% at the 10 mg/L level.

Instrument Error: The maximum DO error caused by calibrating to altitude in increments of 100 feet: ±0.18% (< 0.015 mg/L at 25°C)

B. Humidity:

Errors occur if calibration is performed at less than 100% humidity. The worst possible case would be calibration at 0% humidity. The error varies with the calibration temperature as follows:

Temperature	Calibration Error at 0% humidity
0°C	0.09 mg/L
10°C	0.14 mg/L
20°C	0.21 mg/L
30°C	0.33 mg/L
40°C	0.50 mg/L

Approximating The Error

It is unlikely that the actual error in any measurement will be the maximum possible error. A better error approximation is obtained using a root mean squared (r.m.s.) calculation:

$$\text{r.m.s. error} = \pm[1a^2 + 1b^2 + 2a^2 + 2b^2 + 3a^2 + 3b^2]^{½} \text{mg/L}$$

NOTE: This sample calculation is for a near extreme set of conditions.

7. Troubleshooting

NOTE: An error displayed briefly during the first few seconds after turning the instrument on does NOT indicate a problem.

SYMPTOM	POSSIBLE CAUSE	ACTION
1. Instrument will not turn on	A. Low battery voltage B. Batteries installed incorrectly C. Meter requires service	A. Replace batteries (Page 3) B. Check battery polarity. (Page 3) C. Return system for service (Page 15)
2. Instrument will not calibrate	A. Membrane is fouled or damaged B. Probe anode is fouled or dark C. Probe cathode is tarnished D. System requires service	A. Replace membrane and KCl (Page 6) B. Clean anode (Page 7) C. Clean cathode (Page 7) D. Return system for service (Page 15)
3. Instrument "locks up"	A. Instrument has received a shock B. Batteries are low or damaged C. System requires service	A. Remove battery lid, wait 15 seconds for reset, replace lid. (Page 3) B. Replace batteries (Page 3) C. Return system for service (Page 15)
4. Instrument readings are inaccurate	A. Cal altitude is incorrect B. Salinity setting is incorrect C. Probe not in 100% water saturated air during Cal procedure D. Membrane fouled or damaged E. Probe anode is fouled or dark F. Probe cathode is tarnished G. System requires service	A. Recalibrate w/correct value (Page 8) B. Recalibrate w/correct value (Page 8) C. Moisten sponge and place in Cal chamber w/ probe and Recal (Page 4, 8) D. Replace membrane (Page 6) E. Clean anode (Page 7) F. Clean cathode (Page 7) G. Return system for service (Page 15)
5. LCD displays "LO BAT" or Main display flashes “OFF”	A. Batteries are low or damaged	A. Replace batteries (Page 3)
6. Main display reads “undr”	A. Probe current too low to calibrate B. System requires service	A. Replace membrane and KCl (Page 6) B. Clean anode (Page 7) C. Clean cathode (Page 7) D. Return system for service (Page 15)
7. Main display reads “OVEr”	A. Sample O_2 concentration is more than 20 mg/L B. Probe current too high to calibrate C. System requires service	A. Recalibrate using correct altitude and salinity compensation (Page 8). B. Replace membrane and KCl (Page 6) C. Clean cathode (Page 7) D. Clean anode (Page 7) E. Return system for service (Page 15)

SYMPTOM	POSSIBLE CAUSE	ACTION
8. Main display reads "Er 0"	A. Calibration current out of range B. Instrument's self-test detects improper probe voltage during calibration	A. Replace membrane and KCl (Page 6) B. Clean anode (Page 7) C. Clean cathode (Page 7) D. Return system for service (Page 15)
9. Main display reads "Er 1" or Main display reads “Err” (Secondary display reads “ra”)	A. Instrument's self-test detects a variance in RAM B. System requires service	A. Remove battery lid, wait 15 seconds for reset, replace lid. (Page 3) B. Return system for service (Page 15)
10. Main display reads "Er 2" or Main display reads “Err” (Secondary display reads “ro”)	A. Instrument's self-test detects a variance in ROM checksum B. System requires service	A. Remove battery lid, wait 15 seconds for reset, replace lid. (Page 3) B. Return system for service (Page 15)
11. Main display reads "Er 3" or Main display reads "FAIL" (secondary display reads “eep”)	A. Instrument's self-test detects a system malfunction or component failure B. System requires service	A. Remove battery lid, wait 15 seconds for reset, replace lid. (Page 3) B. Return system for service (Page 15)
12. Main display reads "Er 4"	A. Sample O_2 concentration is more than 20 mg/L B. System requires service	A. Recalibrate using correct altitude and salinity compensation (Page 8). B. Replace membrane and KCl (Page 6) C. Clean anode (Page 7) D. Clean cathode (Page 7) E. Return system for service (Page 15)
13. Main display reads "Er 5"	A. Displayed O_2 concentration is below -0.5 mg/L. B. System requires service	A. Recalibrate using correct altitude and salinity compensation (Page 8). B. Return system for service (Page 15)
14. Main display reads "Er 6"	A. Sample O_2 concentration is over range (% mode) B. System requires service	A. Recalibrate using correct altitude and salinity compensation (Page 8). B. Replace membrane and KCl (Page 6) C. Clean anode (Page 7) D. Clean cathode (Page 7) E. Return system for service (Page 15)
15. Main display reads "Er 7"	A. Displayed O_2 concentration is below -3.0% B. System requires service	A. Recalibrate using correct altitude and salinity compensation (Page 8). B. Return system for service (Page 15)
16. Secondary display reads "Er 8" or Main Display reads “OVEr” (Secondary display reads “ovr”)	A. Sample temperature is more than +45.9°C B. System requires service	A. Reduce the sample temperature B. Return system for service (Page 15)

SYMPTOM	POSSIBLE CAUSE	ACTION
17. Secondary display reads "Er 9" or Main Display reads “OVEr” (Secondary display reads “udr”)	A. Sample temperature is less than -5°C B. System requires service	A. Increase sample temperature. B. Return system for service (Page 15)
18. Main display reads "Er A"	A. Short in probe/cable assembly B. System requires service	A. Replace probe/cable assembly B. Return system for service (Page 15)

8. Warranty And Repair

YSI Model 55 Dissolved Oxygen and Temperature Meters are warranted for two years from date of purchase by the end user against defects in materials and workmanship. YSI Model 55 probes and cables are warranted for one year from date of purchase by the end user against defects in material and workmanship. Within the warranty period, YSI will repair or replace, at its sole discretion, free of charge, any product that YSI determines to be covered by this warranty.

To exercise this warranty, write or call your local YSI representative, or contact YSI Customer Service in Yellow Springs, Ohio. Send the product and proof of purchase, transportation prepaid, to the Authorized Service Center selected by YSI. Repair or replacement will be made and the product returned, transportation prepaid. Repaired or replaced products are warranted for the balance of the original warranty period, or at least 90 days from date of repair or replacement.

Limitation of Warranty

This Warranty does not apply to any YSI product damage or failure caused by (i) failure to install, operate or use the product in accordance with YSI's written instructions, (ii) abuse or misuse of the product, (iii) failure to maintain the product in accordance with YSI's written instructions or standard industry procedure, (iv) any improper repairs to the product, (v) use by you of defective or improper components or parts in servicing or repairing the product, or (vi) modification of the product in any way not expressly authorized by YSI.

THIS WARRANTY IS IN LIEU OF ALL OTHER WARRANTIES, EXPRESSED OR IMPLIED, INCLUDING ANY WARRANTY OF MERCHANTABILITY OR FITNESS FOR A PARTICULAR PURPOSE. YSI's LIABILITY UNDER THIS WARRANTY IS LIMITED TO REPAIR OR REPLACEMENT OF THE PRODUCT, AND THIS SHALL BE YOUR SOLE AND EXCLUSIVE REMEDY FOR ANY DEFECTIVE PRODUCT COVERED BY THIS WARRANTY. IN NO EVENT SHALL YSI BE LIABLE FOR ANY SPECIAL, INDIRECT, INCIDENTAL OR CONSEQUENTIAL DAMAGES RESULTING FROM ANY DEFECTIVE PRODUCT COVERED BY THIS WARRANTY.

YSI Factory Service Centers

United States

YSI Incorporated • Repair Center • 1725 Brannum Lane • Yellow Springs, OH • 45387 • Phone: 937 767-7241 • Fax: 937 767-9353
Endeco/YSI Inc. • 13 Atlantis Drive • Marion, MA • 02738 • Phone: 508 748-0366 • Fax: 508 748-2543

Europe

YSI LTD • Lynchford House • Lynchford Lane • Farnborough, Hampshire • GU14 GLT • Phone: 441 252 514711 • Fax: 441 252 511855

YSI Authorized Service Centers

California

EviroServices & Repair • 1110 Burnett Avenue, Suite D • Concord, CA • 94520 • Phone: 510 609-1088 • Fax: 510 674-8655
Fisher Scientific ISD • 2822 Walnut Avenue, Suite E • Tustin, CA • 92681 • Phone: 800 395-5442

Florida

Aquatic Eco Systems, Inc. • 1767 Benbow Court • Apopka, FL • 32703 • Phone: 407 886-3939 • Fax: 407 886-6787

Georgia

Fisher Scientific ISD • 2775 Horizon Ridge Court • Suwanee, GA • 30174 • Phone: 800 395-5442

Illinois

Fisher • 1600 West Gleenlake Avenue • Itasca, Ill • 60143 • Phone: 800 395-5442

Maine

Q. C. Services • P.O. Box 68 • Harrison, ME • 04040 • Phone: 207 583-2980

Mississippi

Aquacenter • 166 Seven Oaks Road • Leland, MS • 38756 • Phone: 601 378-2861 • Fax: 601 378-2862

New Jersey

Fisher Scientific ISD • 52 Fadem Road • Springfield, NJ • 07081 • Phone: 800 395-5442

Oregon

Q. C. Services • P.O. Box 14831 • Portland, OR • 97293 • Phone: 503 236-2712

Pennsylvania

Fisher Scientific ISD • 585 Alpa Drive • Blawnox, PA • 15238 • Phone: 800 395-5442

8.1. Cleaning Instructions

NOTE: Before they can be serviced, equipment exposed to biological, radioactive, or toxic materials must be cleaned and disinfected. Biological contamination is presumed for any instrument, probe, or other device that has been used with body fluids or tissues, or with waste water. Radioactive contamination is presumed for any instrument, probe or other device that has been used near any radioactive source.

If an instrument, probe, or other part is returned or presented for service without a Cleaning Certificate, and if in our opinion it represents a potential biological or radioactive hazard, our service personnel reserve the right to withhold service until appropriate cleaning, decontamination, and certification has been completed. We will contact the sender for instructions as to the disposition of the equipment. Disposition costs will be the responsibility of the sender.

When service is required, either at the user's facility or at YSI, the following steps must be taken to insure the safety of our service personnel.

1. In a manner appropriate to each device, decontaminate all exposed surfaces, including any containers. 70% isopropyl alcohol or a solution of 1/4 cup bleach to 1 gallon tap water are suitable for most disinfecting. Instruments used with waste water may be disinfected with .5% Lysol if this is more convenient to the user.
2. The user shall take normal precautions to prevent radioactive contamination and must use appropriate decontamination procedures should exposure occur.
3. If exposure has occurred, the customer must certify that decontamination has been accomplished and that no radioactivity is detectable by survey equipment.
4. Any product being returned to the YSI Repair Center, should be packed securely to prevent damage.
5. Cleaning must be completed and certified on any product before returning it to YSI.

8.2. Packing Instructions

1. Clean and decontaminate items to insure the safety of the handler.
2. Complete and include the Cleaning Certificate.
3. Place the product in a plastic bag to keep out dirt and packing material.
4. Use a large carton, preferably the original, and surround the product completely with packing material.
5. Insure for the replacement value of the product.

Cleaning Certificate

Organization _____

Department _____

Address _____

City _____State _____ Zip _____

Country _____ Phone _____

Model No. of Device _____ Lot Number _____

Contaminant (if known) _____

Cleaning Agent(s) used _____

Radioactive Decontamination Certified?

(Answer only if there has been radioactive exposure)

_____Yes _____ No

Cleaning Certified By _____

Name Date

9. Required Notice

The Federal Communications Commission defines this product as a computing device and requires the following notice:

This equipment generates and uses radio frequency energy and if not installed and used properly, may cause interference to radio and television reception. There is no guarantee that interference will not occur in a particular installation. If this equipment does cause interference to radio or television reception, which can be determined by turning the equipment off and on, the user is encouraged to try to correct the interference by one or more of the following measures:

- re-orient the receiving antenna
- relocate the computer with respect to the receiver
- move the computer away from the receiver
- plug the computer into a different outlet so that the computer and receiver are on different branch circuits.

If necessary, the user should consult the dealer or an experienced radio/television technician for additional suggestions. The user may find the following booklet, prepared by the Federal Communications Commission, helpful: "How to Identify and Resolve Radio-TV Interference Problems." This booklet is available from the U.S. Government Printing Office, Washington, DC 20402, Stock No. 0004-000-00345-4.

10. Accessories And Replacement Parts

The following parts and accessories are available from YSI or any Franchise Dealer authorized by YSI.

YSI Order Number	Description
5775	Standard Membrane and KCl kit (1 mil)
5776	High Sensitivity Membrane and KCl kit (.5 mil)
5685	Half Sensitivity Membrane Kit (2 mil)
5680	Probe Reconditioning Kit (sanding tool and disks for cathode cleaning)
5945	O-ring Kit
5520	Carrying Case
055205	Replacement Probe and Cable Assembly (12 feet)
055206	Replacement Probe and Cable Assembly (25 feet)
055229	Replacement Probe and Cable Assembly (50 feet)
055201	Replacement Front Case Cover
055242	Replacement Rear Case Cover
055244	Replacement Battery Cover Kit
055204	Replacement Case Gasket and Screw
055219	Storage Chamber Sponge
115603	Main Board Assembly

11. Appendix A - Solubility Table

Solubility of Oxygen in mg/L in Water Exposed to Water-Saturated Air at 760 mm Hg Pressure.

Salinity = Measure of quantity of dissolved salts in water.

Chlorinity = Measure of chloride content, by mass, of water.

$S(^0/_{00}) = 1.80655 \times \text{Chlorinity } (^0/_{00})$

Temp °C	Chlorinity: 0 Salinity: 0	5.0 ppt 9.0 ppt	10.0 ppt 18.1 ppt	15.0 ppt 27.1 ppt	20.0 ppt 36.1 ppt	25.0 ppt 45.2 ppt
0.0	14.62	13.73	12.89	12.10	11.36	10.66
1.0	14.22	13.36	12.55	11.78	11.07	10.39
2.0	13.83	13.00	12.22	11.48	10.79	10.14
3.0	13.46	12.66	11.91	11.20	10.53	9.90
4.0	13.11	12.34	11.61	10.92	10.27	9.66
5.0	12.77	12.02	11.32	10.66	10.03	9.44
6.0	12.45	11.73	11.05	10.40	9.80	9.23
7.0	12.14	11.44	10.78	10.16	9.58	9.02
8.0	11.84	11.17	10.53	9.93	9.36	8.83
9.0	11.56	10.91	10.29	9.71	9.16	8.64
10.0	11.29	10.66	10.06	9.49	8.96	8.45
11.0	11.03	10.42	9.84	9.29	8.77	8.28
12.0	10.78	10.18	9.62	9.09	8.59	8.11
13.0	10.54	9.96	9.42	8.90	8.41	7.95
14.0	10.31	9.75	9.22	8.72	8.24	7.79
15.0	10.08	9.54	9.03	8.54	8.08	7.64
16.0	9.87	9.34	8.84	8.37	7.92	7.50
17.0	9.67	9.15	8.67	8.21	7.77	7.36
18.0	9.47	8.97	8.50	8.05	7.62	7.22
19.0	9.28	8.79	8.33	7.90	7.48	7.09

Temp °C	Chlorinity: 0 Salinity: 0	5.0 ppt 9.0 ppt	10.0 ppt 18.1 ppt	15.0 ppt 27.1 ppt	20.0 ppt 36.1 ppt	25.0 ppt 45.2 ppt
20.0	9.09	8.62	8.17	7.75	7.35	6.96
21.0	8.92	8.46	8.02	7.61	7.21	6.84
22.0	8.74	8.30	7.87	7.47	7.09	6.72
23.0	8.58	8.14	7.73	7.34	6.96	6.61
24.0	8.42	7.99	7.59	7.21	6.84	6.50
25.0	8.26	7.85	7.46	7.08	6.72	6.39
26.0	8.11	7.71	7.33	6.96	6.62	6.28
27.0	7.97	7.58	7.20	6.85	6.51	6.18
28.0	7.83	7.44	7.08	6.73	6.40	6.09
29.0	7.69	7.32	6.96	6.62	6.30	5.99
30.0	7.56	7.19	6.85	6.51	6.20	5.90
31.0	7.43	7.07	6.73	6.41	6.10	5.81
32.0	7.31	6.96	6.62	6.31	6.01	5.72
33.0	7.18	6.84	6.52	6.21	5.91	5.63
34.0	7.07	6.73	6.42	6.11	5.82	5.55
35.0	6.95	6.62	6.31	6.02	5.73	5.46
36.0	6.84	3.52	6.22	5.93	5.65	5.38
37.0	6.73	6.42	6.12	5.84	5.56	5.31
38.0	6.62	6.32	6.03	5.75	5.48	5.23
39.0	6.52	6.22	5.98	5.66	5.40	5.15
40.0	6.41	6.12	5.84	5.58	5.32	5.08
41.0	6.31	6.03	5.75	5.49	5.24	5.01
42.0	6.21	5.93	5.67	5.41	5.17	4.93
43.0	6.12	5.84	5.58	5.33	5.09	4.86
44.0	6.02	5.75	5.50	5.25	5.02	4.79
45.0	5.93	5.67	5.41	5.17	4.94	4.72

* This table is provided for your information only. It is **NOT** required when calibrating the Model 55 in accordance with the instructions outlined in the chapter entitled *Calibration*.

12. Appendix B - Conversion Chart

To Convert From	To	Equation
Feet	Meters	Multiply by 0.3048
Meters	Feet	Multiply by 3.2808399
Degrees Celsius	Degrees Fahrenheit	(°C × 9/5) + 32
Degrees Fahrenheit	Degrees Celsius	(°F - 32) × 5/9
Milligrams per liter (mg/L)	Parts per million (ppm)	Multiply by 1

YSI incorporated

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A55207D
January 02

Attachment 3

Calibration and Maintenance Logs

pH METER CALIBRATION AND MAINTENANCE LOG

Instrument Manufacturer ____________________

Instrument Model ____________________

Identification Number ____________________

Date/Time	Initials	Water Temperature	pH Standard Used/Expiration	Battery Check	Comments

DISSOLVED OXYGEN METER CALIBRATION AND MAINTENANCE LOG

Instrument Manufacturer ________________________________

Instrument Model ________________________________

Identification Number ________________________________

Date/Time	Initials	Water Temperature	Actual D.O.	Measured D.O.	Battery Check	Membrane Checked/ Replaced	Comments

APPENDIX 15
SOP FOR 24-HR. RUNTIME COMPOSITE SAMPLING (INCLUDES DISCHARGE COMPOSITE SAMPLING FROM PROCESSING FACILITY FOR TWICE WEEKLY POLYCHLORINATED BIPHENYL SAMPLES)

ARCADIS

Standard Operating Procedure: 24-Hour Runtime Composite Sampling

I. Scope and Application

This Standard Operating Procedure (SOP) applies to the collection of processing facility discharge composite samples, using an ISCO sampler, for polychlorinated biphenyl (PCB) analysis during Phase 1 of the Hudson River remedial action. A 24-hour runtime composite sample of the discharge from the dredged sediment dewatering facilities will be collected weekly to assess PCB concentrations.

II. Personnel Qualifications

Field personnel, trained in the use of an ISCO sampler, will collect the composite samples. All field personnel are required to take a 40-hour Occupational Safety and Health Administration (OSHA) Hazardous Waste Operations training course and annual refresher courses, and participate in a medical monitoring program prior to engaging in any field collection activities as required in 29 CFR 1910.120. Additionally, field personnel will be under the direct supervision of qualified professionals who are experienced in performing the tasks required for sample collection.

III. Equipment List

Equipment needed to collect processing facility discharge composite samples for PCB analysis includes:

- ISCO sampler (ISCO 3710VR Refrigerated Sampler or equivalent)
- At least four 2.5-gallon glass, pre-cleaned sample collection vessels (designed for specific ISCO sampler)
- AC power source for ISCO sampler
- Disposable gloves
- Sample containers (two 1-liter amber glass bottles with Teflon®-lined lids from laboratory)
- Plastic (polyethylene) resealable food storage bags

- Plastic (polyethylene) trash bags
- Dedicated Teflon® suction line
- Dedicated, clean cooler with ice
- Box or container for transport of used sample collection vessel
- Field notebook
- Chain of custody forms
- Labels for sample containers
- Permanent marker

IV. Cautions

Sample containers should be packed on ice and stored in a cool, shaded place to maintain a sample temperature of approximately 4ºC, if possible. Ice must be double-bagged to prevent leaks. Sample containers should be stored inside sealable plastic bags to prevent interference from external sources should a container break during transit.

V. Health and Safety Considerations

Health and safety issues are addressed in the site Health and Safety Plan (HASP; Parsons 2008).

VI. Procedures

The ISCO sampler will be operated according to the procedures contained in the operating manual (Attachment 1). The procedure for collecting the composite samples is summarized below:

1. Complete project and sample location information on the Processing Facility Discharge Reporting Form (Figure 2-19).

2. Put on a new pair of disposable gloves.

3. Plug the ISCO sampler in, connect the dedicated Teflon® suction line to the pump tubing and the sample tap, open the sample tap and turn the sampler on.

4. Verify that the refrigerator is set to 4°C.

5. Make sure the ISCO sampler is programmed to collect a 24-hour runtime composite sample with a sample collection frequency of one discrete volume of sample per hour.

6. Return to the sample station 24 hours later.

7. Put on a new pair of disposable gloves.

8. Turn off the sampler.

9. Remove the sample collection vessel from the ISCO sampler.

10. Transfer the composite sample to the appropriate sample containers (i.e., two 1-liter amber glass bottles with Teflon®-lined lids).

11. Affix a label to each sample container and record the following information (in accordance with Appendix 23) on the label: date and time of sample retrieval, sample identification, and analysis method. Note: the sample identification is "Processing Facility Discharge." The analysis method is "EPA Method 608."

12. Seal the sample containers in resealable plastic bags; label the bags with date, time, and sample identification; and place the bags in the cooler with ice.

13. Complete the chain of custody form in accordance with Section 10.1 of the main text.

14. Place the used sample collection vessel in a separate container for delivery to the laboratory for cleaning.

15. Put on a new pair of disposable gloves.

16. Place a clean sample collection vessel (pre-cleaned by the laboratory) in the ISCO sampler.

17. Unplug the ISCO sampler from the power source.

VII. Calibration and Maintenance

Calibration of the ISCO 3710VR Refrigerated Sampler is necessary to provide sample volume accuracy and should occur prior to each use. Calibration will be noted in the field notebook. The specific steps to calibrate the ISCO sampler are presented in the installation and operation guide (Attachment 1).

Maintenance of the ISCO sampler includes both routine and preventative maintenance. General maintenance procedures are provided herein and are detailed in the installation and operation guide (Attachment 1).

Routine maintenance procedures include:

- Clean the interior and exterior of the refrigerator, the controller, bottles, strainer, and tubing.
- Clean the condenser coil and surrounding areas annually.
- Follow the cleaning protocols for priority pollutants and critical sampling. This procedure is detailed below.
- Replace the pump tube when the display shows a warning at 500,000 pump counts or when inspection reveals any cracks or defects.
- Replace the dedicated Teflon® suction line on an annual basis.

Preventative maintenance includes:

- Replace the internal desiccant when the internal case humidity exceeds 30%. The internal case humidity is shown on the indicator visible through the front panel label (the indicator turns pink or white when the humidity level exceeds the printed value).

If experiencing problems with the sampler, contact Teledyne ISCO's Repair Service Department at (402) 464-0231.

VIII. Decontamination of Equipment

The equipment cleaning procedures described herein include pre-field, in-field, and post-field cleaning of sampling equipment, which will be conducted at an established equipment decontamination area (EDA) onsite (as appropriate). Cleaning procedures for sampling equipment will be monitored by collecting field blank samples as specified in the applicable work plan.

The following materials, as required, will be available during field cleaning procedures:

- Health and safety equipment, as required in the site Health and Safety Plan (HASP; Parsons 2008), including personal protective equipment (PPE)
- Distilled/deionized water
- Nonphosphate detergent
- Tap water
- Appropriate cleaning solvent (e.g., hydrochloric acid [HCl], nitric acid [HNO_3], hexane, acetone, isopropanol, methanol)
- Rinsate collection plastic containers
- Plastic overpack drum
- Brushes
- Plastic sheeting
- Aluminum foil
- Large heavy-duty garbage bags
- Spray bottles
- Resealable-type bags
- Handiwipes

- Field notebook

Ensure to rinse equipment thoroughly and allow the equipment to dry before reuse or storage to prevent introducing solvent into sample medium.

Review the material safety data sheets (MSDSs) for the solvents to be used in the decontamination. Avoid use of spray bottles to apply solvent on equipment to minimize potential for introducing vapors into breathing zone. Work in a well-ventilated area and stand upwind while applying solvent to equipment during the decontamination process. Application of solvent to the equipment will be completed in a manner that minimizes potential for exposure to workers. Follow health and safety procedures outlined in the HASP.

A designated area will be established to clean sampling equipment in the field prior to and between sample collection. Equipment cleaning areas will be set up within or adjacent to the specific work area.

The manufacturer suggests the use of decontamination protocols used in National Pollutant Discharge Elimination System (NPDES) compliance monitoring, as described in Attachment 1 and provided below:

- Glass Sample Bottles

    1. One spectro-grade acetone rinse.

    2. Dishwasher cycle (wash and tap water rinse, no detergent).

    3. Acid wash with at least 20% HCl.

    4. Dishwasher cycle (wash and tap water rinse, no detergent).

    5. Replace in covered Teledyne ISCO bases.

- Teflon® Suction Line

    1. Rinse twice with spectro-grade acetone.

    2. Rinse thoroughly with hot tap water using a brush, if possible, to remove particulate matter and surface film.

3. Rinse thoroughly three times with tap water.

4. Acid wash with at least 20% HCl.

5. Rinse thoroughly three times with tap water.

6. Rinse thoroughly three times with distilled water.

7. Rinse thoroughly with petroleum ether and dry by pulling air through the line.

8. Dry overnight in a warm oven (use an oven temperature of lower than 150ºF), if possible.

9. Cap ends with aluminum foil.

- Pump Tubes

1. Rinse by pumping hot tap water through the tube for at least 2 minutes.

2. Acid wash the tube by pumping at least a 20% solution of HCl through the tube for at least 2 minutes.

3. Rinse by pumping hot tap water through the tube for at least 2 minutes.

4. Rinse by pumping distilled water through the tube for at least 2 minutes.

IX. Waste Management

Waste generated during retrieval of the composite samples and during decontamination, such as disposable gloves and other expendables, will be placed in labeled 55-gallon drums onsite.

X. Data Recording and Management

The Processing Facility Discharge Monitoring Reporting Form (Figure 2-19) will be completed. Equipment cleaning and decontamination will be noted in the field notebook. An inventory of the solvents brought onsite and used and removed from the site will be maintained in the files. Containers with decontamination fluids will be labeled.

XI. Quality Assurance

Quality assurance/quality control (QA/QC) procedures are defined in Section 10.2 of this document, and include collecting field QA/QC samples. Field QA/QC samples to be collected are equipment rinse blank samples, field duplicates, and matrix spike samples. Matrix spike samples and field duplicates will be prepared by filling additional appropriately marked containers. Equipment blank samples will be prepared as follows:

1. Put on new disposable gloves.

2. Place a clean sample collection vessel in the ISCO sampler.

3. Slowly pour distilled water into the sampler intake and fill enough of the sample collection vessel to provide sufficient sample volume to fill the sample container.

4. When nearly full, remove the sample collection vessel and distribute to appropriately labeled sample container.

5. After collection, handle equipment blank sample in a manner that is consistent with all other environmental samples.

6. After preparing the equipment blank sample, the sample collection vessel may be reused to collect processing facility discharge samples without cleaning.

XII. References

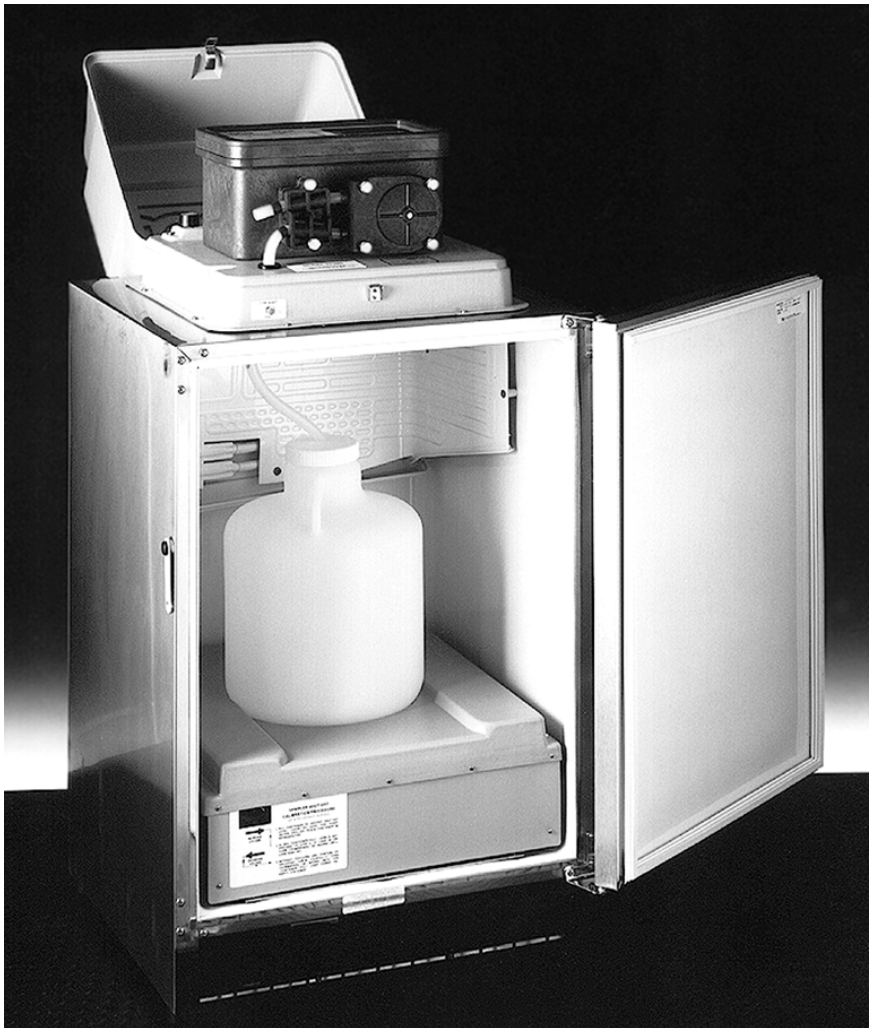
Parsons, 2008. Phase 1 Remedial Action Health and Safety Plan, Hudson River PCBs Superfund Site. Prepared for General Electric Company, Albany, NY. August 2008.

Attachment 1

Teledyne ISCO Installation and Operation Guide

3710R/3750 Refrigerated Sampler

Installation and Operation Guide



TELEDYNE ISCO
A Teledyne Technologies Company

Part #60-3713-046 of Assembly #60-3714-032

Revision FF January 20, 2006

Foreword

This instruction manual is designed to help you gain a thorough understanding of the operation of the equipment. Teledyne Isco recommends that you read this manual completely before placing the equipment in service.

Although Teledyne Isco designs reliability into all equipment, there is always the possibility of a malfunction. This manual may help in diagnosing and repairing the malfunction.

If the problem persists, call or e-mail the Teledyne Isco Technical Service Department for assistance. Simple difficulties can often be diagnosed over the phone.

If it is necessary to return the equipment to the factory for service, please follow the shipping instructions provided by the Customer Service Department, including the use of the **Return Authorization Number** specified. **Be sure to include a note describing the malfunction.** This will aid in the prompt repair and return of the equipment.

Teledyne Isco welcomes suggestions that would improve the information presented in this manual or enhance the operation of the equipment itself.

Teledyne Isco is continually improving its products and reserves the right to change product specifications, replacement parts, schematics, and instructions without notice.

Contact Information

Customer Service

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Fax:	(402) 465-3022	
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Technical Service

Phone:	(800) 775-2965	(Analytical)
	(800) 228-4373	(Samplers and Flow Meters)
Email:	IscoService@teledyne.com	
Return equipment to:	4700 Superior Street, Lincoln, NE 68504-1398	

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Web site:	www.isco.com

Revised September 15, 2005

General Warnings

Before installing, operating, or maintaining this equipment, it is imperative that all hazards and preventive measures are fully understood. While specific hazards may vary according to location and application, take heed in the following general warnings:

⚠ WARNING

This instrument has not been certified for use in "hazardous locations" as defined by the National Electrical Code.

⚠ WARNING

Avoid hazardous practices! If you use this instrument in any way not specified in this manual, the protection provided by the instrument may be impaired; this will increase your risk of injury.

⚠ WARNING

Éviter les usages périlleux! Si vous utilisez cet instrument d'une manière autre que celles qui sont specifiées dans ce manuel, la protection fournie de l'instrument peut être affaiblie; cela augmentera votre risque de blessure.

Hazard Severity Levels

This manual applies *Hazard Severity Levels* to the safety alerts, These three levels are described in the sample alerts below.

⚠ CAUTION

Cautions identify a potential hazard, which if not avoided, may result in minor or moderate injury. This category can also warn you of unsafe practices, or conditions that may cause property damage.

⚠ WARNING

Warnings identify a potentially hazardous condition, which if not avoided, could result in death or serious injury.

⚠ DANGER

DANGER – limited to the most extreme situations to identify an imminent hazard, which if not avoided, will result in death or serious injury.

Hazard Symbols

The equipment and this manual use symbols used to warn of hazards. The symbols are explained below.

Hazard Symbols	
Warnings and Cautions	
	The exclamation point within the triangle is a warning sign alerting you of important instructions in the instrument's technical reference manual.
	The lightning flash and arrowhead within the triangle is a warning sign alerting you of "dangerous voltage" inside the product.
	Pinch point. These symbols warn you that your fingers or hands will be seriously injured if you place them between the moving parts of the mechanism near these symbols.
Symboles de sécurité	
	Ce symbole signale l'existence d'instructions importantes relatives au produit dans ce manuel.
	Ce symbole signale la présence d'un danger d'électocution.
	Risque de pincement. Ces symboles vous avertit que les mains ou les doigts seront blessés sérieusement si vous les mettez entre les éléments en mouvement du mécanisme près de ces symboles
Warnungen und Vorsichtshinweise	
	Das Ausrufezeichen in Dreieck ist ein Warnzeichen, das Sie darauf aufmerksam macht, daß wichtige Anleitungen zu diesem Handbuch gehören.
	Der gepfeilte Blitz im Dreieck ist ein Warnzeichen, das Sei vor "gefährlichen Spannungen" im Inneren des Produkts warnt.
	Vorsicht Quetschgefahr! Dieses Symbol warnt vor einer unmittelbar drohenden Verletzungsgefahr für Finger und Hände, wenn diese zwischen die beweglichen Teile des gekennzeichneten Gerätes geraten.

3710R/3750 Refrigerated Sampler

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3710R/3750 Refrigerated Sampler

Section 1 Introduction

This section contains an overall description of the sampler and a list of technical specifications.

1.1 Description

The 3710R/3710VR/3750 Refrigerated Sampler is a programmable liquid sampler designed for composite sampling. It is one of Teledyne Isco's 3700 Series of portable and refrigerated samplers. The extensive sampling capabilities, flexible programming, and durable construction make the sampler ideally suited for general purpose or priority pollutant sampling.

The sampler, although easy to use, offers a number of very sophisticated features. The following sections introduce key features and provide an overview of the unit's sampling capabilities and a variety of interfacing equipment. Examples of interfacing equipment include Isco Flow meters for flow proportional sampling and sampler enable control, Teledyne Isco Field Printers that print the sampler's program settings and sampling results, and laptop computers which collect and store the same data. A brief discussion of this interfacing equipment is placed at the end of this section.

The 3710R Refrigerated Sampler consists of the 3750 Stainless Steel Refrigerator with the 3710 controller installed on the refrigerator at the factory. The 3710VR Refrigerated Sampler consists of the 3750 Vinyl Refrigerator with the 3710 controller installed at the factory. The controller is housed in the watertight control box mounted on the top of the refrigerator. However, the refrigerator's lower compartment is not watertight.

1.1.1 3710 Controller

The controller consists of a microprocessor with software embedded in a PROM (Programmable Read-Only Memory) and supporting electronics. The controller runs the pump, responds to the keypad, and presents information on the display. It governs all automatic sampling according to user-selectable program settings. The controller also provides for manual control of the sampler; for instance, you can run the pump forward with the PUMP FORWARD key or initiate a manual sample with the MANUAL SAMPLE key.

The control panel, containing the 40-character alphanumeric LCD (Liquid Crystal Display) and keypad, is located on the top of the control box. The 23-position keypad is used to enter program parameters and direct the following controls: on/off, pump reverse, pump forward, stop the pump, start sampling, resume sampling, and display the operating status. A desiccator is installed in the control box to prevent moisture damage to the electronics and pump.

1.1.2 3750 Refrigerator

If you want to convert a presently owned 3710 Portable Sampler into a refrigerated unit, or to have both portable and refrigerated options with the same controller, the 3750 Sampler Refrigerator is available. The 3750 includes all the parts necessary to attach the controller from a portable sampler to the refrigerator.

The exterior of the refrigerator is constructed of either stainless steel or vinyl-clad steel. Foamed-in-place insulation stiffens the sample compartment. The plastic interior will not support bacterial growth or retain odors. Both the controller cover and sample compartment may be individually padlocked. The door has a magnetic gasket which seals against a stainless steel bezel.

The refrigerator's thermostat is calibrated at the factory to be accurate at 39°F (4°C). A forced-air condensing coil and front ventilation allow the unit to be positioned close to a wall or in a corner with clearance required only for the controller cover to open. Wrap-around construction of the evaporator plate provides quick and efficient cooling of the sample compartment. Defrosting is automatic under normal operating conditions. The technical specifications of the 3710R/3710VR/3750 are found in Table 1-1.

1.2 Programmable Features

An intuitive user interface allows the sampler to be programmed for both simple and complex sampling schemes. The LCD prompts you through the programming process by presenting a choice or a question on the sampler's LCD. Programming the sampler is a matter of responding to displayed prompts with the keypad. Two programming modes, "basic" and "extended," are standard with the sampler. The basic programming mode allows you to set up typical sampling routines easily and efficiently.

The extended programming mode expands the versatility of the sampler by providing options which allow you to create complex sampling routines.

The LCD not only prompts you through the programming process, but also allows you to closely monitor a sampling routine as it is executed. The LCD displays pertinent information about the routine – for example, the time of the next sample – and notifies you of any problems encountered during the routine. As the routine progresses, the sampler logs (stores) key information about the results of the routine. The results include the start time, any halt and resume times, time of samples, and cause of any missed samples. This information is accessible during a routine or after a sampling routine is finished. You can view this information from the sampler's display or retrieve it with the Field Printer or a laptop computer running Teledyne Isco's Samplink® software.

1.2.1 Flexible Sampling Intervals

The 3710R/3710VR is designed for composite sampling. Samples may be collected at user-definable time intervals (time-pacing) or at equal flow volume intervals using flow pulse inputs from an external flow meter (flow-pacing). The flow interval may be set

from 1 to 9999 flow pulses. Sampling can be terminated by a weight table shut-off mechanism or by a user-defined number of samples.

The sampler offers two types of time-pacing: uniform and non-uniform. Uniform time-paced samples may be taken at regular time intervals, a sample every 15 minutes, for example. The interval between samples can be set from 1 minute to 99 hours, 59 minutes in 1 minute intervals. Using the extended programming mode, you can specify up to 999 (or bottle volume dependent) non-uniform time intervals in minutes. For example, you can program the sampler to take the first six samples at 10 minutes intervals, then four more samples at 15 minute intervals, and so on. Non-uniform time intervals can be from 1 to 999 minutes in 1 minute intervals. Nonuniform times can be specified in a clock-time format by entering a time and date for each sample. The sampler will accept up to 99 nonuniform clock times.

Additionally, the Sampling Stops and Resumes feature allows you to create an intermittent sampling schedule. With this extended programming feature, you can sample only during key periods of the day. For example, you may wish to sample only during the hours of 6:00 a.m. to 8:00 a.m., and 5:00 p.m. to 7:00 p.m.. You can enter up to 12 sampling stops and 12 resumes. Sampling stops and resumes can be used with both flow- and time-paced routines and with uniform and nonuniform time intervals.

1.2.2 Accurate Sample Volumes

The sampler can be programmed to take sample volumes of 10 to 9990 milliliters. Equipped with the patented LD90 liquid presence detector, the sampler delivers accurate, repeatable sample volumes in changing head conditions. The LD90 is a *non-wetted* liquid presence detector. It detects virtually any pumpable liquid and because it is non-wetted; sample conductivity, viscosity, temperature, and composition do not affect detection. Although it is not normally necessary, samples can be calibrated, if desired.

1.2.3 Flexible Start Times

A sampling routine can be programmed to use a specific start time and date or a start time delay. The sampler will accept a specific start time and date up to one month in advance of the current date. The start time delay is the period between the time you press the START SAMPLING key and the time the routine actually starts. It is adjustable from zero to 9999 minutes.

Other features are available. Program storage allows you to store up to three separate programs, eliminating the need to reprogram the sampler for recurrent sampling routines. A program lock is available for protection from unauthorized program alterations. When enabled, a password must be entered before any program settings can be changed, although program settings can be viewed at any time.

1.2.4 Foreign Languages and Metric Units of Measure

The sampler provides displays in French, German, and Spanish. Additionally, the software supports entries in metric units of measure. Samplers using French and German language displays support metric units for suction line and suction head measurements. Metric units include volumes in milliliters, suction head and suction line length in decimeters, and suction line inside diameter (ID) in millimeters. Samplers operating with English displays support either English or metric units for suction line and suction head measurements. (Sample volume units are always entered in milliliters, regardless of the selected language.)

1.3 Delivery System

The sampler uses a peristaltic pump for sample collection. The sample liquid is under pumped flow at all times; there are no metering chambers or gravity-fed internal tubing. Each sampling cycle includes an air pre-sample purge and a post-sample purge to clear the suction line both before and after sampling. These features make the sampler ideal for both "suspended solids" and "toxic materials" sampling. Cross contamination between samples is minimized and sites for sediment accumulation in the system are eliminated. Materials in contact with the sample fluid are limited to the strainer, suction line, pump tubing, and collection bottles. The system can be easily and safely cleaned by simply replacing relatively inexpensive lengths of tubing.

Pump speed is approximately 250 RPM which generates a velocity sufficient to obtain representative samples. The pumping rate of 3500 ml per minute is generated when using 3/8 inch ID suction line at 3 ft of head. The line transport velocity, using the same suction line and head, is 2.9 ft per second. Volumetric accuracy is not significantly affected by pump speed since the delivered volume is based on a patented electronic count of the number of pump revolutions.

1.3.1 Liquid Detector

The LD90 gives the sampler the ability to deliver accurate, repeatable sample volumes regardless of changing head conditions. Typical sample volumes are accurate to within 10% of the programmed volume and repeatable to within ± 10 ml. The detector and a programmable setting provide for automatic rinsing of the suction line when concerns of cross contamination arise. A programmable setting for sampling retries is available. If the suction line becomes clogged and no liquid is detected in the line, the sampler can be programmed to repeat a purge cycle – up to three times – to clear the clogged line.

1.3.2 Pump Tubing and Suction Lines

The pump tubing is Silastic™ medical grade silicon rubber. Liquid is transferred from the source to the pump through either 1/4- or 3/8 inch ID vinyl or 3/8 inch ID Teflon® suction tubing. The pump tubing and suction lines are easily replaced, minimizing the need for cleaning. The sampler automatically monitors pump tubing wear: a tubing warning indication is reported on the display when the pump revolution count exceeds a user-specified wear limit.

1.3.3 Weight Table Shut-Off

The weight table shut off provides a sampling fail-safe shut-off in case the container is accidentally overfilled. When the container is filled to a selectable, predetermined level, a weight activated control stops the sampling process and a red indicator light illuminates to alert you of the full container.

1.3.4 Strainers

The 3/8 inch ID vinyl suction lines are shipped from the factory with our standard weighted polypropylene strainer installed on one end of the suction line and a tubing coupling on the other end.

Additionally, Teledyne Isco offers two low flow stainless steel strainers for 1/4 inch ID and 3/8 inch ID suction lines.

For sampling from highly acidic flow streams, a weighted plastic CPVC strainer is available.

1.3.5 Bottle Configurations

Four sample containers are available:

- 9400 ml (2.5 gallon) glass container with Teflon lined cap.
- 9400 ml (2.5 gallon) polyethylene container with unlined cap.
- 15,000 ml (4 gallon) polyethylene container with unlined cap.
- 20,800 ml (5.5 gallon) polyethylene container with unlined cap.

1.4 Power Sources

The refrigerator operates from 120 VAC, 60 Hz power (optionally 240 VAC, 50 Hz). A 12 VDC power converter, built into the refrigerator, supplies power to the controller.

In the case of critical sampling, the sampler's controller may be powered by an external 12 VDC battery, as described in Section 2.4, on page 2-5. This allows sampling to continue even if a power failure causes the refrigerator's cooling system to stop functioning. Optionally available from Teledyne Isco is a Power Fail-Safe unit which, under normal conditions, trickle-charges an external battery, and, in the event of a line power failure, supplies 12 VDC power from the battery to the sampler's controller. Consult the factory for details. More information on Teledyne Isco power sources is available in Teledyne Isco's *Power Products Guide*.

1.5 Interfacing Equipment

A full line of accessories and interfacing equipment is available to help you adapt the sampler to your specific application; some of the more common items are briefly noted below. Other key accessories are noted throughout this manual, where appropriate. A full list of accessories is found in Appendix B.

1.5.1 Isco Flow Meters

The 4200 Series Flow Meters, 2100 Series Flow Modules, and 4100 Series Flow Loggers, and UniMag Closed-Pipe Flow Meters, are collectively called "flow meters" in this manual. The sampler will accept flow pulses from all Isco Flow Meters, Flow Modules, and Flow Loggers for flow proportional sampling. Isco Flow

Meters and Flow Loggers are equipped with a sampler enable feature. They can inhibit a sampler until the level of the flow stream reaches a predetermined height or "set point"; when that height is reached, the flow meter enables the sampler and starts the sampling routine. If the level of the stream falls below the set point, the flow meter can disable the sampler and halt the routine.

When equipped with a rain gauge, Isco Flow Meters and Flow Loggers can monitor rainfall. The flow meter can be programmed to enable the sampler when the measured amount of rainfall reaches a predetermined set point.

Set points or pairs of set points — pairs can be level and rainfall rates, level and elapsed time, rainfall and elapsed time, and so on — form the *sampler enable control condition*. A control condition is simply the set of parameters defining the conditions in which a flow meter will enable the sampler. For example, a flow meter can be programmed with a control condition which is satisfied when the flow meter detects ¼ inch of rainfall in 15 minutes. While level control conditions can be entered directly at the flow meter front panel, most control conditions must be downloaded to the flow meter from an IBM® compatible computer running Teledyne Isco's Flowlink® software.

In addition to enable control conditions, Teledyne Isco's Flow Meters and Flow Loggers provide an internal memory module. When programmed with the Flowlink software, the flow meters store level or flow rate readings, rainfall measurements, and sample event data from the samplers. The stored data, which expands the information available from the sampler's results displays, can be retrieved with a computer running the Flowlink software. For more detailed information on sampler enable control conditions and data retrieval, refer to the Flowlink Help files.

1.5.2 Samplink and Laptop Computers

Samplink is designed to run on a laptop computer which can be taken to the sampling installation to collect the data. Samplink collects the data and formats it into two files: a text file and a Flowlink compatible sample event file. The text file can be loaded into a word processor for editing. Samplink's text file contains the same two reports produced by the Field Printer. The first report contains sampler status information and program settings. The second report contains the sampling results. Because the text file is pre-formatted into report form, you can use DOS printing commands to print the file without editing with a word processor. The sample event files can be used with Flowlink to produce sampling reports and graphs.

☑ Note

The Teledyne Isco Field Printer has been discontinued and is no longer sold.

1.5.3 Non-Isco Flow Meters

You can connect certain non-Isco Flow meters directly to a 3700 for flow-paced sampling. The flow meter must have an isolated contact closure of at least 25 milliseconds to provide acceptable flow pulses to the sampler. The frequency of the contact closure must be directly proportional to total flow.

If the flow signal is not compatible with Teledyne Isco's standard, Teledyne Isco offers special interfacing devices. See Sections 4.1.2 and 4.1.3.

1.5.4 Liquid Level Actuator

Another item, the Liquid Level Actuator, is used to provide level sensitive control of the sampler. The actuator can be used as an alternative to a flow meter.

1.6 Technical Specifications, Controls, and Connectors

The technical specifications, controls, and connectors of the 3710R/3710VR/3750 are listed in the following tables. Refer to Figure 2-6, on page 2-6, for a pictorial view of the controls and connectors.

Table 1-1 3710R Technical Specifications, Controls, and Connectors

Physical Specifications	
Physical Size	Height: 45.75 inches (116 cm). Width: 24.25 inches (62cm). Depth: 25 inches (64cm).
Dry weight	145 lb (65.8 kg).
Operational Temperature Range	32°F to 120°F (0°C to 49°C).
Control Box only (does not include refrigerator)	Self Certified NEMA 4X and 6 ratings (Submersible, watertight, dust-tight, and corrosion resistant).
Temperature set point accuracy	± 1.8°F (1°C) at 39°F (4°C).
Pull-down time from 75°F (24°C) to 39°F (4°C)	30 minutes, typical.
Recovery time, door open 1 minute with unit operating at 39°F (4°C), 75°F (24°C) ambient	10 minutes, typical.
Power Specifications	
Sampler Controller Power Requirement	12 VDC AC power converter. Sampler standby current 10 mA, maximum.
Voltage	120 V, 60 Hz (240 Volt, 50/60 Hz available).
Current: Running Starting	2.5 amp, typical 120 volts. (1.25 amp, typical 240 volts 50/60 HZ). 12 amp, typical 120 volts. (6 amp, typical 240 volts).
Controller Internal 3V Lithium Battery Capacity	5 years, minimum (maintains internal logic and program settings).

Table 1-1 3710R Technical Specifications, Controls, and Connectors (Continued)

Pump and Tubing Specifications		
Suction Tubing (intake)	3 to 99 foot lengths of: 1/4-inch ID vinyl 3/8-inch ID vinyl 3/8-inch ID Teflon® lined	
Suction Lift	26 feet (7.9 m), maximum.	
Pumping Rate (at 3 feet of head)	1/4-inch ID suction tubing: 3000 ml/minute. 3/8-inch ID suction tubing: 3500 ml/minute.	
Line Transport Velocity (at 3 feet of head)	1/4-inch ID suction tubing: 5.1 ft/sec. 3/8-inch ID suction tubing: 2.9 ft/sec.	
Clock Specifications		
Real Time Clock Accuracy	1 minute/month, typical.	
Sample Specifications		
Sample Volume Accuracy	With the liquid detector enabled and automatic compensation for head: typically, the greater of ± 10% or ± 20 ml, over a head range of 1 to 12 feet and sampler supply voltage of 10 to 13 volts.	
Sample Volume Repeatability	± 10 ml, typical.	
Sample Frequency	Selectable from one minute to 99 hours, 59 minutes in 1 minute increments between consecutive samples, or from 1 to 9999 flow pulses in single pulse intervals. Up to 999 nonuniform times may be entered in minute intervals or up to 99 times as specific clock times.	
Flow Meter Signal Specifications		
Flow Meter Signal Requirements	5 to 15 volt DC pulse or isolated contact closure of at least 25 milliseconds in duration. (4-20 mA or pulse duration signal may be converted with optional interface unit).	
Controls		
CONTROL	SETTING	FUNCTION
Thermostat	OFF, WARMER, COOLER, 4°C (39°F).	Turns the refrigeration system on/off, selects the sample temperature.
Connectors		
CONNECTOR	TYPE	FUNCTION
12 VDC	2-pin female cable mounted.	12 VDC power supply for sampler.
Printer	6-pin female panel mounted.	Connects 3700R to Teledyne Isco Field Printer or laptop computer.
Flow Meter	6-pin male panel mounted.	Connects 3700R to external flow meter.
Sampler	6-pin female cable mounted.	Connects the flow meter to the sampler's controller.
120 or 240 VAC	3-pin grounded male line cord.	Supplies line voltage for the unit.

3710R/3750 Refrigerated Sampler

Section 2 Setup and Operating Procedures

This section provides the information necessary for everyday operation of the refrigerator. Included are sections covering setup, operation of the refrigerator, and automatic refrigerated sampling.

2.1 Summary of Setup Procedure

The following sections detail the preparations made before using the refrigerator. To place the sampler into operation:

1. Install the sampler.
   Although the suction line can extend to a liquid source up to 99 feet from the sampler, note that the maximum lift for the peristaltic pump with either the Teflon or vinyl line is 26 feet. When installing the sampler, be sure the head — the vertical distance between the level of the liquid source and the pump — is no greater than 26 feet. The pump will not be able to deliver samples for heads of 26 feet or greater.
2. Do not install the refrigerator in a location where the lower compartment could become submerged.
3. Be sure the sampler is connected to a 120 VAC power source. Turn the refrigerator on.
4. Attach the suction line.
5. Place the suction line inlet properly in the liquid source.
6. Connect the sampler to a flow meter, if required.
7. Program the sampler. See Section 3.
8. Calibrate the sample volume, if desired. Section 3.10.11, on page 3-31, contains calibration instructions.)
9. Calibrate the weight table. See Section 2.8.
10. Start the sampling routine.

2.2 Suction Line

The suction line is the piece of tubing that extends from the sampler's pump tubing intake, at the top of the liquid detector, to the liquid source. There are three standard suction lines available: plasticized vinyl tubing in 1/4 inch (0.64 cm) or 3/8 inch (0.94 cm) inside diameters, or FEP Teflon with a polyethylene cover in 3/8 inch inside diameter. The polyethylene cover over the 0.02 inch (0.051 cm) wall Teflon tubing prevents the Teflon liner from kinking or collapsing in service and protects it from abrasion and other damage.

The vinyl suction tubing contains a very low PPM (parts per million) level of phenols. If this affects your samples, use the Teflon suction line.

Both vinyl and Teflon lines can be cut to any length from 3 to 99 feet in 1 foot increments. Cut the suction line in whole foot increments: lengths of 4 feet, not 3.5 feet. The controller will accept only whole numbers as suction line lengths. To ensure the accuracy of the sampler, the suction line length entered must equal that of the actual line measurement. When programming the sampler, you must enter the inside diameter, type, and length of suction line used.

Cut the line to the shortest length feasible: this aids the downhill routing. Avoid loops of coiled suction line which may hold residual amounts of liquid which would cross contaminate sample volumes. A shorter suction line will also extend battery life and pump tube life because a shorter pumping cycle will be needed to deliver the sample volume.

2.2.1 Attaching the Vinyl Suction Line

Vinyl suction line is attached to the pump tubing with the tube coupling as illustrated in Figures 2-1 and 2-2. Two couplings are available, one for each size of vinyl line.

Each coupling has two color coded nylon clamps attached to the stainless steel ferrule. The black clamp secures the pump tube to the coupling. The white clamp secures the suction line. To attach the line or tubing to the coupling, push it onto the appropriate side of the ferrule and tighten the clamp by squeezing the finger pads together. To loosen a clamp, twist the two sides of the clamp until the teeth disengage.

2.2.2 Attaching the Teflon Suction Line

The Teflon line is attached to the pump tubing by inserting the line into the pump tubing and securing it with a suitable clamp.

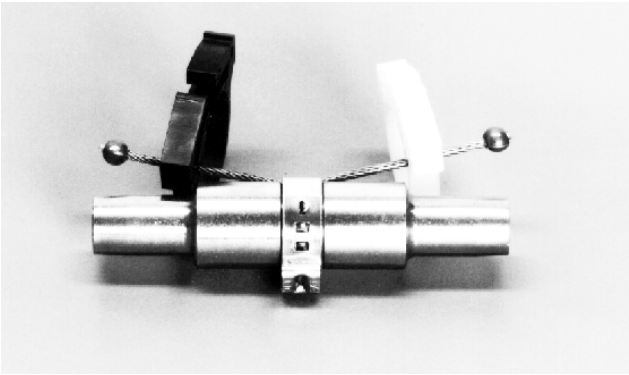


Figure 2-1 Tube Coupling

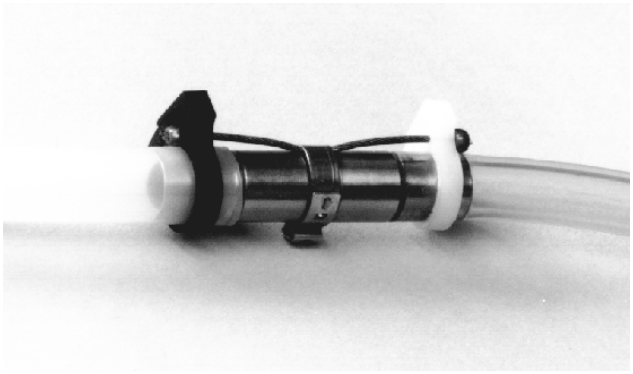


Figure 2-2 Tube Coupling with Suction Line and Pump Tubing

2.2.3 Routing of the Suction Line

Route the suction line from sampler to sampling point so that it slopes continuously downhill. This helps drain the suction line when the peristaltic pump purges the line and minimizes the possibility of cross contamination. When the sampler is used in near freezing temperatures, thoroughly draining the suction line minimizes the possibility of frozen liquid clogging the line.

2.3 Strainers

The 3/8 inch ID vinyl suction lines are shipped from the factory with our standard weighted polypropylene strainer (Figure 2-3) installed on one end of the suction line and a tubing coupling on the other end.

Additionally, Teledyne Isco offers two low flow stainless steel strainers (Figure 2-4) for 1/4 inch ID and 3/8 inch ID suction lines.

For sampling from highly acidic flow streams, a weighted, CPVC plastic-coated strainer is available (Figure 2-5).

The use of the strainer is optional. When heavy suspended solids are involved and flow stream velocities are significant, some field investigation results indicate that more representative samples are obtained without the strainer.

You can purchase bulk suction line without strainers. Refer to the *Accessories List* in the back of this manual. The strainer prevents solid particles larger than a specific diameter from entering and clogging the suction line. Teledyne Isco recommends its use for bottom sampling or sampling from streams containing large solids. The 1/4-inch strainers supplied for use with the 1/4-inch ID suction line have 15/64-inch (0.56 cm) diameter holes. The 3/8-inch strainers supplied for use with the vinyl or Teflon 3/8-inch ID suction line have 23/64-inch (0.9 cm) diameter holes.

2.3.1 Intake Placement

The proper placement of the sampler intake assures the collection of representative samples. Place the intake in the main flow, not in an eddy or at the edge of flow. The vertical position of the intake in the flow is important. An intake at the bottom may result in excess heavy solids and no floating materials, while placement at the top may result in the opposite.

The suction line tends to float in deep flow streams, dislodging the line and strainer. The following chart shows the maximum depths you can submerge the lines and strainers without risks of flotation. At depths exceeding the safe depths, anchor the line and strainer securely.

Table 2-1 Strainers

Strainer	Vinyl 1/4-inch (6 mm)	Vinyl 3/8-inch (9 mm)	Teflon 3/8-inch (9 mm)
Standard Weighted Polypropylene	—	22 feet (6.7 m)	15 feet (4.5 m)
Stainless Steel Low Flow	14 feet (4.3 m)	22 feet (6.7 m)	15 feet (4.5 m)
CPVC	—	4 feet (1.2 m)	4 feet (1.2 m)

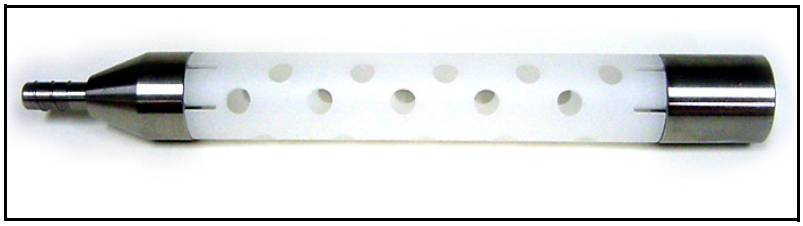


Figure 2-3 Standard Weighted Polypropylene Strainer

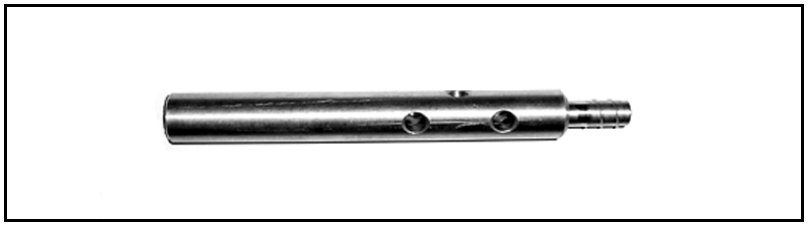


Figure 2-4 Stainless Steel Strainer

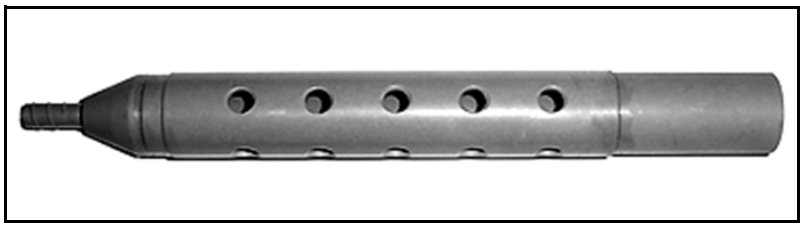


Figure 2-5 CPVC Weighted Strainer

If the strainer is not used, a short piece of thin walled aluminum tubing may be attached to the end of the suction line and the tubing anchored in the flow stream so that the inlet is oriented upstream. The thin wall will provide minimum disturbance of the flow stream and aluminum ions are usually not of concern in analysis. Whether the strainer is used or not, the pre-sample purge cycle should be sufficient to remove any debris which may collect over the strainer or tubing entrance between sampling events.

2.4 Connection to a Power Source

The 3750 operates from 120 VAC, 60 Hz power (optionally 240 VAC, 50 Hz). To provide power for the refrigerator and controller, plug the refrigerator's line cord into an appropriate source. A 12 VDC power converter, built into the refrigerator, supplies power to the controller. A 3V lithium battery, with a minimum service life of 5 years, maintains the controller's real time clock and program settings when power is disconnected.

The sampler's controller may be temporarily powered by an external 12 VDC battery when AC power is not available. Simply disconnect the power cable shown in Figure 2-6, and attach the battery connector to the sampler's power connector. A rechargeable nickel-cadmium battery is most commonly used; however, lead acid batteries are available.

Teledyne Isco's nickel-cadmium battery has an operating capacity of seven standard sampling programs after an 18-hour charge. (A standard sampling program is defined to be 24 samples at a rate of one 200 ml sample per hour, using 10 feet of $^{3}/_{8}$ vinyl suction line at a 5-foot head.)

The lead-acid battery has an operating capacity of 11 standard sampling programs. An Isco 120 VAC 50/60 Hz or 240 VAC 50/60 Hz Power Pack can also power the sampler. Both power packs may also be used to recharge the Teledyne Isco batteries.

2.5 Connection to a Flow Meter or Flow Logger

The sampler's controller must be connected to an external flow meter or flow logger to permit flow proportional sampling. This connection is made to the flow meter connector (shown inFigure 2-6) located on the rear of the control base. A small port is provided on the right side of the control base for routing the flow meter cable. Refer to Sections 4.1.2 and 4.1.3 for information on devices to interface the sampler with non-Isco Flow meters.

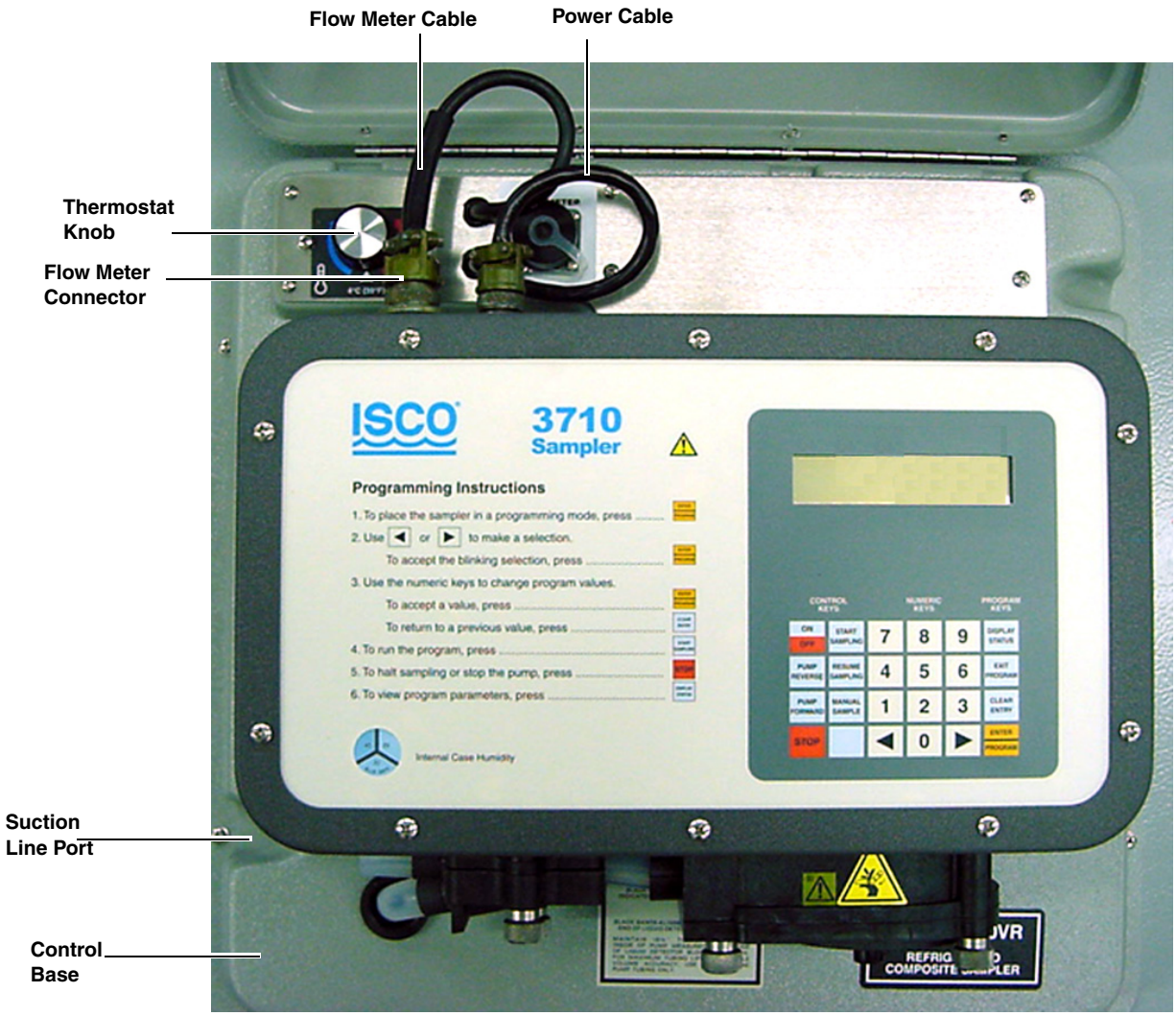


Figure 2-6 Flow Meter Cable Connection and Suction Line Port

2.6 Operation of the Refrigerator

To operate the refrigerator, turn the thermostat knob, shown in Figure 2-6, to the desired sample temperature. The interior air temperature should reach the set value within 20 to 30 minutes. The refrigerator's thermostat is calibrated in sample temperature. That is, if the temperature is set at 4°C (39°F), the temperature of the sample after being in the refrigerator will be 4°C ± 1°C, although the refrigerator air temperature may vary more than this due to the nature of the refrigeration cycle.

> ☑ ***Note***
>
> If the thermostat knob is turned to the lowest setting, the sample may freeze.

2.6.1 Automatic Defrosting

Under normal conditions, you should not need to defrost the refrigerator manually. The cooling coil temperature always cycles from below freezing (when the compressor is running) to above freezing (when the compressor is off) during the normal refrigeration cycle.

If the unit is used in hot, humid conditions, you may need to defrost the unit after several days of operation. Turn the thermostat off and allow the refrigerator to defrost. The refrigerator is equipped with a water diverting tray and a drain tube to route defrost water to an evaporating tray in the rear of the refrigerator. Water in the tray is evaporated by the warm air from the condensing system. The refrigerator compressor may not start immediately when the thermostat is turned on or turned to a lower setting due to the action of the compressor overload relay described in Section 5.10, on page 5-13. After a short time, the compressor will start and initiate the cooling cycle.

2.7 Set Up for Automatic Sampling

Before the unit is ready to be set up for automatic sampling, check that:

1. The control box has been attached to the refrigerator (when necessary).
2. The refrigerator has been connected to a power source.
3. The controller has been connected to an external flow meter (if used).
4. The suction line has been attached to the pump tubing.
5. The weight table shut-off point has been adjusted as described in Section 2.8. An empty sample container has been properly located on the weight table and the pump tube inserted approximately 2 inches into the hole in the container's lid.
6. The thermostat has been adjusted to the desired sample temperature.

2.7.1 Locking

After the sampler has been programmed as desired and the sampling program started, the cover should be closed and latched in place. Locking holes are provided in the controller cover latch and on the refrigerator door to accept padlocks to prevent unauthorized tampering.

2.8 Automatic Sampler Shut-Off

The refrigerator has an adjustable, weight activated sample container table to automatically shut-off the sampling process when the sample container is filled to a predetermined level. When the container is filled to the preset level, sampling stops and the LCD displays alternating messages; the message, "DONE," will alternate with the message, "FLOAT/WEIGHT TRIPPED." Calibrating the automatic shut-off mechanism requires three steps. Refer to Figure 2-7.

1. Fill the container with liquid to the desired shut-off level. Leave at least three inches unfilled. Place the container in its normal position in the bottom of the refrigerator.

2. If the red CONTAINER FULL lamp on the outer front of the refrigerator is off, proceed to step 3. If the lamp is on, turn the black thumbwheel on the front of the weight table to the right until the lamp goes out.
3. Without touching any portion of the weight table, carefully turn the black thumbwheel to the left until the CONTAINER FULL lamp goes on. The calibration procedure is now complete.

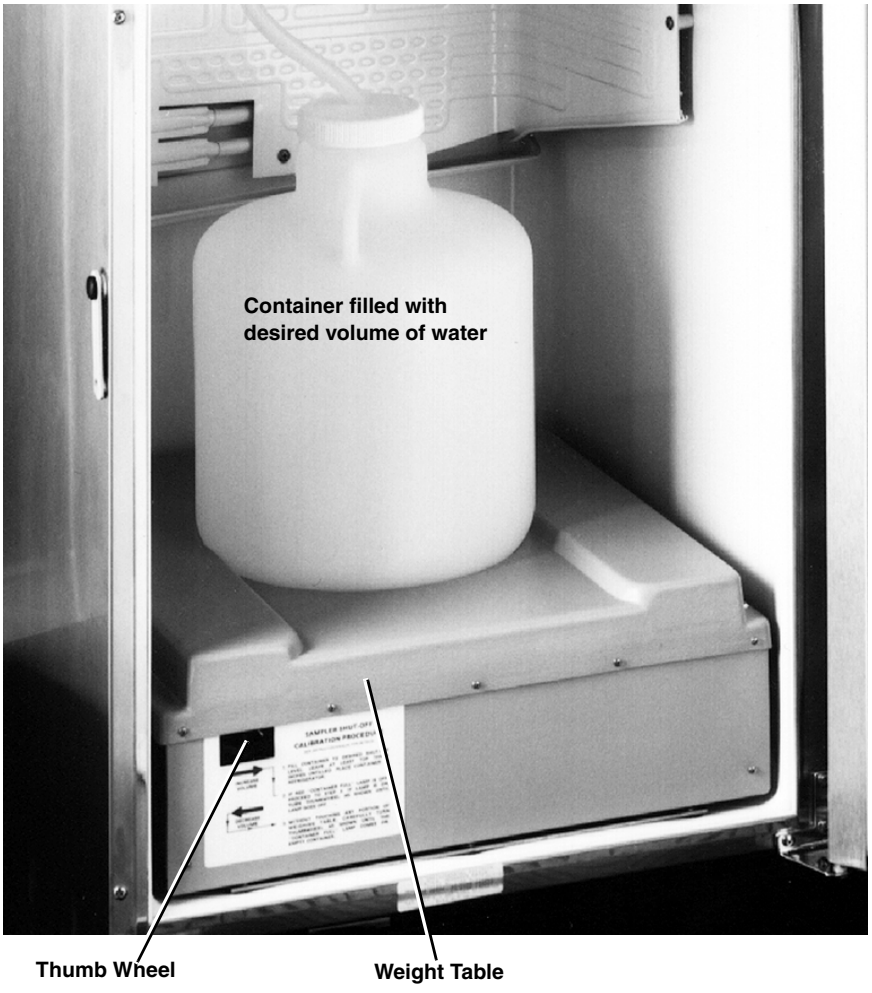


Figure 2-7 Sampler Shut-off Calibration

3710R/3750 Refrigerated Sampler

Section 3 Programming Guidelines

3.1 Introduction

This section discusses the sampling features of the 3710R in detail and covers the procedures used to program the sampler.

We recommend you have a sampler with you when you read this section. The most effective way to learn how to program the 3710 Sampler is to read this section, get a sampler, and experiment. A few minutes in the office or laboratory spent in actually programming the sampler and observing its operation usually proves to be a worthwhile investment of time.

If you are already familiar with the sampling capabilities of the 3710 Sampler, you may prefer to begin with Section 3.5. This section introduces the specifics of programming the sampler.

3.2 Description of Sampling Operations

This information serves to acquaint you with the 3710R Sampler's operation. It introduces you to the types of sampling performed by the sampler and the terminology used to describe those capabilities.

3.2.1 Sample Events and the Sampling Cycle

A sample event is the process of taking a sample. It includes the full sampling cycle. Although the cycle varies according to the program settings which define the sampling routine, the cycle described here follows the typical sequence. This information is presented here to provide you with a frame of reference for the remainder of this section.

1. A sample event is initiated when the interval since the previous sample has expired. For time based intervals, the samples are taken when the internal clock reaches the scheduled time of the sampling event. For flow-paced intervals, the interval is set to the programmed number of pulses received from a flow meter; the sample event begins when the pulses are counted down to zero.
2. The pump rotates in the reverse direction for the pre-sample purge. The pre-sample purge is an air purge of the suction line and inlet which clears the line of any accumulated debris. It also serves to purge residual liquid to avoid cross-contamination of samples.
3. The pump direction changes, pumping in the forward direction to fill the suction line up to the liquid detector.
4. After the suction line has been filled to the liquid detector and liquid has been detected, the sample volume measuring portion of the sampling cycle begins. The pump continues to rotate in the forward direction until the programmed volume of liquid has been delivered to the

sample bottle. (In this manual, the amount of liquid delivered to the bottle is referred to as the "sample volume.")

5. The pump direction again changes, pumping in the reverse direction for the post sample purge. Like the pre-sample purge, the post-sample purge is an air purge of the suction line. After the post-sample purge, the pump then shuts off.
6. The sample interval is reset and the cycle begins again at step 1.

3.3 Types of Samples

The 3710R Sampler is designed to collect composite samples. As noted in Section 1, the 3710R Sampler has two programming modes: basic and extended. The basic programming mode is used for conventional routines which include the types of sampling described in this section. A discussion of the types of sampling available through the extended programming mode is placed in Section 3.4. Composite sampling places individual sample volumes into a single container. Composite sample types can be characterized by sample pacing. Sample pacing refers to the interval between samples.

There are two types of sample pacing: time-pacing and flow-pacing. In time-paced sampling, the interval between samples is a time interval. In flow-paced sampling, the interval between samples is a certain volume of liquid which has passed a measuring point in a flow stream. Flow-paced sampling requires a flow meter. (The 3710 Sampler can be interfaced with Isco Flow meters and certain non-Isco Flow meters.) The flow meter measures the flow quantity and sends a pulse for every predetermined flow quantity to the sampler. The sampler totalizes the number of pulses received from the flow meter and collects a sample when the total reaches a programmed number.

3.4 Sampling Available Through Extended Programming Mode

The extended programming mode expands the variations of sample pacing. The extended features listed below are used in more complex sampling routines. Note, however, that the sampling capabilities described previously in Section 3.3 are available in both the basic and the extended programming modes.

3.4.1 Nonuniform Time Intervals

The 3710R Sampler, through the extended programming mode, can pace samples at nonuniform time intervals. With nonuniform time intervals, samples are taken at irregular intervals, rather than at equal intervals.

Nonuniform time intervals are typically used in runoff studies, often in conjunction with an Isco 1640 Liquid Level Actuator. Nonuniform time intervals permit a number of samples to be collected at short intervals after a rainfall or other event occurs and remaining samples to be collected at widening intervals. For example, when the sampler is used with the actuator in a runoff study, the actuator turns the sampler on when the liquid level of the flow stream rises to contact the actuator's probe. With non-

uniform time intervals, the sampler can collect samples frequently when the flow rate is highest and less frequently as the flow rate decreases.

Nonuniform times can also be used to simulate flow-paced sampling. When the flow rate varies predictably, using nonuniform time intervals allows you to take samples at equal flow volumes. As the flow rate increases, you can take samples at equal flow volumes by *decreas*ing the time interval. As the flow rate decreases, you can *increase* the time interval.

When you use nonuniform times, the time interval between each sample event is individually programmable. You can enter nonuniform times in two ways: in minutes or in clock times. The first method, minutes, allows you to enter the number of sample events spaced at intervals defined in minutes: 12 samples at 5 minute intervals, 6 samples at 10 minute intervals, 4 samples at 15 minute intervals, and so on. You can also enter a specific clock time and date for each sample event: sample event 1 at 6:00 on April 20, sample event 2 at 6:30 on April 20, sample event 3 at 7:15 on April 20. You can specify up to 999 sample events spaced in nonuniform minutes, or up to 99 events specified as clock times. (If a routine requires a large number of nonuniform times, you can save the routine with the program storage feature so that you do not have to re-enter the nonuniform times again.)

3.4.2 Stops and Resumes

The Sampling Stops and Resumes feature, available in the extended programming mode, allows you to create an intermittent sampling schedule. You can program the sampler to stop the routine at a specific time. The routine can then be resumed later. Up to 12 stop times and 12 resume times can be entered. Stops and resumes can be used with time-paced and flow-paced routines and with routines programmed for nonuniform time intervals.

3.5 Programming Introduction

The sampler's programming process is self-prompting. Prompts displayed on the LCD step you through the programming sequence in a logical order, indicating the needed value or option. For example, the sampler will prompt you to enter settings for the interval between samples (select either time-paced or flow-paced intervals); sample volume in ml; and other operating controls. These settings can be changed at any time.

The sampler will accept only appropriate values for the program settings and will reject any unacceptable values. If the unit is turned off or power is disconnected, the settings are retained in the sampler's memory by the lithium battery.

3.6 Operating States

There are three operating states: the standby state where the sampler is waiting for your instructions, the run state where the sampler is running a sampling routine, and the interactive state used to program the sampler. Each state serves a different purpose and is discussed separately.

3.6.1 Standby State

In the standby state, the sampler is waiting for your instructions. From standby, you can start a sampling routine, placing the sampler in the run state. You can also access the interactive state. The standby state is discussed in greater detail on page 63.

3.6.2 Run State

In the run state, the sampling routine is being executed and the sampler is operating under program control. While the sampling routine is executed, the LCD displays a number of messages to communicate the progress of the sampler through the routine. It reports the current time for time-paced routines and the remaining time or pulse count to the next sample. These messages vary according to the sampling routine; a representative set of messages is included with the programming examples placed in Sections 3.7 and 3.8. Table 3-7 also lists run state messages.

As the routine progresses, the sampler creates a log of sampling results that records pertinent information about each sample event. The results include the time and date of each sample, the number of pump counts occurring until liquid is detected for each sample event, and any problems encountered. Results can be retrieved with the Display Status procedure, as explained in Section 3.16. You can retrieve the results in the middle of a routine or when the routine is done. The results remain in the sampler's memory until you start the sampler again. Refer to Section 3.18 for more information on the run state.

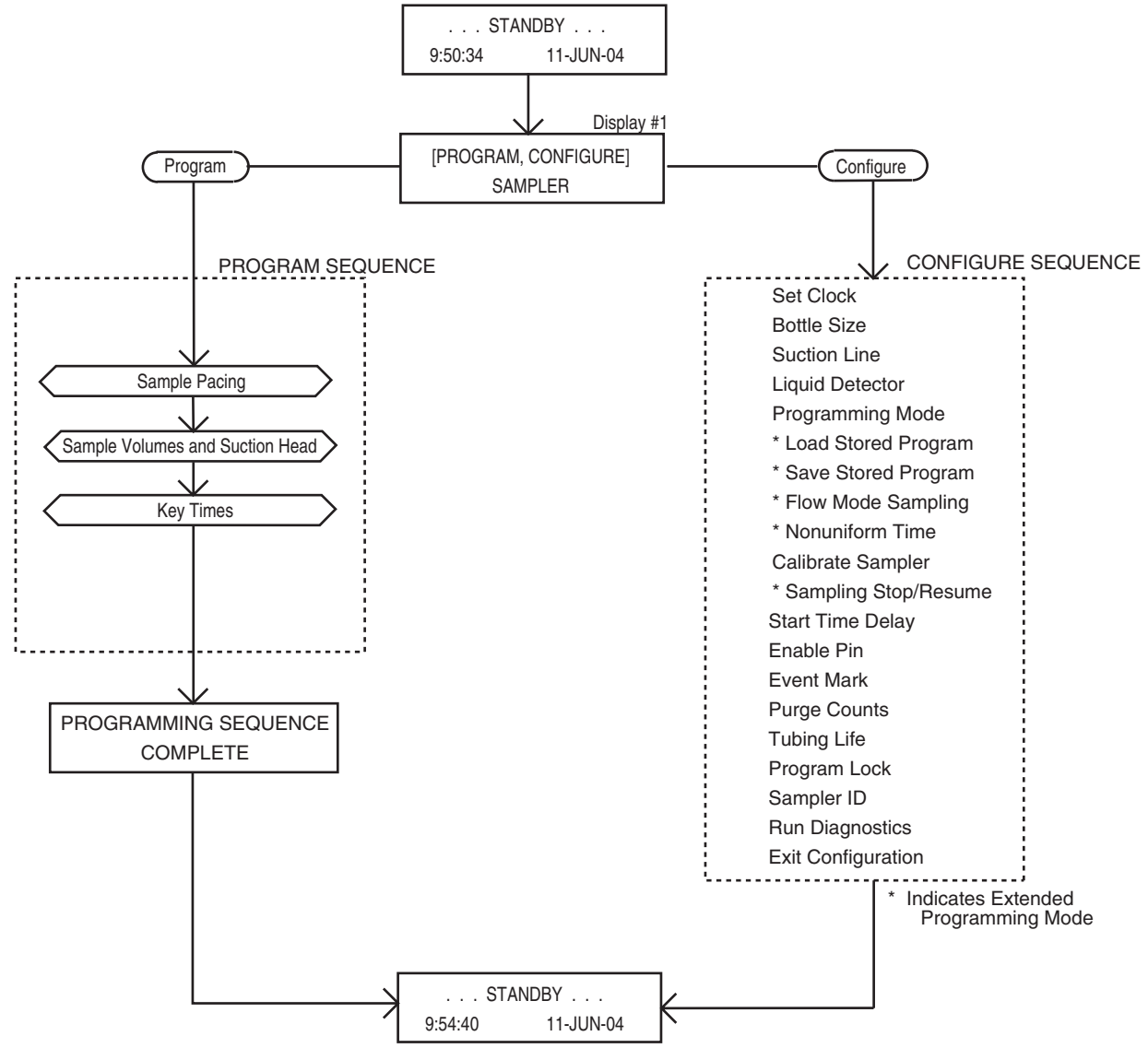


Figure 3-1 Interactive State Structure

3.6.3 Interactive State

The interactive state allows you to program the sampler. The interactive state contains two branches: the program sequence and the configure sequence. Figure 3-1 diagrams the structure of the interactive state. The program sequence is used to define the sampling routine; it allows you to enter the interval between samples, the number of samples, the sample size, and the start time. The configure sequence provides a number of setup options. Some configure options provide equipment specifications: bottle sizes, suction line diameters and lengths, and so on. For example, the 3710R Sampler can be used with different sized bottles: 2.5 gallon or 4 gallon. You must enter the correct bottle size so that the sampler can calculate the range of sample volumes for a given number of samples. This information is used to prevent

overfilling. Other options allow you to set the sampler's real time clock, calibrate the sampler, or enable the password program protection.

3.7 Programming Procedure

The procedure used to program the sampler follows the steps listed below. Note: Because the configuration settings determine portions of the program sequence and affect the accuracy of the sample, check the configuration settings before programming.

1. Determine the equipment you will be using with the sampler. You will need to know the capacity of the bottle and the inside diameter, type (vinyl or Teflon), and length of the suction line. You will need this information when you verify and revise the configuration settings in step 2.
2. Check the configuration settings. From standby, access the interactive state. Select the configure sequence. Check the configuration settings, revising any settings as needed; select basic or extended programming mode. Return to the standby state.
   Example *Checking the Configure Option Settings*, on page 3-17, shows you how to check and revise the configuration settings in the configure sequence. (We recommend you review *Keypad Description* and *Displays* before you work through the programming examples. These sections discuss the functions of the individual keys and how to use the keys when programming the sampler.)

Table 3-1 Configure Option Functions

Configure Option	Availability		Function
	Basic	Extended	
Set Clock	✔	✔	Sets the sampler's real time clock.
Bottle Size	✔	✔	Sets the sampler for portable or refrigerated configuration. Sets the size of the composite bottle.
Suction Line	✔	✔	Sets the type of line (vinyl or Teflon), line diameter (1/4- or 3/8-inch), and line length (3 to 99 ft).
Liquid Detector	✔	✔	Enables/disables liquid detector, sets the number of rinse cycles (0 to 3), enables/disables the suction head entry, and sets the number of sampling retries (0 to 3).
Programming Mode	✔	✔	Sets the programming mode: basic or extended.
Load Stored Program		✔	Loads one of up to three previously saved sampling programs.
Save Current Program		✔	Saves current sampling program.
Flow Mode Sampling		✔	Directs sampler to take a sample at the beginning of a flow-paced program.
Nonuniform Time		✔	Directs sampler to accept nonuniform intervals as specific clock times or in minutes.

Table 3-1 Configure Option Functions

Calibrate Sampler	✔	✔	Enables/disables the calibration sequence.
Sampling Stop/Resume		✔	Enables/disables Sampling Stops and Resumes feature.
Start Time Delay	✔	✔	Sets the start time delay (from 0 to 9999 minutes). If no specific start time is entered in the program sequence, the program will use the entered start time delay. The delay is the amount of time which will elapse after the START SAMPLING key is pressed or after the sampler is enabled.
Enable Pin	✔	✔	Enables/disables the master/slave sampling. Directs the sampler to take a sample when disabled and/or enabled by an Isco Flow Meter or Liquid Level Actuator. Allows you to restart the sampling interval when the sampler is enabled.
Event Mark	✔	✔	Allows you to select one of four types of event marks.
Purge Counts	✔	✔	Adjusts the number of pre-sample and post-sample purge counts.
Tubing Life	✔	✔	Displays the pump tubing life information. Resets the tubing life count.
Program Lock	✔	✔	Enables/disables the password protection for input displays.
Sampler ID	✔	✔	Allows you to enter a 10 character ID number for the sampler.
Run Diagnostics	✔	✔	Tests the RAM, ROM, and pump. Allows for re-initialization of certain program and configure settings.

3. Program the sampler. Again, from standby, access the interactive state. Select the program sequence. Enter the program settings for your routine. The sampler will prompt you through the programming process. When the process is completed, the sampler will automatically return to standby.
   A more detailed discussion of the programming procedure is placed in Section 3.8. Examples *Time-Paced Sampling*, on page 3-19 through *Calibration*, on page 3-23 demonstrate several types of sampling programs in the basic mode. Extended mode sampling programs can be found in Examples *Extended Time-Paced Sampling Using Stops and Resumes*, on page 3-52 through *Reviewing the Sampling Results*, on page 3-58.
4. Install the sampler, if you have not already done so. (The sampler can be programmed on site or in the office before installation.) If desired, connect the sampler to a flow meter or other interfacing equipment. Start the sampler.
5. As the routine is executed, the displays will report the sampler's progress. The programming examples in this manual conclude with the run state displays you should see for each sampling routine. When the routine is done, the sampler will return to standby.
6. Retrieve the filled sample bottle. If desired, use the *Display Status* procedure, discussed in Section 3.16, to examine the sampling results.
7. If you need to reprogram the sampler, follow this procedure from the beginning. If the sampler's current program is correct, start the sampling routine again.

3.7.1 Following Display Cues

Configuring and programming the sampler is as simple as responding to displays on the LCD with the keypad. The sampler will prompt you through many of the entries by presenting a question or a choice on the display. You must respond with the keypad. The LCD and the keypad are located on the 3710 Sampler control panel, shown in Figure 3-2.

A summary of each key's function is placed in Section 3.7.2. For a discussion of the displays presented on the LCD and the way you can use the keypad to interact with the sampler, refer to Section 3.7.6.

3.7.2 Keypad Description

Keys are grouped together on the control panel to assist you in identifying related functions. Control keys are used to manually control the sampler; numeric keys are used to enter program values; programming keys are used to monitor the sampler's status and direct programming activities. In this manual, individual keys are indicated in SMALL CAPITAL LETTERS.

The individual key switches that make up the keypad provide tactile and audible feedback to assure you that the key switch has been successfully actuated. When a key switch is pressed, you can feel the deflection of the spring member in the switch; an audio indicator inside the sampler will beep once. The sampler has a 10-keystroke buffer which, in some cases, allows you to "type ahead" of the display.

3.7.3 Control Keys

Control keys allow you to turn the sampler on or off, start or resume the currently entered program, and control the sampler manually. The functions of the control keys are listed below.

On/Off – Pressing the ON/OFF key when the sampler is off will turn the sampler on, reactivate the display, and place the sampler in the standby state. Pressing the ON/OFF key (when the sampler is on) will halt all sampling activity and clear the display.

Pump Forward – While in the standby state, pressing the PUMP FORWARD key will cause the pump to run continuously in the forward direction. The pump will run until the STOP key is pressed.

Pump Reverse – While in the standby state, pressing the PUMP REVERSE key will run the pump continuously in reverse. The pump will run until the STOP key is pressed.

Stop – The STOP key will stop the pump any time it is running. When the STOP key is pressed in the run state, the sampling routine will be halted, the sampler will be transferred to the standby state, and the "PROGRAM HALTED" message will be displayed. Pressing the STOP key while in the interactive state will access the display's reference number.

Start Sampling – When in the standby state, pressing the START SAMPLING key will begin the sampling program. When entering a sampler ID, the key will type a space.

Resume Sampling – When "PROGRAM HALTED" is displayed, pressing the RESUME SAMPLING key will cause the sampler to continue with the current sample program at the point at which it was halted. When entering a sampler ID, the key will type a period.

Manual Sample – Pressing the MANUAL SAMPLE key will allow you to take a manual sample. The MANUAL SAMPLE key is valid in the standby state, the run state, and when calibrating the sampler. When entering a sampler ID, the key will type a dash (-).

Figure 3-2 3710 Sampler Control Panel

3.7.4 Program Keys

The four program keys are used to enter program settings. Each key's function is listed below.

Display Status – While the sampler is in the standby or run state, pressing the DISPLAY STATUS key will allow you to view the program settings or the sampling results.

Exit Program – Pressing the EXIT PROGRAM key while in the program sequence will return the sampler to standby. Pressing the EXIT PROGRAM key while in the run state will halt the program; the message "PROGRAM HALTED" will be displayed.

Clear Entry – When entering a number, the CLEAR ENTRY key can be used to return to the original entry.

Enter/program – The ENTER/PROGRAM key, while in the standby state, will cause the sampler to enter the interactive state. While at an input display, the ENTER/PROGRAM key will accept an

entered value or a blinking option and direct the sampler to proceed to the next step. Input displays are discussed in *Displays*.

3.7.5 Numeric Keys

The numeric keys consist of 10 digit keys, a LEFT ARROW key, and a RIGHT ARROW key. The digit keys are used to enter quantities. The arrow keys are used to move through the configure option list or program options.

Left Arrow – The LEFT ARROW key is used to select one of two or more program options displayed when the sampler is in the interactive state. When more than one numeric entry is displayed – for example, the hours and minutes of a time setting – the LEFT ARROW can be used to step back to a previously entered value. When entering a number, the LEFT ARROW can be used to erase the most recently entered digit. It is also used to step through display status information and configure option list.

Right Arrow – The RIGHT ARROW key is used to select one of two or more program options displayed in an input display. It is also used to step through display status information and configure option list.

3.7.6 Displays

There are two types of displays: displays which communicate information about the sampler's status and displays which request input. In many cases, you must respond to a display with the keypad.

Informational Displays – Informational displays communicate information about the sampler's status. For example, when the sampler completes a sampling program, a display similar to the illustration below appears. It communicates the sampler's status ("DONE"), the number of samples taken (which will vary according to the program), and the current time and date.

```
DONE . . . 48 SAMPLES
 10:32:34   14-APR-04
```

Input Displays – Input displays can be identified easily because they contain a blinking word or number. The blinking word or number serves as a prompt for input and is said to be "selected." When the input displays shown below first appear, the word "PROGRAM" and the sample volume entry "250" will be blinking. Blinking words or numbers are represented in illustrations of displays with *italic* characters.

```
[PROGRAM, CONFIGURE]
       SAMPLER
```

```
   SAMPLES VOLUMES OF
250  ml EACH  (10 - 990)
```

Display Numbers – Nearly all input displays have a number assigned to them. The number is used to cross reference the input displays with an explanatory listing found in Appendix D,

or in the *3710 Sampler Pocket Guide*. If you have a question about a given input display, you can easily locate the description of the display.

The display number can be accessed by pressing the STOP key when viewing the input display. To see the display number, press the STOP key, read the number from the display, then look up the corresponding number in Appendix D for information on that display. The display number for the program/configure screen above is "1."

Displays With Choices – There are two types of input displays: displays which prompt you to make a choice (between time-paced and flow-paced sampling, for example) and displays which prompt for numeric input (sample volume, for example). In displays which prompt you to make a choice, you must select one of up to four alternatives placed in brackets. The display above prompts you to select the program or the configure sequence. The choices, "PROGRAM" and "CONFIGURE," are placed in brackets.

When an input display prompting for a choice first appears, the blinking word indicates the currently selected choice. If the blinking word is acceptable, press the ENTER/PROGRAM key. If the blinking word is not acceptable, select the preferred choice by pressing the LEFT ARROW or RIGHT ARROW key until the preferred choice is blinking; then press the ENTER/PROGRAM key. The sampler will store the selected choice and advance to the next step.

When the display illustrated above appears, the word "PROGRAM" will be blinking. If "PROGRAM" is acceptable, press the ENTER/PROGRAM key. If "PROGRAM" is not acceptable, press the LEFT ARROW or RIGHT ARROW key until "CONFIGURE" is blinking. Then, press the ENTER/PROGRAM key. The ENTER/PROGRAM key directs the sampler to advance to the next step.

Numeric Input Displays – A numeric input display will prompt for input by blinking the currently stored number. (In the display illustrated above, the number "250" will blink to prompt you to enter a value.) If the blinking number is acceptable, it is not necessary to type the number again: pressing the ENTER/PROGRAM key will store the number and advance the program to the next step. To enter a new number, press the appropriate numeric keys, then press the ENTER/PROGRAM key.

The sampler will not accept a number that exceeds the allowable range of values placed in parentheses on the display. In the next illustration, no less than 10 ml and no more than 990 ml can be entered as a sample volume. If an entered number exceeds the range, the sampler will emit a series of beeps and the original number will reappear. An acceptable value must be entered to advance to the next step.

3.7.7 Editing Numbers

The left arrow key and CLEAR ENTRY key can be used to edit numeric entries if they are used *after* you press a numeric key and *before* you press the ENTER/PROGRAM key. The CLEAR ENTRY

key will clear any typed number and the original number will re-appear. The left arrow will erase the most recently typed number.

Some numeric input displays prompt for more than one value. In the illustration below, the prompt asks for five number entries: hours, minutes, day, month, and year. The left arrow key and RIGHT ARROW key can be used to move back and forth between each of the five entries. Individual entries can be changed, as discussed above. Pressing the right arrow or ENTER/PROGRAM key on the *last* entry will store the values and advance to the next display.

```
 HH:MM      DD-MM-YY
12:33      21-MAR-04
```

3.7.8 Military Times

Times must be entered in military format: to set the sampler's clock to 3:30 p.m., enter a time of 15:30. When the display above first appears, the first two digits, "12," will blink. To enter a new time, type in the new hour: "15." Store the hour entry and advance to minutes by pressing the ENTER/PROGRAM key.

If the month or year entry does not need to be changed, accept the entry by pressing the RIGHT ARROW or ENTER/PROGRAM key. The left arrow key can be used to return to a previous position. Pressing the RIGHT ARROW or ENTER/PROGRAM key on the *last* entry, "04," will store the value and advance to the next display.

3.7.9 Exit Program Key

The user can exit an input display by pressing the EXIT PROGRAM key. If you use the EXIT PROGRAM key, the currently stored setting will not change.

3.8 Programming Examples

The following examples demonstrate the steps used to check the configure option settings and program the sampler for several different sampling routines. The programming examples in this manual present each display in the order in which they appear on the sampler. They are designed to provide you with step-by-step procedures and are provided as models for you to use later when programming the sampler for your "real" applications. Each programming example concludes with the run state displays that appear while that routine is being executed. The run state displays can be used to monitor the sampler's progress through a routine.

There are two sets of examples. Examples for the basic programming sequence are provided in Examples *Time-Paced Sampling*, on page 3-19, through *Calibration*, on page 3-23. Because many of the features of the extended programming mode are affected by selections made in the configure sequence, examples for the extended programming sequence follow the *Configure Sequence*. This section discusses each configure option separately. We recommend you become familiar with the basic programming mode procedure and examples before using the extended programming mode. Most of the procedures used in the

extended programming mode duplicate those of the basic programming mode and are not repeated in the section on extended programming procedures.

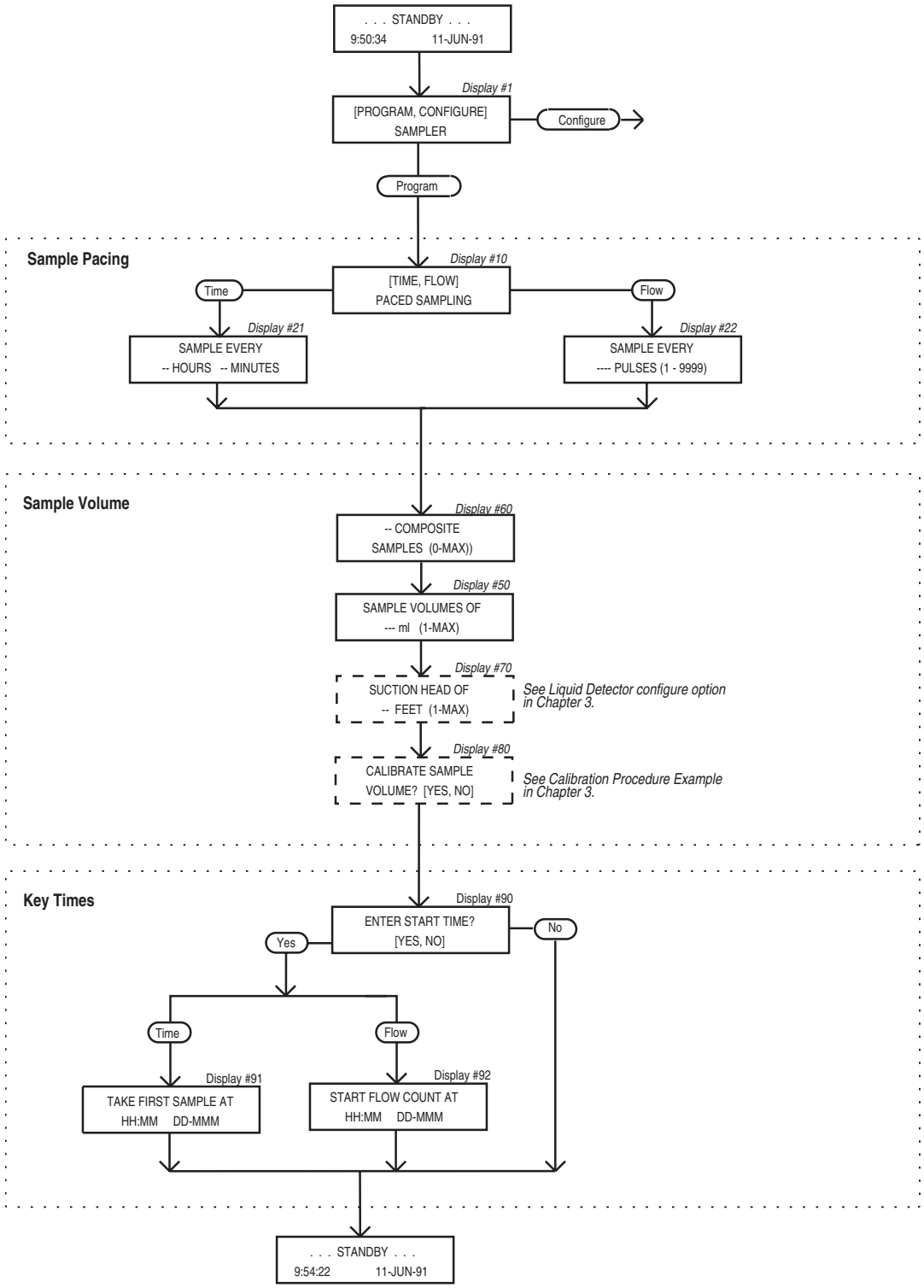


Figure 3-3 Basic Programming Mode: Program Sequence Structure

Examples for both programming modes are accompanied by flow charts. These charts diagram the program sequence structure for each mode. Figure 3-3 charts the Basic Programming Mode structure. Figure 3-5 charts the structure of the Extended Programming Mode. The charts are provided to act as a "map" to the programming process. Both charts are divided into sections – Sample Pacing, Sample Volume, and Key Times –which correspond to the steps listed in the procedure discussed below. Each chart contains the input displays used in the sequence. The input displays on each chart are labeled with their display number so they can be cross-referenced with the listing found in Appendix C.

As noted earlier, the sampler is shipped with a test program and factory configuration settings. The examples in this manual assume that all factory settings are being used, that the sampler will use a 2.5 gallon (9400 ml) container and a 10 foot length of 3/8-inch vinyl suction line. The settings with which your sampler is shipped include settings for the size of bottle ordered and for the size, type, and length of suction line. When you check the configuration settings, make sure the settings match your equipment, not the example.

Most program and configure settings can be re-initialized to factory settings, if desired. Tables 3-5 and 3-4 list the factory settings. A discussion of the re-initialize option, located in the Run Diagnostics configure option, is found in Section 3.10.20. Instructions for re-initializing the sampler are also included as part of Example *Checking the Configure Option Settings*, on page 3-17.

3.9 Basic Programming Procedure

The steps needed to program the sampler in the basic mode follow the procedure outlined below.

1. Turn the sampler on with the ON/OFF key. The sampler always "wakes up" in the standby state. The "STANDBY" message will appear. If the sampler were turned off while running a routine, the "PROGRAM HALTED" message will be displayed. Both messages indicate the sampler is in standby.
2. Press the ENTER/PROGRAM key to access the interactive state. Select "PROGRAM." Refer to Figure 3-3 for displays noted in steps 3 - 6.
   To return to a previous display when programming the sampler, press the EXIT PROGRAM key. The sampler will return to standby. Press the ENTER/PROGRAM key again to re-enter the interactive state. Continue to press the ENTER/PROGRAM key to scroll through the displays until you locate the display in question.
3. Enter the Sample Pacing settings. The sampler will prompt you to select either time- or flow-pacing. Depending on your selection, you will then be prompted to enter the time or flow pulse interval between samples.
   NOTE: If you will be using very short sample intervals, be sure the interval is longer than the duration of the sampling cycle. For truly representative sampling, the interval

in either time- or flow-paced sampling should be longer than the duration of the sampling cycle.
If the intervals are too short, no sample events will be missed, although some events will occur at improper times. The duration of the cycle can be determined by programming the sampler with the desired settings, pressing the MANUAL SAMPLE key, and simply timing the cycle.
When programming the sampler for flow pacing, you must enter the number of pulses that make up the flow interval. If the flow meter has been set to send a pulse once every 1000 gallons, you can program the sampler to collect a sample once every 1000 gallons by entering a flow pulse interval of "1." To collect a sample once every 50,000 gallons, you would enter a sample interval of 50 pulses. Appendix D provides a discussion of some of the calculations needed when determining flow pulse intervals.

4. Enter the Sample Volume settings. The Sample Volume program section will always contain prompts for the number of samples and sample volume. Depending on the selections made in the configure sequence, it may also contain prompts for the suction head and for calibrating the sampler.
   The first display of the Sample Volume section, display #60, prompts you for the number of samples you want deposited in the bottle. The acceptable range for number of samples is 0 to 999; the range is determined by the bottle size entered in the Bottle Size configure option. Enter 0 if you want the sampler to take samples indefinitely until the float shutoff terminates the sampling. If you enter a number greater than zero, the sampler will take samples until it has deposited that number of samples or the float shut off terminates the sampling. The next display prompts you for the sample volume and indicates the range of acceptable volumes. The maximum range of sample volumes is dependent on the number of samples entered in the previous display; it will never exceed 9990 ml.
   When entering the sample volume, the ± 10 ml sample volume repeatability should be kept in mind. Because the entered volume is a "nominal" value, it is prudent to calculate a total sample volume that is somewhat less than the volumetric capacity of the bottle as a safety factor. This will minimize the effects of cumulative error. Refer to Section 3.10.2 for notes on cumulative error and bottle size.
   If you will be using a preservative in the sample bottle, be sure to take the volume of the preservative into account.
   The sampler can be configured, through the Liquid Detector configure option, to add the suction head setting to the program sequence. The suction head display will appear after you enter the sample volume. However, when the head is unknown or variable, the suction head setting should be omitted by disabling the suction head setting in the Liquid Detector configure option. By disabling the setting, you allow the liquid detector to determine the operat-

ing suction head each time a sample is taken.
If you want to calibrate the sample volume, the calibration option must be enabled. To enable this option, select "ENABLE" in the Calibrate Sampler configure option. (Refer to Section 3.10.11.) Enabling the option will add the calibration displays to the Sample Volume program section. The calibration displays are included in Example *Calibration*, on page 3-23.

5. Enter the Key Times settings. In the basic programming mode, you will be asked if you want to enter a start time for the routine. If you select "YES," you will be prompted to enter a specific start time and date. If you select "NO," the sampler will use the start time delay. The start time delay can be set from 0 to 9999 minutes in the Start Time Delay configure option. (See Section 3.10.13.) When you select "NO," the routine will start according to the delay setting in the Start Time Delay configure option. The time remaining between the time you press the START SAMPLING key and the next full minute will pass before beginning the delay countdown. In other words, with a start time delay of one minute, if you press the START SAMPLING key at 10:05:30, the routine will begin the one minute countdown at 10:05:00 and start the routine at 10:06:00.
When the sampler is operating under factory configuration settings and running a time-paced program, the first sample will be taken at the start time for time-paced sampling. This is true whether you enter a specific start time and date, or if you use the start time delay. For flow-paced sampling, however, the flow pulse countdown will begin at the start time and the first sample will be taken when the countdown reaches zero. Refer to the discussion on the *Flow Mode* option, in Section 3.10.10, for additional information.
6. The sampler will automatically return to standby.
7. From standby, start the routine by pressing the START SAMPLING key. This places the sampler into the run state. If you happen to start the routine after the programmed start time, the sampler will allow you to reprogram the start time.
8. Use the run state displays to monitor the sampler's progress.

Before programming the sampler – especially if you are unfamiliar with the settings used in the previous routine, or if you think the settings have been changed – verify the configure option settings. You *must* change the settings if they do not match your bottle size or the suction line used with your unit. Entries suggested in Example *Checking the Configure Option Settings*, on page 3-17, configure the sampler for the 2.5 gallon (9400 ml) container and a 10 foot length of $^{3}/_{8}$-inch ID vinyl suction line, enable the liquid detector, and select the basic pro-

gramming mode. Procedures for re-initializing the program settings and configure options to factory settings are placed in steps 21 to 22.

Example: Checking the Configure Option Settings

1. If the sampler is not already on, press the ON/OFF key to turn it on. The standby display shown here will appear. Press the ENTER/PROGRAM key to access the interactive state. The next display you'll see is shown in Step 2.

```
. . . STANDBY . . .
10:34:50   19-JUN-04
```

2. Access the configure sequence by selecting "CONFIGURE." Select "CONFIGURE" by pressing the RIGHT ARROW key once. When "CONFIGURE" blinks, accept the selection by pressing the ENTER/PROGRAM key.

```
[PROGRAM, CONFIGURE]
        SAMPLER
```

3. The first option displayed is the Set Clock configure option. If the time displayed on the LCD in the standby message is not correct, reset the time with the Set Clock configure option. Press the ENTER/PROGRAM key to access the Set Clock input display.

```
SELECT  OPTION: (← →)
       SET CLOCK
```

4. Use this display to reset the time. Five entries are required. The LEFT ARROW and RIGHT ARROW keys can be used to move back and forth between each of the five entries. Use the arrow keys until the entry you want to change blinks. Type in the new time or date; press the ENTER/PROGRAM key to accept it. Press the RIGHT ARROW or ENTER/PROGRAM key on the *last* entry to store the values and advance to the next display.

```
   HH:MM   DD-MM-YY
10:35:20     19-06-04
```

5. To verify the Bottle Size settings, press the ENTER/PROGRAM key. The display shown in Step *6* will appear.

```
SELECT OPTION: (← →)
     BOTTLE SIZE
```

6. Select "REFRIG." Teledyne Isco 3700 Series portable and refrigerated samplers use the same controller. You would not need to select "PORTABLE" unless you moved the controller to a portable sampler.

```
(PORTABLE, REFRIG
        SAMPLER
```

7. Enter the bottle size here. Enter "9400" for the 2.5 gallon bottles, "15000" for 4 gallon bottle. Press the enter/program key.
   If you enter a number that exceeds the maximum standard bottle size (15000), the message, "WARNING: STANDARD BTL VOLUME EXCEEDED!", will be displayed for a short time. The sampler will then prompt you to confirm the volume entered. This prompt is displayed in step 8.

```
   BOTTLE VOLUME IS
        9400 ml
```

8. Select "YES" if you want to use the nonstandard bottle volume. Select "NO" if you want to revise the entry. The display shown in step 7 will reappear; use it to enter the revised bottle volume. Press the ENTER/PROGRAM key to accept the entry and advance to step 9.

```
15001 ml!  . .. ARE YOU
  SURE?   (YES, NO)
```

9. Press the ENTER/PROGRAM key at this display to access the Suction-Line input displays shown in steps 11 to 13.

```
SELECT OPTION: (← →)
     SUCTION LINE
```

Example: Checking the Configure Option Settings (Continued)

10. Select "1/4" if you are using 1/4-inch suction line, "3/8" if you are using 3/8-inch suction line. Press the ENTER/PROGRAM key to accept the selection. If you select "1/4," you will not see the display shown in step *12*; instead you will be prompted for the suction-line length, as shown in step *13.* (You do not need to specify vinyl line type because only 1/4-inch suction line is available.)

```
SUCTION LINE ID IS
< 1/4, 3/8> INCH
```

11. This display appears when you have selected "3/8" in step *11*. Select "VINYL" if you are using vinyl suction line, "TEFLON" if you are using Teflon suction line. Press the ENTER/PROGRAM key to accept the selection.

```
SUCTION LINE IS
<VINYL, TEFLON>
```

12. Enter the length of the suction line. Do not include the tube coupling or the strainer in the length. Press the ENTER/PROGRAM key to accept the entry and move to step *14*. If you change the suction line settings, the ". . . CALCULATING . . . PUMP TABLE VALUES" message will appear for a short time.

```
SUCTION LINE LENGTH
IS 10 FEET (3 - 99)
```

13. Press the ENTER/PROGRAM key at this display to access the Liquid Detector input displays shown in steps 15 to 18.

```
SELECT OPTION: (← →)
  LIQUID DETECTOR
```

14. Select "ENABLE" to turn on the Liquid Detector on, "DISABLE" to turn off the Liquid Detector. For the purposes of the following examples, select "ENABLE." Press the ENTER/PROGRAM key to accept the selection. You should normally leave the detector enabled unless you suspect it is malfunctioning. If you disable the detector, you will need to enter the suction head in the program sequence.

```
[ENABLE, DISABLE]
 LIQUID DETECTOR
```

15. This display appears when you select "ENABLE" in step *15*. For the purposes of this example, enter "0." Press the ENTER/PROGRAM key to accept the entry. Rinse cycles condition the suction line to reduce cross contamination.

```
0 RINSE  CYCLES (0-3)

```

16. This display appears when you select "ENABLE" in step *15*. For the purposes of the following examples, select "NO" to omit the setting. Press the ENTER/PROGRAM key to accept the selection.

```
ENTER HEAD MANUALLY?
     [YES, NO]
```

17. This display appears when you select "ENABLE" in step 15. For the purposes of this example, set the number of retries to "0." Press the ENTER/PROGRAM key to accept the entry. This setting determines the number of times the sampler will try to detect the presence of liquid for each sample event.

```
RETRY UP TO  0 TIMES
WHEN SAMPLING (0-3)
```

18. To verify the programming mode setting, press the ENTER/PROGRAM key.

```
SELECT OPTION: (← →)
  PROGRAMMING MODE
```

19. Select "BASIC." Press the ENTER/PROGRAM key to accept the selection.

```
[BASIC, EXTENDED]
 PROGRAMMING MODE
```

The steps in Example *Time-Paced Sampling* program the sampler to take 250 ml samples every 15 minutes for a six hour period of time. The sampling routine is to start at 6:00 a.m.

When entering the program settings, you must enter the number of samples required before entering the sample volume. At four samples per hour, the 6 hour period would yield 24 samples. The total sample volume collected at the end of the routine would be 6000 ml (24 samples 250 ml/sample), well within the capacity of the 9400 ml (2.5 gallon) bottle.

Example: Time-Paced Sampling

1. If the sampler is not already on, press the ON/OFF key to turn it on. The standby display shown here will appear. Press ENTER/PROGRAM to access the interactive state.

```
. . . STANDBY . . .
5:34:50  19-JUN-04
```

2. Access the program sequence by selecting "PROGRAM." Because "PROGRAM" will already be selected (blinking), press the ENTER/PROGRAM key to accept it and move to the next step.

```
[PROGRAM, CONFIGURE]
      SAMPLER
```

3. To enter the interval between samples in time increments, select "TIME." If "TIME" is already blinking, press the ENTER/PROGRAM key to accept the selection. If "FLOW" is blinking, press the LEFT ARROW key once so that "TIME" blinks. Then, press the ENTER/PROGRAM key to accept "TIME."

```
    [TIME, FLOW]
  PACED SAMPLING
```

4. This display requires two entries: one for the hours, one for the minutes. Enter "0" to set the hours at zero. Press ENTER/PROGRAM to accept the number "0" and move to the minutes entry shown in step 5.

```
    SAMPLE EVERY
0 HOURS,  1 MINUTES
```

5. Enter "15" to set the minute entry. Press ENTER/PROGRAM to accept the entry.

```
    SAMPLE EVERY
0 HOURS,  15 MINUTES
```

6. Enter the number of samples to be collected: "24". Press ENTER/PROGRAM to accept the entry.

```
    24 COMPOSITE
  SAMPLES (0-470)
```

7. Enter the sample volume: "250." Press ENTER/PROGRAM to accept the entry.

```
  SAMPLE VOLUMES OF
250 ml   (10 - 1000)
```

8. Select "YES" to enter the start time for the routine.

```
  ENTER START TIME?
     [YES, NO]
```

9. Enter the start time and date: 6:00 on April 19.

```
 TAKE FIRST SAMPLE AT
6:00            19-APR
```

After this message is displayed briefly, the sampler will automatically return to the standby state.

```
 PROGRAMMING SEQUENCE
      COMPLETE
```

10. After the sampler is properly installed, press the START SAMPLING key to run the program.

Example: Time-Paced Sampling (Continued)

```
 . . . STANDBY . . .
 5:38:50    19-APR-04
```

The first line of this display indicates the number of the upcoming sample event and the total number of programmed samples. The second line indicates the scheduled time of the upcoming event followed by the current time.

```
    SAMPLE 1 OF 24
AT 6:00        5:39:43
```

When the time to the next sample event has elapsed and the sampler has initiated the sample event, the sampling cycle begins. When the pump reverses for the pre-sample purge, the second line disappears.

```
    SAMPLE 1 OF 24
```

At the end of the pre-sample purge, the pump runs forward to deliver the sample, and the second line appears on the display. This display remains through the end of the post-sample purge.

```
    SAMPLE 1 OF 24
    PUMPING 250 ml
```

At the end of the sample event, the display changes to indicate the number and time of the next event. The current time is reported in the lower right corner.

```
    SAMPLE 2 OF 24
AT 6:15        6:00:33
```

The cycle is repeated for the remainder of the sampling routine.

```
    SAMPLE 2 OF 24
```

```
    SAMPLE 2 OF 24
    PUMPING 250 ml
```

↓
↓

This display appears when the routine is completed. It reports the status of the routine (“DONE”), the total number of sample events, and the current time and date.

```
DONE . . . 24 SAMPLES
6:10:35     21-JUN-04
```

The steps in Example *Flow-Paced Sampling* program the sampler to take 24, 250 ml samples at a flow pulse interval of 10 pulses. The sampling routine is to start according to the start time delay. A discussion of the calculations needed to determine the estimated time interval of flow-paced samples, the number of flow pulses, and sample volume can be found in Appendix D.

Example: Flow-Paced Sampling

1. Press the ENTER/PROGRAM key to reenter the interactive state.

```
      STANDBY . . .
 10:38:50  19-APR-04
```

2. Access the program sequence by selecting "PROGRAM."

```
[PROGRAM, CONFIGURE]
      SAMPLER
```

3. Select "FLOW."

```
      [TIME, FLOW]
   PACED SAMPLING
```

4. Enter "10" to set the pulse interval to 10 pulses. (Note: An entry of "0" will instruct the sampler to take samples until the float shut-off terminates the sampling routine.)

```
      SAMPLE EVERY
 10 PULSES (1 - 9999)
```

5. Enter the number of samples to be collected: "24."

```
     24  COMPOSITE
   SAMPLES ( 0-470)
```

6. Enter the sample volume: "250."

```
   SAMPLE VOLUMES OF
 250 ml   (10 - 1000)
```

7. Select "NO" to use the start time delay set in the configure sequence.

```
   ENTER START TIME?
      [YES, NO]
```

After this message is displayed briefly, the sampler will automatically return to the standby state.

```
 PROGRAMMING SEQUENCE
      COMPLETE
```

8. After the sampler is properly installed, press the START SAMPLING key to run the program.

```
  . . . STANDBY . . .
 10:40:23    19-APR-04
```

This display appears during the start time delay countdown:

```
 START AT 10:42 19-APR
  10:40:35 19-APR-04
```

The first line of this display indicates the number of the upcoming sample event and the total number of programmed samples. The second line indicates the number of pulses remaining to the sample event.

```
SAMPLE     1   OF    24
AFTER         10  PULSES
```

This display indicates that one pulse has been received. The pulse countdown will continue until the next sample event.

```
SAMPLE     1   OF    24
AFTER         9  PULSES
```

Example: Flow-Paced Sampling (Continued)

↓
↓

When the flow countdown reaches zero and the sampler has initiated the sample event, the sampling cycle begins. When the pump reverses for the pre-sample purge, the second line disappears.

```
     SAMPLE 1 OF 24
```

At the end of the pre-sample purge, the pump runs forward to deliver the sample, and the second line appears on the display. This display remains through the end of the post-sample purge.

```
     SAMPLE 1 OF 24
     PUMPING 250 ml
```

At the end of the sample event, the display changes to indicate the number and time of the next event.

```
     SAMPLE 2 OF 24
AFTER          10  PULSES
```

The cycle is repeated for the remainder of the sampling routine.

```
     SAMPLE 2 OF 24
```

```
     SAMPLE 2 OF 24
     PUMPING 250 ml
```

↓
↓

This display appears when the routine is completed. It reports the status of the routine (“DONE”), the total number of sample events, and the current time and date.

```
  DONE . . . 24 SAMPLES
6:10:35         20-APR-04
```

Example *Calibration* demonstrates the method used to calibrate the sampler for a 200 ml sample volume. The Calibrate Sampler configure option must be enabled in the configure sequence before the calibration displays shown below will appear.

Even without calibrating, the 3710 Sampler will deliver accurate sample volumes. If your sample volumes vary significantly with the entered values, check the suction line first. Be sure the line slopes continuously downhill and is draining completely after each pumping cycle. Then, check the suction line entries in the configure sequence to see that they are accurate. The calibration procedure is intended to be for “fine tuning” only.

After you enter the sample volume actually delivered, as shown in step 8, all subsequent sample volumes delivered will be adjusted to correct for the difference between the expected sample volume and the actual volume entered. Clear the adjustment by changing a suction line entry in the Suction Line configure option or by re-initializing the sampler.

Because the sample volume can be calibrated to ± 10 ml, a graduated cylinder should be used to facilitate measurement. A graduated cylinder is available from the factory. Refer to Appendix B for details.

The calibration pump cycle will include rinse cycles and retries, if the sampler is configured to perform them (see Section 3.10.6). This ensures that the calibration procedure includes the pump cycle used while running the sampling program.

Example: Calibration

1. Press the ENTER/PROGRAM key to reenter the interactive state.

```
      STANDBY . . .
  10:38:50  19-APR-04
```

2. Access the program sequence by selecting "PROGRAM."

```
[PROGRAM, CONFIGURE]
      SAMPLER
```

3. Step through the program until the "CALIBRATE SAMPLER?" input display appears (step *4*).

```
     [TIME, FLOW]
   PACED SAMPLING
```

Other program sequence displays.

↓
↓

4. Select "YES."

```
  CALIBRATE SAMPLER?
      [YES, NO]
```

5. Before pressing the MANUAL SAMPLE key, make sure a collection container is underneath the pump tube.

```
  PRESS MANUAL SAMPLE
  KEY WHEN READY . . .
```

6. The sampler will deliver the programmed sample volume.

```
. . . MANUAL SAMPLE . . .
    PUMPING  200 ml
```

7. Measure the actual volume delivered and enter that value here.

```
    200 ml VOLUME
     DELIVERED
```

8. Repeat the procedure if desired by selecting "YES." When you are satisfied with the calibration, select "NO." Under normal conditions, you should not need to repeat the procedure.

```
  CALIBRATE SAMPLER?
      [YES, NO]
```

Other program sequence displays.

↓
↓

Other program sequence displays.

```
  . . . STANDBY . . .
 9:39:50     19-APR-04
```

3.10 Configure Sequence

The configure sequence provides a number of setup options. Some options enable sampling features, some provide reference data, and others affect run state operations.

Example *Checking the Configure Option Settings* shows the procedure used to access the configure sequence. (When you see a "SELECT OPTION: (← →)" display, you are in the configure sequence.) Each option uses at least two displays. The first display lists the option name. The second and any additional displays are input displays. To access an input display, press the ENTER/PROGRAM key while the desired option name is displayed. Once you've accessed the input display, use the keypad to enter numbers and make choices as described in Section 3.7.2 through 3.7.6.

Pressing the EXIT PROGRAM key in the configure option list will return the sampler to standby. Pressing the EXIT PROGRAM key in a configure option *input display* will return you to the list of configure options without changing the display's setting.

By pressing the LEFT ARROW or RIGHT ARROW key at the "SELECT OPTION" display in the configure sequence, you can scroll through the list of configure options without viewing each input display. If you are interested in only one or two options, you can use this method to locate the option of interest quickly.

Each option is discussed below in the order in which it appears when configuring the sampler. Individual input displays and their settings, are discussed separately within the discussion of each option. The name of the setting is placed in the left margin so you can identify each topic. Illustrations of displays are not included in each discussion; however, each discussion includes the display number, should you need to refer to display listing in Appendix C.

3.10.1 Set Clock

The Set Clock option is used to synchronize the sampler's clock with real time. Times must be entered in military time: 9:30 a.m. would be entered as 9:30, 9:30 p.m. would be entered as 21:30. When the year entry is accepted, the seconds will be reset to zero. (*Display #210*)

3.10.2 Bottle Size

The Bottle Size option is used to enter the bottle volume. The option uses two input displays:

- the first display allows you to specify a portable or refrigerated sampler
- the second sets the bottle volume.

The sampler uses the bottle volume to calculate the range of acceptable values in the sample volume input display. It also uses the volume to check for probable overfill when the sampler is programmed for flow-paced sampling.

3.10.3 Portable or Refrigerated Sampler

Because the 3700 Series portable and refrigerated samplers use the same control box, you must specify the type of unit. The 3710R Sampler will be shipped with this setting as "REFRIG-

ERATED." This setting is not changed when you re-initialize the settings. You should not specify "PORTABLE" unless you move the control box to a portable sampler. (*Display #220*)

3.10.4 Bottle Volume

The following chart lists Teledyne Isco's standard bottle sizes for composite samplers. When using Teledyne Isco's bottles, enter the bottle volume setting listed in the third column of the table. The recommended bottle sizes have been adjusted downward. Using the lower, adjusted volume helps prevent overfilling. If you are using a non-standard bottle, enter a bottle volume smaller than the actual bottle capacity. This will help prevent overfilling. (There are approximately 3785 ml per gallon.)

Bottle Configuration	Bottle Size	Bottle Volume Setting
Glass or polyethylene	2.5 gal	9400
1 polyethylene bottle	4 gal	15000
1 polyethylene bottle	5.5 gal	20800

Cumulative Error – The sample accuracy is the greater of 10% of the sample volume or 20 ml and is repeatable to ± 10 ml. Since samples of 150 ml can vary by 10% or ± 15 ml, the cumulative error for 24 samples would be ± 360 ml. If the sampler consistently places 24 sample volumes of 165 ml (150 ml + a 10% variation of 15 ml) in a 3800 ml bottle, the total volume deposited would be 3960 ml, overfilling the bottle by 160 ml. Again, to avoid possible overfilling, enter a bottle volume that is less than the actual bottle capacity.

3.10.5 Suction Line

The Suction Line configure option is used to configure the sampler for the type (vinyl or Teflon), diameter, and length of the suction line used. The volumetric delivery varies with line diameter, type, and length, so it is important that these settings be entered accurately. An incorrect setting will impair the accuracy of the sample volume. These settings are also used to determine the number of post-sample purge counts. It is important to have sufficient counts to completely clear the line.

If you change the current suction line settings, the ". . . CALCULATING . . . PUMP TABLE VALUES" message will appear for a short time. Because the volumetric delivery of the sample varies with the diameter, type, and length of the suction line; the sampler must revise the internal pump tables. The tables are used as reference for the electronic pump count for sample delivery.

There are three types of suction lines available for use with the 3710 sampler: 1/4-inch ID vinyl, 3/8-inch ID vinyl, and 3/8-inch ID Teflon. If you specify 1/4-inch line, the sampler will prompt you

for the line length immediately. If you specify 3/8-inch line, the sampler will prompt you to specify vinyl or Teflon before prompting for the line length. (*Display #'s 230 and 231*)

The sampler will accept suction line lengths of 3 to 99 feet. When measuring the line, do not include the tube coupling or the strainer in the measurement. The line should be cut to even foot lengths. (*Display #232*)

3.10.6 Liquid Detector

The Liquid Detector configure option is used to turn the liquid detector on or off, set the number of rinse cycles, add a suction head setting to the program sequence, and set the number of sampling retries should the suction line become clogged. The option uses four input displays: Enable/Disable Detector, Rinse Cycles, Enter Head Manually, and Sampling Retries.

Enable/Disable Detector – The recommended setting for the Enable/Disable Detector option is "ENABLE." The 3710 Sampler determines the delivered sample volume suction head by counting revolutions of the peristaltic pump rotor. The volume of liquid delivered by one revolution of the pump rotor is a function of the suction head; as the suction head increases, the volume delivered by one revolution of the pump rotor decreases. By enabling the detector, the sampler can accurately determine the operating suction head. It does not have to rely on a programmed suction head value, but can instead begin its volume delivery count when liquid is detected. This minimizes inaccuracies that can occur in changing head conditions, or when measurement of the suction head is difficult to determine accurately.

The disable option is provided should the detector or its associated circuitry become suspect. If the detector is disabled, the manual suction head setting (*Display #70*) is automatically added to the Sample Volume program section in the program sequence. If the detector is disabled, the sampler will use a calculated number of pump counts based on the suction head entry to deliver the correct sample volume. The sampler will operate at diminished accuracy with the detector disabled. (*Display #240*)

Rinse Cycles – The Rinse Cycle setting is available only when the detector is enabled. It is used to set the number of suction line rinses, from 0 to 3. Rinses are used to condition the suction line to reduce cross contamination. During a rinse cycle, the pump draws liquid up through the line until it is detected by the liquid detector. At that point, the pump reverses to purge the line. This cycle is repeated according to the number of rinse cycles entered. (*Display #241*)

Rinse cycles contribute to the wear on pump tubing; therefore, if you use rinse cycles, it may be necessary to replace the tubing more frequently. The Tubing Life configure option (see Section 3.10.17) allows you to monitor pump tubing wear.

Enter Head Manually – Entering the head manually is available as an option when the detector is enabled and allows you to add the suction head entry (*Display #70*) to the program sequence. When the detector is disabled, the Suction Head entry is automatically added to the program sequence. By disabling the

suction head setting, you allow the liquid detector to determine the operating suction head each time a sample is taken. Using the Suction Head entry in conjunction with the liquid detector, *when the head is stable and known accurately*, further increases accuracy of the delivered volume. When the head is variable or unknown, you should select "NO" because an incorrect head setting diminishes the delivered volume accuracy. (*Display #242*)

Sampling Retries – The Sampling Retries option is available as an option when the detector is enabled. It sets the number of times, from 0 to 3, the sampler will try to detect liquid in the line before skipping the sample. This option can be used when sampling liquid with a high concentration of solids which tend to clog the suction line or the strainer. The sampler will also retry the rinse cycle when you are using the Sampling Retry option. (*Display #243*)

Table 3-3 Sampling Capabilities Through the Program Sequence

Pacing	Mode	Feature
Time-Pacing: Uniform Time Intervals	Basic & Extended	Samples taken at regular time intervals from 1 minute to 99 hours, 59 minutes.
Time-Pacing: Nonuniform Clock Time Intervals	Extended	Samples taken at irregular time intervals by specifying the time and date of each sample. You can enter dates as far as one month in advance of the current date.
Time-Pacing: Nonuniform Intervals in Minutes	Extended	Samples taken at irregular time intervals by specifying the amount of time in minutes between each sample. You can enter intervals from 1 to 999 minutes.
Flow-Pacing	Basic & Extended	Samples taken at regular flow intervals. The sampler will totalize flow intervals of 1 to 9,999 pulses.
Volumes and Accuracy		
Number of Samples	Basic & Extended	Number of samples needed to complete the routine. A specific number of samples (up to 999) can be entered or the sampler can be programmed to terminate the routine with the float shut-off.
Sample Volume	Basic & Extended	You can enter volumes from 10 to 9,990 ml.
Suction Head	Basic & Extended	You can enter suction heads from 1 to 20 feet.
Calibration	Basic & Extended	You can calibrate sample volumes if desired.
Key Times		
Start Times	Basic & Extended	You can enter specific start times for both time-paced and flow-paced routines. If you do not enter a start time, Start Time Delay is used.
Stop/Resume Times	Extended	You can perform intermittent sampling by defining sampling stop and resume times. You can enter as many as 12 stop and 12 resume times.
Time-Pacing	Extended	Samples taken at regular time intervals from 1 minute to 99 hours, 59 minutes.

3.10.7 Programming Mode

The Programming Mode option allows you to specify either the basic or extended programming mode. The basic programming mode is used for conventional routines; the extended programming mode can be used for either conventional or more complex routines. (*Display #250*)

Table 3-3 summarizes the sampling features according to the programming mode in the program sequence. Table 3-1 summarizes the features available in the configure sequence.

3.10.8 Load Stored Program

The Load Stored Program option allows you to load one of up to three sampling programs which have been previously saved with the *Save Current Program* configure option, discussed in Section 3.10.9. After loading a program, the sampler will adjust the time settings to current times and dates. Check the settings before starting the program to be sure they are appropriate for your application. (*Display #255*).

The sampler is shipped from the factory with four programs: the current program and three stored programs, numbered from 1 to 3. All four programs contain the factory default program settings. Unless you have previously saved a program under one of the program numbers, loading a program will replace the current program with the factory default settings. When you reinitialize the sampler, all four programs return to the default program settings.

The following example shows you how to load a stored program.

Example: Load Stored Program

1. Press ENTER/PROGRAM to access the interactive state.

```
. . . STANDBY . . .
10:34:50  19-JUN-04
```

2. Access the configure sequence by selecting "CONFIGURE."

```
[PROGRAM, CONFIGURE]
       SAMPLER
```

3. Press the LEFT ARROW or RIGHT ARROW key to scroll through the configure options. The first option displayed is the Set Clock configure option.

```
SELECT OPTION: (← →)
      SET CLOCK
```

↓
↓

4. You can load a stored programmed only when the sampler is configured for the extended programming mode. To verify the programming mode setting, press the ENTER/PROGRAM key.

```
SELECT OPTION: (← →)
  PROGRAMMING MODE
```

5. Select "EXTENDED." Press the enter/program key to accept the selection.

```
[BASIC, EXTENDED]
  PROGRAMMING MODE
```

6. Press ENTER/PROGRAM to access the Load Stored Program configure option.

Example: Load Stored Program (Continued)

```
SELECT OPTION: (← →)
 LOAD STORED PROGRAM
```

7. Select the number of the program you want to load. Select "NONE" when you do not want to load a program.

```
     LOAD PROGRAM
[#1, #2, #3, NONE]
```

8. When the sampler has loaded the program, it will display the next configure option. When you are done configuring the sampler, press EXIT/PROGRAM to return to Standby.

```
SELECT OPTION: (← →)
 SAVE CURRENT PROGRAM
```

9. After you properly install the sampler, press the START SAMPLING key to run the program.

```
  . . . STANDBY . . .
10:37:23    19-JUN-04
```

3.10.9 Save Current Program

The Save Current Program option allows you to assign up to three sampling routines a number and store them. This option eliminates the need to reprogram the sampler for recurrent routines. Only the program settings are saved; if different routines require different configurations, the sampler must be reconfigured for each routine. For example, if the sampler is used at two sites, each requiring a specific sampling routine and different suction line lengths; the sampling routines can be stored for each site, but the suction line length settings must be reentered each time the line changes. (*Display #260*)

The sampler is shipped from the factory with four programs: the current program and three stored programs, numbered from 1 to 3. All four programs contain the factory default program settings. Saving a program will replace the default program with the current settings. Reinitializing the sampler will restore the default program settings. The default program settings are listed in Table 3-5.

☑ *Note*

Saving a program will overwrite a program saved earlier under the same number. Settings for the current program can be viewed with the Display Status procedure.

The following example shows you how to save a program.

Example: Save Current Program

1. Press ENTER/PROGRAM to access the interactive state.

```
. . . STANDBY . . .
10:34:50  19-JUN-04
```

2. Access the configure sequence by selecting "CONFIGURE."

```
[PROGRAM, CONFIGURE]
SAMPLER
```

3. Press the LEFT ARROW or RIGHT ARROW key to scroll through the configure options. The first option displayed is the Set Clock configure option.

```
SELECT OPTION: (← →)
SET CLOCK
```

↓
↓

4. You can save the current program only when the sampler is configured for the extended programming mode. To verify the programming mode setting, press the ENTER/PROGRAM key.

```
SELECT OPTION: (← →)
PROGRAMMING MODE
```

5. Select "EXTENDED." Press the ENTER/PROGRAM key to accept the selection.

```
[BASIC, EXTENDED]
PROGRAMMING MODE
```

6. Press the RIGHT ARROW key to skip the Load Stored Program configure option.

```
SELECT OPTION: (← →)
LOAD STORED PROGRAM
```

7. Press the ENTER/PROGRAM key to access the Save Current Program configure option.

```
SELECT OPTION: (← →)
SAVE CURRENT PROGRAM
```

8. Select the number you want to use as the program "name." Select "NONE" when you do not want to save a program When the sampler has saved the program, it will display the next configure option. When you are done configuring the sampler, press EXIT/PROGRAM to return to Standby.

```
SAVE PROGRAM AS
[#1, #2, #3, NONE]
```

9. When the sampler is properly installed, press the START SAMPLING key to run the program.

```
. . . STANDBY . . .
10:37:23    19-JUN-04
```

3.10.10 Flow Mode Sampling

The Flow Mode Sampling option is used to direct the sampler to take a sample at key times in a flow-paced sampling program.

Sample at Start Time – If you select "YES," the first sample will be taken at the start time entered in the program sequence. If you select "NO," the first sample is delayed until the number of flow pulses, set in the program sequence, have been counted down to zero. (*Display #270*)

Nonuniform Time – The Nonuniform Time option specifies the method in which nonuniform intervals are to be entered in the extended program sequence (*Display #'s 26 or 27*). If you select "CLOCK-TIME," you will be able to enter a specific time and date for each sample event when entering settings in the program sequence. If you select "MINUTES," you will be able to enter nonuniform intervals in minutes. (*Display #280*)

When you enter nonuniform times, you will be prompted to enter the number of nonuniform samples before you enter the nonuniform times. This display replaces the Number of Composite Samples display (*Display #60*) in the program sequence.

3.10.11 Calibrate Sampler

The Calibrate Sampler option is used to add or remove the calibration settings to the program sequence. If you select "ENABLE," the calibration displays will be added to the program sequence and you will be able to precisely calibrate the sample volumes. (*Display #290*)

3.10.12 Sampling Stop/Resume

The Sampling Stop/Resume configure option allows you to add stop and resume settings (*Display #'s 100, 101, and 102*) to the program sequence. The Stop/Resume settings appear in the key time section of the program sequence. (You can enter up to 24 times: 12 stop times and 12 resume times.) For example, the Stop/Resume option allows you to define a sampling routine which will take samples at intervals of 15 minutes between 6:00 a.m. to 8:00 a.m. and between 4:00 p.m. to 6:00 p.m. The stop and resume entries for this routine are shown in Example *Extended Time-Paced Sampling*, on page 3-47.

Enable/Disable – Select "ENABLE" to add the stops and resume settings to the program sequence. (*Display #300*)

Sample at Stop – The Sample at Stop setting is to direct the sampler to take a sample at stop times. (*Display #301*)

Sample at Resume – The Sample at Resume setting is used to direct the sampler to take a sample at resume times. (*Display #302*)

3.10.13 Start Time Delay

The Start Time Delay option is used to set the amount of time in minutes, between the time you press the START SAMPLING key and the time the sampling routine is initiated. The sampler's response varies according to specific entries: "0," "1," and entries greater than 1.

```
---- MINUTE DELAY
TO START (0 - 9999)
```

Display #310

An entry of "0" eliminates the delay to start time; the start time occurs the moment you press START SAMPLING. For example, if you press START SAMPLING at 10:32:15, the sampler will initiate a time-paced sample event at 10:32:15.

However, the sampler will start clocking time intervals at the beginning of the minute (HH:MM:**00**) of the first sample event. If a sampling routine requires 10 minute intervals and you pressed START SAMPLING at 10:32:15, the sampler would begin the time interval at 10:32:00. It would initiate the second sample event at 10:42:00. The sampler would begin the flow interval at 10:32:15 for flow-paced routines.

If you enter a start time delay of "1," the sampler will begin the routine at the beginning of the next minute. Thus, if you pressed START SAMPLING at 10:32:15, the sampler would initiate the sample event at 10:33:00. The sampler would begin time and flow intervals at 10:33:00. If you enter a start time delay of "2," the sampler would begin time or flow intervals at 10:34:00. (*Display #310*)

Note: If you enter a start time, the sampler will disregard the start time delay. The sampler will use the start time delay setting when you do not enter the start time in the program sequence. Care must be taken when using a start time delay of greater than zero when the sampler is being inhibited by another sampler, an Isco Flow Meter, or a Liquid Level Actuator. Refer to Section 3.10.14.

3.10.14 Enable Pin

The Enable Pin option allows you to program the sampler's response to a device controlling pin F of the flow meter connector: for example, an Isco Flow Meter or the Teledyne Isco 1640 Liquid Level Actuator. There are four Enable Pin setup options: Sample Upon Disable, Sample Upon Enable, Reset Sample Interval, and Inhibit Countdown.

Sample Upon Disable – When you are using an Isco Flow Meter or Liquid Level Actuator, "SAMPLE UPON DISABLE?" allows you to direct the sampler to take a sample as soon as the sampler is disabled through pin F. A response of "YES" will cause the sampler to take a sample when the pin is disabled; a response of "NO" will prevent the sampler from taking a sample. (*Display #321*)

The sampler determines an enable or disable condition by monitoring the voltage on pin F. High voltage is interpreted as an enable signal. Low voltage or ground is interpreted as a disable signal.

Sample Upon Enable – When you are using an Isco Flow Meter or Liquid Level Actuator, "SAMPLE UPON ENABLE?" allows you to direct the sampler to take a sample as soon as the sampler is enabled through pin F. A response of "YES" will cause the sampler to take a sample when the pin is enabled. A response of "NO" will prevent the sampler from taking a sample when the pin is enabled. (*Display #322*)

Reset Sample Interval – "RESET SAMPLE INTERVAL?" is used to control the time or flow pulse countdown. If you select "YES," a full sample interval will begin when pin F is enabled. If you select "NO," the interval will not be reset when the sampler is enabled; the interval is then governed by settings entered in

the "INHIBIT COUNTDOWN?" option. If you are sampling on a time-paced basis and wish to synchronize all sampling with real time, do not reset the sample interval. (*Display #323*)

Inhibit Countdown – "INHIBIT COUNTDOWN?" is only applicable when you respond "NO" to "RESET SAMPLE INTERVAL?" The Inhibit Countdown option is used to control the countdown while the sampler is disabled. Select "YES" to freeze the countdown to the next sample. The count will resume when the sampler is enabled. Select "NO" to allow the countdown to continue while the sampler is disabled. (*Display #324*)

3.10.15 Event Mark

The Event Mark option configures the sampler to send an event mark to an interfaced flow meter or other equipment. The sampler will supply a variable duration pulse of up to 700 mA at 12 V on pin E of the flow meter connector. Four types of signals can be sent:

- a pulse at the beginning of the pre-sample purge
- a pulse at the beginning of forward pumping only
- continuous during the entire pump cycle
- continuous during forward pumping only

The type of signal selected from the Event Mark configure option affects the event mark signal on pin E. In Figure 3-4A, a pulse signal is sent at the beginning of the pre-sample purge. In Figure 3-4B, a pulse signal is sent during the sample volume delivery portion of the sample event. In Figure 3-4C, a continuous signal is sent during the entire pump cycle. In Figure 3-4D, a continuous pulse is sent for the duration of the sample volume delivery.

Continuous/Pulse Signal – The Continuous/Pulse setting is used to select either continuous or pulse signals. Pulse signals are three seconds in duration; continuous signals are three seconds or longer and depend on the setting and the pump cycle. (*Display #330*)

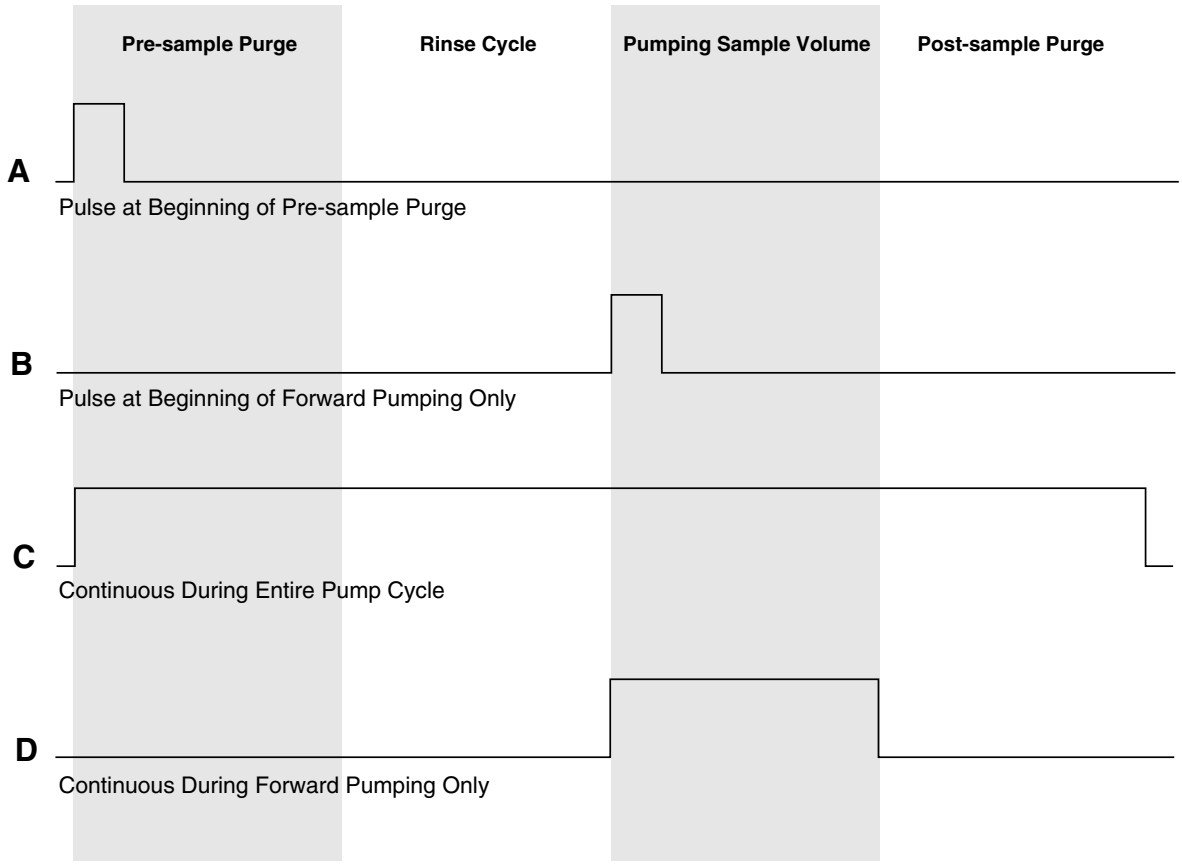


Figure 3-4 Event Mark Signal Output

Continuous Signal Timing – The Pump Cycle/Fwd Pumping settings will appear when you have selected "CONTINUOUS SIGNAL." Select "PUMP CYCLE" when you want a continuous signal transmitted during the entire pump cycle, from the beginning of the pre-sample purge to the end of the post-sample purge. Select "FWD PUMPING" when you want a continuous signal transmitted while the pump is delivering a sample volume. (*Display #331*)

Pulse Signal – The Pulse Signal setting will appear when you have selected "PULSE." Two options are available. The first option, "PURGE," is used to send a pulse at the beginning of the pre-sample purge. The second option, "FWD PUMPING," is used to send a pulse at the beginning of the sample delivery when the pump is running forward. (*Display #332*)

3.10.16 Purge Counts

The Purge Counts option is used to override the number of pump counts needed to clear the suction line in both pre-sample purge and post-sample purge cycles. The pre-sample purge count is normally set to 150 counts and will be reset to this value if the sampler is re-initialized. The post-sample purge count is derived from the suction line diameter and length settings. If your observations indicate that a greater or lesser number of pump counts in either purge is needed, you can change the count settings.

Acceptable entries are between 0 and 9999 for both purges. A purge count can be obtained using the PUMP FORWARD or PUMP REVERSE keys. (*Display #'s 340 and 341*)

3.10.17 Tubing Life

The Tubing Life option is used to set the number of pump counts needed to trigger the "REPLACE PUMP TUBING" warning. The warning will be activated when the pump count reaches the entered value. You must reset the pump counter after replacing the pump tubing. If you consistently experience a tubing failure at a pump count that differs significantly from the current setting, enter that value here. The factory set value of 500,000 pump counts will deliver approximately 500 samples of 200 ml each, using a 3/8-inch × 10 ft vinyl suction line at a 5 ft suction head. (*Display #350, 351, and 352*)

3.10.18 Program Lock

The Program Lock option allows you to protect program and configure settings with a pass-number. Select "ENABLE" to turn the protection on. When the Program Lock is enabled, each protected display can be viewed, but no values can be changed without first entering the pass-number: 3710. Once the pass-number has been entered, you can change any value or setting in either the program or configure sequence. (*Display #360*)

3.10.19 Sampler ID

The Sampler ID option allows you to enter a 10 character identification number (ID) for the sampler. The ID number is used to identify sampling reports produced by the Teledyne Isco Field Printer and in files created by SAMPLINK. The sampler is shipped from the factory with 10 dashes (-) entered for the ID. (*Display #365*)

Acceptable Characters – The ID field will accept digits, dashes, spaces, and periods. You can enter spaces, dashes, and periods with three of the control keys. Enter a space with the START SAMPLING key, a dash (-) with the MANUAL SAMPLE key, and a period with the RESUME SAMPLING key.

3.10.20 Run Diagnostics

Run Diagnostics is used to perform a number of diagnostic functions. This option contains the software revision number; tests the sampler's RAM (Random Access Memory), ROM (Read Only Memory), display, and pump; and allows for re-initializing RAM. The display information is discussed below in the order of appearance.

Software Revision Number – The sampler will display the software revision number for a short period of time.

Test RAM and ROM – The software revision display is replaced by the RAM and ROM test messages. A successful test is indicated by the messages "RAM PASSED TEST" or "ROM PASSED TEST." If either the RAM or ROM fail the test, the sampler will display one of the following messages: "RAM FAILED TEST" or "ROM FAILED TEST" and beep every three seconds until you turn the sampler off. If either the RAM or ROM fail their test, the sampler should be serviced. Contact Teledyne Isco Customer Service for assistance.

LCD Test – After successful RAM and ROM tests, the sampler will then test the LCD by first filling the display with solid rectangles and then printing the alphabet and other characters. Each character position in the display should contain a character.

Pump Test – The next step tests the pump. During the test, the pump will run briefly and the display will indicate an "OFF/ON" number. The number should fall within the range of 50 to 200. If the count falls below 50 or exceeds 200, the pump should be serviced. A count near 100 is typical.

Re-initialize Controller – The final step allows you to re-initialize the sampler. If you select "NO," the sampler will return to the configure option list. If you select "YES," the sampler will reset a number of configuration and program settings, then turn the sampler off. (*Display #371*)

Tables 3-5 and 3-4 list the re-initialized settings. **Not all settings are reset.** Set Clock, Bottle Size, Suction Line, and Sampler ID configure option settings remain unchanged. This reduces the number of settings you would need to change if the sampler were accidently re-initialized. The Pump Count total is not reset to maintain an accurate count for the Tubing Life Warning.

3.10.21 Exit Configuration

This option allows you to leave the configure sequence and return to the standby state. There are no input displays. Press the ENTER/PROGRAM key to exit the configure sequence. The configuration sequence can also be exited at any time using the EXIT PROGRAM key.

3.11 Extended Programming Mode

Sampling capabilities available in the basic programming mode are available in the extended programming mode. (See Table 3-3, on page 3-27.) The extended programming mode provides several additional capabilities: Nonuniform Time pacing, Sampling Stops and Resumes, program storage, and Flow Mode Sampling controls.

The procedure used to program the sampler in the extended mode is the same as the procedure used to program the sampler in the basic programming mode. This procedure is outlined in Section 3.8. There are some exceptions, however. The extended mode modifies the sections of the program sequence to allow you to take advantage of the additional features.

The Sample Pacing program section is extended to include settings for nonuniform times. If you have enabled the Sampling Stops and Resumes configure option, the Key Times section is extended to included displays for sampling stops and resumes.

Each of these extended features is discussed briefly below. You may find it helpful to refer to Figure 3-5, which charts the program sequence in the extended mode.

3.11.1 Extended Mode Sample Pacing

In the extended programming mode, the Sample Pacing section allows you to select flow pacing, or one of two types of time-pacing: uniform or nonuniform. If you select uniform time intervals, the settings for time intervals are identical to the time intervals entered in the basic programming mode.

Nonuniform times allow you to pace the sampler at irregular intervals. Before you enter nonuniform time intervals, you must specify either minutes or clock times in the Nonuniform Times configure option. You can enter nonuniform intervals in two ways. The first method allows you to define the interval between each sample event in minutes. For example, you can program the sampler to take sample #2 after an interval of 10 minutes, sample #3 after an interval of 30 minutes, sample #4 after an interval of 60 minutes, and so on. Sample #1 would be taken at the start time. The second method allows you to enter a specific time and date for each sample event. For example, with nonuniform time pacing, samples can be collected at specific times and dates at irregular intervals: 6:00 a.m. on April 15, noon on April 15, 7:00 a.m. on April 16, and 1:00 p.m. (or 13:00 in military time) on April 16. If you have several sequences of nonuniform times, you can use the program storage feature to save the programs using each sequence.

When you enter nonuniform times, you will be prompted to enter the number of nonuniform samples — "TAKE - - SAMPLES" (*Display 25*) — before you enter the nonuniform times. This display replaces the Number of Composite Samples display (*Display #60*) in the program sequence.

3.11.2 Extended Mode Sample Volumes

The extended mode Sample Volumes section is identical to the basic Sample Volume section. It is modified only when you are using nonuniform times. The Number of Composite Samples display is removed (*Display #60*) as discussed above.

3.11.3 Extended Mode Key Times

The extended mode Key Times section has one additional set of displays which allow you to set up the sampling stop and resume times. The Stops and Resumes settings are available only when you have enabled the Sampling Stop/Resume configure option (see Section 3.10.12). You must first enter the number of stops and resumes, from 0 to 24. (Enter "0" if you want to omit the stop and resume settings without returning to the configure sequence and disabling the Stops and Resumes option.) Then enter the stop and resume clock times. The first entry will be a stop time. Refer to the Key Times section of Figure 3-5, display #'s 100, 101, and 102.

Table 3-4 Factory Program Settings

Program Setting	Display Number	Factory Setting
[TIME, FLOW] PACED SAMPLING	10	TIME
UNIFORM/ NONUNIFORM TIME INTERVALS	11	UNIFORM
SAMPLE EVERY -- HOURS -- MINUTES	21	1 HOUR, 0 MINUTES
SAMPLE EVERY ---- PULSES (1 - 9999)	22	10
TAKE --- SAMPLES (1 - MAX)	25	10
QUANTITY AT INTERVAL 1. -- AT --- MINUTES	27	1 at 60 MINUTES
SAMPLE VOLUMES OF --- ml EACH (10 - *MAX*)	50	200
--- COMPOSITE SAMPLES (0 - *MAX*)	60	10
SUCTION HEAD OF -- FEET (1 - *MAX*)	70	10
ENTER START TIME? [YES, NO]	90	NO

Table 3-5 Factory Configure Option Settings

Configure Option	Display Number	Factory Setting
Set Clock	210	Not Reset
Bottle Size	220, 223	Not Reset
Suction Line	230, 231, 232	Not Reset
Liquid Detector		
Liquid Detector	240	Enable
Rinses	241	0
Enter Head Manually	242	No
# Of Retries	243	0
Programming Mode	250	Basic
Load Stored Program	255	
Save Current Program	260	
Flow Mode Sampling		
Sample At Start Time	270	No
Nonuniform Time	280	Minutes

Table 3-5 Factory Configure Option Settings (Continued)

Configure Option	Display Number	Factory Setting
Calibrate Sampler	290	Disable
Sampling Stop/resume	300	Disable
Sample At Stop Times	301	No
Sample At Resume Times	302	No
Start Time Delay	310	2
Enable Pin		
Master/slave	320	Disable
Sample Upon Disable	321	No
Sample Upon Enable	322	No
Reset Sample Interval	323	No
Inhibit Countdown	324	No
Event Mark		
Continuous /pulse	330	Continuous Signal
Pump Cycle/fwd Only	331	Fwd Pumping Only
Purge/fwd Pumping	332	Fwd Pumping
Purge Counts		
Pre-sample Counts	340	150
Post-sample Counts	341	Based On Line Length
Tubing Life		
Reset Pump Counter	351	No
# Pump Counts	352	Not Reset
Program Lock	360	Disable
Sampler Id	365	Not Reset
Run Diagnostics		
Re-initialize?	371	No

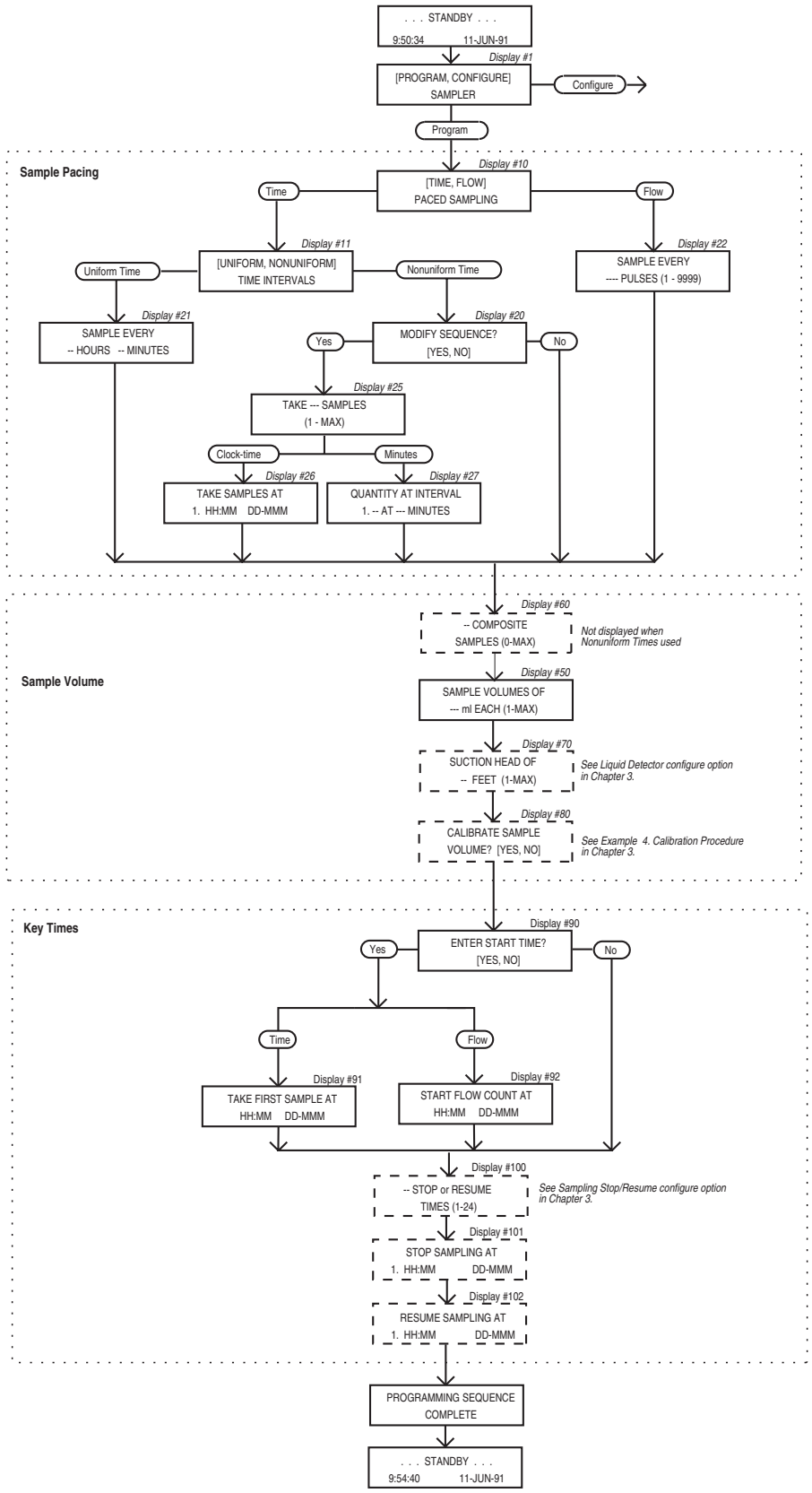


Figure 3-5 Extended Programming Mode: Program Sequence Structure

Determining the Number of Samples with Stops and Resumes – When using stops and resumes, determining the number of samples you want deposited in the container requires a little planning. With a time-paced routine, a sample will always be taken automatically at the *start* time. No sample will be taken at the *stop* time unless you have selected "ENABLE" in the Sample at Stop Time display of the Sampling Stops and Resumes configure option, even if the stop time falls at a scheduled sample event time. No sample will be taken at the *resume* time unless you have selected "ENABLE" in the Sample at Resume display of the Sampling Stops and Resumes option.

When you are using Stops and Resumes with flow-paced routines, a sample will not be taken at the start time, unless you have configured the sampler to do so in the Flow Mode Sampling configure option. With flow-paced routines, no sample will be taken at the stop time unless you have selected "ENABLE" in the Sample at Stop Time display of the Sampling Stops and Resumes option. No sample will be taken at the resume time unless you have selected "ENABLE" in the Sample at Resume display of the Sampling Stops and Resumes option.

If the number of samples deposited is not important to you or if you are using a flow-paced routine for a flow-steam with an unpredictable flow rate, enter "0" in the Number of Composite Samples display (*Display #60*). The sampler will take samples indefinitely, governed by the scheduled stop and resume time. It will be "DONE" at the final stop time or when the float shut-off terminates the routine.

3.12 Start Times

This section discusses the sampler's start times. It begins by outlining the sequence of events preceding the start time for most sampling routines.

3.12.1 Events Preceding Sampling Routine

After you program a sampler, you must start the sampling routine by pressing the START SAMPLING key. However, depending on the program and configure option settings, the sampling routine may not start at soon as you press the key. The "Delay to Start Time" is the period between the time you press START SAMPLING and the start time for the routine. Figure 3-6 diagrams the sequence of events preceding the start time.

The start time for a routine is either the programmed start time or the time at which the delay to start time expires. The programmed start time is determined by entries made in Displays #90, #91, and #92. The delay to start time is determined by the entry in Display #310 of the Start Time Delay configure option. These input displays are illustrated in Table 3-6, on page 3-42.

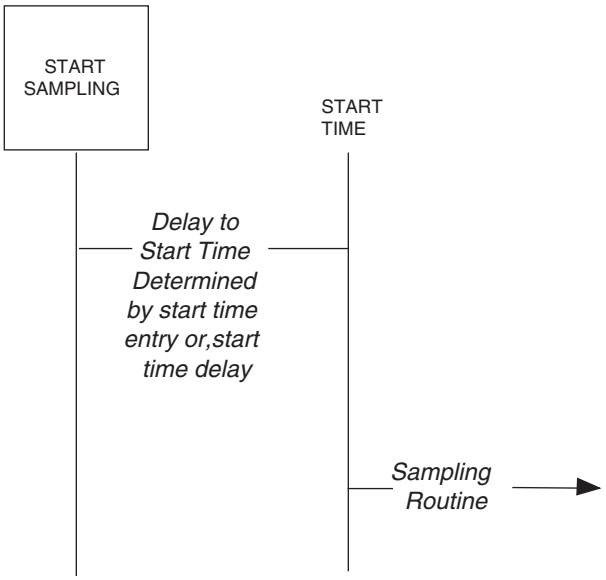


Figure 3-6 Simplified Start Time Diagram

Table 3-6 Start Time Displays

ENTER START TIME? [YES, NO]	**Display #90**
TAKE FIRST SAMPLE AT HH:MM DD-MMM	**Display #91** **(time-paced sampling)**
START FLOW COUNT AT HH:MM DD-MMM	**Display #92** **(flow-paced sampling)**
STORM ENABLED AFTER HH:MM DD-MMM	**Display #93** **(storm-paced sampling)**

Start Time Delay display
(Configure Sequence)

---- MINUTE DELAY TO START (0 - 9999)	**Display #310** **(Start Time Delay configure option)**

☑ *Note*

Unless the sampling routine contains a programmed start time (Displays #91 or #92), the sampler will delay the start time according to the amount of time specified in the Start Time Delay configure option. A programmed start time entry always overrides any settings made in the Start Time Delay configure option.

Isco Flow Meters and Flow Loggers provide two essential functions for certain sampling applications. They send flow-pacing signals — flow pulses — to the sampler for flow-paced sampling. The second function provides disable (inhibit) or enable signals to the sampler. A sampler receiving a disable signal will suspend the sampling routine until it receives an enable signal.

The sampler will *disregard* a disable signal received from a flow meter during the delay to start time. If the sampler is disabled when the start time occurs, it will suspend the routine until it is enabled. Once enabled, the sampler will begin the time or flow intervals. The sampler will initiate a sample event when enabled for all time-paced routines. For flow-paced routines, it will initiate a sample event when the sampler is configured to take a sample upon enable in the Enable Pin configure option (Section 3.10.14).

If the sampler is enabled when the start time occurs, it will begin the routine. The sampler will initiate a sample event at the start time for all time-paced routines. It will initiate a sample event at the start time for flow-paced routines when configured for sample at start time in the Flow Mode configure option (Section 3.10.10). Refer to Figure 3-7, on page 3-45. The diagram shows the sampler's response when enabled or disabled at the start time for most basic and extended mode routines.

3.12.2 Nonuniform Times and Disable Signals

Figure 3-8, on page 3-46, diagrams the sequence of events preceding a routine programmed for nonuniform clock times. Nonuniform clock time programming allows you to enter a specific time and date for each sample event. Samplers programmed with nonuniform clock times may skip a number of samples if disabled for long periods. If the sampler is disabled and subsequently enabled, it will initiate only one event to compensate for the skipped sample events even if several sample event times have been passed.

> ☑ ***Note***
>
> Nonuniform clock time programming is designed to replace flow-pacing when a flow meter is not available at the site. Before using a sampler programmed for nonuniform clock times with a flow meter, be sure flow-pacing is not a more appropriate application.

3.12.3 Manual Sample Key and Programmed Start Times

The sampler will disregard the MANUAL SAMPLE key during the delay to start time and during the disable period. The periods where the sampler disregards disable signals (Delay to Start) and the MANUAL SAMPLE key (when disabled) appear in Figures 3-7 and 3-8.

Entries made in the Start Time Delay configure option affect the start times. See Section 3.10.13.

3.13 Foreign Languages and Metric Units

The 3710 Sampler provides displays in French, Spanish, and German. Additionally, it supports entries in metric units of measure. Metric units include volumes in milliliters, suction head and suction line length in decimeters, and suction line ID in millimeters.

Samplers using French, Spanish, and German language displays support metric units for suction line and suction head measurements. Samplers operating with English displays support either English or metric units for suction line and suction head measurements. (Sample volumes are always entered in milliliters, regardless of the selected language.)

To program the sampler for foreign language displays, begin by placing the sampler in standby. Then, access the language programming sequence by pressing the STOP key five times. The standby display will be replaced by the input display illustrated below.

```
[English, German,
Spanish, French]
```

Select the preferred language from this display. If you select French, Spanish, or German, the sampler will automatically convert English units of measure to metric units and return to standby. If you select English, the input display shown below will appear. Select the units of measure from this display. After you've made the selection, the sampler will convert the units of measure as required and return to standby

```
[U.S., Metric]
    Units
```

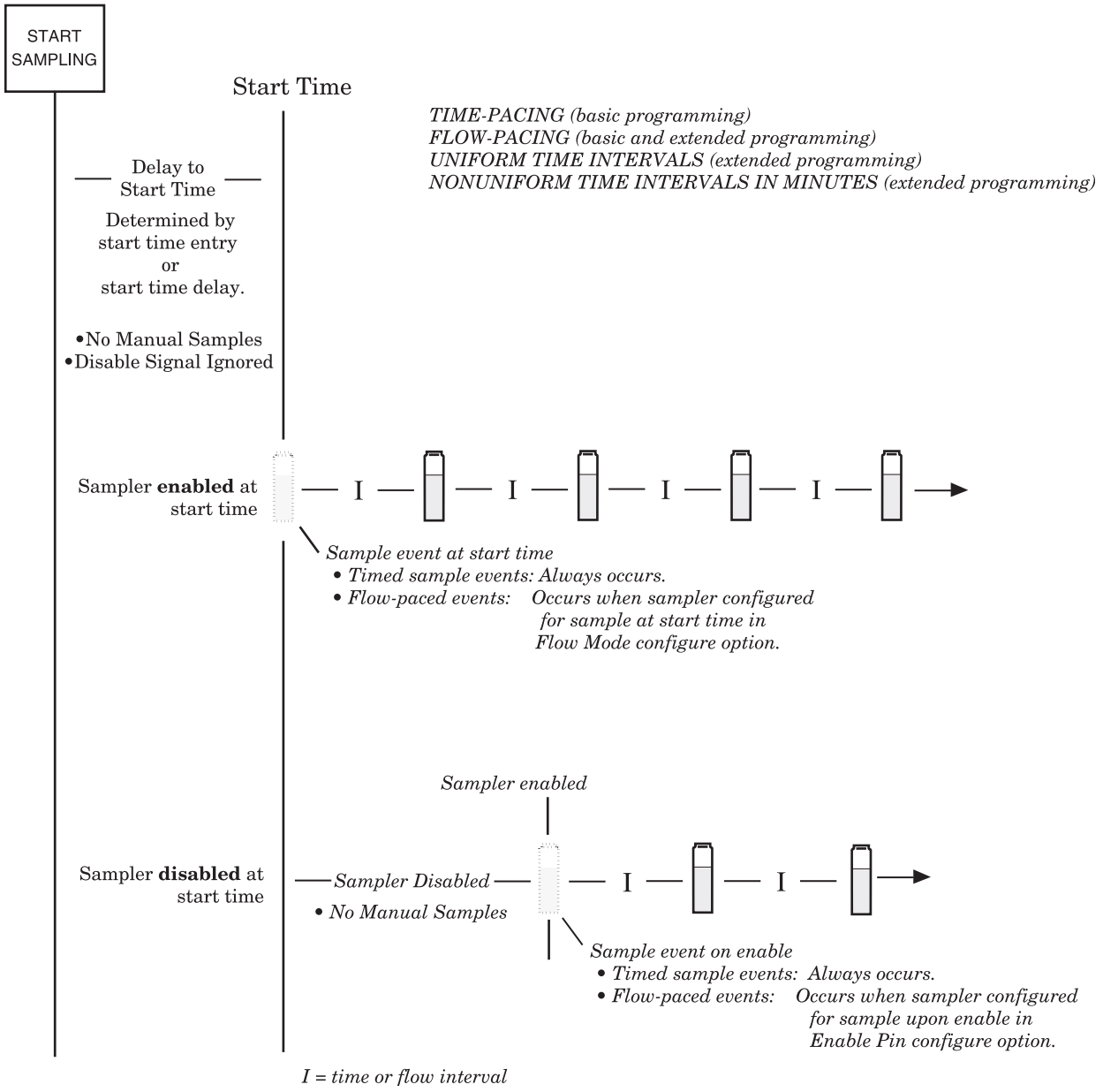


Figure 3-7 Start Time Diagram

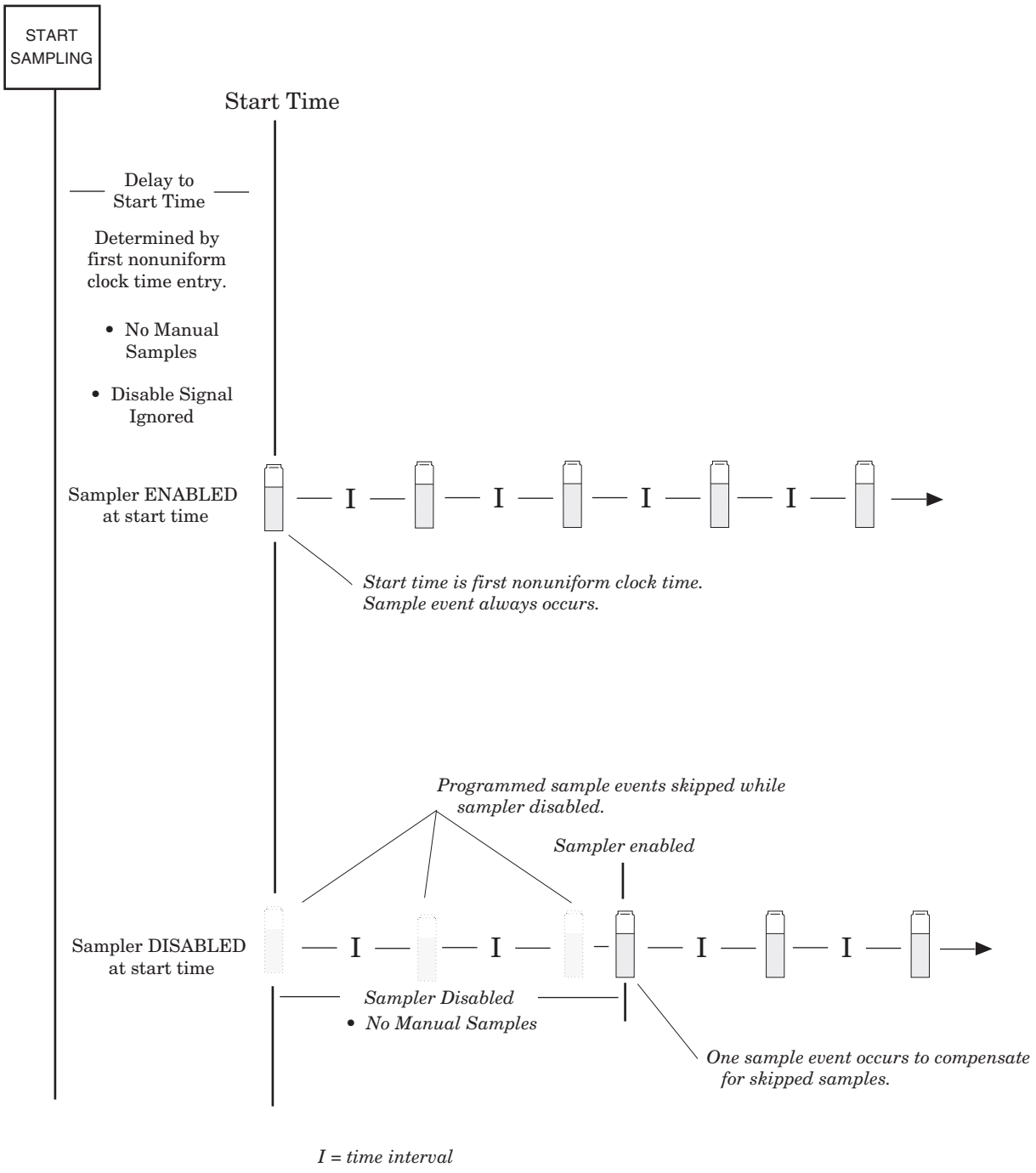


Figure 3-8 Start Time Diagram for Nonuniform Clock Time Routines

3.14 Programming Examples

The examples throughout this section demonstrate the steps used to program the sampler for several different sampling routines in the extended programming mode. Each programming example concludes with the run state displays that appear for that routine. The examples assume you are familiar with the functions of the keys as discussed in Sections 3.7.2 and 3.7.6.

The following example programs the sampler to take 12 time-paced 500 ml samples. Samples are to be taken at uniform time intervals of 30 minutes starting at 8:00 a.m. on the following day.

Example: Extended Time-Paced Sampling

1. Press ENTER/PROGRAM to access the interactive state.

```
. . . STANDBY . . .
10:34:50  19-APR-04
```

2. Access the program sequence by selecting "PROGRAM."

```
[PROGRAM, CONFIGURE]
      SAMPLER
```

3. Select "TIME."

```
[TIME, FLOW]
PACED SAMPLING
```

4. Select "UNIFORM."

```
[TIME, FLOW]
PACED SAMPLING
```

5. Enter "0" to set the hours at zero. Press ENTER/PROGRAM to store the number "0" and move to the minutes entry.

```
     SAMPLE EVERY
0 HOURS,  10 MINUTES
```

6. Enter "30" to set the minutes entry to 30.

```
     SAMPLE EVERY
0 HOURS,  30 MINUTES
```

7. Enter the number of samples to be collected: "12."

```
   12  COMPOSITE
SAMPLES ( 0-470)
```

8. Enter "500" to set the sample volume at 500 ml.

```
  SAMPLE VOLUMES OF
500 ml EACH  (10 - 780)
```

9. Select "YES."

```
ENTER START TIME?
    [YES, NO]
```

10. Enter the start time and date: 8:00 on April 20.

```
TAKE FIRST SAMPLE AT
   8:00   20-APR
```

After this message is displayed briefly, the sampler will automatically return to the standby state.

```
PROGRAMMING SEQUENCE
   COMPLETE . . .
```

When the sampler is properly installed, press the START SAMPLING key to run the program.

Example: Extended Time-Paced Sampling (Continued)

```
  . . . STANDBY . . .
10:37:23    19-APR-04
```

This display appears as the sampler counts down the time remaining to the start time. The first line reports the number of the upcoming sample event and the total number of sample events for the routine. The second line reports the start time at the left and the current time on the right.

```
     SAMPLE 1 OF 12
AT 8:00      10:38:07
```

When the start time occurs, the sampler will take the first sample. The sample event cycle begins with a pre-sample purge. During the purge, the display indicates the sample event number and the number of sample events for the routine.

```
     SAMPLE 1 OF 12

```

As soon as the pump runs forward to deliver the sample volume, the message on the second line appears and remains through the post-sample purge.

```
     SAMPLE 1 OF 12
     PUMPING 500 ml
```

This display appears when the post-sample purge from the previous sample event is completed. It indicates the number of the upcoming sample event. The second line displays the scheduled time for the next event on the left. The current time is displayed on the right.

```
     SAMPLE 2 OF 12
  AT 8:30     8:01:11
```

The cycle of displays is repeated until the sampling routine is done.

↓
↓

When the routine is completed, this message appears. It reports the status of the routine (“DONE”), the total number of sample events, and the current time and date.

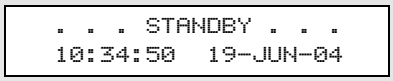
```
 DONE . . . 12 SAMPLES
2:10:35        20-APR-04
```

The following example programs the sampler to take time-paced samples at nonuniform time intervals. This example assumes the sampler is connected to a Liquid Level Actuator which will inhibit the sampler until the liquid level rises to contact the Actuator probe.

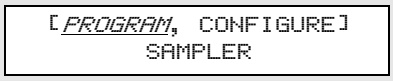
The sampler is to take 20, 100 ml samples: the first samples are to occur at 10 minute intervals for one hour, the following samples at 20 minute intervals for one hour, and the remaining samples at 30 minute intervals. Although this example assumes that nonuniform times are being used with the Actuator, uniform time intervals or flow intervals can be used with the Actuator as well.

Example: Nonuniform Time-Paced Sampling

1. Press ENTER/PROGRAM to access the interactive state.

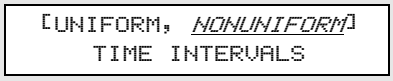


2. Access the program sequence by selecting "PROGRAM."

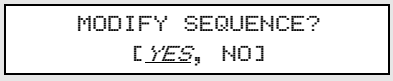


3. Select "TIME."

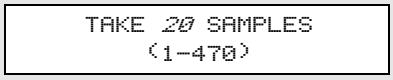
4. Select "NONUNIFORM."



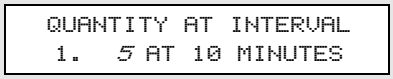
5. Select "YES" to modify the sequence of nonuniform time entries.



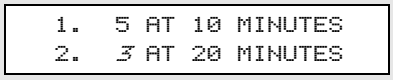
6. Enter the total number of samples: "20." This entry should always include the sample taken at the start time.



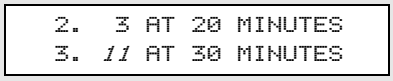
7. Enter the number of samples to occur at the first interval. The sampler is to take samples at 10 minute intervals for one hour or 6 samples in the first hour. Since the first sample is taken at the start time, the remaining five samples will occur at the 10 minute intervals.



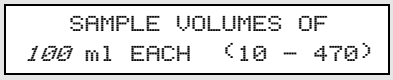
8. When you have completed the first entries, the display will "roll" to move the first interval entries to the first line, and add the second line entries for the next series of samples and intervals. Enter the next entries: "3" samples at "20" minutes.



9. Enter the third set of samples and intervals, "11" samples at "30" minutes.



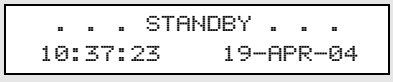
10. Enter "100" to set the sample volume at 100 ml.



11. Select "NO."

After this message is displayed briefly, the sampler will automatically return to the standby state.

12. Press the START SAMPLING key to run the program.



Example: Nonuniform Time-Paced Sampling (Continued)

This display appears while the actuator is inhibiting the sampler. The second line indicates the current time and date.

```
   SAMPLER INHIBITED!
 10:35      20-APR-04]
```

This display appears when the sampler becomes enabled and counts down the time remaining to the start time. The first line reports the number of the upcoming sample event and the total number of sample events for the routine. The second line reports the start time at the left and the current time on the right.

```
     SAMPLE 1 OF 20
 AT 11:26      11:25:47
```

13. When the start time occurs, the sampler will take the first sample. The sample event cycle begins with a pre-sample purge.

```
     SAMPLE 1 OF 20
```

As soon as the pump runs forward to deliver the sample volume, the message on the second line appears. This message remains through the post-sample purge.

```
     SAMPLE 1 OF 20
     PUMPING 100 ml
```

This display appears when the post-sample purge from the previous sample event is completed. It indicates the number of the upcoming sample event. The second line displays the scheduled time for the next event on the left; the current time is displayed on the right.

```
     SAMPLE 2 OF 20
 AT 11:36:     11:26:11
```

The cycle of displays is repeated until the sampling routine is done.

```
              ↓
              ↓
```

When the routine is completed, this message appears. It reports the status of the routine (“DONE”), the total number of sample events, and the current time and date.

```
  DONE . . 20 SAMPLES
8:10:35        21-APR-04
```

Nonuniform times can be entered in either the method shown in the previous example or by specifying a clock time and date for each sample. The abbreviated example below shows the displays used to enter the clock times. (The type of display, clock time or minutes, used in the program sequence is controlled by the settings in the Nonuniform Times configure option; you must specify either clock time or minutes.)

Example: Entering Nonuniform Times as Specific Clock Times

1. Enter the time and date for the first sample event. Times and dates are entered on the second line of the display.

```
TAKE SAMPLES AT
1. 06:00 19-APR
```

2. Enter the time and date for the second sample event. The controller will guess a time at the hour succeeding the previously entered time.

```
1. 06:00 19-APR
2. 07:00 19-APR
```

3. Enter the time and date for the third sample event.

```
2. 06:30 19-APR
3. 07:00 19-APR
```

4. Continue to enter times and dates for each sample event.

↓
↓

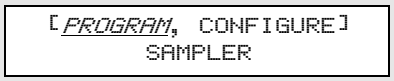
The next example programs the sampler to take time-paced 200 ml samples at uniform time intervals of 15 minutes starting at 6:00 a.m. on the following day. The sampling is to continue from 6:00 a.m. until 8:00 a.m. The sampling will resume again at 11:00 a.m. and continue until 1:30 p.m. It will pause until 4:00 p.m. and continue until 6:00 p.m.

When the sampling is stopped at 6:00 p.m., 24 to 29 samples will have been taken. However, in this particular application, the number of samples is not important, so the sampler will be instructed to take samples indefinitely. This is done by entering "0" in the Number of Samples display as demonstrated in step 7 below. Note: The Sampling Stops and Resumes configure option has settings which allow you to take a sample at the stop and resume times. See Section 3.10.12.

Example: Extended Time-Paced Sampling Using Stops and Resumes

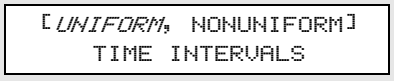
1. Press ENTER/PROGRAM to access the interactive state.

2. Access the program sequence by selecting "PROGRAM."

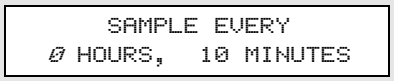


3. Select "TIME."

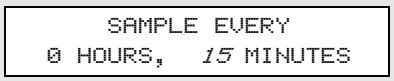
4. Select "UNIFORM."



5. Enter "0" to set the hours at zero. Press ENTER/PROGRAM to store the number "0" and move to the minutes entry.



6. Enter "15" to set the minutes entry to 15.

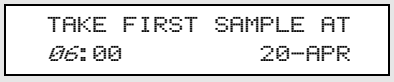


7. Enter "0" so that the sampler will take samples until the last stop time or until the shut-off float terminates the sampling routine.

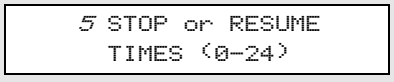
8. Enter "200" to set the sample volume at 200 ml.

9. Select "YES."

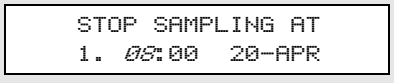
10. Enter the start time and date of the sampling program: 6:00 a.m. tomorrow.



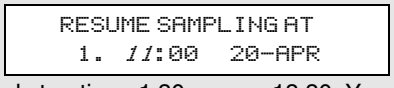
11. Enter "5." There are three stop times and two resume times.



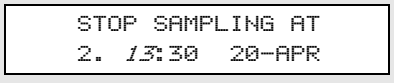
12. Enter the time and date of the first stop time: 8:00 a.m.



13. Enter the time and date the program should resume: 11:00 a.m.



14. Enter the time and date of the second stop time: 1:30 p.m. or 13:30. You must enter the times in military time.



15. Enter the time and date the program should resume: 4:00 p.m. or 16:00 in military time.

Example: Extended Time-Paced Sampling Using Stops and Resumes

```
RESUME SAMPLING AT
 2. 16:00  20-AP
```

16. Enter the final stop time: 6:00 p.m. or 18:00 in military time.

```
STOP SAMPLING AT
3. 18:00  20-APR
```

After this message is displayed briefly, the sampler will automatically return to the standby state.

```
PROGRAMMING SEQUENCE
  COMPLETE . . .
```

17. Press the START SAMPLING key to run the program.

```
. . . STANDBY . . .
10:37:23    19-APR-04
```

This display appears as the sampler counts down the time remaining to the start time. The first line reports the number of the upcoming sample event. The question marks, in the upper right, appear for routines which will take an indeterminate number of samples. The routine will terminate when the float shut-off is triggered. The second line reports the start time at the left and the current time on the right.

```
 SAMPLE 1 OF  ? ? ?
AT 6:00      10:38:07
```

When the start time arrives, the sampler will take the first sample. The sample event cycle begins with a pre-sample purge.

```
 SAMPLE 1 OF  ? ? ?
```

As soon as the pump runs forward to deliver the sample volume, the message on the second line appears. This message remains through the post-sample purge.

```
 SAMPLE 1 OF  ? ? ?
  PUMPING 500 ml
```

This display appears when the post-sample purge from the previous sample event is completed. It indicates the number of the upcoming sample event. The second line displays the scheduled time for the event on the left. The current time is displayed on the right.

```
 SAMPLE 2 OF  ? ? ?
AT 6:15     8:01:11
```

The cycle of displays is repeated until the sampling routine is done.

↓
↓

When the routine is completed, this message appears. It reports the status of the routine (“DONE”), the total number of sample events, and the current time and date.

```
DONE . . . 26 SAMPLES
18:10:35     21-APR-04
```

Example: Program Started Later Than Programmed Start Time

This display informs you of the expired start time. The sampler presents this display for a short time, then advances to the next display.

```
PAST START TIME . . .
```

This display reports the number of samples that will be skipped if you do not change the start time; it appears only if more than one sample event time has passed.

```
1  SAMPLES WILL BE
      SKIPPED
```

1. Select "YES" if you want to change the start time. Select "NO" if missed samples are acceptable.

```
CHANGE START TIME?
    [YES, NO]
```

Display 142

2. This display appears when you select "YES" in display #142 and a sample event is to occur at the start time. Enter the new start time.

```
TAKE FIRST SAMPLE AT
  12:30      19-JUN
```

Display 93

3. This display appears when you select "YES" in display #142 and no sample is to occur at the start time for a flow-paced sampling routine. Enter the new start time.

```
START FLOW COUNT AT
  12:30      19-JUN
```

Display 9

Example: Program Started Later Than Programmed Stop Time

This display informs you of the expired stop time. The sampler presents this display for a short time, then reverts to standby.

```
PAST STOP TIME . . .
  PLEASE REPROGRAM
```

You must access the program sequence to change the expired stop and resume times. Once you've made the changes, start the routine again with the start sampling key.

```
  . . . STANDBY . . .
10:22:34      21-JUN-04
```

3.15 Standby State

A sampler in the standby state is waiting for your instructions. From standby, you can start or resume a sampling program, access the program or configure sequences, take manual samples, and use the DISPLAY STATUS key to review program settings or the results of a sampling routine.

A sampler in standby uses a number of displays to communicate its status. Some of these displays are associated with the function of a specific key; other displays are used to notify you

that a sampling program is done, halted, or has encountered a problem. The standby state displays and valid keys are discussed below.

3.15.1 Standby Display

When you first turn the sampler on, the sampler "wakes up" in the standby state. The standby display, shown below, simply informs you that the sampler is in standby and reports the current time and date.

```
. . . STANDBY . . .
10:37:23    19-APR-04
```

3.15.2 Operable Keys in Standby State

At this point, the following keys are operable: ON/OFF, PUMP REVERSE, PUMP FORWARD, START SAMPLING, MANUAL SAMPLE, DISPLAY STATUS, and ENTER/PROGRAM.

Program Halted – A sampling program can be halted with either the STOP or EXIT PROGRAM key; if this occurs, the sampler will display the halt message shown below. If you halt the program to take a manual sample or to change a setting in the program or configure sequence, the sampler will return to standby. If this is the case, you will not be able to use the RESUME SAMPLING key.

```
. . . PROGRAM HALTED .. .
 10:37:33    19-APR-04
```

Each operable key is listed and discussed below.

On/Off – When in the standby state, this key simply shuts the sampler off.

PUMP FORWARD and PUMP REVERSE – The PUMP FORWARD and PUMP REVERSE keys run the pump forward or in reverse until you interrupt it with the STOP key. While the pump is running, one of the two messages below is displayed, depending on the pumping direction.

```
PUMPING FORWARD . . .
```

```
PUMPING REVERSE . . .
```

When you press the STOP key, the sampler will display a message similar to the one shown here. This message indicates the total number of pump counts that occurred while the pump was running. This information can be used to set the desired number of purge counts required to purge the suction line. See Section 3.10.16. Press any key, except STOP and ON/OFF, to return to the standby display.

```
311 COUNTS FORWARD
```

Manual Sample – You can take manual samples in standby by pressing the MANUAL SAMPLE key. After you press the MANUAL SAMPLE key, the sampler will deliver the programmed sample volume. A manual sample delivers the sample volume currently entered as a programmed setting, and includes the pre-sample and post-sample purges. It will also include any programmed rinses and retries. The sampling process can be stopped with the STOP key at any time. If you press the MANUAL SAMPLE key while a sampling program is in progress, the manual sample will be counted as one of the programmed samples.

While the sample is being delivered, the sampler displays a message similar to the one below. The second line will not appear until the pump begins to pump forward to deliver the sample. The display will revert to standby after the manual sample has been delivered.

```
. . . MANUAL SAMPLE . . .
    PUMPING  200 ml
```

Start Sampling – Once you have programmed and configured the sampler, use the START SAMPLING key to run the sampling program. There are two instances where the sampler will not be able to run the program immediately. These occur when the program has been started after the programmed start time or after one or more programmed stop times.

When you press the START SAMPLING key after a program has been halted, the sampler will give you the choice between resuming the program and starting the program:

```
[START, RESUME]
SAMPLING PROGRAM?
```

Select “START” to start the program from the beginning. Select “RESUME” to resume the program at the point at which it halted. If you do not make a selection from this display within 60 seconds, the sampler will automatically select the currently blinking response. START will re-initialize the display status memory.

Resume Sampling – To resume or restart the program, press the RESUME SAMPLING or START SAMPLING key. When you press the RESUME SAMPLING key, the program will resume at the point it was halted. The display must read “PROGRAM HALTED” for the RESUME SAMPLING key to be active. If any samples were missed during the time the program was halted, the sampler will inform you with the message shown here. The sampler will initiate one sample event if one or more sample events were missed.

```
2 SAMPLES WILL BE
    SKIPPED
```

3.15.3 Additional Displays

There are three additional displays used in the run state. These displays are discussed below.

Done – The sampler will inform you it has completed a program by displaying the message illustrated below. This message is displayed until you press any key, at which time the display will return to the standby message.

```
DONE . . .      24 SAMPLES
10:37:33         19-APR-04
```

Problem Occurred – You will be informed that a problem was encountered during the sampling routine with the message illustrated below. This display will alternate with the "DONE" display at approximately three second intervals until you press any key.

```
PROBLEM OCCURRED . . .
 PRESS DISPLAY STATUS
```

Float Tripped – 3710 Samplers use the display below to notify you that the program finished because the shut-off float was tripped. This display alternates with the "DONE" display at approximately three second intervals.

```
FLOAT/WEIGHT TRIPPED
```

The message shown above is also used in 3700 Series refrigerated samplers. The refrigerated samplers use a weight table to determine when the composite bottle becomes full.

3.16 Display Status

You can access a summary of the current program settings and the results of the most recent sampling routine with the DISPLAY STATUS key. This key is valid in both the run and standby states. The summary of the program settings consists of a number of informational displays describing the settings. The results of the sampling program include information about each sample event and reports problems encountered during the program. This information remains in memory until you start another program.

You can retrieve this information with Teledyne Isco's Field Printer (no longer sold by Teledyne Isco) or a laptop computer running Teledyne Isco's Samplink software. Both methods produce two reports which contain the sampler ID, current status, program settings, and sampling results.

If a sampling routine is in progress when you press the DISPLAY STATUS key, the sampling routine will be suspended. No samples will be taken until you exit Display Status.

If the pump count reaches the number entered for the Tubing Life Warning setting, the Pump Tubing Warning will be displayed. An illustration of the warning is shown below.

```
WARNING: REPLACE
PUMP TUBING!
```

3.16.1 Reviewing or Printing Program Information

The sampler tracks and reports the following items:

- program start time and date
- sample volume
- source of each sample event
- cause of any missed samples
- start time of each sample event
- number of pump counts to liquid detection for each event
- time the routine was completed
- sampler ID
- current time and date
- program settings

Each of these items is illustrated in Example *Reviewing the Sampling Results*.

When you press DISPLAY STATUS, the display shown below follows the pump tubing warning. It allows you to review the program settings or sampling results.

```
[REVIEW, PRINT]
PROGRAM INFORMATION
```

Display #148

Example: Reviewing the Sampling Results

1. Press display status to view the results of the sampling program.

```
DONE . . .  24 SAMPLES
12:34:50     20-JUN-04
```

2. Select "REVIEW."

```
[REVIEW, PRINT]
PROGRAM INFORMATION
```

3. Select "RESULTS."

```
REVIEW PROGRAM [NO,
SETTINGS, RESULTS]
```

4. This display reports the start time and date of the program. Press ENTER/PROGRAM to advance to the next display.

```
PROGRAM STARTED AT
5:30      19-JUN-04
```

5. This display reports the nominal sample volume. Press ENTER/PROGRAM to advance to the next display.

```
200 ml SAMPLES
```

Example: Reviewing the Sampling Results (Continued)

This display reports the number of each sample event. It also reports the source of the event; in this case, the sample was taken at the start time. Press ENTER/PROGRAM to advance to the next display.

```
SAMPLE: 1 OF 24
SOURCE: START
```

6. This display reports the initiation time of the sample and the number of pump counts to liquid detection in the sample delivery cycle. These values indicate changes in the sampling conditions – head changes, for example. Press ENTER/PROGRAM to advance to the next display.

```
TIME: 5:30      19-JUN-04
COUNTS:          280
```

7. Press ENTER/PROGRAM to continue to review the information for the remaining sample events.

↓
↓

8. Press ENTER/PROGRAM to return to the "REVIEW PROGRAM" display.

```
PROGRAM FINISHED AT
12:00       20-JUN-04
```

9. Select "NO" to return to stand.

```
REVIEW PROGRAM [NO,
SETTINGS, RESULTS]
```

```
. . . STANDBY . . .
15:39:50      19-JUN-04
```

Review – Select "REVIEW" to review the program settings and sampling results. The sampler will present the display shown below. Use this display to leave the display status procedure or to review the program settings or sampling results.

```
REVIEW PROGRAM  [NO,
SETTINGS, RESULTS]
```

Display #150

No – Select "NO" to return to the previous operating state. If you entered display status from standby, the standby message will reappear. If you entered display status from the run state, the sampling routine will resume.

Settings – Select "SETTINGS" to review the program settings. Use the LEFT ARROW, RIGHT ARROW, and the ENTER/PROGRAM keys to move through the sampling settings. When the RIGHT ARROW or the ENTER/PROGRAM key is pressed at the last settings display, the "REVIEW PROGRAM" display will reappear.

Results – Select "RESULTS" to review the results of the sampling routine. The first display reports the time and date the sampling program started. Use the LEFT ARROW, RIGHT ARROW, and ENTER/PROGRAM keys to move through the results. If the routine was finished at the time you pressed the DISPLAY STATUS key, the last display will report the time and date the routine ended.

Print – Select "PRINT" from Display #148 to send the current status, program settings, or sampling results to the Teledyne Isco Field Printer. For information on the reports produced by the Field Printer, refer to the *Field Printer Instruction Manual*.

When you select "PRINT," Display #149 appears. Use this display to select the settings or results report. (The sampler will interrupt the reports to take a sample, if necessary.) Select "NO" to return to standby.

```
PRINT PROGRAM [NO,
SETTINGS, RESULTS]
```

Display # 149

The sampler will display one of two messages as it sends the data to the printer. The first message informs you that the transmission is in progress. The second message is a warning which informs you that the sampler is unable to detect the printer. If you see the warning message, check the cable connections between the printer and the sampler.

```
. . . PRINTING . . .
PROGRAM INFORMATION
```

```
PRINT ABORTED
NO PRINTER DETECTED!
```

☑ *Note*

The Teledyne Isco Field Printer is no longer sold. These instructions are intended for users who still own and use Field Printers.

Source of Sample Event – The display illustrated in step 5 of Example *Reviewing the Sampling Results*, on page 3-58, shows the sample event number and the source of the sample event. Source refers to the programmed or configured setting that initiated the sample event. For example, the sampler will report "TIME" as a source if the sample was taken as one of the program's time-paced samples. Eight sources are tracked and reported for a composite sampler:

Time - The sample event was one of the program's time-paced samples.

Flow - The sample event was one of the program's flow-paced samples.

Start - The sample event was initiated at the program's start time.

Resume - The sample event was initiated to compensate for a missed sample which should have occurred while the sampler was halted. If more than one sample event was missed, only one sample will be taken.

Power - The sample event was initiated to compensate for a missed sample which should have occurred while the sampler was without power. If more than one sample was missed, only one sample will be taken.

Enable - The sample event was initiated when the sampler became enabled by a device connected to pin F of the flow meter connector, generally an Isco Flow Meter or Liquid Level Actuator. This source is also reported when the sample was initiated at a programmed resume time. Two different configure option settings control this event: the Sample Upon Enable setting in the Enable Pin configure option and the Sample at Resume setting in the Sampling Stop/Resume configure option.

Manual - The sample event was initiated with the MANUAL SAMPLE key and was counted as one of the programmed sample events.

Disable - The sample event was initiated when the sampler became disabled by a device connected to pin F of the flow meter connector. This source is also reported when the sample was taken at a programmed stop time. Two different configure option settings control this event: the Sample Upon Disable setting in the Enable Pin configure option and the Sample at Stop setting in the Sampling Stop/Resume configure option.

3.17 Error Messages and Missed Samples

The probable cause of any missed sample is reported after the sample number/source display. A missed sample display is illustrated below.

```
SAMPLE MISSED:
NO LIQUID DETECTED!
```

Ten causes are tracked and reported:

Pump "STOP" Key Hit! - The sampler was halted with the STOP key during the sample event.

Pump Jammed! - The sampler was unable to take the sample because the pump jammed.

Started Too Late! - The sampling routine was started after the programmed start time for the first sample. This message is reported for all samples skipped because of an expired start time.

Program Halted! - The sampling routine was interrupted by the STOP or EXIT PROGRAM key when the sample event was to occur.

Power Lost! - The sampler was unable to take the sample because the sampler's power source was disconnected.

Sampler Inhibited! - The sampler was prevented from taking the sample by an inhibit signal sent to the sampler by an Isco Flow Meter or a Liquid Level Actuator.

Float/Weight Tripped! - 3710 Samplers detect overflow with a liquid level float located at the mouth of the composite bottle. If the liquid level of the bottle raises the float past the trip point, the sampler will interrupt the sample event and record the "Float/Weight Tripped" condition.

No More Liquid! - The sampler was unable to take the sample because, in attempting to take the sample, the sampler pumped all liquid from the flow stream.

No Liquid Detected! - The sampler was unable to take the sample because no liquid was detected.

Sampler Shut "Off"! - The sampler was unable to take the sample because it was halted with the ON/OFF key during the sample event.

3.18 Run State

A sampler in the run state is executing the sampler's instructions according to the settings you've entered in the program and configure sequences.

To start a sampling program and place the sampler into the run state, press the START SAMPLING key. While running the sampling program, the sampler will present a number of displays which allow you to monitor the sampler's progress. The displays are listed with a brief explanation in Table 3-7, on page 3-63.

If a problem is encountered while running a sampling routine which has resulted in missed samples, an asterisk will appear in the lower right corner of the display, as illustrated below.

```
     SAMPLE 17 OF 48
AT  6:00       5:42:33 *
```

There is one instance where the refrigerated sampler will enter the run state after the START SAMPLING key is pressed, but will not begin the sampling program. If the sampler is interfaced with a Liquid Level Actuator, or other equipment capable of transmitting an inhibit signal, the sampler will not begin the program until the inhibit signal is suspended. The sampler will use the following display to inform you of these conditions.

```
   SAMPLER INHIBITED!
 10:32          20-APR
```

Table 3-7 Run State Displays: Composite Sampling

SAMPLE 1 OF 12 AT 6:00 5:43:33	Indicates the sample number of the next sample and the total number of samples for time-paced routines. The current time is shown in the lower right corner.
SAMPLE 1 OF 12 AFTER 10 PULSES	Indicates the sample number of the next sample and the total number of samples for flow-paced routines.
SAMPLE 2 OF ??? AT 6:00 5:43:33	Indicates the sample number of the next sample. The question marks indicate the sampler will use the float shut-off to terminate the routine. The second line reports the scheduled time of the upcoming sample event and the current time.
SAMPLE 1 OF ??? AFTER 100 PULSES	Indicates the sample number of the next sample. The question marks indicate the sampler will use the float shut-off to terminate the routine. The second line reports the number of flow pulses remaining until the next sample event.
SAMPLE 2 OF 12 PUMPING 200 ml	Indicates a sample in progress.

3710R/3750 Refrigerated Sampler

Section 4 Options and Interfacing Equipment

This section discusses major options available with the Teledyne Isco 3710R.

4.1 Connections to External Devices

The 3700 Series Samplers can collect samples on a flow-paced basis using flow inputs from an external flow meter. The sampler requires a 5-to-15 VDC pulse of at least 25-millisecond duration to register a flow pulse. Open-channel flow meters are connected to the sampler by attaching a flow meter connect cable to the flow meter connector located on the rear of the sampler. Closed-pipe flow meters are connected to the sampler's Flow Meter port using the Teledyne Isco 4-20 mA Input Interface device (see Appendix B *Accessories*).

Your sampler has an additional connector, labeled "PRINTER," used to connect the sampler to an Isco Field Printer or laptop computer. Both the flow meter connector and the printer connector use the same 6-pin configuration. The printer cable connector accepts both the connector from the field printer and a cable from a field computer or a laptop computer running the Samplink software.

> ☑ ***Note***
>
> The Field Printer has been discontinued and is no longer sold by Teledyne Isco.

4.1.1 Isco Flow Meters and Flow Loggers

You can purchase cables to connect the 3700 samplers to an Isco flow meter, flow logger, or 2100 series flow module. Refer to the *Accessories List* in the back of this manual for details. To make the connection, attach the appropriate cable connector to the flow meter according to directions in the flow meter in instruction manual, attach the other connector to the 6-pin flow meter connector on the rear of the sampler.

> ☑ ***Note***
>
> If a connect cable is not attached to the flow meter or print connectors, be sure that the protective covers are tightly fastened in place.

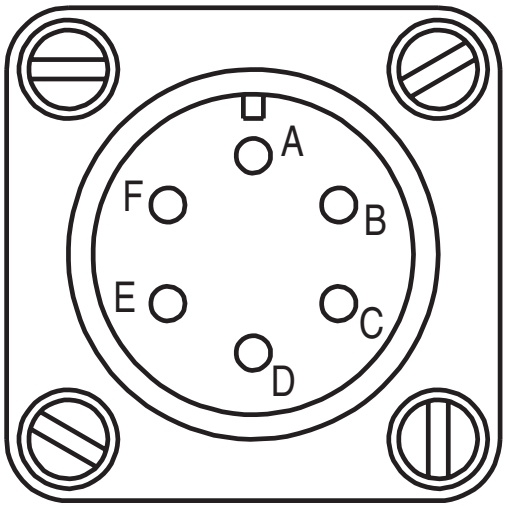


Figure 4-1 6-pin Connector Diagram

Table 4-1 Flow Meter Connector Wiring

A	+12 VDC
B	Common
C	Flow Pulses In
D	Bottle Number Out Master/Slave Out
E	Event Mark Out
F	Inhibit In

Table 4-2 Printer Connector Wiring

A	+12 VDC
B	Common
C	Printer Source
D	Transmit
E	Receive
F	NC

4.1.2 Non-Isco Flow Meters

You can connect certain non-Isco Flow meters directly to a 3710 for flow-paced sampling. The flow meter must have an isolated contact closure of at least 25 milliseconds to provide acceptable flow pulses to the sampler. The frequency of the contact closure must be directly proportional to total flow. Teledyne Isco offers both a connector and cable clamp to connect a non-Isco Flow meter to the 3700 samplers. Connect the flow meter pulse output

to the A and C pins of the 6-pin Flow Meter connector on the 3710 (Figure 4-1). Refer to your flow meter's instruction manual for further details.

Teledyne Isco also offers a connector prewired to a 22-foot (6.7-meter) cable that terminates in two wires. The black wire is connected to pin A; the white wire to pin C.

Note that you will be unable to communicate anything other than the flow pulse contact closure with a non-Isco Flow meter. The non-Isco Flow meter will not be able to interpret event and bottle number information.

If the flow pulse generated by the contact closure on the flow meter is not compatible with Teledyne Isco's standard, contact Teledyne Isco's Special Products Department for an appropriate interface device.

4.1.3 4-20 mA Flow Signals

The 3710 Sampler can also be used with flow meters having other types of outputs, for example, a 4 to 20 mA output directly proportional to the flow rate. However, these flow meters require a special interface device to convert their output signal to one compatible with the 3710 sampler.

The **4–20 mA Sampler Input Interface** converts 4 to 20 mA output signals from both non-Isco Flow meters and closed-pipe flow meters to flow pulses acceptable to the 3710 Sampler.

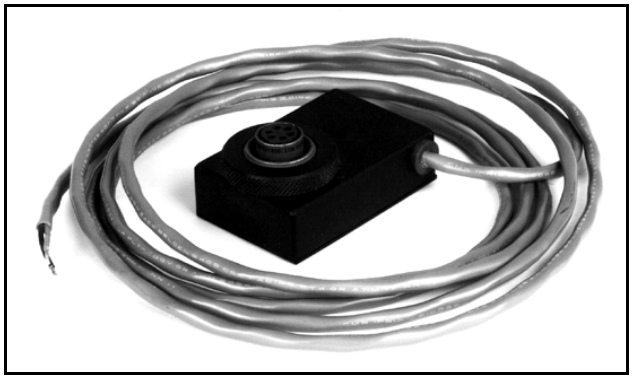


Figure 4-2 4-20 mA Sampler Input Interface

4.1.4 1640 Liquid Level Actuator

The 1640 Liquid Level Actuator is a device used to begin a sampling routine when the liquid level of the sample flow stream reaches a predetermined height. The actuator is used to inhibit sampling according to flow levels; i.e., if the level of the flow stream falls below the actuator's probe, the actuator will inhibit sampling until the level again rises to contact the probe.

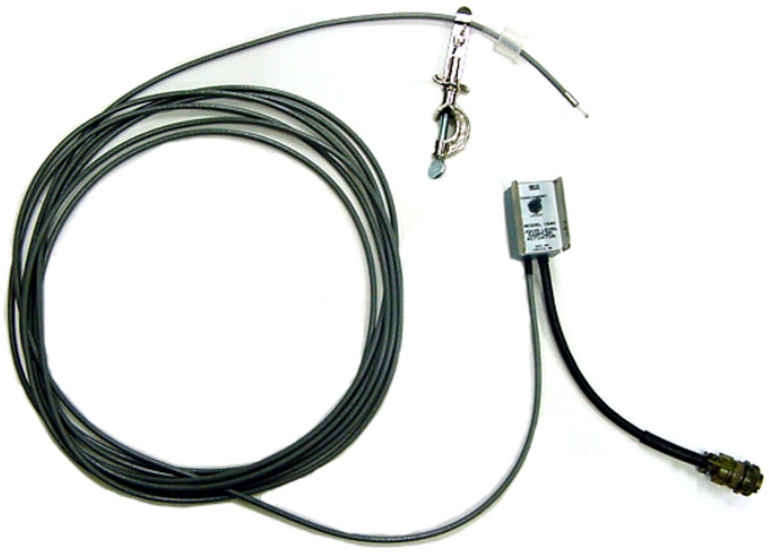


Figure 4-3 1640 Liquid Level Actuator

The actuator can be set to control the sampler in two modes:

Latch Mode – The sampler continues the sampling routine even though the liquid level has receded and liquid no longer contacts the sensor.

Toggle Mode – The sampler will halt the routine when the liquid ceases to contact the sensor.

To connect the actuator to the sampler, attach the actuator cable to the flow meter connector. Refer to Figure 4-1 for the location of the flow meter connector. Refer to the Liquid Level Actuator Instruction Manual for additional information.

The sampler must be configured to respond to the actuator. Refer to the discussion of the Enable Pin configure option (Section 3.10.14).

3710R/3750 Refrigerated Sampler

Section 5 Routine Maintenance and Service

The 3710R/3750 is ruggedly built to withstand difficult field operating conditions and will maintain maximum reliability when these simple maintenance procedures are followed. As with any piece of field operated equipment, preventive maintenance is necessary to keep it functioning properly.

5.1 Weather and Corrosion Resistance

The refrigerator's exterior is fabricated from either Type 304 brushed stainless steel or vinyl clad steel. The remainder of the exposed metal parts are either anodized or Iridited™ aluminum. The controller cover and base are constructed from ABS (acrylonitrile-butadiene-styrene) plastic, as is the bottle locating base. The controller's electronics and mechanisms are protected by a totally sealed Noryl™ (polyphenylene oxide) control box. The control box is rated at NEMA 4X, 6.

The 3710R and the stainless steel 3750 Refrigerator are designed to be operated in relatively hostile environments. They may be directly exposed to wet environments and still function properly. The refrigerator's mechanical and electrical components, and the sampler controller are protected from rain, accidental spray, etc. The 3710VR and the vinyl 3750 Refrigerator offer protection similar to that of the stainless steel model, except to a limited degree. After prolonged exposure, the vinyl clad steel exterior may begin to corrode. This will not cause any functional problems though; only the refrigerator appearance will be damaged.

If the refrigerator is to be operated out-of-doors, in a corrosive atmosphere, or in a wet environment for prolonged periods, it is highly advisable to further protect it with a fabricated shelter or instrument enclosure. Enclosures specifically made for the 3710R/3710VR/3750 are available from COSYSCO (P.O. Box 4837, Walnut Creek, CA 94596, 415-947-5756) and Plasti-Fab (P.O. Box 100, Tualatin, OR 97062, 503-692-5460).

5.2 Cleaning

The following sections present information on cleaning the sample bottles and pump tubing. Information is also included for cleaning the refrigerator's interior, exterior, condenser coil, and bottle locating base.

5.2.1 Tubing

The suction line and pump tubing can be cleaned by placing the end of the suction line in a cleaning solution and pumping this solution through the tubing system using the pump forward and pump reverse keys. Follow with a clean water rinse.

5.2.2 Sample Bottles

The bottles have a wide mouth to facilitate cleaning and can be washed with a brush and soapy water or washed in a dishwasher. The glass bottles can be autoclaved; however, the plastic lids and bottles should **not** be autoclaved.

5.3 Cleaning Protocols for Priority Pollutants

The following sections are excerpted from U.S. Environmental Protection Agency Publications EPA-600/4-77-039 ("Sampling of Water and Wastewater" by Dr. Phillip E. Shelley) to provide an example of sampler cleaning procedures for priority pollutants.

Proper cleaning of all equipment used in the sampling of water and wastewater is essential to ensuring valid results from laboratory analysis.

Cleaning protocols should be developed for all sampling equipment early in the design of the wastewater characterization program. Here also, the laboratory analyst should be consulted, both to ensure that the procedures and techniques are adequate, as well as to avoid including practices that are not warranted in view of the analysis to be performed.

5.3.1 Cleaning Examples

As an example, Lair (1974) has set down the standard operating procedures for the cleaning of sample bottles and field procedures equipment used by USEPA Region IV Surveillance and Analysis field personnel engaged in NPDES compliance monitoring. They are reproduced following for a typical automatic sampler and related sampling equipment.

Teledyne Isco Glass Sample Bottles:

1. One spectro-grade acetone rinse.
2. Dishwasher cycle (wash and tap water rinse, no detergent).
3. Acid wash with at least 20 percent hydrochloric acid.
4. Dishwasher cycle, tap and distilled water rinse cycles, no detergent.
5. Replace in covered Teledyne Isco bases.

Suction Line (1/4 or 3/8 Vinyl):

1. Do not reuse sample tubing. No cleaning required. New sample tubing is to be used for each new sampling setup.
2. Use Teflon tubing where samples for organics are to be collected.

Teledyne Isco Pump Tube:

1. Rinse by pumping hot tap water through tubing for at least 2 minutes.
2. Acid wash tubing by pumping at least a 20 percent solution of hydrochloric acid through tubing for at least 2 minutes.
3. Rinse by pumping hot tap water through tubing for at least 2 minutes.
4. Rinse by pumping distilled water through tubing for at least 2 minutes.

Teflon Tubing:

1. Rinse twice with spectro-grade acetone.

2. Rinse thoroughly with hot tap water using a brush if possible to remove particulate matter and surface film.
3. Rinse thoroughly three times with tap water.
4. Acid wash with at least 20 percent hydrochloric acid.
5. Rinse thoroughly three times with tap water.
6. Rinse thoroughly three times with distilled water.
7. Rinse thoroughly with petroleum ether and dry by pulling room air through tubing.
8. Dry overnight in warm oven (less than 150° F), if possible.
9. Cap ends with aluminum foil.

5.4 Cleaning the Refrigerator

The refrigerator's exterior may be periodically cleaned with soapy water using a sponge or nonmetallic brush to keep it free from corrosive solutions, grease, oil, etc. After cleaning, it should be wiped dry. Automotive wax may be applied to the interior and exterior surfaces of the refrigerator to make them easier to clean and more resistant to corrosion. Do not direct a hose spray toward the underside or into the front grille of the refrigerator. The vacuum formed plastic refrigerator interior may also be cleaned with soapy water as necessary.

Because the refrigerator uses a forced-air system for cooling the compressor and condenser coil; dust, lint, and other debris will be pulled into the unit and will eventually accumulate on the condenser coil and other components in the air circulation path. If the refrigerator is not cleaned periodically, damage due to overheated components may result.

⚠ WARNING

Disconnect the refrigerator's power before performing any service activities

The condenser coil and surrounding areas should be cleaned annually; more frequently under severe operating conditions. To clean,

1. Remove the screws that hold the back panel on to the refrigerator and remove the panel.
2. Vacuum the fan, compressor, and surrounding areas.
3. Check the fan for freedom of movement. Oiling the fan motor is not necessary because the motor bearings are sealed. If the fan motor does not rotate freely, it should be replaced.
4. Replace the back panel.
5. Remove the front grille. Vacuum the condenser coil and surrounding areas.
6. Replace the grille.

5.4.1 Cleaning the Bottle Locating Base and Sample Bottles

The bottle locating base may be cleaned with soapy water and a sponge.

The sample bottles have a wide mouth to facilitate cleaning. The 2.5 gallon glass bottle may be washed with a brush and soapy water then washed in a dishwasher or autoclaved. The 2.5, 4, and 5.5 gallon polyethylene bottles may be washed with a brush and soapy water or washed in a dishwasher, but not autoclaved.

5.5 Pump Tubing

The pump tube serves two functions: it is a pump tube in the peristaltic pump and a distribution tube, routing the sample liquid from the pump outlet to the sample bottle. The pump tube consists of a single piece of medical grade Silastic™ silicone rubber tubing. Medical grade tubing is used because of its superior mechanical properties and because it does not contain any organic materials. Non-medical grade silicone rubber tubing can contain organic vulcanizing agents. During the vulcanizing process, these agents are converted into other compounds which can be leached into the sample. The medical grade silicone rubber tubing supplied by Teledyne Isco for use with the 3710R Sampler **will not** contribute any organic material to the sample.

5.5.1 Inspection of Pump Tubing

The pump tubing is extremely durable. However, the constant mechanical strain placed on the tubing by the peristaltic action of the pump will eventually cause the tubing to fatigue and fail. Inspect the pump tubing periodically for wear inside the pump by removing the cover. Check the tubing for cracks where the pump roller compresses the tubing. Replace it with a new pump tube, if necessary.

⚠ WARNING

Pump may actuate without warning. To avoid injury, sampler must be off when pump housing cover is removed for inspection or tubing replacement.

The inspections should be fairly frequent when the liquid being sampled contains a high percentage of suspended solids. If the liquid is relatively free of solids, the inspections can be less frequent. The Tubing Life configure option reports the number of pump counts elapsed during the life of the pump tube.

☑ Note

The importance of regular tubing replacement cannot be overstated. The key is to replace the tube before failure, not after. When a pump tube ruptures, grit and other abrasive debris can be driven into the pump shaft seal. Over time, this abrasive material will degrade the pump seal, jeopardizing the NEMA 4x 6 rating of the controller.

Failure to maintain the pump tube may result in permanent damage to the sampler. Check the condition of the pump tube regularly and if the tube shows signs of fatigue or wear, replace it immediately. A properly maintained sampler will pro-

vide the years of reliable service that is expected of a Teledyne Isco Sampler.

The amount of tubing (13.5 inches) used in the pump is less than half the total length of the pump tube (47 inches). In some cases, when the tube has not been damaged to the point of leaking, the tube can be used twice by simply turning it around.

☑ Note

The black bands used to assist you in correctly positioning the tubing in the pump and detector are placed on one end only. If you turn the tubing around, you will not be able to use the bands for reference.

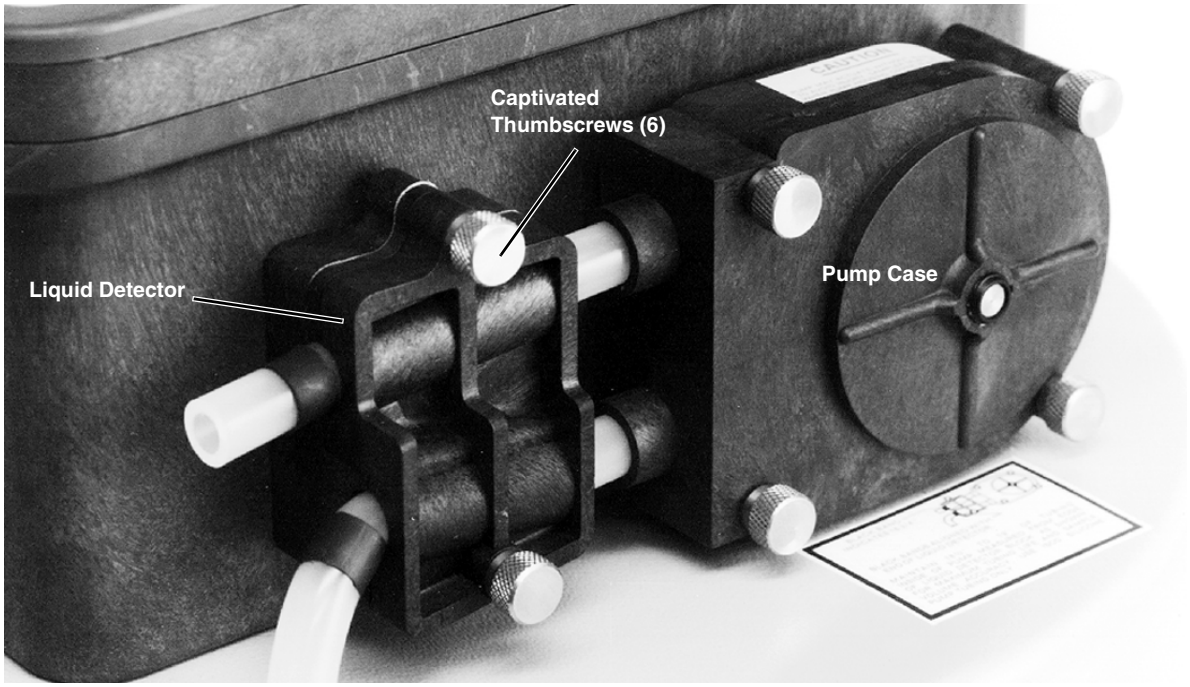


Figure 5-1 Liquid Detector and Pump Case

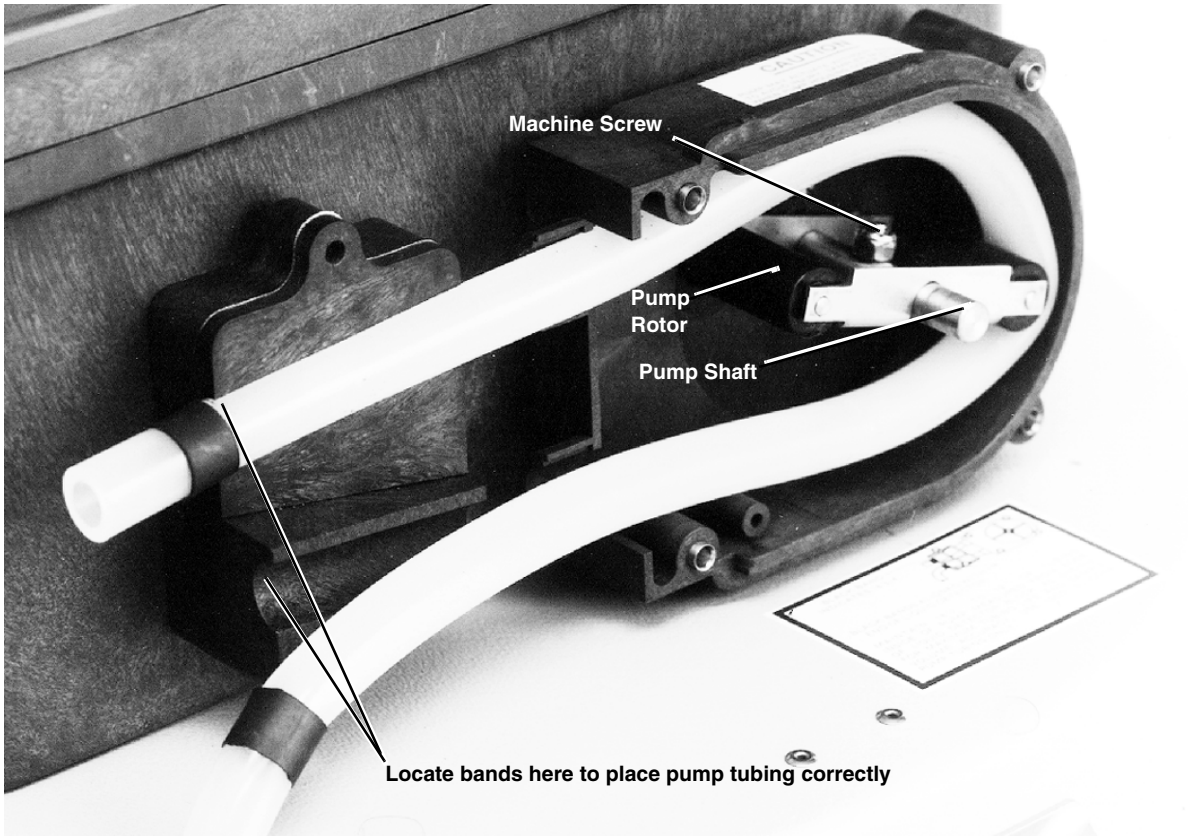


Figure 5-2 Interior of Liquid Detector and Pump Tube

5.5.2 Removing the Pump Tubing

⚠ WARNING

Be sure power is disconnected from the unit before exchanging the pump tubing. The pump is extremely powerful. If the sampler activates the pump while you are manipulating the tubing, serious injury can result.

To remove the tubing:

1. Disconnect power from the unit.
2. Detach the outer cases of the liquid detector and pump by loosening the captivated thumbscrews shown in Figure 5-1. This will expose the pump tubing as shown in Figure 5-2.
3. Pull the tubing away from the detector. Extract the tubing from the pump. The pump rollers can be rotated manually to facilitate the removal of the tubing. After the tubing is removed, clean the interior of the pump case thoroughly.
4. Remove the suction line, if attached, and pull the pump tubing from the pump tube port.

5.5.3 Installing a New Pump Tube

To install new tubing:

1. The pump tube is marked with two black bands. These bands are used to locate the tubing in the detector and pump. Correct placement is critical to prolong the life of the pump tube and to assure efficient operation and accurate sample volumes.
   Facing the liquid detector, place the inner edge of the end band against the upper left inlet of the liquid detector. Place the inner band at the lower outlet of the liquid detector. Figure 5-2 shows the correct placement of the tubing at the liquid detector.
2. Slip the pump tubing under the rollers so that the pump tubing does not interfere with the installation of the outer pump lid.
3. Replace the outer pump lid and tighten the four thumbscrews.
4. Re-check the position of the marker bands and adjust the tubing if the position of the bands indicate the tubing has slipped.
5. Replace the outer case of the liquid detector and tighten the two thumbscrews.
6. Feed the free end of the tube down through the pump tube port.
7. Re-install the suction line, as described in Section 5.6.
8. Reset the Pump Tube count to zero. Refer to the discussion of the *Tubing Life* configure option in Section 3.10.17, on page 3-35.

5.6 Suction Line

It may be desirable to replace the suction line for one of several reasons. The suction line may be worn, cut, contaminated, or otherwise damaged; it should be periodically inspected for damage. In critical sampling, it may be necessary to replace the suction line between sampling programs to avoid cross contamination. When sampling site conditions change, it may be necessary to replace the suction line with a different diameter or type of line (vinyl or Teflon). The vinyl suction line contains a very low PPM (parts per million) level of phenols. If this affects your samples, use the Teflon line.

5.6.1 Cleaning Suction Line

The suction line and the remainder of the pump tube system should be cleaned occasionally as described in Section 5.2.1.

5.6.2 1/4 and 3/8 Inch ID Vinyl Suction Line

The following sections discuss the replacement of the complete suction line-strainer assemblies, the sizing of the suction line, and the assembly and installation of the bulk tubing. The suction line is removed from the pump tubing by detaching the tube coupling, as described in Section 2.2, on page 2-1. If a complete new suction line-strainer assembly of the standard 10 or 25 ft. length is used, it should be installed as described in Section 2.2.

Replacement vinyl suction lines are available from Teledyne Isco in two forms. First, a complete suction line, with strainer and tube coupling, is available in 10 ft. and 25 ft. lengths for each of the 1/4 inch and 3/8 inch ID (Inside Diameter) vinyl suction lines. Second, bulk suction line in the 1/4 inch ID and 3/8 inch ID vinyl tube is available in 100 and 500 ft. rolls.

5.6.3 Bulk Suction Line

If you are using bulk suction line to replace the old line, detach the old line from the tube coupling and remove the strainer. Cut the new suction line to the desired length in one foot increments. The line must be between 3 and 99 feet long. To insure accurate sample volumes, it is important that the line is cut in one foot increments and that the line length is correctly entered in the *Suction Line* configure option (Section 3.10.5, on page 3-25). Screw the strainer into the new suction line. The new suction line can now be installed as described in Section 2.2.

5.6.4 3/8 Inch ID Teflon Suction Line

The suction line is removed from the pump by first loosening the clamp that secures the line to the pump tube and then pulling the suction line out of the pump tube. If a new suction line (either with or without the optional stainless steel strainer) is to be used, it is installed as described in Section 2.2. To install the optional stainless steel strainer, heat the end of the suction line to make it more flexible and carefully screw the strainer's threaded connector into the suction line.

The 3/8 inch ID Teflon suction line is available from Teledyne Isco in line lengths of 10 and 25 feet.

5.7 Internal Desiccant

A humidity indicator, labeled "INTERNAL CASE HUMIDITY," is located in the lower left corner of the control panel. It indicates the amount of moisture present inside the control box. The paper indicator is blue in a dry state.

The control box is a completely sealed unit. It is shipped from the factory with three fresh 4 oz. bags of desiccant installed inside. (The control box does not need to be opened during normal operation.) This desiccant should absorb any moisture which may accumulate in the control box. Thus, the humidity indicator should remain blue under normal conditions. If moisture does accumulate, the numbered areas on the indicator will turn light pink or white, starting with the area numbered "20." This indicates that the relative humidity inside the control box exceeds 20%. As more moisture accumulates, the areas numbered "30" and "40" will turn light pink or white, indicating relative humidities of 30% and 40%.

If the 30% area of the humidity indicator turns light pink or white, the control unit should be opened, inspected for leaks, and the desiccant renewed. This is done by unscrewing the ten screws (indicated in Figure 5-3) around the outer rim of the control box bezel, and carefully lifting the bezel and cover off the control box. The control box contains electronic circuitry which may be damaged by static discharge. Open the control box only in a static free environment.

5.7.1 Renewing the Desiccant

⚠ CAUTION

Desiccant may produce irritating fumes when heated. Observe the following precautions:

- Use a vented oven in a well ventilated room.
- Do not remain in the room while recharging is taking place.
- Use the recommended temperature.

There have been reports of irritating fumes coming from the desiccant during reactivation. While our attempts to duplicate the problem have been unsuccessful, we still urge you to use caution.
Material Safety Data Sheets are provided in Appendix F.

The desiccant is renewed by removing the three bags of desiccant from the control box, as shown in Figure 5-4, and placing them in an oven following the instructions below.

Place a sheet of brown paper on a flat metal sheet. You can use a brown grocery bag and a typical cookie sheet. Place only the bags on the sheet. Do not stack the bags on top of each other or allow them to touch. Place in a vented, circulating forced air, convection oven in a well ventilated room. Allow two inches of air space between the top of the bags and the next metal tray above the bags. Keep the tray a minimum of 16 inches from heating element. Heat the bags at a temperature of 240 to 250°F (116 to 121°C) for 12 to 16 hours. At the end of the time period, the bags should be immediately removed and placed in an air tight container for cooling. The desiccant will be recharged to approximately 80 to 90% of its previous capacity. After repeated recharging, the desiccant bag may require replacement.

Some bags will have the temperature and time for recharging the desiccant printed on the bag. If they differ, use the temperature and time printed on the bag.

Replacement bags of desiccant are available from Teledyne Isco; refer to the Replacement Parts Lists in Appendix A.

Before reinstalling the cover, coat the cover's gasket with a light film of silicone grease to seal the control box. Tighten the ten screws which hold the control box cover and bezel in place using an even cross-torquing pattern.

Figure 5-3 Location of 10 Screws on the Control Box Frame

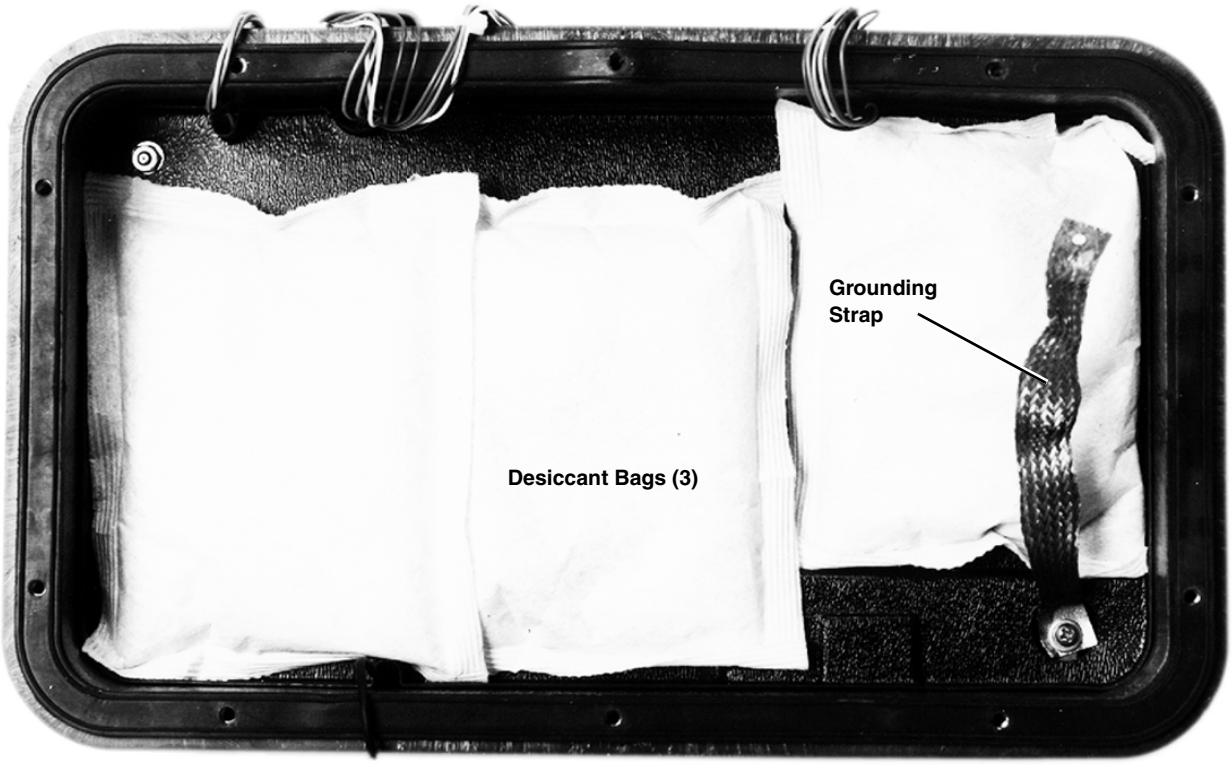


Figure 5-4 Control Box Internal Desiccant

5.8 3710 Controller Mounting

The 3750 Sampler Refrigerator is available to convert a 3710 Portable Sampler into a 3710R Refrigerated Sampler. To do this, remove the control box from the portable sampler following the instructions in the *3710 Portable Samplers Installation and Operation Guide*. Because of the longer distance between the pump discharge and the sample bottle in the refrigerator, the standard 36 inch (92 cm) pump tube must be replaced with the pump tube supplied in the mounting kit. The new pump tube may be installed following the instructions in Section 5.5.3 of this manual.

Once the new pump tube is installed, use the parts supplied in the controller mounting kit and follow the instructions below to prepare and mount the controller on the refrigerator. Refer to Figure 5-5.

1. Turn the controller upside down and screw the four, threaded mounting rods into the four corner feet of the controller. The two middle feet are not used. The controller is now ready to be installed on the refrigerator.
2. Open the controller cover on the top of the refrigerator and orient the controller on the top of the unit so the peristaltic pump and liquid detector face the front of the refrigerator.
3. Carefully insert the threaded rods into the four mating holes on the refrigerator and push the controller down

until it is resting on the refrigerator, install the spacers and wing nuts on the four threaded rods.

4. Feed the pump tube down through the tubing feed through into the interior of the refrigerator and route the pump tube into the distributor arm.
5. Connect the two-pin connector on the power cable to the 12 VDC plug on the controller.

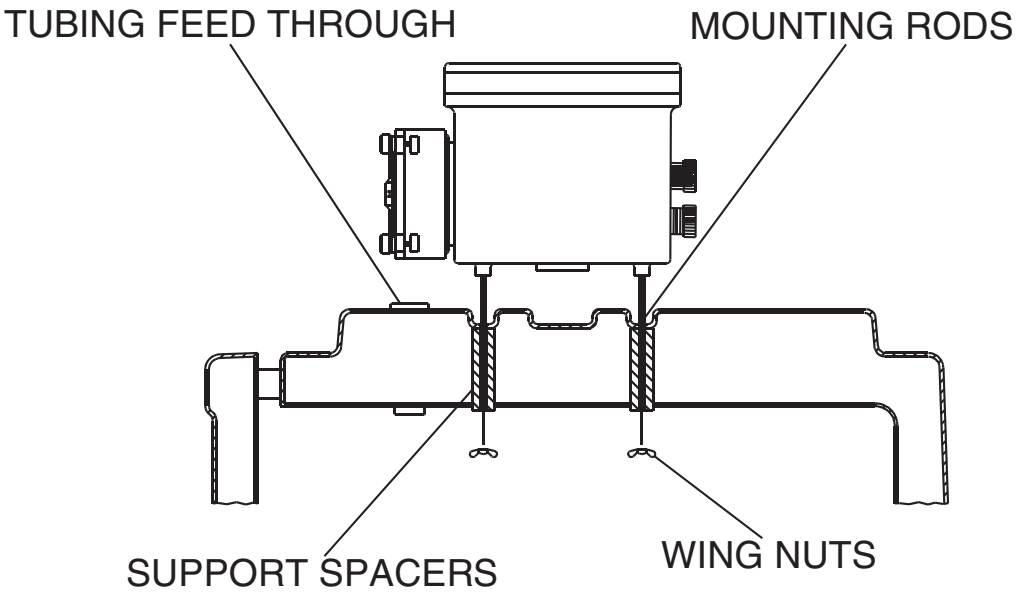


Figure 5-5 Mounting the Control Box

5.9 Servicing

This section provides information to assist you in correcting malfunctions. To view schematic drawings of the circuit boards discussed in this section, first find the serial number on your controller, then go to our web site, **www.isco.com**. Go to Training and Support and select Product Support. Click Automatic Wastewater Samplers. In the left margin, click Schematics. Enter the serial number of your instrument, then click Get Schematics to view a list of PDF files that contain the available schematics. Additionally, you may refer to the **Replacement Parts Lists** and the **Accessories List** for the 3710R/3750 Refrigerated Sampler.

5.10 Refrigerator Electrical System

⚠ WARNING

Disconnect the refrigerator's power before performing any service activities.

Access to the electrical and refrigeration components can be gained by removing the back panel of the refrigerator. Access to the sampler controller's 12 VDC power supply can be gained by laying the refrigerator on its side and removing the bottom plate and back panel.

The refrigerator compressor is equipped with external over-temperature and overload protection, and may fail to start immediately when power to the unit is momentarily interrupted or when the thermostat setting is changed. It is normal for the overload relay to trip repeatedly in these instances, and in no way indicates a malfunction.

5.11 Refrigeration System

The refrigeration system is shown schematically in Figure 5-6. See the refrigerator's serial number label for the charge and type of refrigerant.

⚠ CAUTION

All refrigeration repair work must be performed by a qualified refrigeration technician.
Always purge the system with nitrogen. NEVER USE AIR to purge the system.
Always recover the refrigerant.
When recharging, do not leave a line tap in the refrigeration system because of possible corrosion or leakage problems.

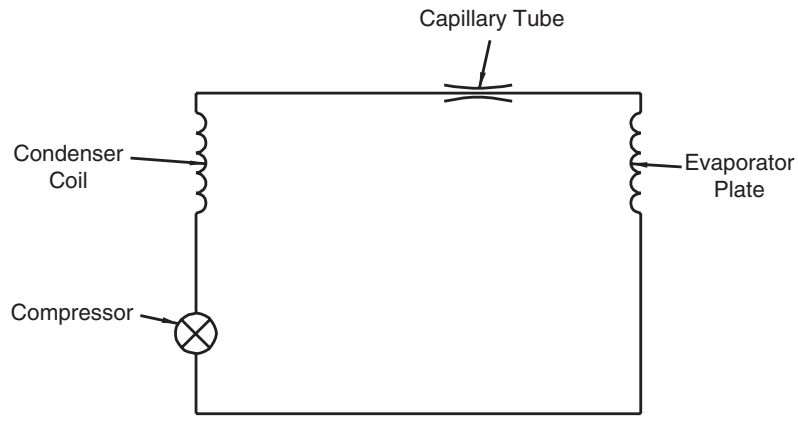


Figure 5-6 Refrigeration Schematic Diagram

5.12 Servicing the 3710 Controller

The electronic circuitry of the 3710R Sampler is solid-state and its reliability is high. If the unit should fail to operate properly, items such as a broken or intermittent connection in the power cable or wiring harness should be suspected.

5.13 If Serious Problems Occur

If the sampler fails to operate properly, call the Teledyne Isco Customer Service Department. The service department will provide information on how to return the sampler to the factory for repair. Contact:

Customer Service Department

Teledyne Isco, Inc.

P.O. Box 82531

Lincoln, NE 68501

Phone: (800) 228-4373

5.14 Access to Electronic Components

⚠ WARNING

Disconnect power from the refrigerator and controller when working on the unit.

To gain access to the electronic components housed in the control box:

1. Disconnect the power source from the sampler.
2. Remove the ten screws around the outer edge of the control box frame.
3. Lift the cover and frame off the control box and turn it over, as shown in Figure 5-7.
4. The control box cover assembly may be disconnected from the control box lower section by disconnecting the five connectors (see Figure 5-7) and the grounding strap.
5. The main circuit board assembly of the 3710 Sampler is protected by an aluminum shield. To remove this shield,

unscrew the stop nut that holds the short grounding strap and unscrew the four screws located in each corner of the shield. Lifting the shield off will then reveal the main circuit board shown in Figure 5-8.

6. To remove the circuit board assembly from the control box cover, unscrew the four hex threaded stand-offs and the phillips head screw, indicated in Figure 5-8. The circuit board may now be pulled away from the control box cover.
7. To completely disconnect the circuit board assembly from the cover, disconnect the connector shown in Figure 5-8.

5.15 Removal of the Pump Gear Case Assembly

The pump gear case assembly is located in the lower section of the control box. To gain access to the pump gear case, follow the instructions in *Access to Electronic Components*. Use the following steps to remove the pump gear case.

1. Remove the liquid detector lid and the pump lid by loosening the captivated thumbscrews on the pump exterior. Figure 5-1 shows the location of the thumbscrews.
2. Remove the pump tubing from the interior of the pump.
3. Remove the pump rotor by loosening the machine screw and locknut attaching the rotor to the pump shaft. Figure 5-2 shows the location of the machine screw. Rotate the rotor until you can reach the screw with a screwdriver inserted through the pump case inlet sleeve.
4. Slide the rotor off the pump shaft.
5. Remove the pump case by unscrewing the four screws on the back of pump's inner case.
6. Lift the pump gear case assembly out of the control box.

5.16 Precautions for Servicing CMOS Circuitry

Most of the circuitry in the 3710 controller is made up of CMOS components. Because of the oxide gate structure of these devices, they are extremely susceptible to destruction caused by the discharge of static electricity through their inputs.

⚠ WARNING

Disconnect power from the refrigerator and controller when working on the unit.

⚠ CAUTION

Keep yourself grounded when handling disassembled equipment.

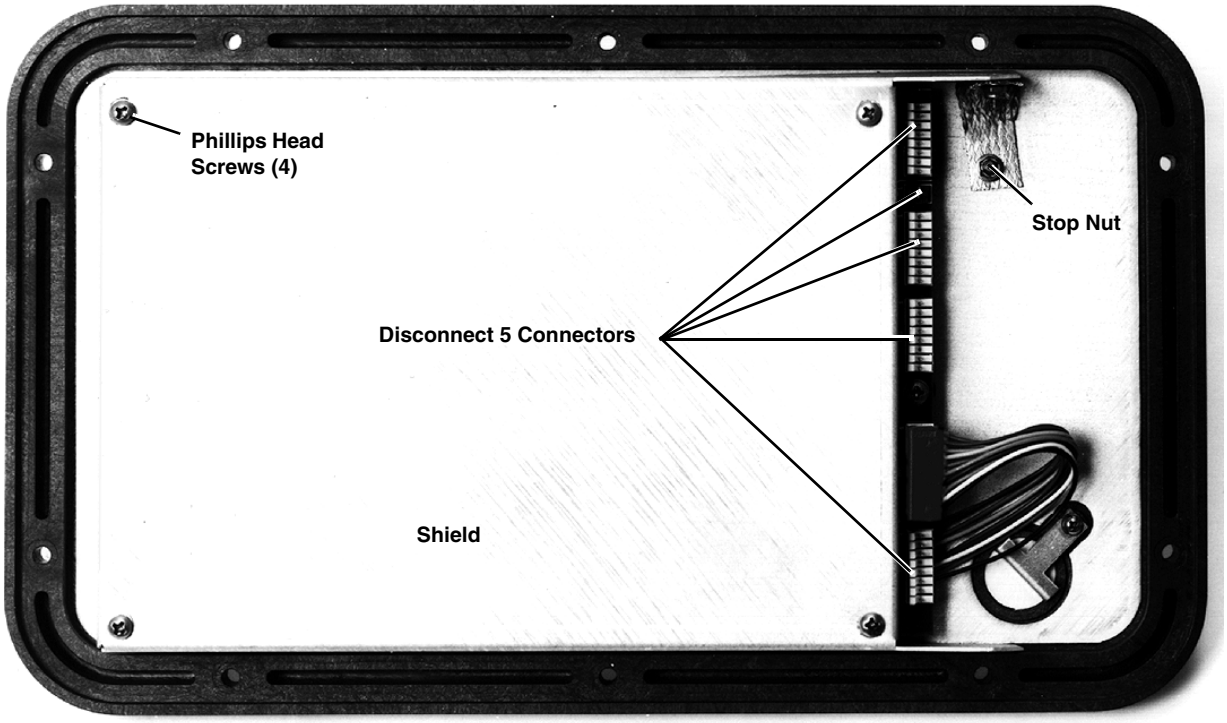


Figure 5-7 Underside of the Control Box Cover

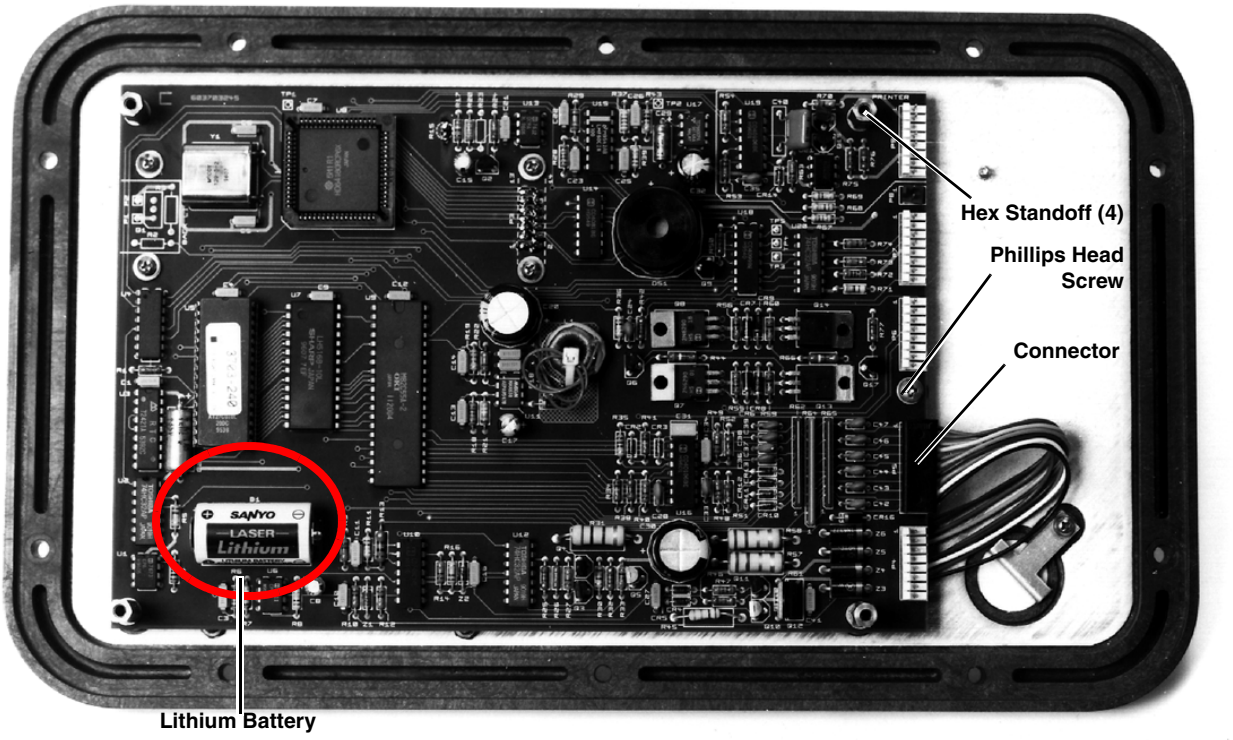


Figure 5-8 Main Circuit Board

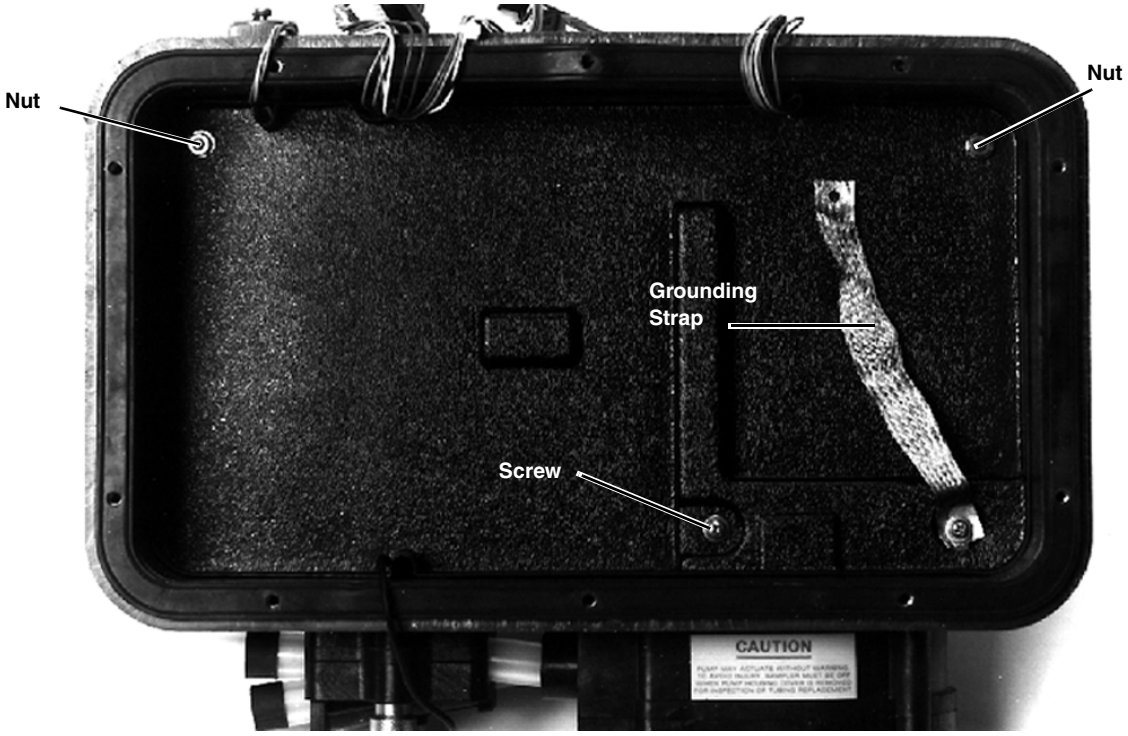


Figure 5-9 Control Box Tray Removal

5.17 Preliminary Electronics Troubleshooting Steps

Following are suggested areas to check before attempting to service the microprocessor CPU and associated circuitry. These checks should be made before looking at the CPU and memory.

1. Supply voltage is correct.
2. Wiring harnesses, connectors, and solder joints are in good condition.
3. Appearance of physical damage, such as burned or broken components, overly hot components, or evidence of water damage.
4. Shorted or open diodes and transistors, especially drive transistors.
5. Voltage regulators working properly.
6. Excessive current draw in some or all the circuitry.
7. Correct input signals to unit.
8. Crystal oscillator operating and at the proper frequency.
9. Reset circuitry working properly.

5.18 Circuit Boards

The following is a general description of the 3710 controller's electronic circuitry. While reading this description, refer to the main circuit board schematic diagram, the case schematic diagram, and the pictorial views of the circuit boards (Figures 5-10 and 5-11).

The 3710 controller is a microprocessor-based device which executes a program stored in ROM. The program (software) is a series of instructions that tell the microprocessor what to do in

order to accomplish the various functions which the sampler must perform. The software is discussed only as is necessary to describe the operation of the circuitry (hardware). The following sections discuss the hardware in greater detail.

A 12 VDC connector on the side of the control box is used to connect to an external 12 V source. A 3.75 Amp PTC device provides circuit protection.

The 3710 controller contains two printed circuit boards: the main board (Figure 5-10) and the pump control board (Figure 5-11). The display module (attached to the main circuit board) also contains a small circuit board. This module is purchased assembled and does not contain any user-serviceable parts. Unless it is being replaced, the display module should not be disturbed.

5.18.1 Main Board

Power is supplied to the circuitry through P4 – pin 1 is ground and pin 2 is 12 V. A 5 V switching regulator (IC U11) is used to obtain a 5 V rail from the 12 V supply. All of the ICs used in the 3710 controller get their operating power from the 5 V rail. IC U11 is also used as a low voltage detector – it constantly monitors the 12 V supply. IC U17, a voltage converter, provides a -5 V supply which is needed for some components.

IC U8 is the microprocessor, IC U5 is the ROM, and IC U7 is the RAM. These three ICs make up the "brains" of the 3710 controller. The microprocessor executes the program stored in ROM. While executing, information (program settings, sample data, etc.) is retrieved from and stored in RAM. A 4.608 MHz crystal oscillator (Y1) sets the microprocessor's execution speed.

The 3710 controller keeps track of time with a real time clock (IC U3). Both the RAM and IC U3 are battery-backed with a lithium battery (B1). IC U1 is a switch which selects between battery and system power.

Three devices allow the microprocessor to communicate with the outside world: the 2 line, 20 characters per line LCD, IC U9, and IC U18. The LCD allows for communication with the user and is connected through P3. IC U13, transistor Q2, thermistor R15, and other components provide the LCD with a temperature compensated driver voltage. By providing temperature compensation, the display quality is optimized over a wide temperature range. IC U9 and IC U18 are I/O devices which allow the microprocessor to: read the keypad, sound the beeper, count pump counts, and other tasks.

A 24 position keypad, connected at P5, is used to direct the microprocessor through the program. Many discrete components along with IC U9 are used to decode pressed keys. All user-originated instructions to the 3710 controller enter the system through the keypad.

The 3710 controller is supplied with a liquid detection system that gives it the ability to accurately deliver specified sample volumes. The liquid detection system consists of a piezoelectric sensor and filtering circuitry. The sensor, mounted on the exterior of the control box, produces a signal proportional to an

induced strain on the pump tubing. This signal is routed through P8 to IC U15 and its associated circuitry where it is massaged into a YES or NO indication of liquid presence. IC U15, containing a switched capacitor low pass filter and two Op Amps, is the main circuit component of the detection system.

A collection of transistors, resistors, and diodes are used to control the distributor motor. The motor control circuitry connects to the distributor through P6 and can drive the distributor in either direction. As the distributor moves, its position is monitored by an optical device mounted to the distributor assembly. IC U20 supplies the necessary current for the optical device.

An RS-232 serial communications port is connected to the system at P9. This port is used to output sampler status, program settings, and sampling results to a printer or an interrogator. IC U21, IC U19, and a handful of discrete components are used to transmit serial information, receive serial information, and sense the presence of the externally connected device.

5.18.2 Pump Control Board

The pump control board (Figure 5-11) is an integral part of the pump assembly and serves two functions: control the pump motor and sense pump revolutions.

The pump motor control consists of a 2-pole double-throw relay (K201) and transistor switches (Q201, Q202, and Q203). The relay is used to change the pumping direction and will run the pump in the reverse direction when in the rest state. Each time the pump runs, the microprocessor sends the pumping direction signal through pin 1 of P7, waits for the relay to change state, then starts the pump by sending a high signal through pin 3 of P7. Waiting for the relay to change state before applying power prevents arcing at the relay contacts.

A key element of the pump revolution count sensor is the LED-phototransistor device (IC201). Whenever the pump is running, power is supplied to IC201. A rotating disk positioned between the LED and phototransistor periodically interrupts the transmitted signal. These interruptions create pulses which are sent back to the main board at pin 8 of P7 to be counted. The microprocessor uses these counts to determine the pumped volume.

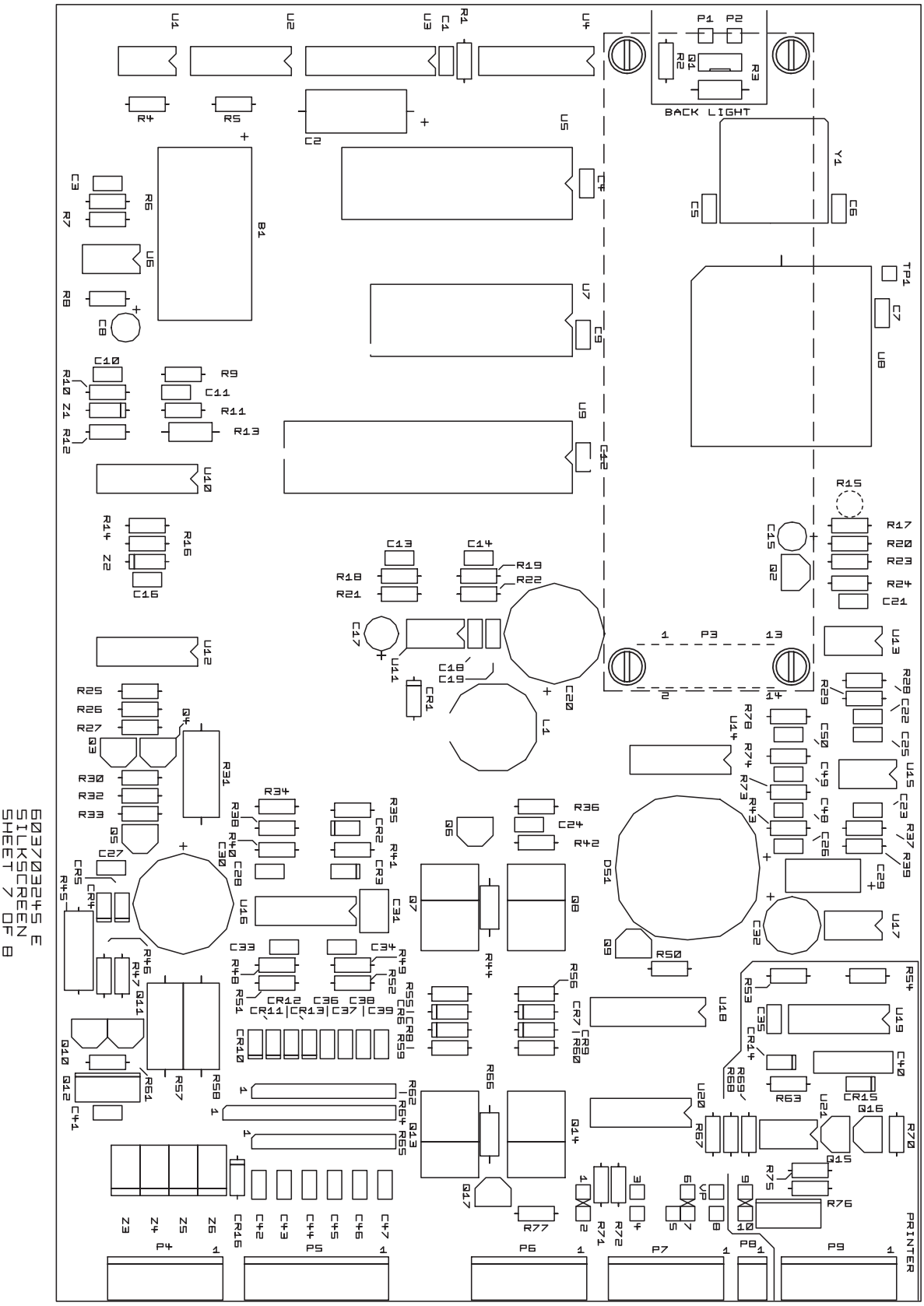


Figure 5-10 3710 Main Circuit Board Component Layout

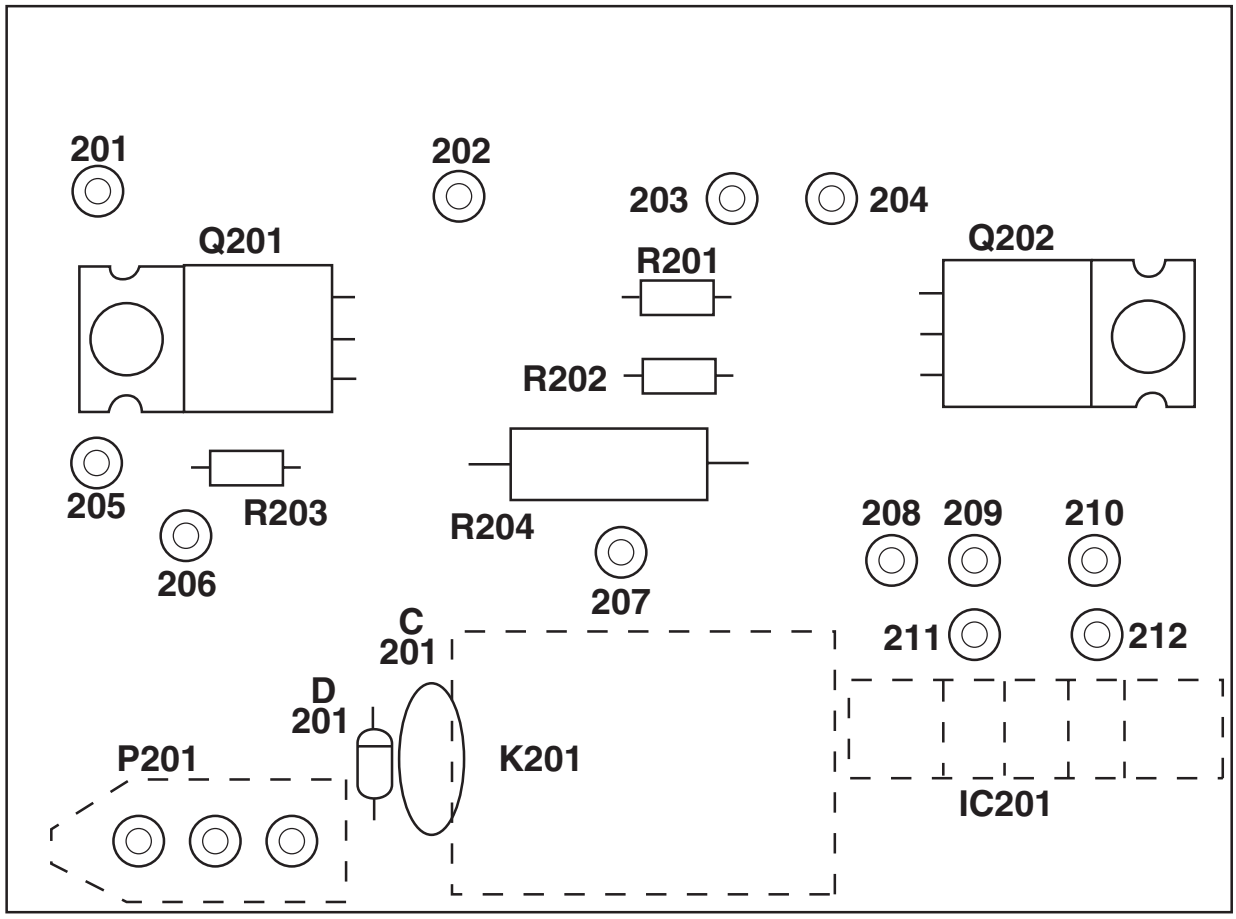


Figure 5-11 Optical Counter PCB Component Layout

5.19 Sample Event Cycle and Delivery of Sample Volumes

The sequence of steps in a typical sequential sample event is described below. Should you suspect a malfunction in the delivery of the sample volumes, this information will assist you in determining the point at which the problem occurs.

1. A sample event is initiated.
2. The pump rotates in the reverse direction to air purge the suction line inlet of any accumulated debris.
3. The pump direction changes, pumping in the forward direction to fill the suction line.
4. After the suction line has been filled to the pump inlet, the sample volume measuring portion of the sampling cycle begins. The pump continues to rotate in the forward direction until the programmed sample volume has been delivered.
5. The pump direction again changes, pumping in the reverse direction to air purge the suction line to avoid cross-contamination of samples. The pump then shuts off.
6. The sampler waits until another sample event is initiated and the cycle begins again at step 1.

5.19.1 Peristaltic Pump

The following is a brief description of the method by which the sample volume is determined. The 3710 Sampler uses a peristaltic pump to transport the sample from the source to the sample bottle. When compared with other suction lift sample gathering methods, a peristaltic pump has numerous advantages: simplicity, reliability, no metering chamber required, easily cleaned, etc.

5.19.2 Volumetric Determination

The 3710 controller determines the volumetric delivery of its peristaltic pump by electronically counting revolutions of the pump rotor. Each revolution of the pump rotor corresponds to a fixed number of "pump counts" and a certain volume of sample liquid. However, the volume of liquid delivered by one revolution of the pump rotor changes with the suction head and the type of suction line. At each sample event, the liquid detection system automatically compensates for changes in suction head and adjusts the volume delivered for each revolution of the pump. Thus, for a given type of suction line, each revolution of the pump rotor results in the delivery of a known amount of sample volume.

5.19.3 Sample Delivery

The sample pumping portion of a sample event consists of three parts: suction line fill, liquid detection, and sample volume delivery. The sampler counts the number of pump revolutions as the suction line fills. At liquid detection, the controller uses that count to determine the proper number of pump revolutions required to deliver the programmed sample volume. It is important to note that the volume delivered by a peristaltic pump can be influenced by a number of factors other than those discussed above. Thus, even with the sophistication of the sample volume measuring functions of the sampler, the volume of sample deposited in the sample bottle may vary from the programmed value. The repeatability of a sample volume from sample to sample (which normally is the most important consideration) will typically be within the ± 10 ml specification stated in Table 1-1, on page 1-7.

An illustrated list of common replacement parts for the 3710R/3710VR/3750 is loacated in Appendix A. When ordering a replacement part, be sure to include the Teledyne Isco part number, a complete description, and the serial number of the unit on which the part is to be used. The controller and the refrigerator are serialized separately. The controller serial number is located on the side of the unit and the refrigerator serial number is located on the inside of the door.

A list of options and accessory parts described throughout this manual can be found in Appendix B. When ordering an option or accessory, be sure to include the part description and the Teledyne Isco part number.

3710R/3750 Refrigerated Sampler

Appendix A Replacement Parts Lists

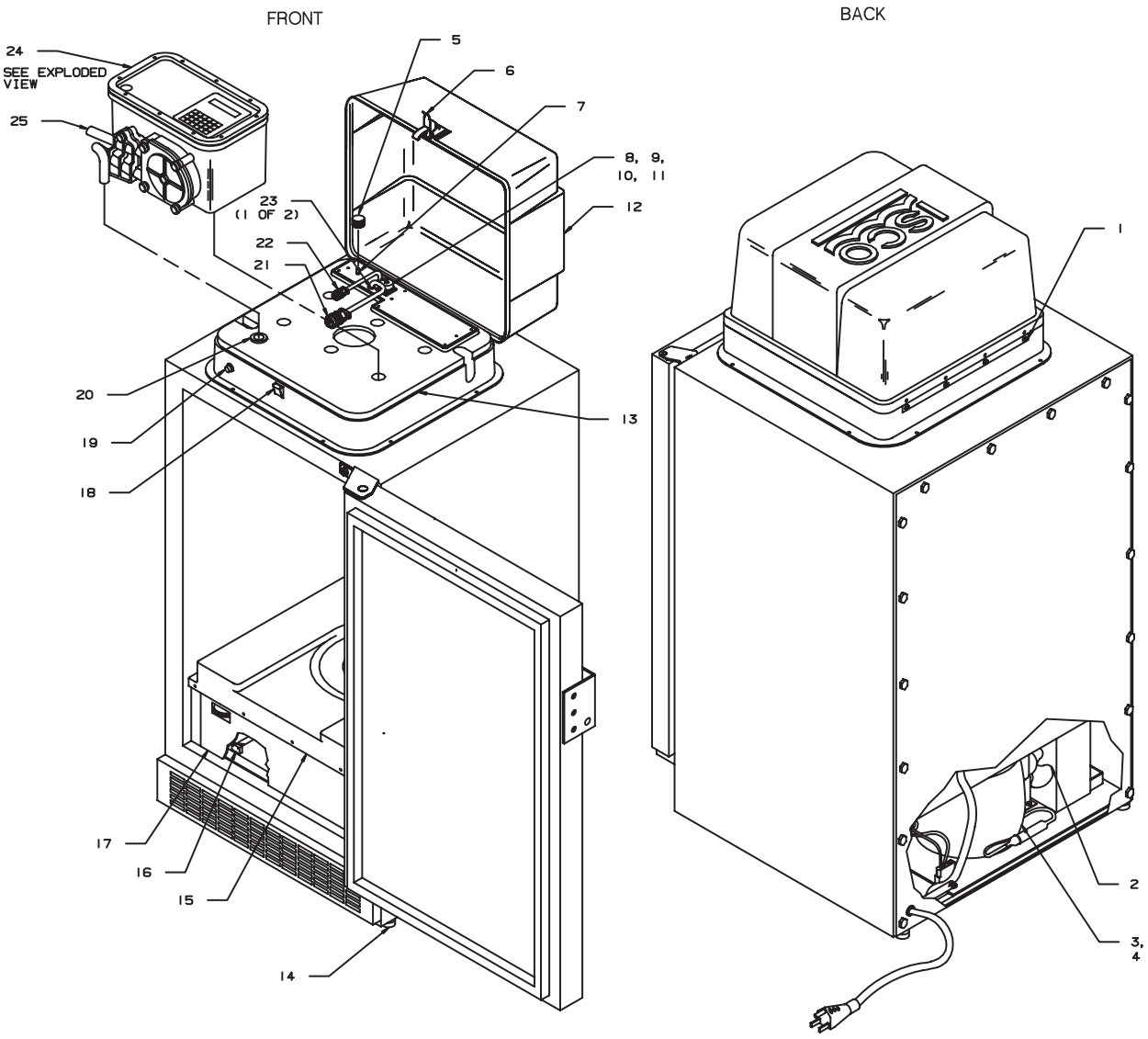
The following appendix contains illustrated replacement parts listings, including part descriptions and order numbers.

Replacement parts can be purchased by contacting Teledyne Isco's Customer Service Department.

Teledyne Isco, Inc.
Customer Service Department
P.O. Box 82531
Lincoln, NE 68501 USA

Phone: (800) 228-4373
(402) 464-0231
FAX: (402) 465-3022

E-mail: IscoInfo@teledyne.com

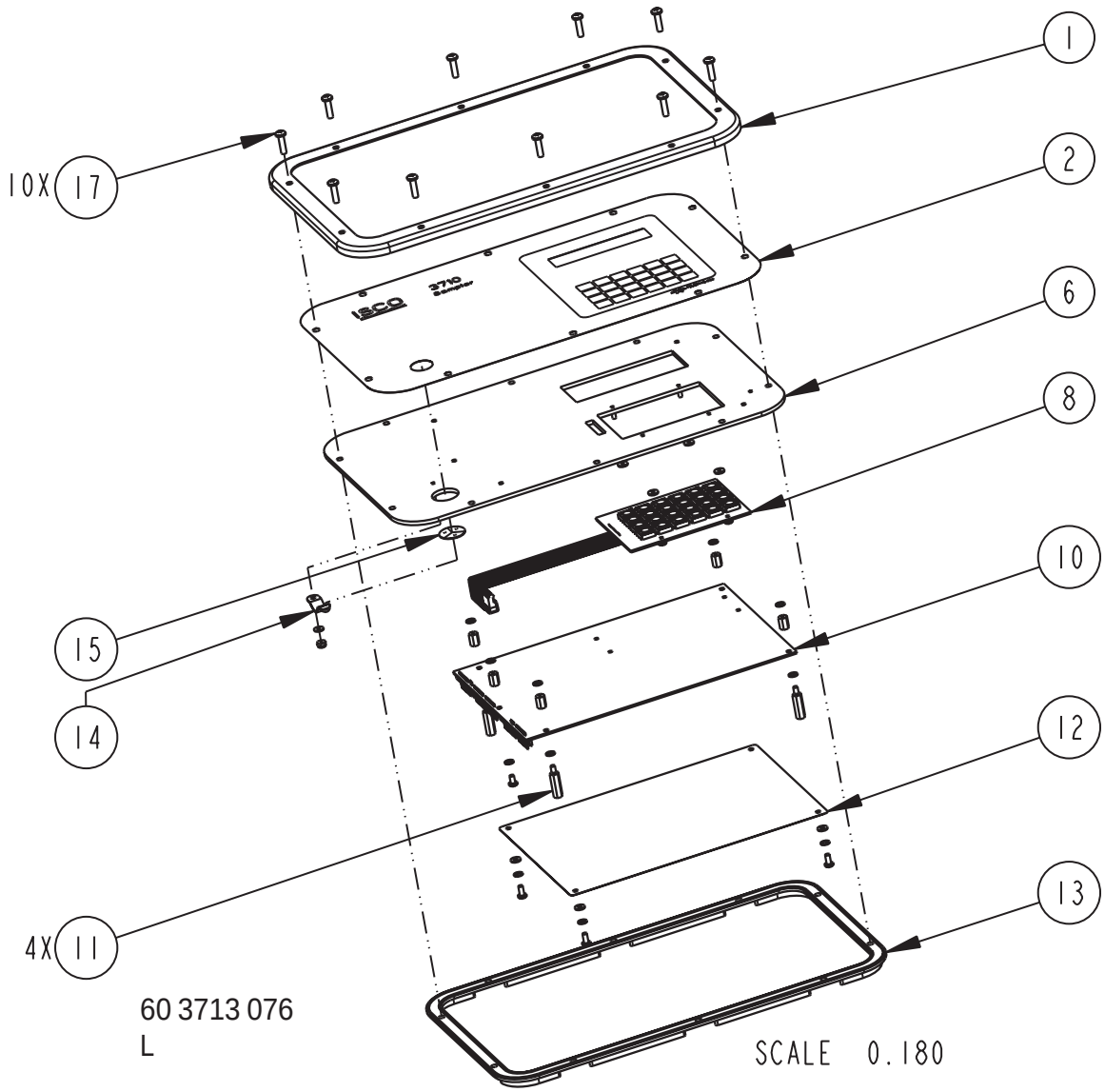


REFRIGERATOR ASSEMBLY

(603713063 REV. E)

ITEM	INVENTORY NO.	DESCRIPTION
1	601623017	COVER HINGE
2	304230100	FAN ASSY - MARVEL 42180093
3	209019006	MARVEL REPL. COMP. - PANASONIC (FROM SN 06539-001)
4	209019007	COMPRESSOR MARVEL 134 (STARTING SN 196E00101)
5	180001201	KNOB PACKAGE
6	109080000	OVER CENTER DRAW LATCH - SOUTHCO
7	692744047	POTENTIOMETER ASSEMBLY
8	140100600	AMP PANEL MT MS3102A-14S-6P
9	609003291	CONNECTOR CAP STRAP
10	603113032	CONNECTOR CAP GASKET MEDIUM
11	603113024	CONNECTOR PROTECTOR CAP MEDIUM
12	602923012	CONTROL COVER
13	602743062	CONTROL BASE
14	601163066	FOOT DELRIN 1-1/4 DIA X 3/4
15	602733011	BOTTLE LOCATING BASE
16	602754009	MICROSWITCH ASSY
17	602934017	FRONT PANEL ASSY
18	609003280	KEEPER LATCH
19	602734013	INDICATING LIGHT ASSY
20	602923038	TUBE FEED THRU
21	602934008	SHUTOFF CABLE ASSY
22	601624010	POWER CABLE ASSY
23	209007505	BSHG SR NYL .300 .500 .090
24	603714001	3710 SAMPLER CONTROLLER
25	603714018	PUMP TUBING ASSY 40-1/2" (FOR SINGLE BOTTLE SAMPLING)
*26	602744035	3740 POWER PACK REPLACE KIT
*27	602744032	REFRIG POWER PACK ASSY

* NOT SHOWN (603713063 REV. E)


10X 17
1
2
6
8
10
15
14
12
13
4X 11
60 3713 076
L
SCALE 0.180

603713076

REPLACEMENT PARTS LIST

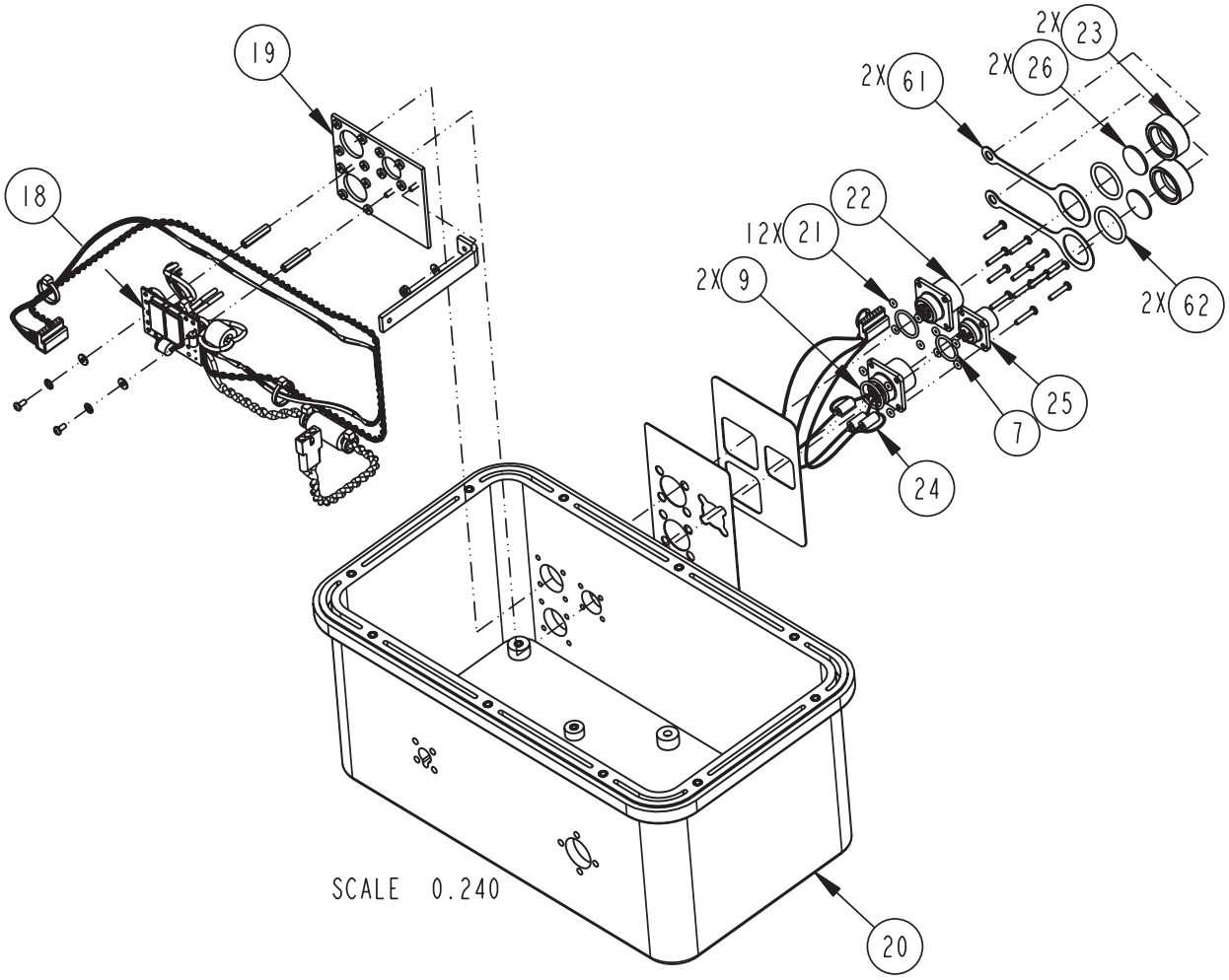
SHEET: 2 OF 7

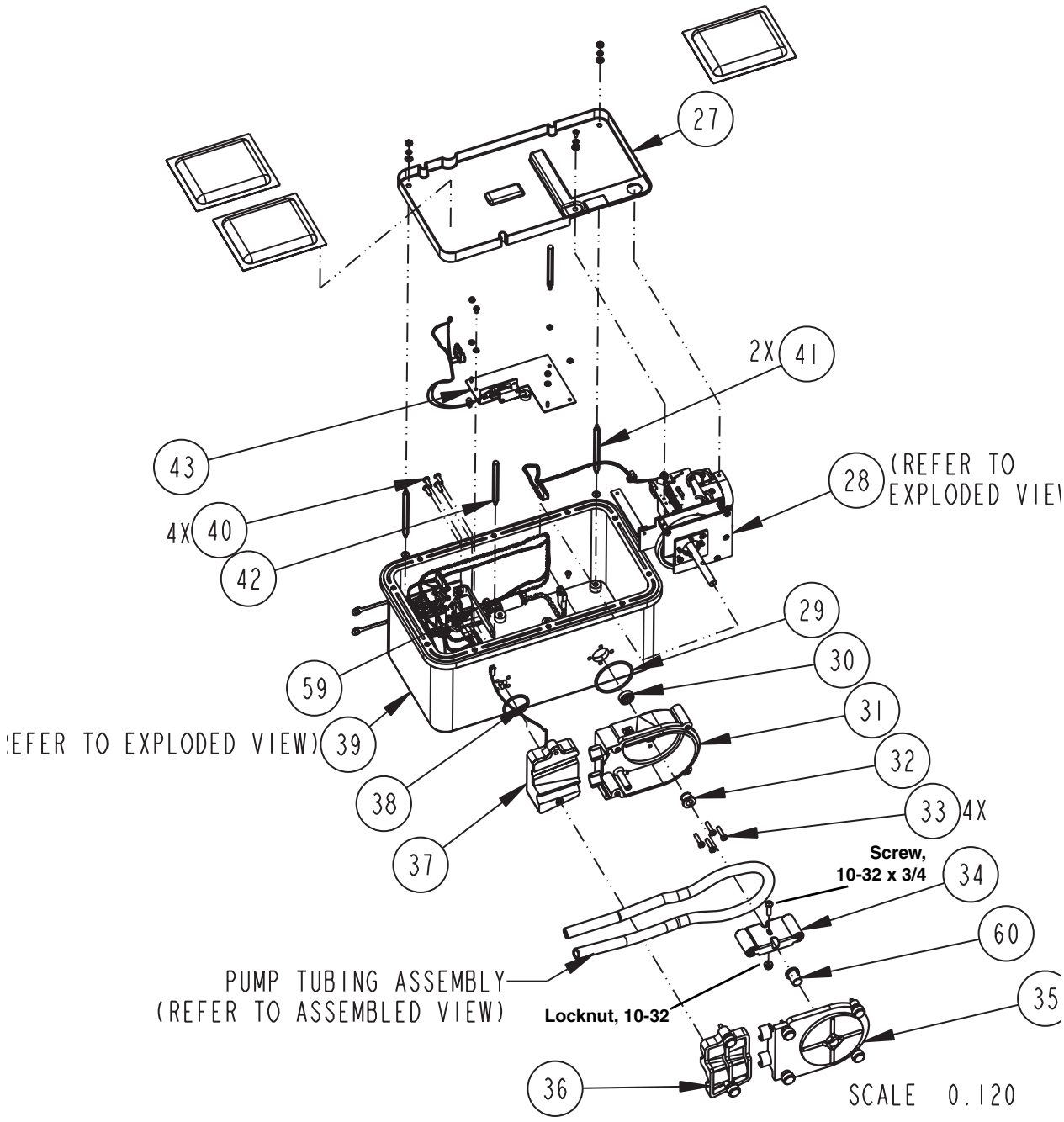
TELEDYNE ISCO, INC.

REV: L | DATE: 06010

ITEM NO.	PART NUMBER	DESCRIPTION
1	693703282	RING TRIM
2	603713004	LABEL CONTROL PANEL
6	603708003	CONTROL PANEL STUD ASSEMBLY
8	693704003	WIRING ASSEMBLY KEYPAD
10	693704180	CIRCUIT BOARD ASSY, 3700 CPU
11	603703028	STANDOFF 1/4 HEX, SST 6-32M/F X .781
12	693703008	ELECTROSTATIC DISCHARGE SHIELD
13	602703010	CONTROL BOX GASKET
14	209902138	TENSION CLIP 3/8 DIA.
15	490001300	HUMIDITY INDICATOR CARD
17	231514510	SCREW CAP SST 8-32 X 5/8
7	202300016	'O' RING .614 ID, .070 CROSS SECTION
9	202307017	'O' RING .676 ID, .070 CROSS SECTION

NOTE: 1. For current prices and quotations on parts, contact Isco Service Department.
2. This list is subject to change without notice.


19
18
2X 23
2X 26
2X 61
22
12X 21
2X 9
2X 62
25
7
24
SCALE 0.240
20


27
2X 41
43
28 (REFER TO EXPLODED VIEW)
4X 40
42
29
30
59
31
EFER TO EXPLODED VIEW) 39
32
38
33 4X
37
Screw, 10-32 x 3/4
34
60
PUMP TUBING ASSEMBLY
(REFER TO ASSEMBLED VIEW)
Locknut, 10-32
35
36
SCALE 0.120

603713076

REPLACEMENT PARTS LIST

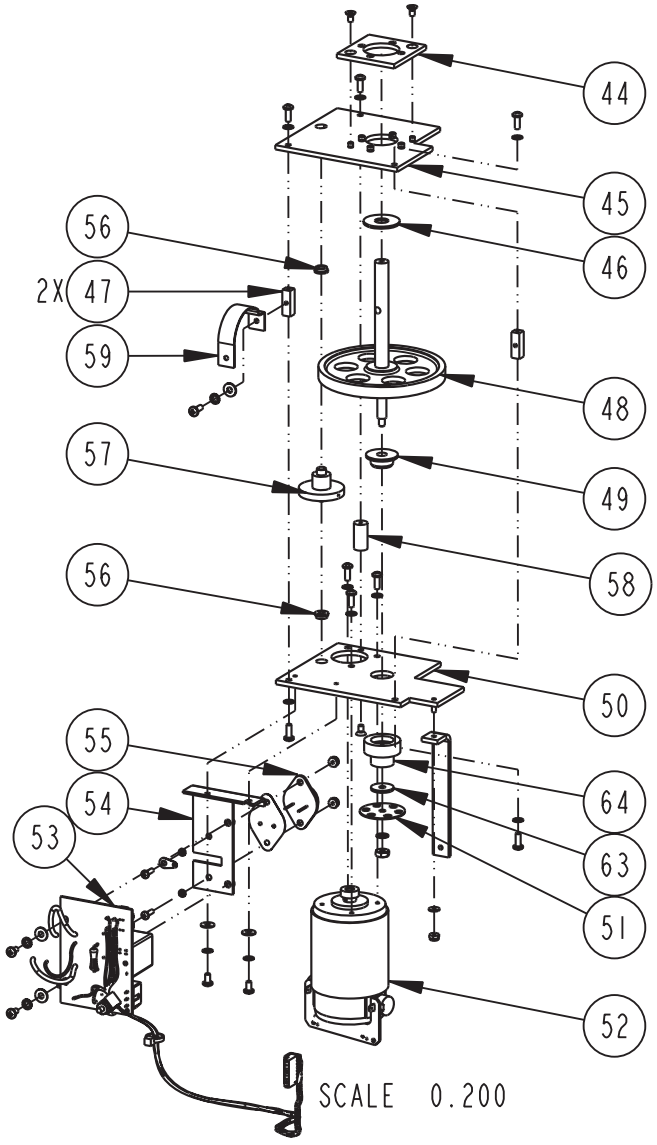
SHEET: 5 OF 7

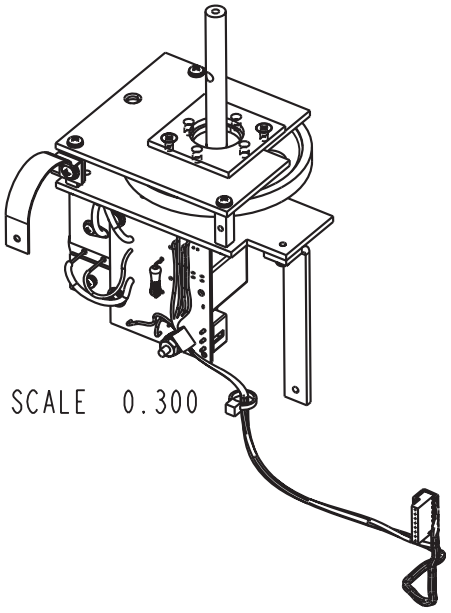
TELEDYNE ISCO, INC.

REV: L | DATE: 06010

ITEM NO.	PART NUMBER	DESCRIPTION
18	603704151	CIRCUIT BOARD ASSEMBLY, POWER SUPPLY CONNECTIONS
19	603704149	BACK PLATE STUD ASSEMBLY, CE
20	603714026	CONTROL BOX MODIFICATION ASSEMBLY
21	202907010	O RING, .100 ID, .070 CROSS SECTION
22	140100600	PLUG, PANEL MOUNT, 6 PIN
23	603113024	CONNECTOR PROTECTOR CAP, MEDIUM
24	603704091	PRINTER CONNECTOR ASSEMBLY
25	140100201	PLUG, PANEL MOUNT, 2 PIN
26	603113032	CONNECTOR CAP GASKET, MEDIUM
27	603703252	DESICCANT TRAY, CE
28	603704154	PUMP GEAR CASE ASSEMBLY, CE
29	202100135	O RING, 1.925 ID, .103 CROSS SECTION,
30	202999903	LIP SEAL, .375 ID X .750 OD
31	603704019	PUMP HOUSING ASSEMBLY, INSIDE
32	603703012	PUMP HOUSING BUSHING
33	231914512	SCREW, MACHINE, 8-32 X 3/4, PAN HEAD, SLOTTED, SST, SELF SEALING, O RING
34	602704019	PUMP ROTOR ASSEMBLY
35	603704017	PUMP HOUSING ASSEMBLY, OUTSIDE
36	603704021	DETECTOR LID ASSEMBLY
37	603704022	DETECTOR BASE ASSEMBLY
38	202401237	O RING, 1.237 ID, .103 CROSS SECTION,
39	603714047	CONTROL BOX SUB-ASSEMBLY, CE
40	231019508	SCREW, MACHINE, 8-32 X 1/2, PAN HEAD, PHILLIPS, SST, SELF SEALING, O-RING
41	602703170	STANDOFF, 6-32 X .25 HEX X 3.00 LONG, MALE, STAINLESS STEEL
42	603714017	SHORT STANDOFF ASSEMBLY
43	603714045	SHUTOFF MICROSWITCH ASSEMBLY, CE
59	603703256	INTERCONNECT STRAP, 5.5"
60	603703278	PUMP HOUSING BUSHING

NOTE: 1. For current prices and quotations on parts, contact Isco Service Department.
2. This list is subject to change without notice.


44
45
56
46
2X
47
59
48
57
49
56
58
50
55
64
54
53
63
51
52
SCALE 0.200


SCALE 0.300

603713076

REPLACEMENT PARTS LIST

SHEET: 7 OF 7

TELEDYNE ISCO, INC.

REV: L | DATE: 06010

ITEM NO.	PART NUMBER	DESCRIPTION
44	602703037	PUMP SHAFT SPACER PLATE
45	602703050	PUMP PLATE
46	602703058	SPACER, .380 ID X 1.00 OD X .060 LONG, DELRIN
47	602703096	STANDOFF, 6-32 X .25 SQUARE X .75 LONG, AL
48	602704010	PUMP SHAFT ASSEMBLY
49	602703076	FLANGED BEARING, .275 ID X .625 OD X .31 LONG
50	603704160	MOTOR PLATE ASSEMBLY, CE
51	602703063	PUMP SHAFT OPTICAL DISK
52	603704172	PUMP MOTOR WITH FILTER ASSEMBLY
53	602704039	CIRCUIT BOARD ASSEMBLY, COUNTER
54	602704048	MOUNTING PLATE ASSEMBLY, OPTICAL COUNTER
55	402025801	TRANSISTOR, 2N5881/2N5882
56	201311200	BEARING, BRONZE, FLANGED, .1891D, .314 OD, 1/8 LONG W/ 3/64 THICK .375 FLANGE
57	602704008	PUMP GEAR SHAFT ASSEMBLY
58	237115000	STANDOFF, 3/16 ROUND, 3/4 LONG, 6-32 FEMALE-FEMALE, AL, CLEAR IRIDITE
59	603703256	INTERCONNECT STRAP, 5.5"
61	609003250	STRAP, DRAIN CAP
62	202400114	'O' RING .612 ID, .103 CROSS SECTION
63	233010804	WSHR, FLAT .171 ID X .625 OD X .060
64	603703291	SPACER, PUMP GEAR CASE ASSEMBLY

NOTE: 1. For current prices and quotations on parts, contact Isco Service Department.
2. This list is subject to change without notice.

3710R/3750 Refrigerated Sampler

Appendix B Accessories

The following appendix contains the most commonly ordered accessories for the 3710R sampler, including part descriptions and order numbers. For additional accessories, contact Teledyne Isco Customer Service or your local sales representative.

Accessories can be purchased by contacting Teledyne Isco's Customer Service Department.

Teledyne Isco, Inc.
Customer Service Department
P.O. Box 82531
Lincoln, NE 68501 USA

Phone: (800) 228-4373
(402) 464-0231
FAX: (402) 465-3022

E-mail: IscoInfo@teledyne.com

B.1 General Accessories

2.5 gallon polyethylene container with cap	299-0013-04
2.5 gallon glass container with cap and Teflon liner	68-2700-005
4 gallon polyethylene container with cap	299-0013-05
Extra Silastic pump tubing, 39.5" length	60-3714-019
Model 3710 Sampler controller with pump tubing	68-3730-005
Extra Pocket Guide, Model 3710R/3710FR	60-3713-049
Extra Silastic pump tubing, bulk 10' length.	68-6700-046
Extra Silastic pump tubing, bulk 50' length.	68-6700-047
Plastic graduated cylinder, 1000 ml, for sample volume calibration	299-0020-00

B.2 Suction Lines and Strainers

3/8" ID x 10' vinyl suction line with standard weighted polypropylene strainer	60-9004-378
3/8" ID x 25' vinyl suction line with standard weighted polypropylene strainer	60-9004-379
3/8" ID x 10' Teflon suction line with protective coating, without strainer	60-1683-146
3/8" ID x 25' Teflon suction line with protective coating, without strainer	60-2703-114
3/8" Standard weighted polypropylene strainer	60-9004-367
1/4" stainless steel low flow strainer only	60-2903-081
3/8" stainless steel low flow strainer only	60-2903-079
Weighted strainer only, 3/8", all plastic CPVC	60-3704-066

1/4" ID vinyl tubing, bulk 100'	68-1680-055
1/4" ID vinyl tubing, bulk 500'	68-1680-056
1/4" ID vinyl tubing, bulk 1000'	68-1680-057
3/8" ID vinyl tubing, bulk 100'	68-1680-058
3/8" ID vinyl tubing, bulk 500'	68-1680-059
1/4" Vinyl suction line accessory kit (required for 1/4" suction lines)	68-3700-006
3/8" Vinyl suction line accessory kit (required for 3/8" suction lines)	68-3700-007

B.3 Power Sources

Model 913 High Capacity Power Pack (120-volt)	60-1684-088
Model 914 Battery-Backed Power Pack (120-volt)	60-3004-130
Model 923 High Capacity Power Pack (240-volt)	60-1684-093
Model 924 Battery-Backed Power Pack (240-volt)	60-3004-160
Model 934 Nickel-Cadmium Battery	60-1684-040
Model 946 Lead-Acid Battery	60-3004-106
Model 948 45-Amp-Hour Battery	68-3000-948
Portable 12-volt DC, 6-Amp Battery Charger for 948 Battery	341-0118-12
Model 961 Battery Charger (120-volt)	60-3004-059
Model 965 Five Station Battery Charger	68-3000-965
Model 954 Solar Panel Battery Charger	68-3000-027
Additional Solar Panel	68-3000-028
Solar Panel Cable (25-foot Length)	60-3004-097
Solar Panel "Y" Cable	60-3004-098
Solar Panel/Interr. Extension Cable	60-2544-028
Connect cable, for external 12 VDC power source; terminates in heavy duty battery clips	60-1394-023

B.4 Interfacing Equipment

1640 Liquid Level Actuator	60-1644-000
Extra Instruction Manual, 1640	60-1644-009
Connect cable, 25', Teledyne Isco sampler to Isco Flow meter	60-3004-107
Connector only, without cable, for use with non-Isco Flow meters having an isolated contact closure proportional to flow	68-1680-060
Same as above, with 22' cable terminating in two wires	60-1394-077
2100 Series Sampler Interface Cable	60-2004-260
4-20 mA Sampler Input Interface (converts analog signal flow meter output as specified by user into pulses acceptable to Teledyne Isco samplers)	60-3704-037
Flowlink Software with manual	call factory
Samplink Sampler Interrogation Software with manual	60-3774-013
Interrogator communications line kit - 9 pin (connects laptop computer with 9 pin serial port to sampler)	60-2544-044
Interrogator communications line kit - 25 pin (connects laptop computer with 25 pin serial port to sampler)	60-2544-040

3710R/3750 Refrigerated Sampler

Appendix C Display Index

> **Note**
>
> To access the display number, press the STOP key while the sampler displays the screen in question. The display numbers are available in the Standby and Program states.

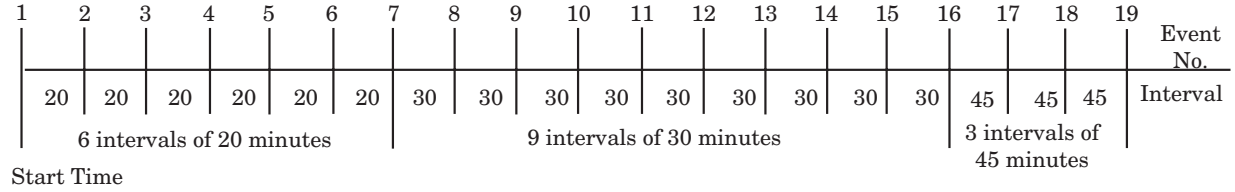


Figure C-1 Time Line

Table C-1 Display Index

This display appears after you press the ENTER/PROGRAM key while in standby. Select "PROGRAM" to access the program sequence. Select "CONFIGURE" to access the configure sequence.

Display 1

```
[PROGRAM, CONFIGURE]
      SAMPLER
```

This informational display appears when you stop the pump with the STOP key after pressing the PUMP FORWARD key. It reports the number of pump counts detected while the pump was in operation. Exit this display by pressing any key except STOP and ON/OFF.

Display 3

```
----- COUNTS FORWARD
```

This informational display appears when you stop the pump with the STOP key after having pressed the PUMP REVERSE key. It reports the number of pump counts detected while the pump was in operation. Exit this display by pressing any key except STOP and ON/OFF.

Display 3

```
----- COUNTS REVERSE
```

This display appears after you select "PROGRAM" in Display #1. Select "TIME" for time-paced sampling, "FLOW" for flow-paced sampling.

Display 10

```
    [TIME, FLOW]
  PACED SAMPLING
```

This display appears only in the extended programming mode and follows Display #10 when you have selected "TIME." Select "UNIFORM" for uniform time intervals, "NONUNIFORM" for nonuniform time intervals.

Display11

```
[UNIFORM, NONUNIFORM]
   TIME INTERVALS
```

Table C-1 Display Index (Continued)

This display follows Display #11 when you have selected "NONUNIFORM." Select "YES" to modify the existing non-uniform intervals. Select "NO" to leave the nonuniform intervals unchanged.

Display 20

```
MODIFY SEQUENCE?
[YES, NO]
```

In the basic programming mode, this display appears after you have selected "TIME" in Display #10. In the extended programming mode, this display appears when you have selected "UNIFORM" in Display #11. Enter the uniform time interval. You need to make 2 entries: The first entry sets the hours, the second sets the minutes.

Display 21

```
SAMPLE EVERY
-- HOURS -- MINUTES
```

This display follows Display #10 when you have selected "FLOW." Enter the flow-pulse interval.

Display 22

```
SAMPLE EVERY
---- PULSES (1 - 9999)
```

This display follows Display #15. Use this display to enter the number of timed sample events in a storm program.

Display 23

```
TAKE -- TIMED
SAMPLE EVENTS (1 - MAX)
```

This display follows Display #23. Enter the time interval between time-paced sample events in a storm program.

Display 24

```
SAMPLE INTERVALS OF
-- MINUTES (1 - 99)
```

This display follows Display #20 when you select "YES" to modify the nonuniform time-interval sequence. Enter the number of sample events to occur at nonuniform time intervals. MAX varies according to the bottle size entered in Display #223

Display 25

```
TAKE --- SAMPLES
(1 - MAX)
```

This display follows Display #25. Enter the nonuniform clock times and dates for each sample event.

Display 26

```
TAKE SAMPLES AT
1.  HH:MM       DD-MMM
```

Enter the number of samples to be taken at each interval. The total quantity you enter will be 1 fewer than the total number of samples, because the first sample, taken at the start time, counts as 1. For example, if you want to take 19 samples (the first 6 at 20-minute intervals, the next 9 at 30-minute intervals, and the remaining 3 at 45-minute intervals), first enter a quantity of 6 at 20 minutes, 9 at 30 minutes, and 3 at 45 minutes. Figure C-1 shows a time line for the sampling routine.

```
QUANTITY AT INTERVAL
1. -- AT --- MINUTES)
```

Enter the size of the sample volume. *MAX* will vary according to the number of samples.

Display 50

```
SAMPLE VOLUMES OF
--- ml EACH  (10 - MAX)
```

Enter the number of composite samples. An entry of "0" instructs the sampler to take samples until a float shut-off terminates the sampling routine.

Display 60

```
--- COMPOSITE
SAMPLES (0 - MAX)
```

This display appears when you select "YES" in Display #242 or select "DISABLE" in Display #240. Enter the measured suction head. *MAX* will be the smaller of the suction line length or "20."

Display 70

```
SUCTION HEAD OF
-- FEET (1 - MAX)
```

Table C-1 Display Index (Continued)

This display appears in the program sequence when you have selected “ENABLE” in Display #290. Select “YES” to use the calibration sequence, “NO” to omit the calibration sequence.

Display 80

```
CALIBRATE SAMPLE
VOLUME?  [YES, NO]
```

This display is part of the calibration sequence. Press the MANUAL SAMPLE key when a collection bottle is underneath the pump tube and the suction line is in place.

Display 81

```
PRESS MANUAL SAMPLE
KEY WHEN READY...
```

This display is part of the calibration sequence. When it first appears, it reports the programmed sample volume. If the measured volume differs from the reported volume, enter the measured volume here.

Display 82

```
--- ml VOLUME
   DELIVERED
```

This display is part of the calibration sequence and appears if the measured volume and the programmed volume differ by a factor of two or more. Select “YES” to confirm the number entered in Display #82. Select “NO” to return to Display #82.

Display 83

```
---ml! ARE YOU
SURE? [YES, NO]
```

Select “YES” to enter a start time. “NO” will begin the sampling routine according to the delay set in Display #310.

Display 90

```
ENTER START TIME?
   [YES, NO]
```

This display appears when you have selected “YES” in Display #90. Enter the start time and date for the first sample event. This display will also appear if you have initiated the routine after a programmed start time so that you can reprogram the start time.

Display 91

```
TAKE FIRST SAMPLE AT
   HH:MM DD-MMM
```

This display appears when you have selected “YES” in Display #90. Enter the start time and date for the flow -pulse countdown. This display will also appear if you have initiated the routine after a programmed start time so that you can reprogram the start time.

Display 92

```
START FLOW COUNT AT
   HH:MM DD-MM
```

This display appears when you select “ENABLE” in Display #300. Enter the number of stop and resume times.

Display 100

```
-- STOP or RESUME
 TIMES  (0 - 24)
```

This display appears when the setting in Display #100 is greater than zero. Enter the appropriate stop time.

Display 101

```
STOP SAMPLING AT
 1.HH:MMDD-MMM
```

This display appears when the setting in Display #100 is greater than one. It follows Display #101. Enter the appropriate resume time.

Display 102

```
RESUME SAMPLING AT
 1.HH:MMDD-MMM
```

This display appears when a routine is halted and you press the start sampling key. Select “START” to start the sampling program at the beginning, “RESUME” to continue the sampling program at the point at which it was halted.

Display 140

```
[START, RESUME]
SAMPLING PROGRAM
```

Table C-1 Display Index (Continued)

This display appears when you have started a routine after the programmed start time. Select "YES" to enter a new start time. Select "NO" to start the routine immediately; some sample events may be missed or late.

Display 142

```
CHANGE START TIME?
[YES, NO]
```

This display appears after you press the display status key. Select "REVIEW" to view the summary of the current program settings and for sampling results. Select "PRINT" to send the current status, program settings, and sampling results to an Isco Field Printer. NOTE: The Teledyne Isco Field Printer is no longer sold, but this function remains available for customers who still have Field Printers. The printed results include data for sample events completed when you pressed the display status key.

Display 148

```
[REVIEW, PRINT] PROGRAM
     INFORMATION
```

This display appears after you select "Print" in Display #148. Select "NO" to return to standby. Select "Settings" to print the settings report. Select "RESULTS" to print the results report.

Display 149

```
PRINT PROGRAM [NO,
SETTINGS, RESULTS]
```

This display appears after you select "REVIEW" in Display #148. Select "NO" to return to the previous operating state. Select "SETTINGS" to view the summary of the current program settings. Select "RESULTS" to view the sampling results for sample events completed at the time you pressed the display status key.

Display 150

```
REVIEW PROGRAM [NO,
SETTINGS, RESULTS]
```

Display #151 is used to identify the displays used to summarize the current program settings which appear when you select "SETTINGS" in Display #150.

Display 151

```
SETTINGS DISPLAYS
```

Display #152 identifies sampling results displays that appear when you select "RESULTS" in Display #150.

Display 152

```
RESULTS DISPLAYS
```

Display #200 is used to identify the displays, which locate each configure option in the configure sequence. Press ENTER/PROGRAM to access the input displays for each option. Use the LEFT ARROW and the RIGHT ARROW keys to move through the options.

Display 200

```
SELECT OPTION (← →)
name of configure option
```

Set Clock configure option. Enter the time and date to set the controller's clock. Use military time. Enter two digits each for the day (DD), month (MM), and year (YY).

Display 210

```
HH:MM DD/MM/YY
HH:MM DD/MM/YY
```

Bottles and Sizes configure option. Select REFRIG if you have a refrigerated base unit. Select PORTABLE only when you are using a 3710 Compact or Standard Sampler.

Display 220

```
[PORTABLE, REFRIG]
     SAMPLER
```

Bottle and Size configure option. Enter the bottle volume in milliliters.

Display 223

```
BOTTLE VOLUME IS
------ ml
```

Bottle and Size configure option. This display appears when you have entered a bottle volume in Display #223 that exceeds a standard Teledyne Isco bottle size.

Display 224

```
----- ml ... ARE YOU
 SURE?  [YES, NO]
```

Table C-1 Display Index (Continued)

Suction Line configure option. Select "1/4" if you are using 1/4-inch suction line, "3/8" if you are using 3/8-inch suction line.

Display 230

```
SUCTION LINE ID IS
[1/4, 3/8] INCH
```

Suction Line configure option. This display appears when you have selected "3/8" in Display #230. Select "VINYL" if you are using vinyl suction line, "TEFLON" if you are using Teflon suction line.

Display 231

```
SUCTION LINE IS
[VINYL, TEFLON]
```

Suction Line configure option. Enter the length of the suction line. Do not include the tube coupling or the strainer in the length measurement.

Display 232

```
SUCTION LINE LENGTH
IS -- FEET (3 - 99)
```

Liquid Detector configure option. Select "ENABLE" to turn on the Liquid Detector, "DISABLE" to turn off the Liquid Detector. If you turn off the detector, you must enter the suction head (Display #70) in the program sequence.

Display 240

```
[ENABLE, DISABLE]
LIQUID DETECTOR
```

Liquid Detector configure option. This display appears when you select "ENABLE" in Display #240. Enter the number of rinse cycles. Rinse cycles condition the suction line to reduce cross-contamination.

Display 241

```
RINSE CYCLES (0 - 3)
```

Liquid Detector configure option. This display appears when you select "ENABLE" in Display #240. Select "YES" to add the suction-head setting (Display #70) to the program sequence. Select "NO" to omit the setting.

Display 242

```
ENTER HEAD MANUALLY?
[YES, NO]
```

Liquid Detector configure option. This display appears when you select "ENABLE" in Display #240. Enter the number of retries: the number of times the sampler will try to detect the presence of liquid for each sample event.

Display 243

```
RETRY UP TO - TIMES
WHEN SAMPLING (0 - 3)
```

Programming Mode configure option. Select "BASIC" to use the basic programming mode. To use the extended programming mode, select "EXTENDED."

Display 250

```
[BASIC, EXTENDED]
PROGRAMMING MODE
```

Load Stored Program configure option. Select the sampling program you want to use. Select "NONE" to exit the display without loading a program.

Display 255

```
LOAD PROGRAM
[#1, #2, #3, NONE]
```

Save Current Program configure option. Select the number with which you want to use to identify the current program when saved. Select "NONE" to exit the display without saving a program.

Display 260

```
SAVE PROGRAM AS
[#1, #2, #3, NONE]
```

Flow Mode Sampling configure option. This setting affects flow-paced sampling routines. Select "YES" to take the first sample at the start time, "NO" to take the first sample at the end of the first flow-pulse interval.

Display 270

```
TAKE SAMPLE AT START
TIME? [YES, NO]
```

Table C-1 Display Index (Continued)

Nonuniform Time configure option. Select "CLOCK TIME" to enter the nonuniform time intervals as clock times (Display #26). Select "MINUTES" to set the nonuniform intervals in minutes (Display #27).

Display 280

```
ENTER INTERVALS IN
[CLOCK TIME, MINUTES]
```

Calibrate Sampler configure option. Select "ENABLE" to add calibration displays to the program sequence. Select "DISABLE" to omit the calibration displays.

Display 290

```
[ENABLE, DISABLE]
CALIBRATE SAMPLE
```

Sampling Stop/Resume configure option. Select "ENABLE" to add the Sampling Stop/Resume settings to the program sequence. Select "DISABLE" to omit the settings.

Display 300

```
[ENABLE, DISABLE]
SAMPLING STOP/RESUME
```

Sampling Stop/Resume configure option. This display appears when you select "ENABLE" in Display #300. Select "YES" to take a sample at stop times. Select "NO" if you do not want a sample event at the stop times.

Display 301

```
SAMPLE AT STOP?
[YES, NO]
```

Sampling Stop/Resume configure option. This display appears when you select "ENABLE" in Display #300. Select "YES" to take a sample at the resume times. Select "NO" if you do not want a sample event at the resume times.

Display 302

```
SAMPLE AT RESUME?
[YES, NO]
```

Start Time Delay configure option. Enter the amount of time, in minutes, you want to delay the start time. This entry affects programs that do not have a programmed start time.

Display 310

```
---- MINUTE DELAY
TO START  (0 - 9999)
```

Enable Pin configure option. Select "YES" to take a sample at the time the sampler becomes disabled. Select "NO" if you do not want a sample event when the sampler becomes disabled.

Display 321

```
SAMPLE UPON DISABLE?
[YES, NO]
```

Enable Pin configure option. Select "YES" to take a sample when the sampler becomes enabled; *i.e.,* ceases to receive an inhibit signal from a flow meter or a Liquid Level Actuator. Note: No sample will be taken if the enable signal is used to initiate the start-time delay countdown. Select "NO" if you do not want a sample event when the sampler becomes enabled.

Display 322

```
SAMPLE UPON ENABLE?
[YES, NO]
```

Enable Pin configure option. Select "YES" to restart the sample interval countdown at the time the sampler is enabled. The interval countdown is determined by the setting if "NO" is selected in Display #324.

Display 323

```
RESET SAMPLE
INTERVAL? [YES, NO]
```

Enable Pin configure option. This display appears if you select "NO" in Display #323. Select "YES" to freeze the sample interval when the sampler becomes disabled. When the sampler is enabled, the interval countdown continues from the point where it had stopped. Select "NO" to let the sample interval countdown continue while the sampler is disabled.

Display 324

```
INHIBIT COUNTDOWN?
[YES, NO]
```

Event Mark configure option. Select "CONTINUOUS SIGNAL" to send a variable-duration event mark signal from pin E of the flow meter connector. Select "PULSE" to send a 3-second event mark signal.

Display 330

```
[CONTINUOUS SIGNAL,
PULSE]
```

Table C-1 Display Index (Continued)

Event Mark configure option. This setting appears when you select “CONTINUOUS SIGNAL” in Display #330. Select “PUMP CYCLE” to transmit the event mark signal during the entire pump cycle, including any programmed rinses and retries. Select “FWD PUMPING ONLY” to send the signal when the pump is delivering a sample volume only.

Display 331

```
DURING [PUMP CYCLE,
 FWD PUMPING ONLY]
```

Event Mark configure option. This setting appears when you select “PULSE” in Display #330. Select “PURGE” to transmit an event mark signal to a flow meter at the beginning of the pre-sample purge. Select “FWD PUMPING” to transmit a signal when the pump switches forward to deliver the sample volume.

Display 332

```
AT THE BEGINNING OF
[PURGE, FWD PUMPING]
```

Purge Counts configure option. Enter the number of pre-sample pump counts needed to purge the suction line. This value is set to 150 when the controller is reinitialized.

Display 340

```
--- PRE-SAMPLE
COUNTS (0 - 9999)
```

Purge Counts configure option. Enter the number of post-sample pump counts needed to purge the suction line. The Controller derives the number that initially appears in this display from the suction line ID and length entered in Display #230 and #232.

Display 341

```
--- POST-SAMPLE
COUNTS (0 - 9999)
```

Tubing Life configure option. This informational display communicates the pump counts elapsed since the last reset and the counts required to trigger the Pump Tubing Warning. Exit this display by pressing any key.

Display 350

```
------- PUMP COUNTS,
WARNING AT -------
```

Tubing Life configure option. After changing the pump tube, select “YES” to reset the pump counter to zero. Select “NO” to leave the counter unchanged.

Display 351

```
--- POST-SAMPLE
COUNTS (0 - 9999)
```

Tubing Life configure option. Enter the number of pump counts required to trigger the pump-count warning if the factory setting is not suitable. This value is set to 500,000 when the controller is reinitialized.

Display 352

```
------- PUMP COUNTS
    TO WARNING
```

Program Lock configure option. Select “ENABLE” to turn on the program lock. If you enable the program lock, input displays are protected by a pass-number: 3700. The controller will not allow you to make any changes to a program or configure sequence setting until you enter the pass-number when requested. Select “DISABLE” to turn the program lock off.

Display 360

```
[ENABLE, DISABLE]
  PROGRAM LOCK
```

Sampler ID configure option. Enter the sampler identification here. The sampler will accept as many as 10 characters, including periods (press resume sampling), dashes (press manual sample), and spaces (press start sampling).

Display 365

```
SAMPLER ID NUMBER IS
     __________
```

Run Diagnostics configure option. Select “YES” to “reinitialize” (reset) the controller: the entire RAM – with the exception of the configure option settings for current pump-count total, number of bottles, bottle size, suction-line length, and sampler ID – will be reset to factory settings. Select “NO” the leave the settings unchanged.

Display 371

```
RE-INITIALIZE?
  [YES, NO]
```

3710R/3750 Refrigerated Sampler

Appendix D Calculating Flow Increment Between Samples

The 3710R Sampler will accept flow-proportional inputs from an external flow meter, flow module, or flow logger. These electronic flow-input signals are transmitted to the sampler at fixed increments of total flow, for example, every 10,000 gallons. Each time 10,000 gallons of liquid flows past the flow meter, it sends a signal to the sampler, which registers it as a single flow pulse. You can program the sampler to totalize any number of flow pulses from 1 to 9,999 before initiating a sampling event. For example, if the sampler were programmed to totalize 5 flow pulses and each flow pulse represented 10,000 gallons of total flow, a sample would be collected each time 50,000 gallons (5 flow pulses of 10,000 gallons each) had passed the flow meter.

Time Interval Known – If the desired average time interval between individual samples is known, the flow increment between samples can be determined by calculating how much flow (based on the average flow rate) occurs during that time interval. For example, assume that the average flow is 2.5 MGD and it is desired to collect a sample every 30 minutes. The flow increment between samples is calculated:

2.5 MGD = 2,500,000 GAL/DAY

2,500,000 GAL/DAY X 1 DAY/24 HR X 1 HR/60 MIN = 1736 GAL/MIN

736 GAL/MIN X 30 MIN/SAMPLE = 52,080 GAL/SAMPLE

Thus, the desired flow increment between samples is approximately 52,000 gallons.

Number of Samples Known – Alternatively, if the total number of samples to be collected over the total sampling period is known, the flow increment between samples can be determined by calculating how much total flow will occur during the sampling period, and dividing this by the total number of samples to be collected. For example, assume that the average flow is 1.75 MGD, that the composite sampling period is 2 days, and that it is desired to collect 100 individual samples. The flow increment between samples is calculated:

1.75 MGD = 1,750,000 GAL/DAY

1,750,000 GAL/DAY X 2 DAYS = 3,500,000 GAL

3,500,000 GAL ÷ 100 SAMPLES = 35,000 GAL/SAMPLE

Thus, the desired flow increment between samples is approximately 35,000 gallons.

Calculation of Number of Flow Pulses – Once the desired flow increment between samples is known, the number of flow pulses to be programmed into the sampler may be calculated, assuming that the volume of the flow pulses from the flow meter is known. The number of flow pulses is calculated by dividing the flow increment between samples by the volume of each flow pulse. Using the first example above, the flow increment between samples was calculated as 52,000 gallons; assume that each flow pulse represents 10,000 gallons of flow. The number of flow pulses to be programmed into the sampler is calculated:

52,000 GAL ÷ 10,000 GAL/FLOW PULSE = 5.2 FLOW PULSES

Rounding this to an even number results in 5 flow pulses to be programmed into the sampler. This in turn results in a flow increment between samples of 50,000 gallons (5 flow pulses × 10,000 gallons/flow pulse).

Total Number Of Samples – To calculate the total number of samples to be collected, three quantities must be known: the average flow rate, the flow increment between samples (calculated above), and the total time over which the composite sample is to be collected. The total number of samples to be collected is determined by first calculating the total flow volume over the sampling period, and then dividing this by the flow increment between samples. For example, assume that the average flow is 2.5 MGD, the flow increment between samples is 50,000 gallons, and the composite sample is to be collected over a 24 hour period. The total flow volume over a 24 hour period is:

2.5 MGD = 2,500,000 GAL/DAY

2,500,000 GAL/DAY X 1 DAY = 2,500,000 GAL

The total number of samples to be collected in this 24 hour period is then calculated:

2,500,000 GAL ÷ 50,000 GAL/SAMPLES = 50 SAMPLES

Thus, based on an average flow of 2.5 MGD, 50 samples will be collected.

Calculation of Sample Volume – To calculate the volume of each individual sample, the volume of the composite sample container being used and the total number of samples to be collected (calculated above) must be known. The individual sample volume is calculated by simply dividing the volume of the composite sample container being used by the total number of samples to be collected. For example, assume that a 2.5 gallon (9,400 ml) plastic container is being used, and that a total of 50 samples are to be collected in it. The individual sample volume is then calculated:

9400 ML ÷ 50 SAMPLES = 188 ML

Sample Volume Considerations – Thus, a sample volume of 188 ml will result in the desired composite sample. Because of the basic uncertainty of the delivered sample volume exactly matching the programmed nominal sample volume and the 10 ml sample repeatability, it is good practice to select a nominal sample volume which is slightly smaller than the calculated sample volume. This is to prevent overfilling of the sample container. In the example, an individual nominal sample volume of 125 ml might be a prudent choice. For critical applications, calibration of the sample volume can be used. It is important to select an individual sample volume which will not result in an overfilled sample container under worst-case conditions.

The nominal volume of the composite sample may be calculated by multiplying the programmed nominal sample volume by the total number of samples to be collected. In the example:

125 ML/SAMPLE X 50 SAMPLES = 6,250 ML

This calculated total volume may vary from the actual total volume because of variations in the actual volume of each individual sample. The total time needed to collect the 50 individual samples may vary from the desired 24 hour period because of variations in the average flow rate from the 2.5 MGD figure used in these calculations.

3710R/3750 Refrigerated Sampler

Appendix E Glossary

Composite sampling – In composite sampling, multiple sample volumes are placed in bottle sets. Typically, composite sampling uses a single container. A composite sample represents an average of the characteristics of the flow stream for the elapsed time of sampling.

Controller – The controller, housed within the molded control box, is a collection of electronic components, which govern the actions of the sampler. It includes the microprocessor, RAM (Random Access Memory), ROM (Read Only Memory) and its imbedded software, the LCD (Liquid Crystal Display), and the keypad.

Cross contamination – Cross contamination occurs when portions of previous samples are mixed with the current sample. For example, cross contamination results when residual amounts of sample remain in the suction line or pump tube from a previous sample event.

Event mark – An event mark is a signal that the sampler sends to a flow meter or other device a each sample event. Each time the flow meter receives an event mark pulse, the flow meter places a mark on the its recording chart. Marking the recording chart cross-references the charted flow with the sample events.

Post-sample purge – Post-sample purge refers to the suction line purge that follows the delivery of the sample volume(s). It is also called post-purge.

Pre-sample purge – Pre-sample purge refers to the suction line purge that precedes the delivery of the sample volume(s). It is also called pre- purge.

Real-time clock – A real-time clock can be set to the actual time and date.

Sample event – A sample event consists of the complete sampling cycle resulting in the collection and distribution of one or more equal sample volumes. A sample event includes pre-sample and post-sample purges, line rinses, liquid detection retries, and deliveries of sample volumes. No more than one sample volume is placed in any one bottle during a sample event.

Sample volume – The sample volume is the discrete, programmed amount of sample delivered to each bottle. A single sample event may deliver several sample volumes.

Sampling routine – A sampling routine, also called a sampling program, is the process of taking samples according to the program settings you enter when programming and configuring the controller. The program settings define the sample pacing, distribution, volume, and key clock times.

Selection – A selection is represented by a blinking word or number in an input display. The blinking selection indicates the current choice or value. Selections are accepted and stored by pressing the enter/program key.

Suction head – Suction head is the vertical distance from the surface of the flow stream to the pump inlet.

3710R/3750 Refrigerated Sampler

Appendix F Material Safety Data Sheets

This appendix provides Material Safety Data sheets for the internal desiccant used in the 3710 controller.

Specific questions regarding the use and handling of these products should be directed to the manufacturer listed in the MSDS.

101 Christine Drive
Belen, New Mexico 87002
Phone: (505) 864-6691
Fax: (505) 861-2355

SÜD-CHEMIE
Performance Packaging

ISO 9002

MATERIAL SAFETY DATA SHEET -- September 28, 1998
SORB-IT®
Packaged Desiccant

SECTION I -- PRODUCT IDENTIFICATION

Trade Name and Synonyms:	Silica Gel, Synthetic Amorphous Silica, Silicon, Dioxide
Chemical Family:	Synthetic Amorphous Silica
Formula:	$SiO_2.x\ H_2O$

SECTION II -- HAZARDOUS INGREDIENTS

Components in the Solid Mixture

COMPONENT	CAS No	%	ACGIH/TLV (PPM)	OSHA-(PEL)
Amorphous Silica	63231-67-4	>99	PEL - 20 (RESPIRABLE), TLV – 5	LIMIT – NONE, HAZARD - IRRITANT ˝

Synthetic amorphous silica is not to be confused with crystalline silica such as quartz, cristobalite or tridymite or with diatomaceous earth or other naturally occurring forms of amorphous silica that frequently contain crystalline forms.

This product is in granular form and packed in bags for use as a desiccant. Therefore, no exposure to the product is anticipated under normal use of this product. Avoid inhaling desiccant dust.

SECTION III -- PHYSICAL DATA

Appearance and Odor:	White granules; odorless.
Melting Point:	>1600 Deg C; >2900 Deg F
Solubility in Water:	Insoluble.
Bulk Density:	>40 lbs./cu. ft.
Percent Volatile by Weight @ 1750 Deg F:	<10%.

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SORB-IT®
Packaged Desiccant

SECTION IV -- FIRE EXPLOSION DATA

Fire and Explosion Hazard - Negligible fire and explosion hazard when exposed to heat or flame by reaction with incompatible substances.

Flash Point - Nonflammable.

Firefighting Media - Dry chemical, water spray, or foam. For larger fires, use water spray fog or foam.

Firefighting - Nonflammable solids, liquids, or gases: Cool containers that are exposed to flames with water from the side until well after fire is out. For massive fire in enclosed area, use unmanned hose holder or monitor nozzles; if this is impossible, withdraw from area and let fire burn. Withdraw immediately in case of rising sound from venting safety device or any discoloration of the tank due to fire.

SECTION V -- HEALTH HAZARD DATA

Health hazards may arise from inhalation, ingestion, and/or contact with the skin and/or eyes. Ingestion may result in damage to throat and esophagus and/or gastrointestinal disorders. Inhalation may cause burning to the upper respiratory tract and/or temporary or permanent lung damage. Prolonged or repeated contact with the skin, in absence of proper hygiene, may cause dryness, irritation, and/or dermatitis. Contact with eye tissue may result in irritation, burns, or conjunctivitis.

First Aid (Inhalation) - Remove to fresh air immediately. If breathing has stopped, give artificial respiration. Keep affected person warm and at rest. Get medical attention immediately.

First Aid (Ingestion) - If large amounts have been ingested, give emetics to cause vomiting. Stomach siphon may be applied as well. Milk and fatty acids should be avoided. Get medical attention immediately.

First Aid (Eyes) - Wash eyes immediately and carefully for 30 minutes with running water.

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SORB-IT®
Packaged Desiccant

NOTE TO PHYSICIAN: This product is a desiccant and generates heat as it adsorbs water. The used product can contain material of hazardous nature. Identify that material and treat accordingly.

SECTION VI -- REACTIVITY DATA

Reactivity - Silica gel is stable under normal temperatures and pressures in sealed containers. Moisture can cause a rise in temperature which may result in a burn.

SECTION VII --SPILL OR LEAK PROCEDURES

Notify safety personnel of spills or leaks. Clean-up personnel need protection against inhalation of dusts or fumes. Eye protection is required. Vacuuming and/or wet methods of cleanup are preferred. Place in appropriate containers for disposal, keeping airborne particulates at a minimum.

SECTION VIII -- SPECIAL PROTECTION INFORMATION

Respiratory Protection - Provide a NIOSH/MSHA jointly approved respirator in the absence of proper environmental control. Contact your safety equipment supplier for proper mask type.

Ventilation - Provide general and/or local exhaust ventilation to keep exposures below the TLV. Ventilation used must be designed to prevent spots of dust accumulation or recycling of dusts.

Protective Clothing - Wear protective clothing, including long sleeves and gloves, to prevent repeated or prolonged skin contact.

Eye Protection - Chemical splash goggles designed in compliance with OSHA regulations are recommended. Consult your safety equipment supplier.

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MATERIAL SAFETY DATA SHEET -- September 28, 1998
SORB-IT®
Packaged Desiccant

SECTION IX -- SPECIAL PRECAUTIONS

Avoid breathing dust and prolonged contact with skin. Silica gel dust causes eye irritation and breathing dust may be harmful.

* No Information Available

HMIS (Hazardous Materials Identification System) for this product is as follows:

Health Hazard	0
Flammability	0
Reactivity	0
Personal Protection	HMIS assigns choice of personal protective equipment to the customer, as the raw material supplier is unfamiliar with the condition of use.

Material Safety Data Sheet

Indicating Silica Gel

Identity (Trade Name as Used on Label)

Manufacturer : MULTISORB TECHNOLOGIES, INC. (formerly Multiform Desiccants, Inc.)	MSDS Number* : M75
Address: 325 Harlem Road Buffalo, NY 14224	CAS Number* :
Phone Number (For Information): 716/824-8900	Date Prepared: July 6, 2000
Emergency Phone Number: 716/824-8900	Prepared By* : G.E. McKedy

Section 1 - Material Identification and Information

Components - Chemical Name & Common Names (Hazardous Components 1% or greater; Carcinogens 0.1% or greater)	%*	OSHA PEL	ACGIH TLV	OTHER LIMITS RECOMMENDED
Silica Gel SiO_2	98.0	6mg/m^3 (total dust)	10mg/m^3 (total dust)	
Cobalt Chloride	>2.0	0.05mg/m^3 (TWA cobalt metal dust & fume)	.05mg/m^3 (Cobalt, TWA)	
Non-Hazardous Ingredients				
TOTAL	100			

Section 2 - Physical/Chemical Characteristics

Boiling Point	N/A	Specific Gravity (H_20 = 1)	2.1
Vapor Pressure (mm Hg and Temperature	N/A	Melting Point	N/A
Vapor Density (Air =1)	N/A	Evaporation Rate (_____=1)	N/A
Solubility in Water	Insoluble, but will adsorb moisture.	Water Reactive	Not reactive, but will adsorb moisture.
Appearance and Odor	Purple crystals, no odor.		

Section 3 - Fire and Explosion Hazard Data

Flash Point and Methods Used	N/A	Auto-Ignition Temperature	N/A	Flammability Limits in Air % by Volume	N/A	LEL	UEL
Extinguisher Media	Dry chemical, carbon dioxide and foam can be used.						
Special Fire Fighting Procedures	Water will generate heat due to the silica gel which will adsorb water and liberate heat.						
Unusual Fire and Explosion Hazards	When exposed to water, the silica gel can get hot enough to reach the boiling point of water. Flooding with water will reduce the temperature to safe limits.						

Section 4 - Reactivity Hazard Data

STABILITY ☐**Stable** ☐**Unstable**	Conditions To Avoid	Moisture and high humidity environments.
Incompatibility (Materials to Avoid)	Water.	
Hazardous Decomposition Products	Carbon dioxide, carbon monoxide, water	
HAZARDOUS POLYMERIZATION ☐May Occur	Conditions To Avoid	None.

*Optional

Section 5 - Health Hazard Data

PRIMARY ROUTES OF ENTRY	☐Inhalation ☐Skin Absorption	☐Ingestion ☐Not Hazardous	**CARCINOGEN LISTED IN**	☐NTP ☐IARC Monograph	☐OSHA ☐Not Listed
HEALTH HAZARDS	Acute	May cause eye, skin and mucous membrane irritation.			
	Chronic	Prolonged inhalation may cause lung damage.			
Signs and Symptoms of Exposure	Drying and irritation.				
Medical Conditions Generally Aggravated by Exposure	Asthma.				
EMERGENCY FIRST AID PROCEDURES - Seek medical assistance for further treatment, observation and support if necessary.					
Eye Contact	Flush with water for at least 15 minutes.				
Skin Contact	Wash affected area with soap and water.				
Inhalation	Remove affected person to fresh air.				
Ingestion	Drink at least 2 glasses of water.				

Section 6 - Control and Protective Measures

Respiratory Protection (Specify Type)	Use NIOSH approved dust mask or respirator.		
Protective Gloves	Light cotton gloves.	Eye Protection	Safety glasses.
VENTILATION TO BE USED	☐ Local Exhaust	☐Mechanical (General)	☐Special
	☐Other (Specify)		
Other Protective Clothing and Equipment	None.		
Hygienic Work Practices	Avoid raising dust. Avoid contact with skin, eyes and clothing.		

Section 7 - Precautions for Safe Handling and Use/Leak Procedures

Steps to be Taken if Material Is Spilled Or Released	Sweep or vacuum up and place the spilled material in a waste disposal container. Avoid raising dust.
Waste Disposal Methods	Dispose in an approved landfill according to federal, state and local regulations.
Precautions to be Taken In Handling and Storage	Cover promptly to avoid blowing dust. Wash after handling.
Other Precautions and/or Special Hazards	Keep in sealed containers away from moisture. The silica gel will readily adsorb moisture.

*Optional Indicating Silica Gel

3710R/3750 Refrigerated Sampler

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*Teledyne Isco One Year Limited Factory Service Warranty **

Teledyne Isco warrants covered products against failure due to faulty parts or workmanship for a period of one year (365 days) from their shipping date, or from the date of installation by an authorized Teledyne Isco Service Engineer, as may be appropriate.

During the warranty period, repairs, replacements, and labor shall be provided at no charge. Teledyne Isco's liability is strictly limited to repair and/or replacement, at Teledyne Isco's sole discretion.

Failure of expendable items (e.g., charts, ribbon, tubing, lamps, glassware, seals and filters), or from normal wear, accident, misuse, corrosion, or lack of proper maintenance, is not covered. Teledyne Isco assumes no liability for any consequential damages.

Teledyne Isco specifically disclaims any warranty of merchantability or fitness for a particular purpose.

This warranty applies only to products sold under the Teledyne Isco trademark and is made in lieu of any other warranty, written or expressed.

No items may be returned for warranty service without a return authorization number issued from Teledyne Isco.

This warranty does not apply to the following products: Process Analyzers, SFX 3560 SFE Extractor, 6100 VOC Sampler.

The warrantor is Teledyne Isco, Inc. 4700 Superior, Lincoln, NE 68504, U.S.A.

*** This warranty applies to the USA and countries where Teledyne Isco Inc. does not have an authorized dealer. Customers in countries outside the USA, where Teledyne Isco has an authorized dealer, should contact their Teledyne Isco dealer for warranty service.**

In the event of instrument problems, always contact the Teledyne Isco Service Department, as problems can often be diagnosed and corrected without requiring an on-site visit. In the U.S.A., contact Teledyne Isco Service at the numbers listed below. International customers should contact their local Teledyne Isco agent or Teledyne Isco International Customer Service.

Return Authorization

A return authorization number must be issued prior to shipping. Following authorization, Teledyne Isco will pay for surface transportation (excluding packing/crating) both ways for 30 days from the beginning of the warranty period. After 30 days, expense for warranty shipments will be the responsibility of the customer.

Shipping Address: Teledyne Isco, Inc. - Attention Repair Service
4700 Superior Street
Lincoln NE 68504 USA

Mailing address: Teledyne Isco, Inc.
PO Box 82531
Lincoln NE 68501 USA

Phone: Repair service: (800)775-2965 (lab instruments)
(800)228-4373 (samplers & flow meters)
Sales & General Information (800)228-4373 (USA & Canada)

Fax: (402) 465-3001

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APPENDIX 16
SOP FOR NEAR-FIELD PCB RELEASE MECHANISM SAMPLING

APPENDIX 16
STANDARD OPERATING PROCEDURE FOR NEAR-FIELD PCB RELEASE MECHANISM SAMPLING

1.1 Scope & Application

This Standard Operating Procedure (SOP) is applicable to the collection of water column samples downstream of dredging operations for total suspended solid (TSS) and dissolved and particulate polychlorinated biphenyl (PCB) analyses as part of a special study for the Hudson River Remedial Action Monitoring Program (RAMP). The objective of this study is to determine the nature of PCB release during dredging (sediment resuspension/particle-associated or dissolved phase). This study will examine whether near-field TSS concentrations can be considered a reliable indicator of PCB releases due to dredging-related activities. If so, real-time TSS surrogate measurements taken at near-field stations may be used: 1) to identify when modifications of dredging activities to reduce resuspension are needed; and 2) to anticipate when elevated PCB concentrations may be expected at far-field monitoring stations.

1.2 Summary of Method

The study will be carried out at multiple locations so that a range of dredging conditions can be evaluated, including different sediment types (cohesive and non-cohesive) and PCB concentrations, and the range of dredge types used for Phase 1 dredging. Water samples will be collected and filtered to measure dissolved and particulate PCB concentrations within the resuspended sediment plume generated by active dredging operations. Discrete monitoring of each study area will be performed on three occasions, spaced approximately 2 days apart.

1.3 Health and Safety Warnings

Health and safety issues are addressed in the project Health and Safety Plan (HASP; Parsons 2008).

1.4 Contamination and Interferences

- Cross contamination
- Improper sample collection
- Rupture of filter

1.5 Personnel Qualifications

All field personnel are required to take a 40-hour OSHA Hazardous Waste Operations training course and annual refresher courses, and participate in a medical monitoring program prior to engaging in any field collection activities as required in 29 CFR 1910.120. Additionally, field personnel will be under the direct supervision of qualified professionals who are experienced in performing the tasks required for sample collection.

1.6 Equipment and Supplies

Sample collection equipment:

- Sampling vessel equipped w/GPS (WAAS enabled)
- Peristaltic pump (2 required)
- Teflon (or equivalent) pump tubing (for PCB and organic carbon sampling)
- Clear vinyl pump tubing (for TSS sampling)
- Downrigger or similar device to maintain depth of pump tubing (2 required)
- 25 ml graduated cylinder
- 250 ml graduated cylinder
- Stainless steel pressure filtration apparatus
- 4 L amber glass pre-cleaned containers
- 142 mm, 0.7 µm glass fiber filters (cleaned) in Petri dish
- Forceps
- YSI 6000 series multi-parameter probe, or equivalent
- Decontamination supplies
- Lap top computer
- Field note book
- Printer
- Re-sealable food storage bags

- Sample labels
- Cooler
- Ice
- Temperature blank

1.7 Water Sample Collection

Sampling Locations

Sampling locations are defined in Section 9.2 and Figures 9-1 and 9-2 of the RAM QAPP, and include five special study areas; four in the Northern Thompson Island Pool (NTIP) and one to the east of Griffin Island (EGIA). Samples will be collected from one upstream (background) station and from three downstream transects at each special study area. Sampling locations will be laid out in the field as follows:

Background Location

The background station will be adjacent to the upstream near-field monitoring station (if one is used at the operation being studied). If no upstream near-field monitoring station is available a location for collecting the background sample will be determined as follows:

1. Obtain the approximate coordinates of the dredging operation from the dredge operator or navigate the sampling vessel as close as possible to the dredging operation and determine the coordinates using GPS (WAAS enabled).
2. Determine the approximate distance from the dredging operation to the nearest shore using GPS.
3. Position the sampling vessel at a location approximately 100 m upstream of the dredging operation, and the same approximate distance from the shoreline as the dredge. Secure the vessel at this position using an anchor or spuds.

Downstream Transect Locations

Three transects will be placed downstream of the dredging activity (perpendicular to flow). These transects will be located at approximately 30 m, 100 m and 300 m downstream of the dredging operation. The procedure to delineate the transects is presented below:

1. Navigate the sampling vessel approximately 30 m downstream of the dredging operation.

2. Deploy the continuous reading turbidity probe to the approximate mid-depth of the water column.
3. Move the vessel laterally across the river along a line approximately 30 m downstream of the dredge at idle speed, and collect turbidity data to delineate the lateral extent of the plume. The plume will be defined as the area of the river that exhibits turbidity that is a minimum of 10 NTUs above background conditions.
4. Obtain coordinates using the GPS at the approximate end points of the lateral extent of the plume at the 30 m transect.
5. Calculate the total width of the plume along the transect. Multiply the plume width by 0.17. Then, starting from one of the transect end points, move the vessel toward the center of the plume along the transect this distance and anchor a buoy at that location. Repeat this procedure starting at the opposite transect end point. Samples will be collected along the transect between these two buoys (samples will only be collected from the central 2/3 of the plume).
6. Repeat steps 1-5 at the 100 m and 300 m transects.

Sampling Frequency and Methods

Discrete monitoring of each study area shall be performed on three occasions, spaced approximately 2 days apart.

Background Sampling

Samples will be collected at the background station as follows:

1. Navigate the sampling vessel to the background station and secure the vessel in place using anchors or spuds.
2. Two peristaltic pumps will be used. Place Teflon tubing (or equivalent) in one pump ("PCB sampling pump") and clear vinyl tubing in the other ("TSS sampling pump"). Attach the pump intake tubing from both pumps and a YSI 6000 Series multi-parameter probe (or equivalent) to a downrigger or similar device and lower to 0.2 of the water depth. Begin collecting data for DO, conductivity, temperature, pH, and turbidity. These measurements shall be logged at a minimum frequency of one minute.
3. Set up a decontaminated stainless steel pressure filtration apparatus on the boat. The filtration unit will be capable of accepting 142 mm diameter filters.

4. Prior to installing a filter, add approximately 0.5-L of river water to the reservoir of the filtration unit. Rinse the filtration unit by gently swirling the water, and discard the rinsate.
5. Carefully place a clean, pre-weighed filter onto the filtration unit using forceps in a manner that will not deform or perforate the filter. The filters (142 mm Whatman GF/F 0.7 micron glass fiber filter or equivalent) will be obtained from the analytical laboratory prior to each sampling event. The laboratory will prepare the filters by heating in the laboratory at 450°C for a minimum of 1 hour, allow the filters to cool, weighing, and placing them in new Petri dish. The tare weight of each filter will be written on the Petri dish.
6. Connect the discharge from the PCB sampling pump to the inlet side of the filtration unit.
7. Start the PCB sampling pump and check the flow rate by capturing the discharge from the filtration unit in a graduated cylinder and calculate flow based on the volume collected per unit of time. Adjust the pumping rate until it reaches approximately 130 ml/min. Check the flow in the TSS sampling pump using the same procedure, and adjust to approximately 65 ml/min.
8. Collect the filtrate in a clean 4-L amber glass container (two required) by placing the filtration unit discharge tubing in the top of the container. Collect the discharge from the TSS sampling pump in a clean 4-L container (plastic or glass).
9. Check the discharge rate from the filtration unit and the TSS sampling pump visually on a frequent basis, and calibrate the flow every 10 minutes (or more frequently if flow appears to be decreasing) by temporarily diverting the flow into the graduated cylinder. Adjust the PCB sampling pump to maintain a flow of approximately 130 ml/min. out of the filtration unit. If this rate cannot be achieved, turn off the pump and change the filter. If necessary, adjust the TSS sampling pump to maintain a flow of 65 ml/min.
10. If filter changes are required, disconnect the pump intake tubing and allow all sample in the reservoir to pass through the filter, then release the pressure, disassemble the filtration unit, and put in a new filter. Remove the filter with forceps and place back in the Petri dish that was supplied with the filter. Label the Petri dish with pertinent information, as described in Section 10.1 of the QAPP.

11. Install a new filter and continue the filtration until 4-L of sample collected from 0.2 of the water depth has been filtered (approximately 30 minutes), and approximately 2-L of water has been collected from the TSS sampling pump.
12. Turn off both pumps and move the depth of the sampler intake tubing and multi-parameter probe to 0.8 of the water depth. Restart the pump and continue the filtration. Changing filters between the 0.2 and 0.8 water depth sample intake locations is not necessary.
13. Continue to pump and filter as described in steps above until 4-L of sample have been collected at the 0.8 water depth.
14. Label the 4-L containers in accordance with the procedures specified in Section 10.1 of the QAPP. The filtrate contained in the two 4-L containers will be submitted and analyzed as a single sample (dissolved PCB and organic carbon analysis).

Transect Sampling

Samples will be collected at the transect stations as follows:

1. Navigate the sampling vessel to one of the 30 m transect end point buoys and hold the boat near that position using the engine.
2. Prepare the pump, tubing, filtration unit, and containers as described in steps 2-7 above.
3. Collect samples as specified in steps 8-14 above, except the boat will move as the samples are obtained. As soon as the equipment is ready to collect and filter samples, start the pump and begin moving the boat laterally across the transect (between the buoys) at idle speed. Adjust the depth of the pump intake tubing as required to maintain an approximate sampling depth of 0.2 of the total water depth as the boat is moving. When the second end point is reached, reverse direction head back toward the first end point. Continue to move the boat at idle speed back and forth across the transect until the approximately 4-L of sample has been collected.
4. Repeat sample collection in the same manner specified above at 0.8 of the total water depth.
5. When sample collection at the 30 m transect is complete, samples will be obtained from the 100 m and 300 m transects by repeating steps 1-4.

1.8 Sample Handling and Preservation

Sample containers will be labeled prior to sample collection in accordance with labeling requirements specified in Section 10.1. The filtrate and a whole water sample will be collected in 4-L containers, which will be submitted directly to the laboratory. Filters will be contained in Petri dishes supplied with the filters from the laboratory. After labeling, place each container in a re-sealable food storage bag, and place in a cooler with ice to chill the samples to approximately 4°C. A temperature blank will be placed in each cooler for use by the laboratory to measure the temperature of samples upon submittal. Samples will be hand delivered to the laboratory at the end of each day (unless requested otherwise by the laboratory). Chain of custody procedures will be followed, as specified in Section 10.1 of the QAPP. Samples will be submitted for PCB and TSS analysis in accordance with Appendices 28 and 30.

1.9 Data and Records Management

Data from water sample collection will be recorded in a field database using a laptop computer as described in Section 10.5.1 of the QAPP. Upon completion of sampling at one location, all data from the location will be entered into the database. Blank field log sheets can also be used to record information manually in case of difficulties with data entry using the computer are encountered. Manually recorded data will be transcribed into the field database at the end of each day. Additionally, data logged by the multi-parameter probe will be downloaded into the database upon completion of each sampling event.

1.10 Quality Control and Quality Assurance (QA/QC)

Field QA/QC samples (blind duplicate and matrix spike samples) will be collected as part of the RAMP at the same time that the samples for field filtration are collected. Therefore, these samples will provide adequate QA/QC for the program; no additional field QA/QC samples will be collected during the Near-Field PCB Release Mechanism Special Study.

1.11 References

Parsons. 2008. Phase 1 Remedial Action Health and Safety Plan, Hudson River PCBs Superfund Site. Prepared for General Electric Company, Albany, NY. August 2008.

APPENDIX 17
SOP FOR NON-TARGET DOWNSTREAM AREA CONTAMINATION SAMPLING

APPENDIX 17
STANDARD OPERATING PROCEDURE FOR NON-TARGET DOWNSTREAM AREA CONTAMINANT SAMPLING

1.1 Scope & Application

This Standard Operating Procedure (SOP) is applicable to the collection of sediment samples as part of a special study for the Hudson River Remedial Action Monitoring Program (RAMP). The purpose of this program is to determine the extent to which resuspension induced by dredging activities results in the movement of polychlorinated biphenyls (PCBs) to areas that are immediately downstream and is a potential source of future contamination of the water column and downstream surficial sediment. The sediment samples will be analyzed for total mass, with a subset of samples analyzed for Aroclor-based PCBs using Method GEHR8082 and particulate organic carbon (POC) using the Lloyd Kahn Method.

1.2 Summary of Method

Sediment deposition will be monitored by deploying sediment traps at the stations described below. The sediment traps will be deployed from a boat using an underwater video system. The traps will be lowered gently to the bottom of the river, and allowed to rest on an approximately level area. Multiple traps will be deployed to provide data on both a spatial and temporal basis.

1.3 Health and Safety Warnings

Health and safety issues are addressed in the project Health and Safety Plan (HASP; Parsons 2008).

1.4 Contamination and Interferences

- Cross contamination
- Improper sample collection

1.5 Personnel Qualifications

All field personnel are required to take a 40-hour OSHA Hazardous Waste Operations training course and annual refresher courses, and participate in a medical monitoring program prior to engaging in any field collection activities as required in 29 CFR 1910.120. Additionally, field personnel will be under the direct supervision of qualified professionals who are experienced in performing the tasks required for sample collection.

1.6 Equipment and Supplies

Equipment needed for the collection of sediment trap samples includes:

- Sampling vessel equipped w/GPS (WAAS enabled)
- Underwater video system
- Sediment traps
- Telescoping poles and associated tools for trap deployment and retrieval
- 4-L, wide-mouth amber glass pre-cleaned containers
- 2 gallon re-sealable food storage bags
- Decontamination supplies
- Laptop computer
- Field note book
- Printer
- Sample labels
- Label Printer
- Cooler
- Ice
- Temperature blank

1.7 Sediment Sample Collection

Sampling Locations

The study areas and conceptual layout for the sediment traps is presented in Section 9.3 of the QAPP. Coordinates for each sediment trap location will be determined using GIS. The location and spacing of the sediment traps may have to be adjusted to prevent placement of sediment traps in the navigational channel.

Sampling Frequency and Methods

The monitoring period for each study area will extend over the entire time that the study area is being dredged. Six rounds of data will be obtained at approximately equal time intervals. The length of these time intervals will be determined by subdividing the estimated time required to dredge the target area by 6. The frequency of monitoring may be adjusted during the study to reflect the actual dredging progress.

Sediment Trap Deployment

The sediment traps will be deployed in pairs. Initial deployment of the sediment traps will be performed as follows:

1. Obtain the target coordinates of each sediment trap and program into the GPS (WAAS enabled).
2. Navigate the sampling vessel to within approximately 10 ft. of each target location using the GPS. Secure the vessel in position using spuds.
3. Mark the sediment traps in a unique manner so that each trap can be identified in the future.
4. Gently lower a sediment trap to the bottom of the river using a rope or telescoping pole equipped with a hook. Use the underwater video system to confirm that the sediment trap is placed in a stable position on the bottom. Deploy a second sediment trap in the same manner, placing it adjacent to the first trap. Designate one of the traps to be the primary trap and the other as the secondary trap. The primary trap will be sampled during each data collection round; the secondary trap will only be sampled during the final data collection round. Record the date, time, and sediment trap IDs deployed at each location in the field database.
5. Record the actual coordinates in the field database for the sediment trap pair location and anchor a small buoy (labeled with the sediment trap IDs) at the location.

Sediment Trap Retrieval (Data Collection Rounds 1-5)

1. Navigate the sampling vessel to a sediment trap location using GPS and/or visually to the buoy marking the location. Secure the vessel using spuds.
2. Use the underwater video system to locate the sediment trap pair, identify the ID of each trap, and confirm that the traps have remained in an undisturbed state.

3. If visible sediment is observed in the trap gently raise the primary trap to the deck of the sampling vessel using a telescoping pole equipped with a hook or similar device.
4. Decant the water that overlies the sediment that has accumulated in the trap to the extent possible without losing solids. Pour the remaining water and sediment from the trap into a wide mouth 4-L glass container. Label the container with the appropriate sediment trap ID.
5. Rinse the trap with distilled water prior to redeployment. Redeploy the trap by gently lowering it to the bottom of the river, and confirming that it is in a stable position with the underwater video system.

Sediment Trap Retrieval (Data Collection Round 6)

1. Retrieve and sample both the primary and secondary sediment traps using the same technique specified in Steps 1 through 5, above.
2. Clean the traps and store for future use. Remove the buoy and associated anchor.

1.8 Sample Handling and Preservation

Sample containers will be labeled prior to sample collection in accordance with labeling requirements specified in Section 10.1. The 4-L containers will be submitted directly to the laboratory. After sample has been transferred to the pre-labeled, amber glass 4-L container, place each container in a re-sealable food storage bag, and place in a cooler with ice to chill the samples to approximately 4°C. A temperature blank will be placed in each cooler for use by the laboratory to measure the temperature of samples upon submittal. Samples will be hand delivered to the laboratory at the end of each day (unless requested otherwise by the laboratory). Chain of custody procedures will be followed, as specified in Section 10.1 of this QAPP. The sediment collected on the primary traps from this study will be analyzed for mass of solids (Appendix 60). The sediment collected in the secondary traps will be analyzed for Aroclor PCBs (Appendix 49), POC (Appendix 59), and mass of solids (Appendix 60).

1.9 Data and Records Management

All data from sediment trap sample collection will be recorded in a field database using a laptop computer, as described in Section 10.5 of the QAPP. Upon deployment or collection of a sediment trap, all data from the event will be entered into the database. Blank field log

sheets can also be used to record information manually in case difficulties with data entry using the computer are encountered. Manually recorded data will be transcribed into the field database at the end of each day.

1.10 Quality Control and Quality Assurance (QA/QC)

Two additional sediment traps will be deployed for QA/QC purposes for each of the three area studies. One of these traps will be placed adjacent to a primary sediment trap, and the other will be placed adjacent to a secondary trap. These additional traps will provide blind duplicate samples during each round of data collection, and will be handled and analyzed in the same manner as the other sediment traps.

1.11 References

Parsons. 2008. Phase 1 Remedial Action Health and Safety Plan, Hudson River PCBs Superfund Site. Prepared for General Electric Company, Albany, NY. August 2008.

APPENDIX 18
SOP FOR ELECTRONIC DATA DELIVERABLE (EDD)

APPENDIX 18
STANDARD OPERATING PROCEDURE FOR THE LABORATORY ELECTRONIC DATA DELIVERABLE (EDD)

1.1 Introduction

The purpose of this document is to describe the processing of the analytical data received from the laboratory and includes the required specifications of the electronic data deliverable (EDD) format.

1.1.1 File Format

All data from the laboratory must be transmitted in an ASCII file using a tab-delimited standard format. Maximum length of text fields is indicated in the parentheses below in the *Column Datatype* column. If the information is less than the maximum length, do not pad the record with spaces.

Each record must be terminated with a carriage return/line feed (i.e., standard DOS text file). The file can be produced using any software with the capability to create ASCII files. Date is reported as MM/dd/yyyy (month in year/day in month/four digit year) and time as HH:mm (hour in day:minute in hour). Time uses a 24-hour clock, thus 3:30 p.m. will be reported as 15:30.

Four files are required: one each for laboratory samples, tests, results, and batches. The files must have valid DOS (8.3) filenames. The filename extensions are used to indicate the file type as follows:

*.SMP for laboratory sample rows

*.TST for test rows

*.RES for result rows

*.BCH for batch rows

The 8-character filenames for the lab generated files must be the same for each group of four files. If a file needs to be resubmitted after error corrections the file name must remain the

same as that of the original submittal. All four files will be prepared and loaded into the database together in one group.

1.1.2 Data Integrity Rules

If a field is to be considered part of the primary key of a table, it is indicated below by the presence of "PK" in the PK column. The combination of values in each primary key must be unique within the file. Referential integrity must be enforced between files and between these files and existing records (field information) in the project database. The foreign key relationships in the EDD files are listed below:

1. If a sys_sample_code in the .TST file references a field sample, the sys_sample_code and lab_anl_method_name fields of that line of the .TST file constitute a foreign key that references the primary key of an existing field sample test request record in the project database.
2. If a sys_sample_code in the .TST file references a laboratory sample, the sys_sample_code of that line of the .TST file is a foreign key that references the primary key of the .SMP file.
3. The sys_sample_code, lab_anl_method_name, analysis_date, analysis_time, total_or_dissolved, column_number, and test_type fields of the .RES file constitute a foreign key that references the primary key of the .TST file.
4. The sys_sample_code, lab_anl_method_name, analysis_date, analysis_time, total_or_dissolved, column_number, and test_type fields of the .BCH file is a foreign key that references the primary key of the .TST file.

1.1.3 Controlled Vocabulary

Many of the fields are populated with controlled values; that is, their content must be one of a set of defined text strings. Where this is the case it is indicated in the tables below with a "Yes" in the *Ref. Value* column. The set of defined values for each controlled value field are listed in Table 10.2.

Setting the value of certain controlled value fields will restrict the value of other controlled value fields in the same line to a particular value. This is the case with the lab_anl_method_name and prep_method columns of the .TST file. Table 10.2a lists the

prep_method value that must be specified along with a given lab_anl_method_name value; if no prep_method value is given in Table 10.2a, then a null value should be used for the particular record.

Tables 10.2b-e list the controlled values for target analytes that must be reported for each analytical method. Results for these analytes must have the "TRG" result type. Note that chemical_name is not a controlled value and is added to Tables 10.2b-e for clarity.

Controlled values for surrogate compounds for analytical methods are listed in Table 10.2a *Analytical Methods-Surrogates*. Results for these analytes must also be reported for the analytical methods listed in Table 10.2a. Results for surrogate analytes must have the "SUR" result type.

1.1.4 Null Format

Many fields are optional. When a field is not listed as required, this means that a null value may be appropriate. A null value is represented in the EDD file as and empty field and is delimited by two immediately adjacent tab delimiters. The null value must still be surrounded by tabs. In other words, the number of fields is always the same, whether or not there are null fields in the file.

1.2 Naming Convention of Samples

Field samples being submitted to the data management system follow a standard naming structure. Sample names are composed of four distinct components separated by hyphen characters. As an example, a water column field sample ID of 'WFF-SCHU-060412-AT001' contains the four components:

- WFF
- SCHU
- 060412
- AT001

There will be no hyphens within any of the individual components.

Lab QC sample IDs will have the same four component structure as field sample IDs. The Lab QC sample ID will be constructed by replacing the third component of any sample name on the chain of custody with the concatenation of LABQC and the relevant sample delivery group id. The fourth component of the Lab QC sample ID will be the internal laboratory sample ID. For example a method blank QC sample (A3910), delivered in sample delivery group 'COC06040084', for a batch containing the sample mentioned above would look like 'WFF-SCHU-LABQCCOC06040084-A3910'. The sample ID has a maximum of 60 characters available to it. It is the responsibility of the laboratory to ensure that the ID strings are within the size limits.

1.3 Examples

Below are examples of sample types to be used in the project, showing when QC fields need to be populated and when it is not necessary to populate QC fields.

QC fields in a normal field sample (i.e., Sample_type_code = ENV)

The following table shows a subset of the fields in the result file for a normal field sample. Notice that all QC fields are blank.

cas_rn	Result Value	QC Original Conc	QC Spike Added	QC Spike Measured	QC Spike Recovery	QC Dup Original Conc	QC Dup Spike Added	QC Dup Spike Measured	QC Dup Spike Recovery
93-76-5	1.56								
94-75-7	3.17								
94-82-6	2.31								

QC fields in a normal field sample with surrogates (i.e., Sample_type_code = ENV)

The following table shows a subset of the fields in the result file for a normal field sample. Notice that QC fields are blank except on surrogate rows.

cas_rn	Result Value	Result Unit	Result Type Code	QC Original Conc	QC Spike Added	QC Spike Measured	QC Spike Recovery
93-76-5	1.56	mg/l	TRG				
94-75-7	3.17	mg/l	TRG				
PHEN2F		mg/l	SUR		12.5	12.9	103

QC fields in a matrix spike (i.e., Sample_type_code = MS)

The following table shows some of the fields in the result file for a matrix spike sample. Notice that all "dup" QC fields are blank. The qc_rpd field (data column not shown) is left blank for these rows.

cas_rn	Result Value	QC Original Conc	QC Spike Added	QC Spike Measured	QC Spike Recovery	QC Dup Original Conc	QC Dup Spike Added	QC Dup Spike Measured	QC Dup Spike Recovery
93-76-5	5.36	1.56	4.18	5.36	90.9				
94-75-7	7.15	3.17	4.18	7.15	95.2				
94-82-6	5.66	2.31	4.22	5.66	79.3				

QC fields in a matrix spike duplicate (i.e., Sample_type_code = MSD)

The following table shows a subset of the fields in the result file for a matrix spike duplicate sample. Notice that all "dup" QC fields are completed. The qc_rpd field (data column not shown) is required for these rows.

cas_rn	Result Value	QC Original Conc	QC Spike Added	QC Spike Measured	QC Spike Recovery	QC Dup Original Conc	QC Dup Spike Added	QC Dup Spike Measured	QC Dup Spike Recovery
93-76-5	5.70					1.56	4.23	5.70	97.8
94-75-7	7.62					3.17	4.23	7.62	105
94-82-6	5.33					2.31	4.13	5.33	73.1

QC fields in an LCS (i.e., laboratory control sample, blank spike, Sample_type_code = LCS)

The following table shows a subset of the fields in the result file for an LCS sample. The qc_rpd field (data column not shown) is left blank for these rows.

cas_rn	Result Value	QC Original Conc	QC Spike Added	QC Spike Measured	QC Spike Recovery	QC Dup Original Conc	QC Dup Spike Added	QC Dup Spike Measured	QC Dup Spike Recovery
93-76-5			5.00	5.26	105				
94-75-7			1.00	1.02	102				
94-82-6			12.5	12.9	103				

Retests

The following table shows how to report retests in an example where a sample was retested at dilution. The first two constituents (75-25-2, and 67-66-3) are reported in the initial test, and constituent 95-95-4 in the diluted retest. The other results would be "turned off" by setting the reportable_result field to "No". Surrogate results, however, are flagged as reportable ("Yes") in both the initial test records and for any retest records.

Test_type	cas_rn	result_value	reportable_result
Initial	75-25-2	1.2	Yes
Initial	67-66-3	3.4	Yes
Initial	95-95-4	100	No
Reanalysis	75-25-2		No
Reanalysis	67-66-3		No
Reanalysis	95-95-4	78.3	Yes

Second Columns

The following table shows how to report first and second column confirmation results. The first and third constituents (75-25-2, and 95-95-4) are reported in the first column, and constituent 67-66-3 is reported in the second column. The other results would be "turned off" by setting the reportable_result field to "No".

column_number	cas_rn	result_value	reportable_result
1C	75-25-2	1.2	Yes
1C	67-66-3	3.4	No
1C	95-95-4	5.6	Yes
2C	75-25-2	1.3	No
2C	67-66-3	3.7	Yes
2C	95-95-4	5.4	No

Units

Units are to be reported consistently for the duration of the project. The result_unit field is required to be reported as specified in the controlled values. Associated measurements (i.e., reporting detection limit, method detection limit) must be reported consistently with the result units.

Sample Import Format

#	Attribute Name	Column Datatype	PK	Required	Ref Value	Attribute Definition
1	sys_sample_code	Text(25)	PK	required		Unique sample identifier. Each sample must have a unique value. For matrix spike, matrix spike duplicate, and laboratory replicate samples, this field must be populated as follows: COC#, which is "COC" followed by a number, then a dash (-), then the Item#, which is a sequential three digit number that is typed on the Chain-of-Custody to the left of each sample (i.e., COC042602-001), followed by "MS" for matrix spike, "SD" for matrix spike duplicate, or "LR" for laboratory replicate. This table must contain all laboratory - generated samples, including lab blanks, blank spikes, matrix spikes, matrix spike duplicates, and laboratory replicates.
2	lab_sample_id	Text(60)		required		Laboratory sample identifier. **The sample naming convention, as described in Section 1.2, must be followed.** **Each line of the file with matching lab_sample_id values must have the same values for sample_type_code, sample_matrix_code, sample_source, parent_sample_code, sample_date, sample_time, and comment.**
3	sample_type_code	Text(10)		required	Yes	Code which distinguishes between different types of sample. For valid value list, consult the controlled values supplied for the project.
4	sample_matrix_code	Text(10)		required	Yes	Code which distinguishes between different types of sample matrix.

#	Attribute Name	Column Datatype	PK	Required	Ref Value	Attribute Definition
						The matrix of the sample as analyzed may be different from the matrix of the sample as retrieved (e.g., TCLP leachates), so this field is required at the sample level. For valid value list, consult the controlled values supplied for the project.
5	sample_source	Text(10)		required	Yes	Must be "Lab" for laboratory QC samples..
6	parent_sample_code	Text(25)		required if applicable		The value of sys_sample_code that uniquely identifies the field sample that was the source of this sample. For example, the value of this field for a laboratory replicate sample would identify the normal field sample of which this sample is a replicate. **Required** in the laboratory EDD for all laboratory "clone" samples (i.e. matrix spikes, matrix spike duplicates, and lab replicates). **Must be null** for samples that have no parent (i.e., method blanks and lab control samples).
7	comment	Text(255)				Sample comments as necessary.
8	sample_date	Date				**Must be a null field for this project.**
9	sample_time	Time				**Must be a null field for this project.**
10	standard_solution_source	Text(20)				Textual description of the source of standard solutions as needed for certain laboratory samples (e.g., LCS).

Test Import Format

#	Attribute Name	Column Datatype	PK	Required	Ref. Value	Attribute Definition
1	sys_sample_code	Text(25)	PK	required		Unique sample identifier. Identifies the sample that the test was performed on.
2	lab_anl_method_name	Text(35)	PK	required	Yes	Laboratory analytical method name or description. For valid value list, consult the controlled values supplied for this project.
3	analysis_date	Date	PK	required		Date of sample analysis in MM/dd/yyyy format.
4	analysis_time	Time	PK	required		Time of sample analysis in 24-hr (military) HH:mm format.
5	total_or_dissolved	Text(1)	PK	required	Yes	Must be either "T" for total (metal) concentration, "D" for dissolved / filtered (metal) concentration, or "N" for organic (or other) constituents for which neither "total" nor "dissolved" is applicable.
6	column_number	Text(2)	PK	required	Yes	Must be either "1C" for first column analyses, "2C" for second column analyses, or "NA" for analyses for which neither "1C" nor "2C" is applicable. If any "2C" tests are reported, then there must be a corresponding "1C" tests present. Laboratories will be reporting which of the two columns is to be considered "primary". This distinction is handled by the "reportable_result" field in the result table (see section 1.3).
7	test_type	Text(10)	PK	required	Yes	Type of test. Valid values include "initial", "reextract", and "reanalysis".

#	Attribute Name	Column Datatype	PK	Required	Ref. Value	Attribute Definition
8	lab_matrix_code	Text(10)		required	Yes	Code which distinguishes between different types of lab sample matrix. The matrix of the sample as analyzed may be different from the matrix of the sample as retrieved (e.g., TCLP leachates). For valid value list, consult the controlled values supplied for this project.
9	analysis_location	Text(2)		required	Yes	Must be either "FI" for field instrument or probe, "FL" for mobile field laboratory analysis, or "LB" for fixed-based laboratory analysis.
10	basis	Text(10)		required	Yes	Must be either "Wet" for wet-weight basis reporting, "Dry" for dry-weight basis reporting, or "NA" for tests for which this distinction is not applicable.
11	dilution_factor	Number		required		Effective test dilution factor. Must be greater than zero.
12	prep_method	Text(35)		required if applicable	Yes	Laboratory sample preparation method name or description. For valid values consult the controlled values list supplied for the project. Selection of analytical test method may require the specification of a particular preparation method. To determine when this requirement applies consult the controlled values list supplied for the project.
13	prep_date	Date		required if applicable		Date of sample preparation in MM/dd/yyyy format. **Required** when the prep_method is not null.
14	prep_time	Time		required if applicable		Time of sample preparation in 24-hr (military) HH:mm format. **Required** when the prep_method is not null.

#	Attribute Name	Column Datatype	PK	Required	Ref. Value	Attribute Definition
15	leachate_method	Text(15)				Laboratory leachate generation method name or description. A list of valid method names is not required for the laboratory EDD unless otherwise specified by the project manager.
16	leachate_date	Date		required if applicable		Date of leachate preparation in MM/dd/yyyy format. **Required** when the leachate_method is not null.
17	leachate_time	Time		required if applicable		Time of leachate preparation in 24-hr (military) HH:mm format. **Required** when the leachate_method is not null.
18	lab_name_code	Text(10)		required	Yes	Unique identifier of the laboratory. For valid value list, consult the controlled values supplied for this project.
19	data_package_level	Text(10)		required	Yes	Data package level. Possible values are “A”, “B”, or “AB”.
20	lab_sample_id	Text(20)		required		Internal laboratory sample identifier.
21	percent_moisture	Number		required		Percent moisture of the sample portion used in this test. Numeric format is "NN.MM", (e.g., 70.1% is reported as "70.1" and not as "70.1%"). Must be between 0 and 100.
22	subsample_amount	Number		required		Amount of original sample used in sample preparation. Must be greater than zero.

#	Attribute Name	Column Datatype	PK	Required	Ref. Value	Attribute Definition
23	subsample_amount_unit	Text(15)		required	Yes	Unit of measurement for sub-sample amount. Must use standard unit abbreviations (see controlled values list supplied for the project). The capitalization specified for the unit abbreviation must be followed. The standard ASCII character "u" will be used in place of the Greek letter µ (mu) to indicate "micro."
24	analyst_name	Text(30)				Name or initials of laboratory analyst. This is an optional field for the laboratory EDD unless otherwise specified by the project manager.
25	instrument_id	Text(50)				Instrument identifier. This is an optional field for the laboratory EDD unless otherwise specified by the project manager.
26	sample_receipt_date	Date		required if applicable		Date of sample collection in MM/dd/yyyy format. **Must be null** for laboratory samples (i.e. matrix spike, matrix spike duplicate, lab replicate, method blank, and lab control sample). **Required** for field samples.
27	sample_receipt_time	Time		required if applicable		Time of sample collection in 24-hr (military) HH:mm format. **Must be null** for laboratory samples (i.e. matrix spike, matrix spike duplicate, lab replicate, method blank, and lab control sample). **Required** for field samples.
28	sample_delivery_group	Text(15)		required		Sample delivery group id. Every row of the file must contain the same sample_delivery_group.
29	comment	Text(255)				Comments about the test as

#	Attribute Name	Column Datatype	PK	Required	Ref. Value	Attribute Definition
						necessary.
30	final_volume	Number				The final amount/volume of the sample, extract, or digestate after sample preparation.
31	final_volume_unit	Text(15)		required if applicable	Yes	Unit of measure of final_volume. Must use standard unit abbreviations (see controlled values list supplied for the project). The capitalization specified for the unit abbreviation must be followed. The standard ASCII character "u" will be used in place of the Greek letter µ (mu) to indicate "micro." **Required** if the final_volume is **not** null. **Must be null** if the final_volume is null.

Result Import Format

#	Attribute Name	Type	PK	Required	Ref. Value	Attribute Definition
1	sys_sample_code	Text(25)	PK	required		Unique sample identifier. Identifies the sample that the test was performed on.
2	lab_anl_method_name	Text(35)	PK	required	Yes	Laboratory analytical method name or description. For valid value list, consult the controlled values supplied for the project.
3	analysis_date	Date	PK	required		Date of sample analysis in MM/dd/yyyy format.
4	analysis_time	Time	PK	required		Time of sample analysis in 24-hr (military) HH:mm format.
5	total_or_dissolved	Text(1)	PK	required	Yes	Must be either "T" for total (metal) concentration, "D" for dissolved/filtered (metal) concentration, or "N" for organic (or other) constituents for which neither "total" nor "dissolved" is applicable.
6	column_number	Text(2)	PK	required	Yes	Must be either "1C" for first column analyses, "2C" for second column analyses, or "NA" for analyses for which neither "1C" nor "2C" is applicable.
7	test_type	Text(10)	PK	required	Yes	Type of test. Valid values include "initial", "reextract", and "reanalysis".
8	cas_rn	Text(15)	PK	required	Yes	Chemical Abstracts Registry Number for the parameter if available. Otherwise consult the controlled values supplied for this project.
9	chemical_name	Text(60)				Name of the parameter. Used only in manual review of EDD.
10	result_value	Number		required if applicable		Analytical result reported at the project specified number of significant digits. **Must be null** for non-detects. **Required** for any result not qualified as non-detect.
11	result_error_delta	Text(20)				Error range applicable to the result value; typically used only for radiochemistry results.

#	Attribute Name	Type	PK	Required	Ref. Value	Attribute Definition
12	result_type_code	Text(10)		required	Yes	Must be either "TRG" for a target or regular result, and "SUR" for surrogates.
13	reportable_result	Text(10)		required	Yes	Must be either "Yes" for results which are considered to be reportable, or "No" for non-reportable results. For target analytes, any given sys_sample_code / cas_rn combination must have only one reportable result record (i.e. reportable_result = “Yes”).
14	detect_flag	Text(1)		required	Yes	Must be either "Y" for detected analytes or "N" for non-detected.
15	lab_qualifiers	Text(7)			Yes	Qualifier flags assigned by the laboratory. For valid value list, consult the controlled values supplied for the project.
16	organic_yn	Text(1)		required	Yes	Must be either "Y" for organic constituents or "N" for inorganic constituents.
17	method_detection_limit	Number		required		Detection limit that reflects conditions such as dilution factors and moisture content.
18	reporting_detection_limit	Number		required		Concentration level above which results can be quantified with confidence. Reflects conditions such as dilution factors and moisture content.
19	quantitation_limit	Number		required		Concentration level above which results can be quantified with confidence. Reflects conditions such as dilution factors and moisture content.
20	result_unit	Text(15)		required	Yes	Unit of measure of result_value. Must use standard unit abbreviations (see controlled values list supplied for the project). The capitalization specified for the unit abbreviation must be followed. The standard ASCII character “u” will be used in place of the Greek letter µ (mu) to indicate “micro.”

#	Attribute Name	Type	PK	Required	Ref. Value	Attribute Definition
						Note that the project may require certain test results to be reported in specific units. For details on when this requirement applies consult the controlled values supplied for this project.
21	detection_limit_unit	Text(15)		required	Yes	Unit of measure of method_detection_limit, reporting_detection_limit, and quantitation_limit. The capitalization specified for the unit abbreviation must be followed. Must use standard unit abbreviations (see controlled values list supplied for the project). The standard ASCII character "u" will be used in place of the Greek letter µ (mu) to indicate "micro." Note that this project requires that detection_limit_unit be the same as result_unit.
22	tic_retention_time	Text(8)				Retention time in seconds for tentatively identified compounds. TICs will not be used on this project.
23	result_comment	Text(255)				Result specific comments as necessary.
24	qc_original_conc	Number		required if applicable		The concentration of the analyte in the original (un-spiked) sample. **Required** for matrix spike, matrix spike sample results. If original (un-spiked) sample is a non-detect, then populate this field with a zero as opposed to the detection limit. If using an original sample result that is less than the reporting limit for background correction, then populate this field with the below reporting limit

#	Attribute Name	Type	PK	Required	Ref. Value	Attribute Definition
						original sample result, as opposed to zero.
25	qc_spike_added	Number		required if applicable		The concentration of the analyte added to the original sample. **Required** for matrix spike, laboratory control sample, performance evaluation, and surrogate compound results.
26	qc_spike_measured	Number		required if applicable		The measured concentration of the analyte. Use zero for spiked compounds that were not detected in the sample. **Required** for matrix spike, laboratory control samples, performance evaluation, and surrogate compound results.
27	qc_spike_recovery	Number		required if applicable		The percent recovery calculated for the spiked compounds. **Required** for matrix spike, laboratory control sample, performance evaluation, and surrogate compound results. Report as percentage (e.g., report "120%" as "120").
28	qc_dup_original_conc	Number		required if applicable		The concentration of the analyte in the original sample. **Required** for matrix spike duplicate and lab replicate results. If original sample is a non-detect, then populate this field with a zero as opposed to the detection limit. For matrix spike duplicates, if using an

#	Attribute Name	Type	PK	Required	Ref. Value	Attribute Definition
						original sample result that is less than the reporting limit for background correction, then populate this field with the below reporting limit original sample result, as opposed to zero.
29	qc_dup_spike_added	Number		required if applicable		The concentration of the analyte added to the original sample. **Required** for matrix spike duplicates.
30	qc_dup_spike_measured	Number		required if applicable		The measured concentration of the analyte in the duplicate. **Required** for matrix spike duplicates. Use zero for spiked compounds that were not detected in the sample.
31	qc_dup_spike_recovery	Number		required if applicable		The duplicate percent recovery calculated for spiked compounds. **Required** for matrix spike duplicates. Report as percentage (e.g., report "120%" as "120").
32	qc_rpd	Number		required if applicable		The relative percent difference calculated between original and lab duplicate results. **Required** for matrix spike duplicate and lab replicate results. Report as percentage (e.g., report "120%" as "120").
33	qc_spike_lcl	Number		required if applicable		Lower control limit for QC spike recovery. **Required** for matrix spike, matrix spike duplicate, performance evaluation, laboratory control sample, and

#	Attribute Name	Type	PK	Required	Ref. Value	Attribute Definition
						surrogate compound results. Report as percentage (e.g., report "120%" as "120").
34	qc_spike_ucl	Number		required if applicable		Upper control limit for QC spike recovery. **Required** for matrix spike, matrix spike duplicate, laboratory control sample, performance evaluation, and surrogate compound results. Report as percentage (e.g., report "120%" as "120").
35	qc_rpd_cl	Number		required if applicable		Relative percent difference control limit **Required** for matrix spike duplicate and lab replicate results. Report as percentage (e.g., report "120%" as "120").
36	qc_spike_status	Text(10)		required if applicable	Yes	Used to indicate whether the spike recovery was within control limits. Use the "*" character to indicate failure, otherwise leave blank. **Required** for matrix spike, performance evaluation, laboratory control sample, and surrogate compound results that are outside of the QC spike control limits,
37	qc_dup_spike_status	Text(10)		required if applicable	Yes	Used to indicate whether the duplicate spike recovery was within control limits. Use the "*" character to indicate failure, otherwise leave blank.

#	Attribute Name	Type	PK	Required	Ref. Value	Attribute Definition
						Required for matrix spike duplicate results that are outside of the QC spike control limits.
38	qc_rpd_status	Text(10)		required if applicable	Yes	Used to indicate whether the relative percent difference was within control limits. Use the "*" character to indicate failure, otherwise leave blank. **Required** for matrix spike duplicate and lab replicate results with relative percent difference than is greater than the QC RPD control limit.
39	calibration_compliant	Text(1)		required	Yes	A flag indicating if the calibration associated with the result is in compliance. Use 'N' to indicate that the calibration was out of compliance and 'Y' otherwise.

Batch Import Format

#	Attribute Name	Column Datatype	PK	Required	Ref. Value	Attribute Definition
1	sys_sample_code	Text(25)	PK	required		Unique sample identifier. Identifies the sample that the test was performed on.
2	lab_anl_method_name	Text(35)	PK	required	Yes	Laboratory analytical method name or description. For valid value list, consult the controlled values supplied for this project.
3	analysis_date	Date	PK	required		Date of sample analysis in MM/dd/yyyy format.
4	analysis_time	Time	PK	required		Time of sample analysis in 24-hr (military) HH:mm format.
5	total_or_dissolved	Text(1)	PK	required	Yes	Must be either "T" for total (metal) concentration, "D" for dissolved/filtered (metal) concentration, or "N" for organic (or other) constituents for which neither "total" nor "dissolved" is applicable.
6	column_number	Text(2)	PK	required	Yes	Must be either "1C" for first column analyses, "2C" for second column analyses, or "NA" for analyses for which neither "1C" nor "2C" is applicable.
7	test_type	Text(10)	PK	required	Yes	Type of test. Valid values include "initial", "reextract", and "reanalysis".
8	test_batch_type	Text(10)	PK	required	Yes	Lab batch type. Valid values include "Prep", "Analysis", and "Leach".
9	test_batch_id	Text(20)		required		Unique identifier of lab batches. The test_batch_id must uniquely identify a batch across the entire project. No batch id can be re-used. This requires that batch ids remain unique amongst laboratories contracted on the project.

APPENDIX 18
STANDARD OPERATING PROCEDURE FOR THE LABORATORY ELECTRONIC DATA DELIVERABLE (EDD)

1.1 Introduction

The purpose of this document is to describe the processing of the analytical data received from the laboratory and includes the required specifications of the electronic data deliverable (EDD) format.

1.1.1 File Format

All data from the laboratory must be transmitted in an ASCII file using a tab-delimited standard format. Maximum length of text fields is indicated in the parentheses below in the *Column Datatype* column. If the information is less than the maximum length, do not pad the record with spaces.

Each record must be terminated with a carriage return/line feed (i.e., standard DOS text file). The file can be produced using any software with the capability to create ASCII files. Date is reported as MM/dd/yyyy (month in year/day in month/four digit year) and time as HH:mm (hour in day:minute in hour). Time uses a 24-hour clock, thus 3:30 p.m. will be reported as 15:30.

Four files are required: one each for laboratory samples, tests, results, and batches. The files must have valid DOS (8.3) filenames. The filename extensions are used to indicate the file type as follows:

*.SMP for laboratory sample rows

*.TST for test rows

*.RES for result rows

*.BCH for batch rows

The 8-character filenames for the lab generated files must be the same for each group of four files. If a file needs to be resubmitted after error corrections the file name must remain the

same as that of the original submittal. All four files will be prepared and loaded into the database together in one group.

1.1.2 Data Integrity Rules

If a field is to be considered part of the primary key of a table, it is indicated below by the presence of "PK" in the PK column. The combination of values in each primary key must be unique within the file. Referential integrity must be enforced between files and between these files and existing records (field information) in the project database. The foreign key relationships in the EDD files are listed below:

1. If a sys_sample_code in the .TST file references a field sample, the sys_sample_code and lab_anl_method_name fields of that line of the .TST file constitute a foreign key that references the primary key of an existing field sample test request record in the project database.
2. If a sys_sample_code in the .TST file references a laboratory sample, the sys_sample_code of that line of the .TST file is a foreign key that references the primary key of the .SMP file.
3. The sys_sample_code, lab_anl_method_name, analysis_date, analysis_time, total_or_dissolved, column_number, and test_type fields of the .RES file constitute a foreign key that references the primary key of the .TST file.
4. The sys_sample_code, lab_anl_method_name, analysis_date, analysis_time, total_or_dissolved, column_number, and test_type fields of the .BCH file is a foreign key that references the primary key of the .TST file.

1.1.3 Controlled Vocabulary

Many of the fields are populated with controlled values; that is, their content must be one of a set of defined text strings. Where this is the case it is indicated in the tables below with a "Yes" in the *Ref. Value* column. The set of defined values for each controlled value field are listed in Table 10.2.

Setting the value of certain controlled value fields will restrict the value of other controlled value fields in the same line to a particular value. This is the case with the lab_anl_method_name and prep_method columns of the .TST file. Table 10.2a lists the

prep_method value that must be specified along with a given lab_anl_method_name value; if no prep_method value is given in Table 10.2a, then a null value should be used for the particular record.

Tables 10.2b-e list the controlled values for target analytes that must be reported for each analytical method. Results for these analytes must have the "TRG" result type. Note that chemical_name is not a controlled value and is added to Tables 10.2b-e for clarity.

Controlled values for surrogate compounds for analytical methods are listed in Table 10.2a *Analytical Methods-Surrogates*. Results for these analytes must also be reported for the analytical methods listed in Table 10.2a. Results for surrogate analytes must have the "SUR" result type.

1.1.4 Null Format

Many fields are optional. When a field is not listed as required, this means that a null value may be appropriate. A null value is represented in the EDD file as and empty field and is delimited by two immediately adjacent tab delimiters. The null value must still be surrounded by tabs. In other words, the number of fields is always the same, whether or not there are null fields in the file.

1.2 Naming Convention of Samples

Field samples being submitted to the data management system follow a standard naming structure. Sample names are composed of four distinct components separated by hyphen characters. As an example, a water column field sample ID of 'WFF-SCHU-060412-AT001' contains the four components:

- WFF
- SCHU
- 060412
- AT001

There will be no hyphens within any of the individual components.

Lab QC sample IDs will have the same four component structure as field sample IDs. The Lab QC sample ID will be constructed by replacing the third component of any sample name on the chain of custody with the concatenation of LABQC and the relevant sample delivery group id. The fourth component of the Lab QC sample ID will be the internal laboratory sample ID. For example a method blank QC sample (A3910), delivered in sample delivery group 'COC06040084', for a batch containing the sample mentioned above would look like 'WFF-SCHU-LABQCCOC06040084-A3910'. The sample ID has a maximum of 60 characters available to it. It is the responsibility of the laboratory to ensure that the ID strings are within the size limits.

1.3 Examples

Below are examples of sample types to be used in the project, showing when QC fields need to be populated and when it is not necessary to populate QC fields.

QC fields in a normal field sample (i.e., Sample_type_code = ENV)

The following table shows a subset of the fields in the result file for a normal field sample. Notice that all QC fields are blank.

cas_rn	Result Value	QC Original Conc	QC Spike Added	QC Spike Measured	QC Spike Recovery	QC Dup Original Conc	QC Dup Spike Added	QC Dup Spike Measured	QC Dup Spike Recovery
93-76-5	1.56								
94-75-7	3.17								
94-82-6	2.31								

QC fields in a normal field sample with surrogates (i.e., Sample_type_code = ENV)

The following table shows a subset of the fields in the result file for a normal field sample. Notice that QC fields are blank except on surrogate rows.

cas_rn	Result Value	Result Unit	Result Type Code	QC Original Conc	QC Spike Added	QC Spike Measured	QC Spike Recovery
93-76-5	1.56	mg/l	TRG				
94-75-7	3.17	mg/l	TRG				
PHEN2F		mg/l	SUR		12.5	12.9	103

QC fields in a matrix spike (i.e., Sample_type_code = MS)

The following table shows some of the fields in the result file for a matrix spike sample. Notice that all "dup" QC fields are blank. The qc_rpd field (data column not shown) is left blank for these rows.

cas_rn	Result Value	QC Original Conc	QC Spike Added	QC Spike Measured	QC Spike Recovery	QC Dup Original Conc	QC Dup Spike Added	QC Dup Spike Measured	QC Dup Spike Recovery
93-76-5	5.36	1.56	4.18	5.36	90.9				
94-75-7	7.15	3.17	4.18	7.15	95.2				
94-82-6	5.66	2.31	4.22	5.66	79.3				

QC fields in a matrix spike duplicate (i.e., Sample_type_code = MSD)

The following table shows a subset of the fields in the result file for a matrix spike duplicate sample. Notice that all "dup" QC fields are completed. The qc_rpd field (data column not shown) is required for these rows.

cas_rn	Result Value	QC Original Conc	QC Spike Added	QC Spike Measured	QC Spike Recovery	QC Dup Original Conc	QC Dup Spike Added	QC Dup Spike Measured	QC Dup Spike Recovery
93-76-5	5.70					1.56	4.23	5.70	97.8
94-75-7	7.62					3.17	4.23	7.62	105
94-82-6	5.33					2.31	4.13	5.33	73.1

QC fields in an LCS (i.e., laboratory control sample, blank spike, Sample_type_code = LCS)

The following table shows a subset of the fields in the result file for an LCS sample. The qc_rpd field (data column not shown) is left blank for these rows.

cas_rn	Result Value	QC Original Conc	QC Spike Added	QC Spike Measured	QC Spike Recovery	QC Dup Original Conc	QC Dup Spike Added	QC Dup Spike Measured	QC Dup Spike Recovery
93-76-5			5.00	5.26	105				
94-75-7			1.00	1.02	102				
94-82-6			12.5	12.9	103				

Retests

The following table shows how to report retests in an example where a sample was retested at dilution. The first two constituents (75-25-2, and 67-66-3) are reported in the initial test, and constituent 95-95-4 in the diluted retest. The other results would be "turned off" by setting the reportable_result field to "No". Surrogate results, however, are flagged as reportable ("Yes") in both the initial test records and for any retest records.

Test_type	cas_rn	result_value	reportable_result
Initial	75-25-2	1.2	Yes
Initial	67-66-3	3.4	Yes
Initial	95-95-4	100	No
Reanalysis	75-25-2		No
Reanalysis	67-66-3		No
Reanalysis	95-95-4	78.3	Yes

Second Columns

The following table shows how to report first and second column confirmation results. The first and third constituents (75-25-2, and 95-95-4) are reported in the first column, and constituent 67-66-3 is reported in the second column. The other results would be "turned off" by setting the reportable_result field to "No".

column_number	cas_rn	result_value	reportable_result
1C	75-25-2	1.2	Yes
1C	67-66-3	3.4	No
1C	95-95-4	5.6	Yes
2C	75-25-2	1.3	No
2C	67-66-3	3.7	Yes
2C	95-95-4	5.4	No

Units

Units are to be reported consistently for the duration of the project. The result_unit field is required to be reported as specified in the controlled values. Associated measurements (i.e., reporting detection limit, method detection limit) must be reported consistently with the result units.

Sample Import Format

#	Attribute Name	Column Datatype	PK	Required	Ref Value	Attribute Definition
1	sys_sample_code	Text(25)	PK	required		Unique sample identifier. Each sample must have a unique value. For matrix spike, matrix spike duplicate, and laboratory replicate samples, this field must be populated as follows: COC#, which is "COC" followed by a number, then a dash (-), then the Item#, which is a sequential three digit number that is typed on the Chain-of-Custody to the left of each sample (i.e., COC042602-001), followed by "MS" for matrix spike, "SD" for matrix spike duplicate, or "LR" for laboratory replicate. This table must contain all laboratory - generated samples, including lab blanks, blank spikes, matrix spikes, matrix spike duplicates, and laboratory replicates.
2	lab_sample_id	Text(60)		required		Laboratory sample identifier. **The sample naming convention, as described in Section** Error! Reference source not found.**, must be followed.** **Each line of the file with matching lab_sample_id values must have the same values for sample_type_code, sample_matrix_code, sample_source, parent_sample_code, sample_date, sample_time, and comment.**
3	sample_type_code	Text(10)		required	Yes	Code which distinguishes between different types of sample. For valid value list, consult the controlled values supplied for the project.
4	sample_matrix_code	Text(10)		required	Yes	Code which distinguishes between

#	Attribute Name	Column Datatype	PK	Required	Ref Value	Attribute Definition
						different types of sample matrix. The matrix of the sample as analyzed may be different from the matrix of the sample as retrieved (e.g., TCLP leachates), so this field is required at the sample level. For valid value list, consult the controlled values supplied for the project.
5	sample_source	Text(10)		required	Yes	Must be "Lab" for laboratory QC samples..
6	parent_sample_code	Text(25)		required if applicable		The value of sys_sample_code that uniquely identifies the field sample that was the source of this sample. For example, the value of this field for a laboratory replicate sample would identify the normal field sample of which this sample is a replicate. **Required** in the laboratory EDD for all laboratory "clone" samples (i.e. matrix spikes, matrix spike duplicates, and lab replicates). **Must be null** for samples that have no parent (i.e., method blanks and lab control samples).
7	comment	Text(255)				Sample comments as necessary.
8	sample_date	Date				**Must be a null field for this project.**
9	sample_time	Time				**Must be a null field for this project.**
10	standard_solution_source	Text(20)				Textual description of the source of standard solutions as needed for certain laboratory samples (e.g., LCS).

Test Import Format

#	Attribute Name	Column Datatype	PK	Required	Ref. Value	Attribute Definition
1	sys_sample_code	Text(25)	PK	required		Unique sample identifier. Identifies the sample that the test was performed on.
2	lab_anl_method_name	Text(35)	PK	required	Yes	Laboratory analytical method name or description. For valid value list, consult the controlled values supplied for this project.
3	analysis_date	Date	PK	required		Date of sample analysis in MM/dd/yyyy format.
4	analysis_time	Time	PK	required		Time of sample analysis in 24-hr (military) HH:mm format.
5	total_or_dissolved	Text(1)	PK	required	Yes	Must be either "T" for total (metal) concentration, "D" for dissolved / filtered (metal) concentration, or "N" for organic (or other) constituents for which neither "total" nor "dissolved" is applicable.
6	column_number	Text(2)	PK	required	Yes	Must be either "1C" for first column analyses, "2C" for second column analyses, or "NA" for analyses for which neither "1C" nor "2C" is applicable. If any "2C" tests are reported, then there must be a corresponding "1C" tests present. Laboratories will be reporting which of the two columns is to be considered "primary". This distinction is handled by the "reportable_result" field in the result table (see section **Error! Reference source not found.**).
7	test_type	Text(10)	PK	required	Yes	Type of test. Valid values include "initial", "reextract", and "reanalysis".

#	Attribute Name	Column Datatype	PK	Required	Ref. Value	Attribute Definition
8	lab_matrix_code	Text(10)		required	Yes	Code which distinguishes between different types of lab sample matrix. The matrix of the sample as analyzed may be different from the matrix of the sample as retrieved (e.g., TCLP leachates). For valid value list, consult the controlled values supplied for this project.
9	analysis_location	Text(2)		required	Yes	Must be either "FI" for field instrument or probe, "FL" for mobile field laboratory analysis, or "LB" for fixed-based laboratory analysis.
10	basis	Text(10)		required	Yes	Must be either "Wet" for wet-weight basis reporting, "Dry" for dry-weight basis reporting, or "NA" for tests for which this distinction is not applicable.
11	dilution_factor	Number		required		Effective test dilution factor. Must be greater than zero.
12	prep_method	Text(35)		required if applicable	Yes	Laboratory sample preparation method name or description. For valid values consult the controlled values list supplied for the project. Selection of analytical test method may require the specification of a particular preparation method. To determine when this requirement applies consult the controlled values list supplied for the project.
13	prep_date	Date		required if applicable		Date of sample preparation in MM/dd/yyyy format. **Required** when the prep_method is not null.
14	prep_time	Time		required if applicable		Time of sample preparation in 24-hr (military) HH:mm format. **Required** when the prep_method is not null.

#	Attribute Name	Column Datatype	PK	Required	Ref. Value	Attribute Definition
15	leachate_method	Text(15)				Laboratory leachate generation method name or description. A list of valid method names is not required for the laboratory EDD unless otherwise specified by the project manager.
16	leachate_date	Date		required if applicable		Date of leachate preparation in MM/dd/yyyy format. **Required** when the leachate_method is not null.
17	leachate_time	Time		required if applicable		Time of leachate preparation in 24-hr (military) HH:mm format. **Required** when the leachate_method is not null.
18	lab_name_code	Text(10)		required	Yes	Unique identifier of the laboratory. For valid value list, consult the controlled values supplied for this project.
19	data_package_level	Text(10)		required	Yes	Data package level. Possible values are “A”, “B”, or “AB”.
20	lab_sample_id	Text(20)		required		Internal laboratory sample identifier.
21	percent_moisture	Number		required		Percent moisture of the sample portion used in this test. Numeric format is "NN.MM", (e.g., 70.1% is reported as "70.1" and not as "70.1%"). Must be between 0 and 100.
22	subsample_amount	Number		required		Amount of original sample used in sample preparation. Must be greater than zero.

#	Attribute Name	Column Datatype	PK	Required	Ref. Value	Attribute Definition
23	subsample_amount_unit	Text(15)		required	Yes	Unit of measurement for sub-sample amount. Must use standard unit abbreviations (see controlled values list supplied for the project). The standard ASCII character "u" will be used in place of the Greek letter µ (mu) to indicate "micro."
24	analyst_name	Text(30)				Name or initials of laboratory analyst. This is an optional field for the laboratory EDD unless otherwise specified by the project manager.
25	instrument_id	Text(50)				Instrument identifier. This is an optional field for the laboratory EDD unless otherwise specified by the project manager.
26	sample_receipt_date	Date		required if applicable		Date of sample collection in MM/dd/yyyy format. **Must be null** for laboratory samples (i.e. matrix spike, matrix spike duplicate, lab replicate, method blank, and lab control sample). **Required** for field samples.
27	sample_receipt_time	Time		required if applicable		Time of sample collection in 24-hr (military) HH:mm format. **Must be null** for laboratory samples (i.e. matrix spike, matrix spike duplicate, lab replicate, method blank, and lab control sample). **Required** for field samples.
28	sample_delivery_group	Text(15)		required		Sample delivery group id. Every row of the file must contain the same sample_delivery_group.
29	comment	Text(255)				Comments about the test as necessary.

#	Attribute Name	Column Datatype	PK	Required	Ref. Value	Attribute Definition
30	final_volume	Number				The final amount/volume of the sample, extract, or digestate after sample preparation.
31	final_volume_unit	Text(15)		required if applicable	Yes	Unit of measure of final_volume. Must use standard unit abbreviations (see controlled values list supplied for the project). The standard ASCII character "u" will be used in place of the Greek letter µ (mu) to indicate "micro." **Required** if the final_volume is **not** null. **Must be null** if the final_volume is null.

Result Import Format

#	Attribute Name	Type	PK	Required	Ref. Value	Attribute Definition
1	sys_sample_code	Text(25)	PK	required		Unique sample identifier. Identifies the sample that the test was performed on.
2	lab_anl_method_name	Text(35)	PK	required	Yes	Laboratory analytical method name or description. For valid value list, consult the controlled values supplied for the project.
3	analysis_date	Date	PK	required		Date of sample analysis in MM/dd/yyyy format.
4	analysis_time	Time	PK	required		Time of sample analysis in 24-hr (military) HH:mm format.
5	total_or_dissolved	Text(1)	PK	required	Yes	Must be either "T" for total (metal) concentration, "D" for dissolved/filtered (metal) concentration, or "N" for organic (or other) constituents for which neither "total" nor "dissolved" is applicable.
6	column_number	Text(2)	PK	required	Yes	Must be either "1C" for first column analyses, "2C" for second column analyses, or "NA" for analyses for which neither "1C" nor "2C" is applicable.
7	test_type	Text(10)	PK	required	Yes	Type of test. Valid values include "initial", "reextract", and "reanalysis".
8	cas_rn	Text(15)	PK	required	Yes	Chemical Abstracts Registry Number for the parameter if available. Otherwise consult the controlled values supplied for this project.
9	chemical_name	Text(60)				Name of the parameter. Used only in manual review of EDD.
10	result_value	Number		required if applicable		Analytical result reported at the project specified number of significant digits. **Must be null** for non-detects. **Required** for any result not qualified as non-detect.
11	result_error_delta	Text(20)				Error range applicable to the result value; typically used only for radiochemistry results.

#	Attribute Name	Type	PK	Required	Ref. Value	Attribute Definition
12	result_type_code	Text(10)		required	Yes	Must be either "TRG" for a target or regular result, and "SUR" for surrogates.
13	reportable_result	Text(10)		required	Yes	Must be either "Yes" for results which are considered to be reportable, or "No" for non-reportable results. For target analytes, any given sys_sample_code / cas_rn combination must have only one reportable result record (i.e. reportable_result = “Yes”).
14	detect_flag	Text(1)		required	Yes	Must be either "Y" for detected analytes or "N" for non-detected.
15	lab_qualifiers	Text(7)			Yes	Qualifier flags assigned by the laboratory. For valid value list, consult the controlled values supplied for the project.
16	organic_yn	Text(1)		required	Yes	Must be either "Y" for organic constituents or "N" for inorganic constituents.
17	method_detection_limit	Number		required		Method detection limit.
18	reporting_detection_limit	Number		required		Detection limit that reflects conditions such as dilution factors and moisture content.
19	quantitation_limit	Number		required		Concentration level above which results can be quantified with confidence. Reflects conditions such as dilution factors and moisture content.
20	result_unit	Text(15)		required	Yes	Unit of measure of result_value. Must use standard unit abbreviations (see controlled values list supplied for the project). The standard ASCII character “u” will be used in place of the Greek letter µ (mu) to indicate “micro.” Note that the project may require certain test results to be reported in specific units. For details on when this

#	Attribute Name	Type	PK	Required	Ref. Value	Attribute Definition
						requirement applies consult the controlled values supplied for this project.
21	detection_limit_unit	Text(15)		required	Yes	Unit of measure of method_detection_limit, reporting_detection_limit, and quantitation_limit. Must use standard unit abbreviations (see controlled values list supplied for the project). The standard ASCII character "u" will be used in place of the Greek letter µ (mu) to indicate "micro." Note that this project requires that detection_limit_unit be the same as result_unit.
22	tic_retention_time	Text(8)				Retention time in seconds for tentatively identified compounds. TICs will not be used on this project.
23	result_comment	Text(255)				Result specific comments as necessary.
24	qc_original_conc	Number		required if applicable		The concentration of the analyte in the original (un-spiked) sample. **Required** for matrix spike, matrix spike sample results. If original (un-spiked) sample is a non-detect, then populate this field with a zero as opposed to the detection limit. If using an original sample result that is less than the reporting limit for background correction, then populate this field with the below reporting limit original sample result, as opposed to zero.
25	qc_spike_added	Number		required if applicable		The concentration of the analyte added to the original sample.

#	Attribute Name	Type	PK	Required	Ref. Value	Attribute Definition
						Required for matrix spike, laboratory control sample, and surrogate compound results.
26	qc_spike_measured	Number		required if applicable		The measured concentration of the analyte. Use zero for spiked compounds that were not detected in the sample. **Required** for matrix spike, laboratory control samples, and surrogate compound results.
27	qc_spike_recovery	Number		required if applicable		The percent recovery calculated for the spiked compounds. **Required** for matrix spike, laboratory control sample, and surrogate compound results. Report as percentage (e.g., report "120%" as "120").
28	qc_dup_original_conc	Number		required if applicable		The concentration of the analyte in the original sample. **Required** for matrix spike duplicate and lab replicate results. If original sample is a non-detect, then populate this field with a zero as opposed to the detection limit. For matrix spike duplicates, if using an original sample result that is less than the reporting limit for background correction, then populate this field with the below reporting limit original sample result, as opposed to zero.
29	qc_dup_spike_added	Number		required if applicable		The concentration of the analyte added to the original sample.

#	Attribute Name	Type	PK	Required	Ref. Value	Attribute Definition
						Required for matrix spike duplicates.
30	qc_dup_spike_measured	Number		required if applicable		The measured concentration of the analyte in the duplicate. **Required** for matrix spike duplicates. Use zero for spiked compounds that were not detected in the sample.
31	qc_dup_spike_recovery	Number		required if applicable		The duplicate percent recovery calculated for spiked compounds. **Required** for matrix spike duplicates. Report as percentage (e.g., report "120%" as "120").
32	qc_rpd	Number		required if applicable		The relative percent difference calculated between original and lab duplicate results. **Required** for matrix spike duplicate and lab replicate results. Report as percentage (e.g., report "120%" as "120").
33	qc_spike_lcl	Number		required if applicable		Lower control limit for QC spike recovery. **Required** for matrix spike, matrix spike duplicate, laboratory control sample, and surrogate compound results. Report as percentage (e.g., report "120%" as "120").
34	qc_spike_ucl	Number		required if applicable		Upper control limit for QC spike recovery. **Required** for matrix spike, matrix spike

#	Attribute Name	Type	PK	Required	Ref. Value	Attribute Definition
						duplicate, laboratory control sample, and surrogate compound results. Report as percentage (e.g., report "120%" as "120").
35	qc_rpd_cl	Number		required if applicable		Relative percent difference control limit **Required** for matrix spike duplicate and lab replicate results. Report as percentage (e.g., report "120%" as "120").
36	qc_spike_status	Text(10)		required if applicable	Yes	Used to indicate whether the spike recovery was within control limits. Use the "*" character to indicate failure, otherwise leave blank. **Required** for matrix spike, laboratory control sample, and surrogate compound results that are outside of the QC spike control limits,
37	qc_dup_spike_status	Text(10)		required if applicable	Yes	Used to indicate whether the duplicate spike recovery was within control limits. Use the "*" character to indicate failure, otherwise leave blank. **Required** for matrix spike duplicate results that are outside of the QC spike control limits.
38	qc_rpd_status	Text(10)		required if applicable	Yes	Used to indicate whether the relative percent difference was within control limits. Use the "*" character to indicate failure, otherwise leave blank.

#	Attribute Name	Type	PK	Required	Ref. Value	Attribute Definition
						Required for matrix spike duplicate and lab replicate results with relative percent difference than is greater than the QC RPD control limit.
39	calibration_compliant	Text(1)		required	Yes	A flag indicating if the calibration associated with the result is in compliance. Use 'Y' to indicate the calibration is in compliance and 'N' otherwise.

Batch Import Format

#	Attribute Name	Column Datatype	PK	Required	Ref. Value	Attribute Definition
1	sys_sample_code	Text(25)	PK	required		Unique sample identifier. Identifies the sample that the test was performed on.
2	lab_anl_method_name	Text(35)	PK	required	Yes	Laboratory analytical method name or description. For valid value list, consult the controlled values supplied for this project.
3	analysis_date	Date	PK	required		Date of sample analysis in MM/dd/yyyy format.
4	analysis_time	Time	PK	required		Time of sample analysis in 24-hr (military) HH:mm format.
5	total_or_dissolved	Text(1)	PK	required	Yes	Must be either "T" for total (metal) concentration, "D" for dissolved/filtered (metal) concentration, or "N" for organic (or other) constituents for which neither "total" nor "dissolved" is applicable.
6	column_number	Text(2)	PK	required	Yes	Must be either "1C" for first column analyses, "2C" for second column analyses, or "NA" for analyses for which neither "1C" nor "2C" is applicable.
7	test_type	Text(10)	PK	required	Yes	Type of test. Valid values include "initial", "reextract", and "reanalysis".
8	test_batch_type	Text(10)	PK	required	Yes	Lab batch type. Valid values include "Prep", "Analysis", and "Leach".
9	test_batch_id	Text(20)		required		Unique identifier of lab batches. **Each line of the file with matching test_batch_id values must have the same test_batch_type value.**

APPENDIX 19
SOP FOR DATA PACKAGE DELIVERABLE

OBJECTIVE

This Standard Operating Procedure (SOP) describes the requirements for the data packages that will be generated as part of the Remedial Action Monitoring Program (RAMP). This SOP applies to the contractor(s) involved in analytical data generation and reporting. All data packages generated for the RAMP must be provided in an Adobe Acrobat (.PDF) file format.

SECTION A-9 DATA PACKAGE DELIVERABLES

The following sections describe in detail the types of data packages designed for the Remedial Action Monitoring Program. These details are provided to allow several participating laboratories to produce data packages that are similar in format, order of presentation, and content. The data packages detailed in Section A-9.1 have been developed based on deliverables specified in the US EPA Contract Laboratory Program Statement of Work (CLP SOW). The CLP SOW has additional details concerning data packages that are specific to the CLP analyses. The most recent Statement of Work should be referenced for details concerning CLP-style data packages. Note: the summary forms provided in these data packages should be in similar format and content to the Contract Laboratory Program (CLP) forms listed (as references) next to the form title. These CLP forms references are only provided as guidance on content and format and should be modified by the laboratory to meet specific method requirements. Section A-9.2 provides details concerning specific contents of the data deliverables described in Section A-9.1.

The data package deliverables are as follows:

Level B - Fully documented data package.

The Level B package resembles the information required by the CLP SOW. This type of package includes a cover letter, SDG narrative, field Chain-of-Custody Records, analytical results summaries, a glossary of qualifier codes and summary forms for quality control procedures and all sample and quality control raw data to support the results reported.

A-9.1 Data Package Contents and Order of Presentation

The laboratory will be required to submit supporting documentation for the reported analytical results. The supporting documentation and the analytical results will be reported in one of two data package delivery categories. The categories are defined below. The data package deliverables must be submitted in the order in which the deliverables appear in the text. The laboratory need not include the documentation for any fraction not required for an SDG.

A-9.1.1 General Format for Level B Deliverables

The Level B Sample Data Package shall include data for analyses of all samples in one SDG, including field samples, reanalyses, secondary dilutions, blanks, laboratory control samples, matrix spikes, matrix spike duplicates, and/or laboratory duplicates. The complete Sample Data Package is divided into the units as described below. Units for each analytical fraction have been detailed. If the analysis of that fraction was not required for samples in the SDG, the fraction-specific unit is not a required deliverable. The Sample Data Package must be complete before submission and must be consecutively paginated. The Sample Data Package will be arranged in the following order:

A) Cover Letter/Letter of Transmittal signed by the laboratory manager.

B) Title Page

C) Table of Contents

D) Sample Delivery Group (SDG) Narrative

This document shall be clearly labeled "SDG Narrative" and shall contain: laboratory name; SDG number; GE sample identifications; laboratory sample numbers; and detailed documentation of any quality control, sample, shipment, and/or analytical problems encountered in processing (preparing and analyzing) the samples reported in the data package. A glossary of qualifier codes used in the SDG must also be provided.

The laboratory must also include any technical and administrative problems encountered, corrective actions taken and method of resolution, and an explanation of all flagged edits (i.e., exhibit edits) on quantitation reports.

Additionally, the SDG Narrative must be signed and dated by the laboratory manager.

E) Field Chain-of-Custody Records and Sample Receipt Documentation Log

Copies of field Chain-of-Custody Records for all samples within the SDG must be included in the deliverables. A description of the condition and temperature of the

samples upon laboratory receipt (*i.e.*, custody seal condition, container status) must be provided for each Chain-of-Custody Record/sample cooler.

F) GC/MS Volatile Organic Data.

1. Quality Control (QC) Summary.

a. Surrogate Percent Recovery Summary (modified CLP SOW288 Form II VOA).

b. Matrix Spike/Matrix Spike Duplicate Summary (modified CLP SOW288 Form III VOA).

c. Laboratory Control Sample Summary (modified CLP SOW288 Form III VOA).

d. Method Blank Summary (modified CLP SOW288 Form IV VOA) -- arranged in chronological order by date of analysis of the blank, by instrument.

e. GC/MS Tuning and Mass Calibration Summary (modified CLP SOW288 Form V VOA) -- arranged in chronological order, by instrument.

f. Internal Standard Area and Retention Time Summary (modified CLP SOW288 Form VIII VOA) -- arranged in chronological order, by instrument.

2. Sample Data

Sample data shall be arranged in packets consisting of the Analytical Results Summaries followed by the raw data for volatile samples. These sample packets should then be placed in increasing alphanumeric order by GE sample identification. The order of each sample packet is as follows:

a. Target Compound Results (modified CLP SOW288 Form I VOA).

b. Reconstructed total ion chromatogram (RIC) and quantitation reports.

c. Copies of raw spectra and copies of background-subtracted mass spectra of each target compound identified in the sample and corresponding background-subtracted target compound standard mass spectra.

d. Exhibit work sheet (including example calculations showing how sample results are calculated using the initial calibration and sample responses for at least one sample).

3. Standards Data

a. Initial Calibration Data (modified CLP SOW288 Form VI VOA and associated volatile standard RICs and quantitation reports) -- for all initial calibrations associated with analyses in the SDG, in chronological order, by instrument. If a curve equation is utilized,

the laboratory must provide the curve equation and coefficient of determination.

b. Continuing Calibration Data (modified CLP SOW288 Form VII VOA and associated volatile standard RICs and quantitation reports) -- for all continuing calibrations associated with analyses in the SDG, in chronological order, by instrument.

4. Raw QC Data

a. For each GC/MS tuning and mass calibration (in chronological order, by instrument):

1. Bromofluorobenzene (BFB) bar graph spectrum.

2. BFB mass listing.

b. Method/Storage Blank Data - in chronological order, by instrument:

i. Target Compound Results (modified CLP SOW288 Form I VOA).

ii. RIC and quantitation reports.

iii. Copies of raw spectra and copies of background-subtracted mass spectra of each target compounds identified in the blank

and corresponding background-subtracted target compound standard mass spectra.

c. Laboratory Control Sample Data:

i. Target Compound Results (modified CLP SOW288 Form I VOA).

ii. RIC and quantitation reports.

d. Matrix Spike Data:

i. Target Compound Results (modified CLP SOW288 Form I VOA).

ii. RIC and quantitation reports.

e. Matrix Spike Duplicate Data:

i. Target Compound Results (modified CLP SOW288 Form I VOA).

ii. RIC and quantitation reports.

G) GC/MS Semivolatile Organic Data

1. QC Summary

a. Surrogate Percent Recovery Summary (modified CLP SOW288 Form II SV).

b. Matrix Spike/Matrix Spike Duplicate Summary (modified CLP SOW288 Form III SV).

c. Laboratory Control Sample Summary (modified CLP SOW288 Form III SV).

d. Method Blank Summary (modified CLP SOW288 Form IV SV) -- arranged in chronological order by date of analysis of the blank, by instrument.

e. GC/MS Tuning and Mass Calibration Summary (modified CLP SOW288 Form V SV) -- arranged in chronological order, by instrument.

f. Internal Standard Area and Retention Time Summary (modified CLP SOW288 Form VIII SV-1, SV-2) -- arranged in chronological order, by instrument.

2. Sample Data

Sample data shall be arranged in packets consisting of the Analytical Results Summaries, followed by the raw data for semivolatile samples. These sample packets should then be placed in increasing alphanumeric order by GE sample identification. The order of each sample packet is as follows:

a. Target Compound Results (modified CLP SOW288 Form I SV-1, SV-2).

b. RIC and quantitation report.

c. Copies of raw spectra and copies of background-subtracted mass spectra of each target compound identified in the sample and corresponding background-subtracted target compound standard mass spectra.

d. UV traces from Gel Permeation Chromatography (GPC) chromatograms cleanup (if performed).

e. Exhibit work sheet (including example calculations showing how sample results are calculated using the initial calibration and sample responses for at least one sample).

3. Standards Data

a. Initial Calibration Data (modified CLP SOW288 Form VI SV-1, SV-2 and associated semivolatile standard RICs and quantitation reports) -- for all initial calibrations associated with analyses in the SDG, in chronological order, by instrument. If a curve equation is utilized, the laboratory must provide the curve equation and coefficient of determination.

b. Continuing Calibration Data (modified CLP SOW288 Form VII SV-1, SV-2 and associated semivolatile standard RICs and quantitation reports) -- for all continuing calibrations associated with analyses in the SDG, in chronological order, by instrument.

4. Raw QC Data

a. For each GC/MS tuning and mass calibration (in chronological order, by instrument):

i. Decafluorotriphenylphosphine (DFTPP) bar graph spectrum.

ii. DFTPP mass listing.

b. Blank Data -- in chronological order, by instrument:

i. Target Compound Results (modified CLP SOW288 Form I SV-1, SV-2).

ii. RIC and quantitation reports.

iii. Copies of raw spectra and copies of background-subtracted mass spectra of each target compounds identified in the blank and corresponding background-subtracted target compound standard mass spectra.

c. Laboratory Control Sample Data:

i. Target Compound Results (modified CLP SOW288 Form I SV-1, SV-2).

ii. RIC and quantitation reports.

d. Matrix Spike Data:

i. Target Compound Results (modified CLP SOW288 Form I SV-1, SV-2).

ii. RIC and quantitation reports.

e. Matrix Spike Duplicate Data

i. Target Compound Results (modified CLP SOW288 Form I SV-1, SV-2).

ii. RIC and quantitation reports.

H) GC Organochlorine Pesticide Data

1. QC Summary

a. Surrogate Percent Recovery Summary (modified CLP SOW288 Form II PEST).

b. Matrix Spike/Matrix Spike Duplicate Summary (modified CLP SOW288 Form III PEST).

c. Laboratory Control Sample Summary (modified CLP SOW288 Form III PEST).

d. Method Blank Summary (modified CLP SOW288 Form IV PEST) -- arranged in chronological order by date of analysis of the blank, by instrument.

2. Sample Data

Sample data shall be arranged in packets consisting of the Analytical Results Summaries followed by the raw data for organochlorine pesticide samples. These sample packets should then be placed in increasing alphanumeric order by GE sample identification. The order of each sample packet is as follows:

a. Analytical Results Summary (modified CLP SOW288 Form I PEST).

b. Copies of organochlorine pesticide chromatograms.

c. Copies of organochlorine pesticide chromatograms from second GC column confirmation (if performed).

d. GC integration reports or data system printouts.

e. Exhibit work sheet (including example calculation showing how sample results are calculated using initial calibration standard and sample responses for at least one sample).

f. UV traces from GPC cleanup (if performed).

g. If organochlorine pesticides are confirmed by GC/MS, the laboratory must submit copies of raw spectra and copies of background-subtracted mass spectra of target compounds that are identified in the sample and corresponding background-subtracted target compound standard mass spectra. For multi-component pesticides confirmed by GC/MS, the laboratory will submit mass spectra of three major peaks of multi-component compounds from samples and standards.

3. Standards Data

a. Analytical Sequence Form -- in chronological order, by GC column, by instrument for all samples and quality control analyses.

b. Initial Calibration Data (Initial Calibration Summary Form [inclusive of retention time windows, calibration factors, %RSDs, %Ds, etc.], organochlorine pesticide standard chromatograms, and integration reports) -- for each initial calibration associated with SDG in chronological order, by GC column, by instrument. If a curve equation is utilized, the laboratory must provide the curve equation and coefficient of determination.

c. Continuing Calibration Data (Continuing Calibration Summary Form [inclusive of retention time windows, calibration factors, %RSDs, %Ds, etc.], organochlorine pesticide standard chromatograms, and integration reports) -- for each continuing calibration associated with SDG in chronological order, by GC column, by instrument following the associated initial calibrations.

d. 4,4′-DDT and Endrin Breakdown Data (Percent Breakdown Summary Form, organochlorine pesticide chromatograms and integration reports) -- for each standard associated with SDG in chronological order by GC column, by instrument.

4. Raw QC Data

a. Blank Data -- in chronological order, by instrument:

i. Target Compound Results (modified CLP SOW288 Form I PEST).

ii. Organochlorine pesticide chromatograms and integration reports.

b. Laboratory Control Sample Data:

i. Target Compound Results (modified CLP SOW288 Form I PEST).

ii. Organochlorine pesticide chromatograms and integration reports.

c. Matrix Spike Data:

i. Target Compound Results (modified CLP SOW288 Form I PEST).

ii. Organochlorine pesticide chromatograms and integration reports.

d. Matrix Spike Duplicate Data:

i. Target Compound Results (modified CLP SOW288 Form I PEST).

ii. Organochlorine pesticide chromatograms and integration reports.

e. UV traces from GPC cleanup (if performed).

i. UV traces for the initial calibration standards and blanks. Compound names shall be written over the peaks or printed over the peaks, or retention times shall be written over the peaks, and a separate table listing compounds and retention times shall be provided.

ii. Chromatographs and data system reports for all standards used to quantify compounds in the GPC blanks.

iii. Chromatographs and data system reports for the GPC calibration check solution and all standards used to quantify compounds in the GPC calibration check solution.

f. Raw Florisil® data, arranged in chronological order.

i. Chromatographs and data system reports for the analysis of the Florisil® cartridge performance check.

ii. Chromatographs and data system reports for the standards used to quantify compounds in the Florisil® cartridge performance check analysis (*i.e.*, INDA, INDB, and the 2,4,5-trichlorophenol standards).

I) GC Polychlorinated Biphenyl (PCB) Data

1. QC Summary

a. Surrogate Percent Recovery Summary (modified CLP SOW288 Form II PEST).

b. Matrix Spike/Matrix Spike Duplicate Summary (modified CLP SOW288 Form III PEST).

c. Laboratory Control Sample Summary (modified CLP SOW288 Form III PEST).

d. Method Blank Summary (modified CLP SOW288 Form IV PEST) -- arranged in chronological order by date of analysis of the blank, by instrument.

2. Sample Data

Sample data shall be arranged in packets consisting of the Analytical Results Summaries followed by the raw data for PCB samples. These sample packets should then be placed in increasing alphanumeric order by GE sample identification. The order of each sample packet is as follows:

a. Analytical Results Summary (modified CLP SOW288 Form I PEST).

b. Copies of PCB chromatograms.

c. Copies of PCB chromatograms from second GC column confirmation (if performed).

d. GC integration reports or data system printouts. The integration reports or data system printouts must include all peaks not just the peaks corresponding to the target analytes.

e. Exhibit work sheets (including example calibration showing how sample results are calculated using initial calibration and sample responses for at least one sample).

f. UV traces from GPC (if performed).

g. If PCBs are confirmed by GC/MS, then the laboratory must submit copies of raw spectra and background-subtracted mass spectra of target compounds that are identified in the sample and corresponding background-subtracted target compound standard mass spectra. The laboratory will submit mass spectra of three major peaks of multi-component compounds from samples and standards for each PCB result confirmed by GC/MS.

3. Standards Data

a. Analytical Sequence Form -- in chronological order, by GC column, by instrument for all samples and quality control analyses.

b. Initial Calibration Data -- Initial Calibration Summary Form (inclusive of retention time windows, calibration factors, %RSDs, %Ds, etc.), PCB standard chromatograms, and integration reports for each initial calibration associated with SDG in chronological order, by GC column, by instrument. If a curve equation is utilized, the laboratory must provide the curve equation and coefficient of determination.

c. Continuing Calibration Data -- Continuing Calibration Summary Form (inclusive of retention time windows, calibration factors, %RSDs, %Ds, etc.), PCB standard chromatograms, and integration reports for each continuing calibration associated with SDG in chronological order, by GC column, by instrument following the associated initial calibration.

4. Raw QC data

a. Blank Data -- in chronological order, by instrument:

i. Target Compound Results (modified CLP SOW288 Form I PEST).

ii. PCB chromatograms and integration reports.

b. Laboratory Control Sample Data:

i. Target Compound Results (modified CLP SOW288 Form I PEST).

ii. PCB chromatograms and integration reports.

c. Matrix Spike Data:

i. Target Compound Results (modified CLP SOW288 Form I PEST).

ii. PCB chromatograms and integration reports.

d. Matrix Spike Duplicate Data:

i. Target Compound Results (modified CLP SOW288 Form I PEST).

ii. PCB chromatograms and integration reports.

e. UV traces from GPC cleanup (if performed).

i. UV traces for the initial calibration standards and blanks. Compound names shall be written or printed over the peaks, or retention times shall be written over the peaks, and a

separate table listing compounds and retention times shall be provided.

ii. Chromatographs and data system reports for all standards used to quantify compounds in the GPC blanks.

iii. Chromatographs and data system reports for the GPC calibration check solution and all standards used to quantify compounds in the GPC calibration check solution (or used to assess the Aroclor pattern).

f. Raw Florisil® data, arranged in chronological order:

i. Chromatographs and data system reports for the analysis of the Florisil® cartridge performance check.

ii. Chromatographs and data system reports for the standards used to quantify compounds in the Florisil® cartridge performance check analysis (*i.e.*, INDA, INDB, and the 2,4,5-trichlorophenol standards).

J) GC Herbicide Data

1. QC Summary

a. Surrogate Percent Recovery Summary ("CLP SOW288-like" Form II PEST).

b. Matrix Spike/Matrix Spike Duplicate Summary ("CLP SOW288-like" Form III PEST).

c. Laboratory Control Sample Summary ("CLP SOW288-like" Form III PEST).

d. Method Blank Summary ("CLP SOW288-like" Form IV PEST) -- arranged in chronological order by date of analysis of the blank, by instrument.

2. Sample Data

Sample data shall be arranged in packets consisting of the Analytical Results Summaries followed by the raw data for herbicide samples. These sample packets should then be placed in increasing alphanumeric order by GE sample identification. The order of each sample packet is as follows:

a. Analytical Results Summary ("CLP SOW288-like" Form I PEST).

b. Copies of herbicide chromatograms.

c. Copies of herbicide chromatograms from second GC column confirmation (if performed).

d. GC integration reports or data system printouts.

e. Exhibit work sheets (including example calculation showing how sample results are calculated using initial calibration and sample responses for at least one sample).

f. UV traces from GPC (if performed).

g. If herbicides are confirmed by GC/MS, the laboratory must submit copies of raw spectra and copies of background-subtracted mass spectra of target compounds that are identified in the sample and corresponding background-subtracted target compound standard mass spectra.

3. Standards Data

a. Analytical Sequence Form -- in chronological order, by GC column, by instrument for all samples and quality control analyses.

b. Initial Calibration Data (Initial Calibration Summary Form [inclusive of retention time windows, calibration factors, %RSDs, %Ds, etc.], herbicide standard chromatograms, and integration reports) -- for each initial calibration associated with SDG in chronological order, by GC column, by instrument. If a curve equation is utilized, the laboratory must provide the curve equation and coefficient of determination.

c. Continuing Calibration Data (Continuing Calibration Summary Form [inclusive of retention time windows, calibration factors, %RSDs, %Ds, etc.], herbicide standard chromatograms, and integration

reports) -- for each continuing calibration associated with SDG in chronological order, by GC column, by instrument following the associated initial calibrations.

4. Raw QC Data

a. Blank Data -- in chronological order, by instrument:

i. Target Compound Results ("CLP SOW288-like" Form I PEST).

ii. Herbicide chromatograms and integration reports.

b. Laboratory Control Sample Data:

i. Target Compound Results ("CLP SOW288-like" Form I PEST).

ii. Herbicide chromatograms and integration reports.

c. Matrix Spike Data:

i. Target Compound Results ("CLP SOW288-like" Form I PEST).

ii. Herbicide chromatograms and integration reports.

d. Matrix Spike Duplicate Data:

i. Target Compound Results ("CLP SOW288-like" Form I PEST).

ii. Herbicide chromatograms and integration reports.

e. UV traces from GPC cleanup (if performed).

i. UV traces for the initial calibration standards and blanks. Compound names shall be written or printed over the peaks, or retention times shall be written over the peaks and a separate table listing compounds and retention times shall be provided.

ii. Chromatographs and data system reports for all standards used to quantify compounds in the GPC blanks.

iii. Chromatographs and data system reports for the GPC calibration check solution and all standards used to quantify compounds in the GPC calibration check solution (or used to assess the Aroclor pattern).

K) GC/MS Dioxin/Furan Data

1. Quality Control (QC) Summary

a. Matrix Spike/Matrix Spike Duplicate Summary.

b. Ongoing Precision and Recovery (ORP) Summary.

c. Method Blank Analysis Summary.

2. Sample Data

Sample data shall be arranged in packets consisting of the Analytical Results Summaries followed by the raw data for dioxin/furan samples. These sample packets should then be placed in increasing alphanumeric order by GE sample identification. The order of each sample packet is as follows:

a. Analytical Results Summary.

For each sample including peak retention times, ion ratios, reported concentrations, Estimated Detection Limit (EDL) designation, and internal standard recoveries.

b. Calculation of Toxicity Equivalence.

c. Dioxin/Furan Review Worksheet and Quantitation Report. The quantitation reports must include all information required to reproduce reported positive results and EDL results.

d. Extracted Ion Current Profile (EICP) Chromatograms.

e. Second Column Confirmation Data (if necessary; will include A-9.1.1.K, Section 2, items a, b, c, and d).

f. Exhibit work sheets (including example calibration showing how sample results are calculated using initial calibration and sample responses for at least one sample. The calculations should cover positive results and EDL results).

3. Standards Data

a. Mass spectrometer performance standard data for each calibration associated with the SDG, in chronological order by GC column, by instrument.

b. Window-defining mix and isotope ratio data for each calibration associated with the SDG, in chronological order by GC column, by instrument. The retention time windows must be summarized for reference.

c. Isomer Specificity Test Standard Summary and raw data in chronological order by GC column, by instrument.

d. Initial Calibration Data (Initial Calibration Summary Form, quantitation report, and EICP Chromatograms) for each initial calibration associated with the SDG, in chronological order by GC column, by instrument. If a curve equation is utilized, the laboratory must provide the curve equation and coefficient of determination.

e. Continuing Calibration Data (Continuing Calibration Summary Form, quantitation report, and EICP Chromatograms) for each continuing calibration associated with the SDG, in chronological order, by GC column, by instrument.

4. Raw QC Data

a. Blank Data -- in chronological order, by instrument:

i. Analytical Results Summary.

For each blank including peak retention times, ion ratios, reported concentrations, EDL designation, and internal standard recoveries.

ii. Dioxin/Furan Review Worksheet and Quantitation Report.

iii. EICP Chromatograms.

b. OPR Standard Data:

i. Analytical Results Summary.

For each OPR standard including peak retention times, ion ratios, reported concentrations, EDL designation, and internal standard recoveries.

ii. Dioxin/Furan Review Worksheet and Quantitation Report.

iii. EICP Chromatograms.

c. Matrix Spike Data:

i. Analytical Results Summary.

For each matrix spike including peak retention times, ion ratios, reported concentrations, EDL designation, and internal standard recoveries.

ii. Dioxin/Furan Review Worksheet and Quantitation Report.

iii. EICP Chromatograms.

d. Matrix Spike Duplicate Data:

i. Analytical Results Summary.

For each matrix spike duplicate including peak retention times, ion ratios, reported concentrations, EDL designation, and internal standard recoveries.

ii. Dioxin/Furan Review Worksheet and Quantitation Report.

iii. EICP Chromatograms.

5. GC/MS Instrument Run Logs.

L) Inorganic Data for ICP or ICP/MS

1. Cover Page for the Inorganic Analyses Data Package.

2. Sample Results Summaries (modified CLP SOW390 Form I-INs) -- for all samples in the SDG, arranged in increasing alphanumeric order by GE sample identification.

3. Quality Control and Quarterly Verification of Instrument Parameters Summaries:

a. Initial and Continuing Calibration Verification summaries (modified CLP SOW390 Form II [PART 1]-INs).

b. Detection Limit Standards summaries (if performed, modified CLP SOW390 Form II [PART 2]-INs).

c. Blanks summaries (modified CLP SOW390 Form III-INs).

d. ICP Interference Check Sample summaries (modified CLP SOW390 Form IV-INs).

e. Matrix Spike/Matrix Spike Duplicate Sample Recovery summary (modified CLP SOW390 Form V [PART 1]-IN).

f. Post-Digest Spike Sample Recovery forms (modified CLP SOW390 Form V [PART 2]-IN).

g. Duplicates summary (modified CLP SOW390 Form VI-IN).

h. Laboratory Control Sample summary (modified CLP SOW390 Form VII-IN)

i. Method of Standard Addition Results summary (modified CLP SOW390 Form VIII-IN).

j. ICP Serial Dilution summary (modified CLP SOW390 Form IX-IN).

k. Method Detection Limits (MDL) and Reporting Limits (modified CLP SOW390 Form X-IN).

l. ICP Interelement Correction Factors (if performed, modified CLP SOW390 Form XI [PART 1]-IN).

m. ICP Linear Ranges (if performed, modified CLP SOW390 Form XII-INs).

n. Preparation Logs (modified CLP SOW390 Form XIII-INs).

o. Analytical Run Logs (modified CLP SOW390 Form XIV-INs).

4. ICP/MS Data Package will also include the following additional forms. The forms for ICP analysis listed A-9.1.1.K Sections 1-3 are also required using the SOW1091-LCIN protocol.

a. Linear Range Standard Summary (if performed, modified CLP For IV-LCIN).

b. ICP and ICP/MS Interference Check Sample (modified CLP Form VI-LCIN).

c. ICP/MS Tuning and Response Factor Criteria (modified CLP Form XIV-LCIN).

d. ICP/MS Internal Standards Summary (modified Form XV-LCIN).

5. Raw Data

For each reported value, the contracted laboratories will provide all raw data used to obtain that value. This applies to all required QA/QC measurements, instrument standardization, and all sample analysis results. This statement does not apply to the Quarterly Verifications Parameters submitted as part of each data package (Section A-9.1.1.L, items 3k-3m). Raw data must contain all instrument readouts used for the sample results. Each exposure or instrumental reading must be provided, including those readouts that may fall below the MDL. All AA and ICP instruments must provide a legible hard copy of the direct real-time instrument readout (*i.e.*, strip charts, printer tapes, etc.). A photocopy of the instrument's direct sequential readout must be included. A hard copy of the instrument's direct instrument readout for cyanide must be included if the instrumentation has the capability.

The order of raw data in the data package shall be ICP-AES, ICP/MS, flame AA, furnace AA, mercury, and cyanide. All flame and furnace AA data will be grouped by element.

M) Wet Chemistry/Conventionals Data

The wet chemistry data will be arranged in the following order by individual parameter requested for the samples in the SDG.

1. Analytical Results Summaries -- for all samples in the SDG, arranged in increasing alphanumeric order by GE sample identification.

2. Quality Control Summaries

   a. Initial and Continuing Calibration Verification summaries.

   b. Blanks summaries.

   c. Spike Sample/Spike Duplicate Recovery summary.

   d. Duplicates summary.

   e. Laboratory Control Sample summary.

   f. Analytical Run Logs for instrumental analyses.

3. Raw Data

   For each reported value, the contracted laboratories will provide all raw data (instrument printouts or logbook pages) used to obtain that value. This applies to all required QA/QC measurements, instrument standardization, as well as all sample analysis results. Raw data must contain all instrument readouts/logbooks pages used for the sample results. Each exposure or instrumental reading must be provided, including those readouts/logbook pages that may fall below the quantitation limit. A photocopy of the instrument's direct sequential readout must be included if the instrumentation has the capability.

P) Preparation Logs

1. TCLP Extraction Logs (if TCLP extraction was performed).

2. Volatile Extraction Logs (if medium-level volatile analyses were performed).

3. Semivolatile Extraction Logs.

4. Organochlorine Pesticide/PCB Extraction Logs.

5. Herbicide Extraction Logs.

6. Dioxin/Furan Extraction Logs.

7. Metals Digestion Logs.

8. Wet Chemistry Preparation Logs (by parameter).

A-9.2 Deliverables Reporting Requirements for GC/MS Volatile and Semivolatile Organic Analyses

The laboratory will be required to submit the following information as support documentation for the reported analytical results. The quality control summary forms must include the acceptance criteria (*i.e*., recovery ranges, relative percent difference limits, *etc*.) and spike-added amounts (where applicable). Additionally, the quality control summary

forms must indicate any recoveries that are outside of the acceptance criteria. The raw data associated with the samples, blanks, and standards must clearly identify the GE sample identifier, the laboratory sample number, the instrument, the laboratory file number for the analysis, and the peak areas/heights and retention times that correspond to the compounds of interest observed in all analyses reported. If the requirement of a summary form is not applicable to a particular sample, standard, or blank, the requirement should still appear on the form; however, no entry will be necessary on the form for that sample, standard, or blank.

A) 1. An analysis summary of the results for all target compounds for all sample analyses, matrix spike analyses, matrix spike duplicate analyses, laboratory control sample analyses, and method/storage blank analyses must be supplied. The summary must include an entry for each target compound, date(s) and time(s) of analysis, GE sample identification, laboratory sample number, date of sample collection, sample matrix, sample weight, sample percent solids, heated or unheated purge, column type(s), column internal diameter, dilution factor, solid extract volume, solid aliquot volume, concentration units, and sample results. For semivolatile analyses, date of sample extraction, final extract volume, injection volume, and an indication of whether the GPC cleanup was performed (yes/no) is also required. If positive results below the lowest calibration standard are reported, they must be flagged as estimated ("J") on the analysis summary. "Not-detected" results will be represented by the GE required quantitation limit and a "U" flag. If a compound was detected in a sample as well as in the method blank associated with the sample, the result must be flagged with a "B" on the summary form. Additionally, if a dilution is performed on a sample because a target compound is above the calibration range, then the positive result for

the particular compound should be flagged with a "D." If the compound is still above the calibration rage after a dilution is performed on the sample, then the compound should be flagged with an "E."

2. The raw data for the sample analyses, method blank analyses, and storage blank analyses by GC/MS methodologies will include the RICs, mass spectra for all target compounds identified, and quantitation reports for the target compounds and surrogates. The raw data for the matrix spike and matrix spike duplicate analyses will include the RIC and quantitation report for the target compounds. These are required only for Level B Deliverables.

B) A surrogate percent recoveries summary for all of the reported analyses (samples, blanks, *etc*.). The surrogate recovery forms should be segregated by method (*i.e*., high-level solid samples separate from low-level solid samples). The summary form should also include the surrogate recovery limits and the laboratory should flag the compounds that do not meet the recovery limits, on the summary form.

C) A matrix spike/matrix spike duplicate concentration and percent recovery/relative percent difference summary for each matrix spike/matrix spike duplicate pair analyzed. The matrix spike/matrix spike duplicate summary form will indicate the GE identification of the unspiked sample, the MS/MSD sample, the spike concentrations, the matrix, and the concentrations of the compounds present in the unspiked sample and the MS/MSD sample. The summary form should also include the MS/MSD recovery criteria and RPD criterion. The laboratory should flag the compounds that do not meet the criteria. A similar form for the LCS must be included with the deliverables.

D) A method/storage blank summary form for each method/storage blank which identifies the samples associated with each method/storage blank. The date of analysis, time of analysis, file number, and matrix of the method/storage blank must also be reported on the summary form. Storage blanks are only required for volatiles analysis.

E) 1. A GC/MS tuning summary which summarizes the percent abundances for the mass ions of interest and the acceptance criteria for the mass ions. Additionally, the summary must include a list of the sample and QC sample analyses (sample names, file numbers, and dates and times of analysis) associated with the GC/MS tune. The summary should indicate the instrument identification, date and time of analysis, column type, diameter of the column, and the type of purge (heated or unheated for volatiles) used to analyze the samples.

2. The raw data for the GC/MS tuning summary, consisting of a summary of the mass ion abundances and a mass spectral representation of the tuning peak.

F) 1. For the internal standard calibration method, an initial calibration summary for each initial calibration performed, summarizing all of the relative response factors for each calibration standard, the average relative response factor, and the relative standard deviation among the relative response factors. If a calibration curve equation is utilized, the laboratory must summarize the curve equation and the coefficient of determination. Additionally, the summary should indicate the compounds that must meet a minimum relative response factor or a maximum relative standard deviation

criterion and the compounds that did not meet the acceptance criteria. The summary should indicate the instrument identification, the file identifications of the analyses, the dates and times of calibration commencement and completion, column type, diameter of the column, and the type of purge (heated or unheated for volatiles) used to analyze the samples.

2. The raw data for the initial calibration, consisting of the reconstructed ion chromatogram and the raw quantitation report for each calibration standard. This is a requirement for the Level B Deliverables only.

G) 1. For the internal standard calibration method, a continuing calibration summary for each continuing calibration standard analyzed, summarizing the average relative response factors of the initial calibration associated with the continuing calibration standard, the relative response factors of the continuing calibration standard, and the percent differences between the average relative response factors of the initial calibration and the relative response factors of the continuing calibration. If calibration curve equations are utilized the laboratory must summarize the true concentration, observed concentration, and the percent drift. Additionally, the summary must indicate the compounds that are subject to a minimum relative response factor criterion, the compounds that are subject to a maximum percent difference criterion, and the compounds that did not meet the acceptance criteria. The summary should indicate the instrument identification, the date of the initial calibration, the date and time of analysis, column type, diameter of the column, and the type of purge (heated or unheated for volatiles) used to analyze the samples.

2. The raw data for the continuing calibration, consisting of the reconstructed ion chromatogram and the raw quantitation report for each calibration standard. This is a requirement only for the Level B Deliverables.

H) An internal standard area counts summary, containing a summary of the area counts and retention times for the internal standards for a continuing calibration. The summary must indicate the acceptance windows for the internal standard retention times and area counts. This summary must supply a comparison of the continuing calibration internal standards to the mid-level initial calibration internal standards. Additionally, the summary must include a listing of the internal standard retention times and area counts for all of the samples, method blanks, matrix spikes, and matrix spike duplicates associated with the continuing calibration standard.

I) A copy of all of the extraction log information for semivolatiles is required. At a minimum, the extraction information must include the date the extraction was started, the date the extraction was completed, the initial sample weight or volume, final extraction volume, laboratory sample number, the amount and concentration of surrogate spike added, and the amount and concentration of matrix spike solution added. Additionally, the extraction log should indicate if a cleanup procedure was performed on the sample. If a medium-level extraction was performed for the volatiles analysis, all extraction logs for this analysis will be required. For volatile organics analyses that require weighing sample aliquots in the field, copies of the field measurement documentation will be included in this section.

A-9.3 Deliverables Reporting Requirements for Organochlorine Pesticide, PCB, and Herbicide Analysis

The laboratory will be required to submit the following information as support documentation for the reported analytical results. The quality control summary forms must include the acceptance criteria (i.e., recovery ranges, relative percent difference limits, etc.) and spike-added amounts (where applicable). Additionally, the quality control summary forms must indicate any recoveries that are outside of the acceptance criteria. The raw data associated with the samples, blanks, and standards must clearly identify the GE sample identification, the laboratory sample number, the instrument, the laboratory file number for the analysis, and the peak areas/heights and retention times that correspond to the compounds of interest observed in all analyses reported. If the requirement of a summary form is not applicable to a particular sample, standard or blank, the requirement should still appear on the form; however, no entry will be necessary on the form for that requirement.

A) 1. An analysis summary of the concentrations of all target compounds for all sample analyses, matrix spike analyses, matrix spike duplicate analyses, and blank analyses. The blank analyses must consist of all of the extraction (method) blank analyses, injection blank analyses, and any blanks associated with cleanup procedures. The summary must include dates and times of analysis, GE sample identifications, laboratory sample numbers, dates of sample collection, date of sample receipt, dates of sample extraction, sample matrices, sample weights or volumes, sample percent solids, column types, column internal diameters, dilution factors, initial extract volumes/weights, final extract volumes, concentration units, the type of cleanup performed, and sample results. If positive results below the lowest calibration standard are reported, they must be flagged as estimated ("J") on the analysis summary. "Not-detected" results will be represented by the GE required quantitation limit and a "U" flag. If a compound was detected in a sample as well as in the method blank associated with the sample, the result must be

flagged with a "B" on the summary form. Additionally, if a dilution is performed on a sample because a target compound is above the calibration range then the positive result for the particular compound should be flagged with a "D." If the compound is still above the calibration range after a dilution is performed on the sample, then the positive result for the compound should be flagged with an "E."

2. The raw data for the sample analyses, matrix spike analyses, matrix spike duplicate analyses, and blank analyses, consisting of the chromatograms indicating the surrogate peaks and target compound peaks and quantitation reports for the target compounds and surrogates. This is a requirement only for the Level B Deliverables.

B) A surrogate percent recovery summary for all of the reported analyses (samples, blanks, *etc*.). The surrogate recovery forms should be segregated by matrix and method (*i.e*., medium-level solid samples separate from low-level solid samples). The summary form should also include the surrogate recovery limits and the laboratory should flag the compounds that do not meet the recovery limits on the summary form.

C) A matrix spike/matrix spike duplicate concentration and percent recovery/relative percent difference summary for each matrix spike/matrix spike duplicate pair analyzed. The matrix spike/matrix spike duplicate summary form will indicate the GE identification of the unspiked sample, the MS/MSD sample, the spike concentrations, the matrix, and the concentrations of the compounds present in the unspiked sample and the MS/MSD sample. The summary form should also include the MS/MSD recovery criteria and RPD criterion. The laboratory should flag the

compounds that do not meet the criteria. A similar form for the LCS should be included with the deliverables.

D) A method blank summary form for each method blank, identifying the samples associated with each method blank. The date, time, lab file number, and matrix of the method blank must also be reported on the summary form.

E) Initial Calibration Data: A summary of the initial calibration retention times, mean retention time, and a retention time window for all target compounds and surrogates must be provided for all initial calibrations. A second summary of the initial calibration standard calibration factors, average calibration factors, and relative standard deviations for all target compounds and surrogates must also be provided for all initial calibrations. If a calibration curve equations is utilized the laboratory must supply the curve equation and the coefficient of determination. Both summaries should include the SDG number, instrument identification, GC column type and diameter, date(s) of analysis, the concentration level for each initial calibration standard (as a multiplication factor of the low calibration standard), and the acceptance limit for the relative standard deviation. Copies of the pesticide, herbicide, and PCB standard chromatograms and integration reports associated with summaries should immediately follow the summary (only for the Level B Deliverables). Each initial calibration associated with the SDG must be presented in chronological order, by GC column and by instrument.

F) Continuing Calibration Data: A summary of the observed retention times, calculated compound concentrations, true concentrations, percent differences, and retention time window from the initial calibration (or from the daily retention time window update) must be provided for all continuing calibration standards. If calibration

curve equations are utilized the laboratory must summarize the true concentration, observed concentration, and the percent drift. The summary should list the SDG number, GC column type and diameter, date and time of analysis, laboratory sample number, initial calibration dates, and acceptance limits. Copies of the pesticide, herbicide, and PCB standard chromatograms and integration reports associated with summaries should immediately follow the summary (only for the Level B Deliverable). Each continuing calibration associated with an SDG must be presented in chronological order, by GC column and by instrument.

G) 4,4′-DDT and Endrin Breakdown Data (organochlorine pesticides only): A summary of the observed 4,4′-DDT, endrin, and combined percent breakdowns must be presented for each breakdown check performed. (Alternatively, if this data is obtained from a continuing calibration standard rather than a specific breakdown standard, this information may be reported on the associated continuing calibration summary form.) The summary should list the SDG number, GC column type and diameter, date and time of analysis, laboratory sample number, initial calibration dates, and acceptance limits. Copies of the pesticide/PCB standard chromatograms and integration reports associated with summaries should immediately follow the summary (only for the Level B Deliverables). Each breakdown summary associated with an SDG must be presented in chronological order, by GC column and by instrument.

H) A summary of the analytical sequence for each column and instrument used for the analysis of the project samples. The summary must contain the GC column number, the internal diameter of the column, initial calibration dates associated with the sequence, the instrument identification, the mean retention time(s) for the surrogate(s) utilized, a listing of the GE sample names, the laboratory sample

numbers, dates and times of analysis, and the retention times for the surrogate(s). The summary should also indicate the retention time window for all surrogates used and any surrogate retention times that do not meet the acceptance criterion. The summary must contain all of the analyses for the samples, blanks, initial calibration standards, and continuing calibration standards associated with the sequence. All sequences will begin with an initial calibration and will terminate with a continuing calibration or breakdown check standard that meets all acceptance criteria.

I) When a GPC cleanup procedure is required for the samples, a summary for each check standard associated with the GPC calibration. The summary must contain the GPC column identification, the calibration date of the GPC column, the GC column(s) used for the analysis of the standard, the GC column internal diameter, the theoretical concentrations of the compounds in the GPC standard, the observed concentrations of the GPC standard, the percent recovery for each compound in the GPC standard, the GE sample identification, laboratory sample number, and the date(s) of analysis for all samples associated with the GPC standard. The limits for each compound in the GPC standard should be listed on the summary form. The laboratory should flag any compound if the percent recovery was not within the control limits.

J) When a Florisil® cartridge cleanup procedure is required for the samples, a summary for each check standard associated with a Florisil® cartridge lot. The summary must contain the Florisil® cartridge lot number, the date of analysis of the Florisil® cartridge check standard, the GC column(s) used for the analysis of the standard, the GC column internal diameter(s), the theoretical concentrations of the compounds in the Florisil® cartridge check standard, the observed concentrations of the Florisil® cartridge check standard, the percent recovery for each compound in

the Florisil® cartridge check standard, the GE sample identifications, the laboratory sample number, and the date(s) of analysis for all samples in the data deliverable associated with each lot of Florisil® cartridges.

K) Second column confirmation may be performed for all pesticide, PCB, and herbicide analyses when there is a positive result reported for a project sample. When the laboratory performs a dual column quantitative analysis for organochlorine pesticides, PCBs, and herbicides, a summary of the identified compounds and observed concentrations for the two columns utilized for sample analyses is required. The summary must contain the GE sample identification, the laboratory sample number, the dates and times of analysis, the instruments used for analysis, the GC columns, the GC column internal diameters, the retention time windows for each peak used to quantitate the compound, the observed retention time for each peak used to quantitate the compound, the calculated concentration for each peak used, the mean concentration for each column for each compound identified, and the percent difference between the mean concentrations calculated for each column.

If the percent difference between the results for the analyte from the two GC columns is greater than 40% for the analysis, then the higher of the two values is reported and flagged with a "P." Finally, the "C" flag is used when the identification of a pesticide result is confirmed by GC/MS.

A-9.4 Deliverables Reporting Requirements for Dioxin/Furan Analyses

The laboratory will be required to submit the following information as support documentation for the reported analytical results. The quality control summary forms must include the acceptance criteria (*i.e*., recovery ranges, relative percent difference limits, *etc*.)

and spike-added amounts (where applicable). Additionally, the quality control summary forms must indicate any recoveries that are outside of the acceptance criteria. The raw data associated with the samples, blanks, and standards must clearly identify the GE sample identifier, the laboratory sample number, the instrument, the laboratory file number for the analysis, and the peak areas/heights and retention times that correspond to the compounds of interest observed in all analyses reported. The raw data must provide all information necessary to reproduce all reported positive and EDL results. If the requirement of a summary form is not applicable to a particular sample, standard, or blank, the requirement should still appear on the form; however, no entry will be necessary on the form for that requirement.

A) 1. An analysis summary of the results for all target compounds for all sample analyses, second column confirmation analyses, matrix spike analyses, ORP standard analyses, and method blank analyses must be supplied. The summary must include an entry for each target 2,3,7,8-substituted compound and total homologue concentrations, date(s) and time(s) of analysis, GE sample identification, laboratory sample number, date of sample collection, date of sample preparation, sample matrix, sample weight, sample percent solids, column type(s), column internal diameter(s), dilution factor, concentrated extract volume, concentration units, peak retention times, isotope ratios, and sample results. If positive results below the lowest calibration standard are reported, they must be flagged as estimated ("J") on the analysis summary. "Not-detected" results will be represented by the EDL and a "U" flag. If a compound was detected in a sample as well as in the method blank associated with the sample, the result must be flagged with a "B" on the summary form. Additionally, if a dilution is performed on a sample because a target compound is above the calibration range, then the

positive result for the particular compound should be flagged with a "D". If the compound is still above the calibration rage after a dilution is performed on the sample, the positive result for the compound should be flagged with an "E".

2. The raw data for the sample analyses and method blank analyses by GC/MS methodologies, consisting of the EICP, quantitation reports for the target compounds, the associated areas or height for each peak within the established retention time window, and all other information required to reproduce all reported positive and EDL results. The raw data for the matrix spike and matrix spike duplicate analyses will include the EICP chromatogram and quantitation report for the target compounds.

B) A matrix spike concentration and percent recovery summary for each matrix spike analyzed is required. The matrix spike summary form will indicate the GE identification of the unspiked sample, the sample, the matrix, and the concentrations of the compounds present in the unspiked and spiked sample. The summary form should also include the MS recovery criteria. The laboratory should mark the compounds that do not meet the specified criteria. A similar form for the OPR standard should be included with the deliverables.

C) A method blank summary form for each method blank that identifies the samples associated with each method blank. The date of extraction, date of analysis, time of analysis, lab file number, sample weight, and matrix of the method blank must also be reported on the summary form.

D) A mass spectrometer performance summary for each mass spectrometer performance standard analyzed should identify the sample number, lab file identification, date and time of analysis, instrument identification, GC column identification, and static resolving power.

E) A window defining mix summary form for each window defining analysis should identify the sample number, lab file identification, date and time of analysis, instrument identification, and GC column identification. This form should include the retention time of the first eluting and last eluting isomer for each congener group.

F) An isomer specificity test standard summary should identify the sample number, file number, instrument ID, date and time of analysis, the GC column and instrument identification, and the percent valley determination between $^{13}C_{12}$-2,3,7,8-TCDD and $^{13}C_{12}$-1,2,3,4-TCDD. In addition, if second column confirmation is required, percent valley for 2,3,7,8-TCDD and the closest isomers should be calculated and reported.

G) A summary of the analytical sequence for each column and instrument used for the analysis of the project samples. The summary must contain the GC column number, the internal diameter of the column, initial calibration dates associated with the sequence, the instrument identification, a listing of the GE sample names, the laboratory sample numbers, and dates and times of analysis. The summary must contain all of the analyses for the samples, blanks, initial calibration standards, and the continuing calibration standards associated with the sequence.

H) 1. An initial calibration summary for each initial calibration performed, summarizing all of the relative response factors for each calibration standard,

the average relative response factor, and the relative standard deviation among the relative response factors. If calibration curve equations are utilized, the laboratory must supply the curve equation and coefficient of determination. Additionally, the summary should indicate maximum relative standard deviation and minimum relative response factor criteria as well as the compounds that did not meet the acceptance criteria. The summary should indicate the instrument identification, the dates and times of calibration commencement and completion, column type, and diameter of the column.

2. The raw data for the initial calibration, consisting of the EICPs and the raw quantitation report for each calibration standard.

I) 1. A continuing calibration summary for each continuing calibration standard analyzed, summarizing the average relative response factors of the initial calibration associated with the continuing calibration standard, the relative response factors of the continuing calibration standard, and the percent differences between the average relative response factors of the initial calibration and the relative response factors of the continuing calibration, and the isotope ratios and retention times. If calibration curve equations are utilized the laboratory must summarize the true concentration, observed concentration, and the percent drift. Additionally, the summary must indicate the compounds that are subject to a minimum relative response factor criterion, the compounds that are subject to a maximum percent difference criterion, and the compounds that did not meet the acceptance criteria. The summary should indicate the instrument identification, the date

of the initial calibration, the date and time of analysis, column type, and diameter of the column.

2. The raw data for the continuing calibration, consisting of the EICPs and the raw quantitation report for each calibration standard.

A-9.5 Deliverables Reporting Requirements for Inorganic Analyses

The laboratory will be required to submit the following information as support documentation for the reported analytical results. The quality control summary forms must include the acceptance criteria (*i.e.*, recovery ranges, relative percent difference limits, *etc*.) and spike-added amounts (where applicable). Additionally, the quality control summary forms must indicate any quality control results that are outside the acceptance criteria. All instrument raw data printouts for the points discussed below must be provided in an orderly fashion. This applies to all required QA/QC measurements, and instrument standardization, as well as sample analysis results. Additionally, all associated extraction, digestion, and distillation logs must be supplied. The order of the raw data in the data package shall be ICP-AES, ICP/MS, flame AA (if performed), furnace AA (if performed), and mercury. All flame and furnace AA data shall be grouped by element. All raw data shall be grouped by analysis date for all analytical results.

A) 1. A sample reference list for all samples present in an SDG. This reference list must summarize and correlate the laboratory sample number, the GE designated sample identification, and any laboratory code (*i.e.*, truncation of GE designated sample number by the laboratory) for each sample in an SDG.

2. A Table of Contents listing page numbers associated with information such as:

   a. Methodology Summary

   b. Case Narrative

   c. Sample Results

   d. Quality Control Data

   e. Verification of Instrument Parameters

   f. Preparation and Analysis Logs

   g. Raw Data, including but not limited to:

      i. ICP-AES, ICP/MS, Flame AA, GFAA, and Mercury Data

      ii. Digestion Logs

      iii. Confirmation Data

   h. Chain-of-Custody Records

B) Analysis summaries of the concentrations of all target analytes for all sample analyses. The summary must include the GE designated sample number, the laboratory sample number, date of sample collection, date of sample receipt, sample

matrix, sample percent solids, concentration units, sample results, data qualifier codes, analysis method codes, description of sample before and after analysis, and any comments relating to the sample.

C) A summary of the initial and continuing calibration verifications for each calibration performed. This summary will include the concentrations observed as well as the true value of the analyte in the initial and continuing calibrations. A percent recovery will be summarized based on the observed and true values for each analyte.

D) A summary of the Detection Limit (DL) standard analyses for both Atomic Absorption (AA) and Inductively Coupled Plasma (ICP) analyses. This summary will include the concentrations observed as well as the true value of the analyte in the DL standard. A percent recovery will be summarized based on the observed and true values for each analyte.

E) A summary of the initial and continuing laboratory blank analyses for each calibration performed. This summary will include the concentrations (positive or negative) observed of any analyte in the initial and continuing blank analyses at values greater than the MDL. The summary should also include the concentrations of any analyte observed in the laboratory preparation blank associated with each calibration sequence performed by the laboratory.

F) A summary of the ICP interference check sample analysis for each analytical sequence performed. This form will summarize the true and found values (positive, negative, or zero) of all analytes present in Solutions A and AB of the ICP interference check sample analysis. This form will also summarize the percent recoveries of the analytes/interferences present in the standards.

G) A summary of the pre-digestion matrix spike analysis. This form will summarize the percent recovery control limit for each analyte. Also, the sample result, the spike sample result, and the spike-added amount must be summarized on this form for all parameters analyzed. The laboratory-calculated percent recovery as well as the laboratory qualifier stating whether the calculated percent recovery was within control limits must also be summarized on this form.

H) A summary of the post-digestion matrix spike analysis. This form will require the same information described in item G.

I) A summary of the laboratory duplicate analysis. This form will summarize the percent differences observed between the sample and laboratory duplicate analyses. The appropriate control limits must be specified by the laboratory, and a summary of the sample and laboratory duplicate analyses must be provided. The percent solids for the sample and the duplicate sample should be included on the summary form.

J) A summary of the Laboratory Control Sample (LCS) analysis. This form will summarize the percent recovery, control limits, and true and found values for the solid sample analyses.

K) A summary of any required Method of Standard Additions (MSA) determinations. This form will summarize the concentrations and absorbencies of all samples and analytes that require analysis by MSA. The correlation coefficient for the MSA analysis will be calculated and summarized on this form. Also, the sample concentration determined from the MSA determination will be summarized on this form.

L) A summary of the ICP Serial Dilution analyses performed by the laboratory. This summary will show the result of the initial sample analysis (in aqueous units, as observed from the raw data), the result of the five-fold serial dilution analysis, and the percent difference between the two analyses.

M) The summaries necessary for the verification of instrument parameters. These include an Method Detection Limit and Reporting Limit Summary, an ICP Interelement Correction Factor Summary (if performed) for each ICP used for analysis, and an ICP Linear Range Summary (if performed) for each ICP used for analysis.

N) The analysis log summaries. These include a Sample Preparation log that provides the sample identification; the preparation date; the sample weight (in grams) used; and the digestion volume (in mL) used and an Analysis Run Log that provides the instrument identification, the sample identification, any dilution factors employed in the analysis, the date and time of analysis, the method of analysis, and the parameters analyzed. Additionally, the GFAA post-digestion analytical spike sample recoveries are listed on the Analysis Run Log.

A-9.6 Deliverables Reporting Requirements for Wet Chemistry/Conventionals Analysis

The laboratory will be required to submit the information detailed in Sections A-9.5 A) -C), A-9.5, E) and A-9.5, G) - J) and A-9.5-N as support documentation for the reported analytical results. The quality control summary forms must include the acceptance criteria (*i.e*., recovery ranges, relative percent difference limits, *etc*.) and spike-added amounts (where applicable). Additionally, the quality control summary forms must indicate any quality control results that are outside the acceptance criteria. All instrument raw data

printouts for the points discussed in the above mentioned sections must be provided in an orderly fashion. This applies to all required QA/QC measurements, and instrument standardization, as well as sample analysis results. Additionally, a direct sequential readout must be included if the instrument has the capability.

APPENDIX 20
TSS SURROGATE STUDY SUMMARY

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1 INTRODUCTION

1.1 Introduction

This report has been prepared on behalf of the General Electric Company (GE) to present the results of bench scale laboratory studies that have been performed to develop semi-quantitative relationship(s) between total suspended solids (TSS) and a surrogate parameter(s) for use in the near- and far-field compliance monitoring that GE will perform as part of the Remedial Action Monitoring Plan (RAMP) for Phase 1 dredging. The surrogate parameter data will be collected in near real time, and will be used to estimate TSS concentrations in the Hudson River upstream and downstream of dredging operations. These estimates will in turn be used to evaluate the extent of sediment resuspension caused by dredging operations, allowing the assessment of any associated affects on water quality and serve as an indicator of compliance with standards developed by the United States Environmental Protection Agency (USEPA). The relationship(s) between TSS and a surrogate parameter(s) developed through the studies discussed in this report are incorporated in the Remedial Action Monitoring Quality Assurance Project Plan (RAM QAPP), which also sets forth the procedures to be used to maintain and update the relationship(s) through the course of Phase 1 dredging.

1.2 Background

During Phase 1 dredging, GE will be required to monitor polychlorinated biphenyls (PCBs), TSS, dissolved and particulate organic carbon, metals, and field water quality parameters, as part of the requirements of USEPA's Engineering Performance Standards for Resuspension (RPS; USEPA 2004). In particular, in-river water column monitoring will be performed to evaluate achievement of the RPS, which has been designed to limit the impacts of dredging on water quality. As the PCBs in the sediment are primarily associated with sediment particles (i.e., PCBs bound to the solid phase), monitoring TSS downstream of dredging activities provides a useful qualitative indicator of potential PCB release via resuspension. The RPS establishes TSS threshold criteria in both the near-field (i.e., within 300 m of dredging) and far-field (i.e., greater than one mile downstream of dredging), that if exceeded, trigger additional compliance monitoring and the evaluation of engineering controls. Should a significant PCB release accompany TSS concentrations that exceed the RPS criteria, additional engineering controls (including temporarily shutting down the dredging

operation) may be implemented, and downstream public users of Hudson River water may be notified that PCB concentrations in river water may exceed the criteria specified in the RPS (RAM Scope at Pages 2-16 and 2-28).

Effective control of dredging operations will require implementation of appropriate response actions as soon as practical after confirmation that TSS concentrations have exceeded criteria at near-field monitoring stations. Monitoring for compliance of the RPS TSS criteria by direct TSS measurements alone is problematic. It may take up to 24 hours to collect water samples at compliance locations, transport those samples to a field or analytical laboratory, perform the TSS analyses, and report the results to field management and oversight personnel. Therefore, continuous measurement of a surrogate TSS parameter accompanied by an appropriate method for using these data to estimate near real-time TSS concentrations will improve control of the dredging project and promote compliance with the RPS TSS criteria. GE has performed this special study to identify an appropriate real-time surrogate parameter and procedure for estimating TSS concentrations during Phase 1.

1.2.1 Near-Field Special Studies

The RPS specifies near-field special studies that include bench scale laboratory tests designed to assess the relationship between TSS and two real-time surrogate parameters (turbidity and particle volume). These tests include settling column and serial dilution tests performed in accordance with the work plan prepared for this study by GE (QEA 2005) which was submitted to USEPA on November 15, 2005. As required in the RPS, the testing specified in the work plan was based on United States Army Corps of Engineers (USACE) procedures (Thackson and Palermo 2000; Earhart 1984), and focused on areas of the river that are designated for Phase 1 dredging operations.

1.2.1.1 Sample Collection

To obtain sediment for the testing, data collected during the Sediment Sampling and Analysis Program (SSAP) were evaluated to identify locations in the river that contain sediment with characteristics that are appropriate for testing. Target locations for cores to be collected for the TSS study were selected based on analysis of geotechnical data, visual grain size and color descriptions, and PCB data. The goal was to select cores that are representative of the

Phase 1 dredge areas and have a high content of the targeted primary sediment type while considering the variability of the sediment matrix existing in each sediment type category. A summary of this evaluation, target core sample locations, and sampling procedures are presented in a Technical Memorandum dated October 14, 2005 (Attachment A). A total of 24 cores - 8 cores in each sediment type category were collected for the study.

1.2.1.2 Sample Preparation and Selection

Upon collection, the cores were stored in the processing laboratory at the Ford Edward plant site until they were processed on December 19, 2005. During processing, the cores were cut at the depth of contamination, homogenized, visually characterized, and photographed. Samples of the homogenized sediment were submitted to analytical laboratories for grain size analysis, total organic carbon analysis, and moisture content analysis. The cores were collected, described, and processed in accordance with the procedures used in the SSAP.

Of the 24 cores collected, 3 were selected from each sediment type category for the testing (total of 9 cores). The laboratory and processing data were evaluated to select the cores that were the most appropriate for use in the testing. The results of this evaluation are presented in a Technical Memorandum dated February 7, 2006 (Attachment B), and are summarized in Table 1-1. The table includes core IDs sorted by targeted primary sediment type, along with the results of grain size, TOC, moisture content, and bulk density analysis. Additionally, visual characterization results, wet and dry sediment weight, and approximate median particle size diameter are included. Records highlighted in blue identify cores that were used in the testing.

1.2.2 Far-Field Special Studies

The RPS also requires the development a surrogate relationship for suspended sediments at far-field locations. This relationship will be developed using data collected as part of the Baseline Monitoring Program (BMP; QEA and ESI 2004) and during testing conducted during the automated sampling station pilot study to be conducted in 2006. The activities described in the Statement of Work (QEA 2005) for the pilot testing will be used to supplement the weekly TSS and turbidity results at a single far-field location by collecting a series of samples and turbidity measurements.

It is anticipated that the BMP and the proposed testing of the pilot automated sampling station will provide sufficient data to establish a semi-quantitative relationship between TSS and turbidity at the background and far-field stations under baseline conditions prior to Phase 1 dredging. GE will evaluate the far-field TSS and turbidity data upon completion of the automated sampling station pilot test. The results of this evaluation will be presented to USEPA in an update to the Phase 1 RAM QAPP.

1.3 OBJECTIVES

The overall objective of this special study is to develop a semi-quantitative relationship for the correlation of analytical measurements of TSS with surrogate field measurements in the near-field to be applied during Phase 1 dredging. An ancillary objective of the study that is addressed in this report is to compare the semi-quantitative relationships of TSS and real-time surrogate parameters for different sediment types to evaluate the sufficiency of using a single near-field surrogate relationship.

Other ancillary objectives include:

- Compare the surrogate relationship(s) for near-field TSS and turbidity with the initial far-field relationship(s) developed using paired data collected under the BMP.
- Evaluate the particle size distribution of suspended sediment under baseline conditions.

2 METHODS

Conducting the TSS/Surrogate Special Study included performing settling column and serial dilution tests in accordance with the work plan (QEA 2005). These tests examine TSS, turbidity, and particle volume as TSS concentrations decline due to settling (column test) or dilution (serial dilution test). Sediments resuspended in the field during dredging operations are subject to both settling and dilution and the tests allow examination of the impact of both processes on the relationship between TSS and turbidity or particle volume. These tests were performed in March 2006 in the processing laboratory at the GE Fort Edward facility. As described in Attachment B, 9 sediment core samples were selected from a group of 24 core samples that were collected from the Hudson River in November 2005. During each test, three sets of samples were collected for TSS, turbidity, and particle volume distribution analysis. The purpose of these tests was to generate data for use in evaluating the relationship between TSS and a surrogate (turbidity or particle volume) over a wide range of sediment types and particle concentrations.

Cores discussed in this report will be referred to by the order in which they have been processed. This order was determined by the median diameter of particles present in the core. Core 1 contained particles with the smallest overall median diameter; while Core 9 contained the largest. The list of the core IDs and the order in which they were processed is presented in Table 2-1.

2.1 Settling Column Tests

During the settling column testing, the settling of resuspended sediment was studied over a 24-hour period; dilution of the resuspended sediment by clean river water was not evaluated. Sampling time intervals were selected to bracket the approximate time of travel between a working dredge, near-field monitoring stations (100 and 300 meters downstream) and a far-field monitoring station (1 mile downstream minimum) under a range of flow velocities that are anticipated during active dredging. Settling column test was performed in a manner similar to procedures specified by the USEPA and USACE (USEPA and USACE 1998).

2.1.1 Equipment

The tests were performed using an acrylic column approximately 8-ft. high and 12 in. in diameter (Figure 2-1). The column was equipped with a mechanical mixing device with a speed regulator and was tested for leaks prior to its use (Figure 2-1). The column was equipped with seven sample ports located at 12-in. intervals, starting 1-ft. off the bottom, and continuing up to the 7-ft. level (Figure 2-2). The working volume of the column was approximately 150 L. Samples were collected from the upper six ports during the tests; the port located 1-ft. off the bottom was not used to withdraw any samples because of its proximity to the settled sediment/water interface.

2.1.2 Procedures

Each test was initiated by filling the settling column up to the approximate 7-ft. level with water, and then a predetermined volume of sediment to the column was added, followed by topping off the column up to the 7.5-ft. level with water (Figure 2-3). The water used for the testing was collected from the Hudson River at the Fort Edward yacht basin (Figure 2-4) under normal low flow conditions. The water was taken to the processing laboratory and allowed to reach room temperature overnight. The sediment used in the study was stored at the processing facility in sealed five-gallon pails since it was collected in November of 2005. Prior to each test, the sediment was homogenized and sieved through a wire mesh to eliminate particles larger than approximately 0.25 in. (Figure 2-4). The amount of sediment needed for the settling column test was calculated on a dry weight basis by accounting for the moisture content of the samples, as reported as part of the geotechnical analysis of each core. A balance was then used to weigh the correct amount of sample (Figure 2-4) to achieve an initial TSS concentration of approximately 10,000 mg/L in the column.

After the sediment and water was placed in the column, the mixer was started. The speed of the mixer was adjusted until the sediment and water mixture was visually homogeneous. The mixing device was then turned off and samples were collected from all six sampling ports as quickly as possible. Ports were sampled from top (Port 1) to bottom (Port 6); sample collection typically required approximately two to three minutes. In addition to the sample collected immediately after the mixer was turned off (time = 0 min.) additional samples were withdrawn after settling times of 5, 10, 20, 30, 60, 90, 120, 180, and 360 minutes and

approximately 24 hours (Figure 2-5). During the first 30 minutes of testing, one sample from each port was collected, thereafter; samples were only collected from Ports 1, 3, and 6 until the test was completed. Depending on the testing schedule, the 24-hour sample was occasionally collected after approximately 22 hours to facilitate starting a subsequent test within normal working hours.

Samples were withdrawn by opening the valve on each sampling port, and collecting the sample in clear 350 ml plastic containers (Figure 2-2). The contents of the bottles were sub sampled for analysis. Of the 350 ml of sample, up to 100 ml was used for the particle volume analysis (depending on particle concentration), approximately 30 ml were used for the turbidity measurements, and the remainder was sent to Northeast Analytical, Inc. (NEA) for TSS analysis. Analytical procedures are discussed in Section 2.3.

The overall volume of water withdrawn during each of the nine settling tests resulted in a decrease of approximately 3.5 in. in the water level compared to the initial height of the water in the column. After the conclusion of each test, the column was drained into a holding tank, allowed to settle, and characterized prior to discharge to the GE Fort Edward wastewater treatment system. At the end of the study, the remaining sediment contained in the tank was placed in drums managed as PCB waste by GE.

2.1.3 Observations

After the mixing device was turned off, the larger particles began settling immediately. Since the mixing device was always turned off prior the first sample withdrawal, the time = 0 samples were not fully representative of the initial conditions in the column, as a significant amount of sediment settled before the samples could be collected. This resulted in the initial TSS concentrations being less than the target concentration of 10,000 mg/L for the tests, with the exception of Core 1, which contained the highest fraction of fine grained sediment. The rapid settling of large particles appeared to create highly variable conditions within the column early in the tests (typically first 20 minutes).

The settling characteristics of two cores (Cores 5 and 8) were significantly different than for the remaining cores. Figures 2-6 and 2-7 depict what appears to be flocculation occurring in

the column. A time series that illustrates the settling that occurred in Cores 5 and 8 is presented in Figures 2-8 and 2-9, respectively. In both cases, little sediment remained in suspension after the first 20 minutes of the test. This however was not true for the rest of the cores, which remained turbid throughout the 24-hour testing period. A time series of photos taken of Core 9 (Figure 2-10) illustrates that significant turbidity remained in the column at the end of the test. This trend was similar to that observed during testing of Cores 1, 2, 3, 4, 6, and 7.

2.2 Serial Dilution Tests

The purpose of the serial dilution tests was to examine TSS, turbidity, and particle volume as TSS concentrations declined due to dilution with Hudson River water. Serial dilution tests were conducted using techniques similar to those recommended by the USACE (Earhart 1984).

2.2.1 Equipment

The dilution tests were performed in a two liter transparent plastic mixing vessel outfitted with a sampling port and a variable speed mechanical mixer (Figure 2-11).

2.2.2 Procedure

Preparation for the dilution study test was identical to the preparation described in Section 2.1.2 for the settling column test. Hudson River water used in the dilution test came from the Rogers Island area where it was collected under normal low flow conditions and allowed to sit at room temperature about 24 hours before the beginning of each test. The sediment used in the study was homogenized, and then sieved through a wire mesh to eliminate particles larger than approximately 0.25 in.

The test was initiated by adding a pre-determined amount of sediment to the mixing vessel containing 1 L of Hudson River water. The initial target suspended solids concentration was approximately 10,000 mg/L. The water/sediment mixture was then mixed continuously; the speed of the mixer was adjusted until the sediment appeared to be uniformly distributed within the water in the mixing vessel. A 350-ml sample was then withdrawn for TSS and particle volume analysis, while a 50-ml sample was withdrawn for turbidity measurement

(400 ml total). Then, 400 ml of Hudson River water was added back to the mixing vessel to dilute the original suspension. The sample was mixed and another 400 ml aliquot was removed from the vessel for analysis. This procedure was repeated 20 times, resulting in progressively lower TSS concentrations (Figure 2-12). Three additional dilutions were then performed, using increased volumes (800 ml), resulting in TSS concentrations that approach baseline conditions in the Hudson River.

2.2.3 Observations

Large particles (>0.25 in.) were screened out prior to the test; however, sand particles up to 0.25 in. remained in the sediment samples (Figure 2-13). Although aggressive mixing techniques were employed, it was difficult to maintain a homogenous particle suspension in the sampling vessel. As a result, samples withdrawn for analysis contained quantities of large particles that were not representative of the test vessel as a whole and varied randomly during the dilution sequence. The random incorporation of one or more large particles in samples likely affected the accuracy of the TSS data. This observation is supported by the results of the data quality evaluation (Section 3.1.1) which suggests that the nature of the sediment resulted in significant variability of the analytical data.

2.3 Analytical Methods

The samples collected during the TSS Surrogate Special Study were analyzed for TSS, turbidity, and particle volume. TSS analysis was performed by NEA. Turbidity and particle volume measurements were performed on site in the processing laboratory during the course of the study.

2.3.1 TSS

TSS analyses were performed by NEA in accordance with USEPA Method 160.2. The majority of samples submitted to NEA for TSS analysis had a volume 200 ml or more, with the exception of duplicate samples collected during the dilution study. The volume of the duplicate samples sent for TSS analysis was typically lower than 200 ml because only 400 ml was withdrawn after each dilution and this amount had to be split between the original sample and its duplicate. In addition both samples had to be analyzed for turbidity and particle volume before they were sent for TSS analysis. Sample size limitations resulted in

NEA reporting elevated detection limits; however, only 17 of 670 samples were reported as not detected. Of these, the highest detection limit was approximately 2.5 mg/L. The samples were maintained at 4°C until submitted to NEA for analysis.

2.3.2 Turbidity

2.3.2.1 Instrumentation

A bench top turbidity meter (Hach 2100AN IS) was used to measure turbidity in NTU in the surrogate study samples (Figure 2-14). This instrument was selected because it has a wide measurement range (0.1 to 10,000 NTU), and is reported to provide data that is comparable to turbidity probes designed for in situ deployment, such as the YSI 1636 (currently used for the BMP). The turbidity measurements were made in the ratio mode, in which the signals from four detectors are mathematically processed to improve the instruments calibration stability, measurement range, and the ability to measure turbidity in the presence of color. At the beginning of the study the instrument was calibrated using a StablCal Stabilized Formazin Calibration Kit, which contained ampoules with stabilized Formazin suspensions of <0.1, 20, 200, 1000, 4000, and 7500 NTU. Gelex Secondary Standards were used throughout the study to verify the proper calibration of the instrument. The instrument calibration was considered acceptable as long as the turbidity values of the secondary standard turbidity were within + 5% of the values assigned to them at the time of previous calibration. Because the turbidities of the individual Gelex samples never exceeded the 5% limit, the original calibration curve was used throughout the whole surrogate study.

2.3.2.2 Sample Preparation and Analysis

For logistical purposes, the samples collected for turbidity analysis were handled slightly differently during the settling and dilution studies. During the dilution study, samples were collected directly into the 50 ml sample cells that came with the turbidimeter and analyzed immediately after collection (Figure 2-11). During the settling column study, samples were collected in 350-ml bottles. Approximately 50 ml were withdrawn from each container for turbidity analysis (Figure 2-14). The contents of each bottle were thoroughly mixed before the 50-ml subsample was poured into the sample cell. The surface of the sample cell was wiped dry and the sample was placed in the Hach turbidity meter and the sample cover was

placed over the sample (Figure 2-14). The data were recorded in an electronic spreadsheet as it was collected.

When samples contained a significant fraction of coarse grained particles, the withdrawal of a representative subsample and its subsequent turbidity analysis were affected by rapid settling of larger particles. Typically, large particles settled out before a representative subsample could be collected. Additionally, large particles present in the subsample tended to settle to the bottom of the turbidity meter sample cell before a stable turbidity measurement could be obtained. It is likely that turbidity was underestimated during the early phases of both the settling column and serial dilution tests, when TSS concentrations were the highest and the settling column contained a significant fraction of large particles.

2.3.2.3 Turbidimeter Comparison Study

The YSI turbidity probe (Figure 2-15) was used to analyze a subset of samples to verify that its performance is comparable to the performance of the Hach bench-top turbidimeter. The YSI probe operates on a similar principle to the bench top turbidimeter; using the same incident light wave length to irradiate the analyzed sample. Prior its use, the YSI probe was calibrated with three different calibration standards: 0.1, 40, and 1000 NTU.

The sediment of one core from each sediment category (SI, FS, and MS) was used to compare the performance of the two turbidity probes. Specifically, samples for the comparison study were prepared from Cores 1, 4, and 9. The sediment from each core was first mixed with water to generate a mixture with a TSS concentration of approximately 10,000 mg/L. Then the mixture was allowed to settle for several minutes prior to withdrawing a sample from the supernatant. This sample did not contain any large particles and therefore could be easily diluted further with water to obtain dilutions covering a range of TSS concentrations from high to near background levels. Each dilution was prepared from the previous sample by mixing 50% of its volume with equal amount of the river water. Up to 10 dilutions were prepared for each sample depending on the initial concentration of silt and clay in the first sample.

The YSI turbidity probe is less convenient to use in the laboratory setting than the bench top turbidimeter. The probe consists of three main parts – sensor, sample cup, and the

instrument control module (Figure 2-15). Prior to each measurement, the sensor, and the cup were thoroughly rinsed in river water. Then the sample was poured in the sample cup and the turbidity probe was submerged inside the cup (Figure 2-15). After the instrument stabilized, the turbidity reading was recorded; the cup and the probe were rinsed with river water. The sample was then diluted with river water, and the procedure was repeated. Dilutions continued to be prepared and analyzed until the turbidity reading of the analyzed sample approached baseline levels in the river water.

Figure 2-16 presents the results of the turbidimeter comparison study in the form of a cross plot (Panel A) and relative percent difference (RPD) comparisons (Panels B, C, D). The cross plot (Figure 2-16, Panel A) depicts a comparison of turbidity data collected by the Hach instrument with data collected with the YSI turbidity probe. Because the operating range of the YSI probe is 0-1000 NTU, two Core 1 samples that exceeded the probe's operating range were excluded from RPD evaluations. Panel B in Figure 2-16 presents turbidity RPDs for individual cores and samples; the average RPDs for each core are noted at the bottom. The data suggest that Core 1 turbidities measured by the Hach instrument and the YSI probe compared the best (RPD = 8.9%) while Core 4 and 9 turbidities compared worse at 31.4% and 33.6%, respectively. Panels C and D in Figure 2-16 present the range of RPDs calculated for samples with low particle concentrations (Hach turbidities <50 NTU) and high particle concentrations (50< Hach turbidity <1000 NTU). The panels show that RPDs in samples with higher turbidities (Figure 2-16, Panel C) tend to be lower than in less turbid samples (Figure 2-16, Panel D), where small differences in turbidity measurements can lead to high RPDs. No particle volume data were collected during the comparison study; however, the relatively high RPDs for Cores 4 and 9 may be related to measurement technique differences (YSI turbidities took longer to measure than the Hach turbidities). Larger particles may have settled out of the samples before the measurements could be taken. In addition, average RPDs calculated from duplicate turbidities measured using only the Hach instrument were significantly lower (4.77% - 12.3%, Table 3-1) than RPDs of samples collected by two different instruments (see above). This may suggest some differences in the results obtained between the Hach and YSI instruments.

2.3.2.4 Decontamination

The bench-top turbidity measurements were performed using three sets of new, scratch free sample cells provided by the manufacturer. After each measurement the cells were emptied out and submerged in clean, soapy water where they were allowed to soak. After several minutes of soaking the vials were rinsed with tap water, and allowed to dry prior to reuse (Figure 2-14). Immediately prior to each measurement, the surface of the sample cell was wiped off and placed in the instrument. To achieve consistent results, the sample cells were aligned with the sample holder in accordance with the manufacturer's recommendations prior to each measurement (Figure 2-14). Field blanks prepared from distilled water were used to check for contamination.

2.3.3 Particle Volume

2.3.3.1 Instrumentation

The particle volume distributions were analyzed using a LISST 100X (Laser In-Situ Scattering and Transmissometry) Type-C instrument with 5-cm optical path obtained from Sequoia Scientific, Inc. (Figure 2-17). This instrument is based on laser diffraction technology and reports particle volumes in 32 particle size classes logarithmically distributed over the range particle diameters from 2.5 to 500 um. The instrument is designed to work in a concentration range between 100 to 500 mg/L TSS, and is insensitive to color and particle composition. For laboratory use, the instrument was outfitted with a small volume (100 ml) horizontal mixing chamber according to specifications provided by the manufacturer (Figure 2-18). During particle volume distribution measurements, particles were kept in suspension by a rotating stirrer bar placed at the bottom of the mixing chamber. The speed of the rotation of the stirrer was adjusted manually. Sequoia Scientific, Inc. provided the software required for data collection and instrument operation, and calibration.

2.3.3.2 Sample Preparation

The samples for particle volume analysis were withdrawn from the 350-ml bottles used to collect samples during the settling column and serial dilution study. The contents of each bottle were homogenized by mixing prior sample withdrawal. Due to the large percentage of samples that had TSS concentrations that exceeded the upper range of the LISST

(approximately 500 mg/L), around 70% of the samples had to be diluted before analysis. The higher dilutions (1:100 – 5:100) were prepared by withdrawing a mixed sub-sample with a 5-ml syringe from the 350 ml collection bottles and diluting it with river water in a 100-ml graduated cylinder. The lower dilutions (1:10) were prepared with 10-ml and 100-ml graduated cylinders. The samples were then poured into the LISST mixing chamber.

The LISST mixer was operated manually in a manner to homogenize the samples during analysis as thoroughly as possible based on visual observations. For Cores 1 through 6, the mixer was used continuously. For Cores 7 through 9, the mixer was only used to measure samples containing coarser particles. The use of the mixer was reduced for the three last cores because the particle volume distributions of field blanks suggested the presence of sand-sized particles. These particles did not appear to exist in the samples and their presence was attributed to bubble generation created by the motion of the stirrer.

Typically, samples were collected, diluted, and analyzed on the same day with the exception of the samples from Cores 1 and 2. These samples were very turbid and therefore required more time to prepare and analyze. Based on the results of experimentation performed during the testing, samples that were stored for longer periods of time appeared to have undergone changes in particle volume distribution. The increase of large-grained particles over time may have been the result of flocculation of smaller particles in the sample containers.

2.3.3.3 Data Collection

Prior to sample analysis, background scatter was evaluated to assess the optics alignment and the performance of the LISST instrument, as recommended by the manufacturer. The spectrum was measured on distilled water and was compared with the factory provided background scatter file. This comparison indicated that the instrument was functioning properly; the background file was subtracted during post-processing of the data to obtain true particle scatter.

To perform an analysis, approximately 100 ml of sample was placed in the mixing chamber and mixed as described in Section 2.3.3.2, above. An external mechanical switch was then used to activate the instrument. When the switch was set to 1, the instruments internal

Flash Card recorded a raw binary file (DAT) every time a sample was illuminated by a pulse. After particle volume distributions from several pulses were collected the mechanical switch was set back to 0, and the data collection was terminated. After data collection, the raw binary file from the LISST data logger was downloaded to a computer for further data processing. The LISST software was used to convert the raw data into particle size distribution (PSD) files which could be viewed on the screen and placed into space delimited ASCI files which contained all the processed volume data. The ASCI files were used to generate LISST volume distributions presented in this report.

2.3.3.4 Decontamination

After samples were analyzed for particle volumes, they were drained from the mixing chamber through tubing attached at the bottom of the chamber. A small brush was used to clean the optical windows of the LISST instrument and the whole chamber was rinsed thoroughly with distilled water. Occasionally, the brush was also used prior volume measurement to remove the small bubbles that formed on the optics. In general, samples from the same core were analyzed in two separate batches with samples from the dilution study processed before the samples from the settling study. Within each batch, samples were analyzed from the lowest concentration to highest (in the opposite order than they were collected). A distilled water field blank was prepared and analyzed every 20 samples to check for cross contamination by suspended solids particles.

3 DATA QUALITY EVALUATION

3.1 Introduction

This section focuses on evaluating the quality of the three data sets collected during the surrogate study: TSS, turbidity, and particle volume distributions. The purpose of this evaluation is to identify any deficiencies in data quality; the effect of these deficiencies on the usability of the data is discussed in Section 4. The primary indicator of data quality is the results of duplicate and field blank samples which were collected at a rate of 1 duplicate and 1 field blank per 20 environmental samples. The field blank values represent a measure of background contamination in the sample. The duplicate data are used to calculate the Relative RPD between the parent and the duplicate data sets. RPD values provide an indicator of the precision of the sample collection and analytical procedures. In addition, for the LISST data, the optical transmission coefficient will be also discussed. A summary of the results of the data quality evaluation are presented in Table 3-1.

3.1.1 TSS Data Quality

There is good agreement between the parent and the duplicate TSS samples collected during the settling column study (Figure 3-1, top panel). The plot below (Figure 3-1, bottom panel) shows the probability distributions of the RPD values. The average RPD between the parent and duplicate samples for which detectable TSS concentrations were reported is 14.2%. The range of RPDs for TSS analyses that is commonly accepted during data validation for environmental studies is between 0% and 20% and 15 of the 21 data pairs have RPDs within this range. No field blank samples were submitted for TSS analysis.

The agreement between parent and duplicate samples collected during the serial dilution testing was poor. Figure 3-2 presents a cross plot of the parent and duplicate data sets (top panel) and probability distributions of the RPDs between the sets (bottom panel). The top panel shows the regression line for the duplicate data and the bottom panel shows the range of RPD values for the data set. The average RPD for TSS data collected is 62.7% and eight of the nine data pairs have RPDs greater than 20%. The accuracy of the TSS measurements in the serial dilution study was affected by the random inclusion or exclusion of one or more large particles in the samples. The presence of large grained particles in many of the samples combined with the continuous mixing technique resulted in the intermittent inclusion of

large particles in the samples withdrawn for TSS analysis. Due to the sensitivity of the TSS analysis, the inclusion of even one large grained particle could have a significant effect on analytical results.

3.1.2 Turbidity Data Quality

The average RPD between parent and duplicate turbidity measurements for the settling column testing was very good at 4.8% (Figure 3-3.). The average RPD for the serial dilution testing was 12.3% (Figure 3-4). The field blank data for the settling column testing and the serial dilution testing are summarized in Figure 3-5. These data demonstrate that the decontamination procedures were effective; turbidity values in field blanks were consistently less than 1 NTU during both series of tests.

3.1.3 Particle Volume Data Quality

Results of duplicate particle volume analyses performed during the settling column study are presented in Figure 3-6. The average RPD between parent and duplicate particle volume measurements is 20.7% which is the highest RPD of the three datasets for the settling column tests. The probability plot in Figure 3-6 (bottom panel) suggests the higher average RPD can be attributed to two outliers. Figure 3-7 presents the results of the RPD analysis for the serial dilution testing; the average RPD between the parent and duplicate particle volume data is 24.7%. The average RPD appears to be biased high by two outliers in the data set.

Field blank particle volume distributions for the settling column testing and the serial dilution testing are shown in Figures 3-8a through 3-8f. The volume of particles detected in field blanks is presented in Figure 3-9. The LISST field blank particle volume was <3 uL/L for more than 80% of the samples; the highest particle volume measured in a field blank was approximately 7.6 uL/L. These levels would not have a significant impact on the data if the particle volumes were homogenously distributed among all the particle size classes. However, the data suggest that the measurable particle volumes in the field blanks occurred primarily in the last four bins (Bins 29 through 32) of the particle distribution spectra collected by the LISST instrument. This condition appears in a number of field blanks analyzed in the first part of the study; however, this trend is minimized in Cores 7, 8, and 9 when the use of magnetic stirrer was discontinued in the field blanks. Bins 29 through 32

contain the volumes of particles with diameters in the range from 281.2 to 501.8 um. Based on visual observations and in consideration of the decontamination procedures followed in the study, it is unlikely that samples were contaminated with particles of this size. Observations made during the testing suggest that the large particles detected in the field blanks may have actually been bubbles introduced into the sample by the stirrer.

An additional indicator of data quality for the particle volume analysis is optical transmission. The optical transmission of the LISST is defined as the percentage of light entering the water from the transmit window that reaches the receive window. This parameter is reported for each sample measurement and can be found in the 41st column of the ASC file. Optical transmission is a measure of data quality because it can provide us with information regarding multiple scatter on particles present in an analyzed sample. Multiple scatter occurs in samples with high particle concentrations when light scattered by one particle gets re-scattered by another. When multiple scatter occurs the particle volume spectrum becomes less representative of the particles present in the sample.

According to the manufacturer, multiple scatter occurs when optical transmission is below 30%. The volume distribution error is small but noticeable when optical transmission is between 30% and 10%; below 10% the error is significant. Typically, for samples with optical transmission <10%, no volume distributions are reported and samples must be diluted and reanalyzed. The amount of dilution necessary was typically based on turbidity results which provided a good indicator of particle volume in each sample. At very low particle concentrations (when the optical transmissions are 98% or higher) the reported volume measurements also have limitations because the low amount of scattered light makes it difficult to mathematically estimate particle volumes correctly. All field blank data collected in this study had transmission coefficients >98%; however, the accuracy of these data appear to be sufficient to evaluate data quality.

With the exception of Cores 1 and 2, the optical transmissions measured in the surrogate study samples were over 30%. Prior to the testing performed on Core 3, the significance of the optical transmission coefficient was not fully understood. Therefore, samples from Cores 1 and 2 with optical transmissions <30% were re-analyzed. Figures 3-10 and 3-11 present the differences in particle volume distributions between samples with optical transmission

<30% and the same re-analyzed samples with higher optical transmissions achieved by further dilutions for Cores 1 and 2, respectively. The plots depict sample volume data for six separate particle size fractions (in percent of total sample volume) for samples collected from Port 1 of the settling column. It appears that the size of particles increased over time, primarily shifting from clay-sized particles to silt-sized particles. This indicates that samples should be analyzed for particle volumes as soon as possible after collection; the apparent shift in particle size may have been a result of flocculation in the sample containers over time (Sections 2.1.3 and 2.3.3.2).

4 ANALYTICAL SENSITIVITY AND DATA NORMALIZATION

4.1 Introduction

The three data sets collected during this study use different techniques to estimate the amount of suspended solids:

- TSS reflects the mass of all particles (dry) >0.45 um in size.
- Turbidity is an expression of the optical property that causes light to be scattered and absorbed by particles suspended in the sample rather than transmitted in straight lines.
- Particle volume data set consists of volumes of particles in 32 size classes. This primary measurement can be converted to mass if particle densities in all size classes are known.

4.2 Method Sensitivities

4.2.1 TSS

TSS is directly proportional to the number, size, and specific gravity of particles contained in a water sample; it includes the organic fraction (algae, detritus) and inorganic fraction (clay, silt, sand) retained after passing the sample through a 0.45µm filter. As discussed in Section 3, TSS measurements are sensitive to the presence of large particles in a sample. The accuracy of the TSS measurements in this study was affected by the random inclusion or exclusion of one or more large particles in the samples. It was not possible to maintain a uniform distribution of the coarser sand particles in the samples during the testing.

4.2.2 Turbidity

4.2.2.1 Particle-Light Interactions

Turbidity is affected by particle-light interactions. Turbidity has been found to be directly proportional to the number and the surface area of particles present in a suspension, however, it has been found to be inversely proportional to the size of the particles present in the suspension (Connor 1992; Gibbs 1992). The turbidity measurements performed using and OBS-3 turbidity probe are sensitive to particle diameter (D):

$$Turbidity \sim 8.3*(D)^{-0.6} \quad (4\text{-}1)$$

The OBS-3 works on principles similar to those of the instrument used in this study, therefore it is reasonable to expect that the relationship between turbidity and particle size is similar for the two instruments. The equation suggests that turbidity measurements will be much more sensitive to clay or colloidal particles than to larger particles such as silt or sand. The sensitivity of turbidity measurements to particle diameter may affect correlations between turbidity and TSS.

Another factor that affects the turbidity measurement is the relationship between the particle diameter and the wave length (λ) of the incident light. The light scattered from particles with a diameter of approximately 1 micron is typically concentrated in the forward direction with sharp maxima and minima scatter showing at wider angles. This pattern starts to change as particles become smaller. The scatter pattern on particles with $D \sim 1/4\lambda$ becomes somewhat peanut shaped with some light scattered under wider angles while the scatter on very small particles such as colloids with $D \sim 1/10\lambda$ is much more spatially uniform. In other words, the 90° scatter on particles much smaller than the wavelength of incident light yields higher turbidities than scatter on larger particles. This behavior can be observed in filtered samples if colloid concentrations are sufficiently high.

Turbidity is also sensitive to sample-specific parameters such as particle color, shape, and relative refractive index (D&A Instrument Company 2006). Particle color affects the ability of particles to reflect or absorb light. Lighter colored particles such as sand tend to reflect light, darker particles tend to absorb it. Smooth, spherical-shaped particles will provide more predictable optical response than irregularly-shaped particles. More scatter will also occur as the difference between the refractive indexes of the particle and the sample fluid increases.

4.2.2.2 Turbidimeter Design

In turbidimeters whose incident light consists of a full spectrum of wavelengths, the scatter pattern is rather complex because each wavelength tends to scatter on each particle size slightly differently. Therefore, in this study a turbidimeter with narrow range of incident light wavelengths (870 ± 30nm) was selected to generate a more consistent scatter pattern that would be easier to interpret. Other optical design parameters that affect turbidity measurements are the number and position of the scatter detectors, and color sensitivity of

the photocell. Because turbidity measurements are sensitive to both turbidimeter design and particle-light interactions, turbidity measurements performed on the same sample by two individual instruments using a different optical design can not be directly compared.

4.2.2.3 Testing Conditions

In addition to the sensitivities affecting the turbidity measurements described above, the turbidity measurements in this study were affected by the conditions experienced as a result of the design of the study. The high starting concentrations (10,000 mg/L) used in the tests combined with the presence of large grained particles in many of the samples resulted in rapid settling of solids. Despite aggressive mixing techniques, solids were observed settling in the sample chamber of the turbidimeter before a stable turbidity measurement could be obtained. This condition was observed to be most prevalent in the first 10 to 20 minutes of each settling column test, and the first 5 to 10 dilutions of the serial dilution tests.

4.2.3 Particle Volume

The LISST instrument measures volume distributions in 32 log-spaced particle size classes of particles with diameters between 2.5 to 500 microns. The instrument uses the Mia scatter theory to analyze multi-angle scattering. It reports particle content as a volume of particles per liter; the particles are assumed to be spherical in shape. The mass of the particles can be estimated by assigning an assumed density to the particles. Particle volume measurements are, similarly to turbidity, the result of particle-light interactions; however, they are not dependent on particle color as well as particle size and concentration as long as the instrument operates in appropriate concentration and particle diameter range specified by the manufacturer.

4.2.3.1 Particle Shape

Available laser diffraction technologies deliver accurate measurements of volume distributions only for perfectly spherical particles. Non-spherical particles, such as suspended sediment particles, reduce the accuracy of diffraction measurements by widening the diffraction patterns on the detector and therefore making it more difficult to estimate volume distributions accurately. Empirical calibration correction procedures are available; however, they are not feasible for use in an environment with a highly variable particle size,

which is the focus of this study. The magnitude of this sensitivity has not been quantified for this study.

4.2.3.2 Particle Size

The LISST -100X, Type C instrument used in this study is capable of measuring particle sizes ranging from clay to medium sand. Particles outside this range were also reported at either the large or small particle end; however, the accuracy of these measurements is limited. This may have had a minor effect on the overall particle volume measurements, especially in samples with high concentrations of small clay particles (<2.5 um) and colloids, or in samples with greater than medium sand particles (>500 um).

4.2.3.3 Particle Concentration

The volume measurements from the LISST instrument are based on the assumption that light is scattered only once before it reaches the detector. At very high particle concentrations, multiple-scattering occurs and the detectors will detect an unrealistic volume spectrum, depending on the magnitude of the optical transmission coefficient (Section 3.1.3). Similarly, at very low particle concentrations (when the optical transmission is 98% or higher) the low amount of scattered of light makes it mathematically difficult to estimate the particle volumes correctly. The sensitivity of the optical transmission coefficient to particle size is due to particle-light interactions which change with particle size. Because the same volume of small particles has a much greater cross-sectional area than same volume of larger particles, multiple-scatter occurs at much lower concentrations for small particles than it does for larger particles.

According to Sequoia Scientific, Inc., the LISST 110X, Type C instrument used for this study was equipped with a five centimeter optical path. This optical path will be reduced to the 30% transmission level at particle concentrations in the range of several hundred mg/L of fine silt; while for larger particles it will take several thousands of mg/L to reduce the transmission to this level. This sensitivity was addressed by diluting samples prior to analysis (Section 2.3.3.2).

4.2.3.4 Persistence of Large Particles over Time

The LISST data indicates that sand-sized particles were present throughout the duration of the settling test (Figures 4-1a through 4-1i) in several cores. However, sand-sized particles are expected to settle out in the settling column within the first few minutes of a test. The potential causes of the persistence of large particles in were: 1) low optical transmission coefficient; 2) interference by bubbles generated by the stirrer rotation; or 3) the flocculation of small particles either in the column prior sampling or in the sample container prior analysis resulting in large particles with very low densities.

The volumes of large particles reported in samples with optical transmissions <10% may have been incorrect because the multiple scatter spectra does not accurately represent the existing particle distributions. However, in the whole study there were only six samples with transition coefficient <10% that were collected after 30 minutes of settling; these samples were considered unreliable and therefore were excluded from all analyses.

The occurrence of changes in particle size over time was identified when samples from Core 1 and Core 2 were re-analyzed due to low transmission coefficients in the original analyses. The comparison of the original and reanalyzed volume spectra revealed changes in the proportion of the silt and clay fractions – over time, the clay fraction decreased while larger particle fractions increased. This condition appears to be the result of flocculation that occurred in the sample containers over time. To evaluate the magnitude of the effects of flocculation, a comparison between data from the first 32, 28, and 21 bins was performed using data collected after the first 20 minutes of the settling column tests. Figures 4-2a through 4-2c suggest that the correlation between TSS and particle volume data improves when the larger particles are eliminated from the overall particle volume. This result is also likely influenced with the elimination of large particles measured in the last four bins of the volume spectra, as identified in the field blank analysis (assumed to be the result of mixer-induced bubbles; Section 3.1.3).

4.3 DATA TO BE USED FOR REGRESSION ANALYSIS

The sensitivities of the analytical methods due to the nature of the TSS and the measurement conditions are summarized in Table 4-1. These sensitivities complicate developing

correlations between TSS, turbidity, and/or particle volume, as each analytical method exhibits its own manner of sensitivity. Additionally, some of the data are of questionable quality for reasons discussed in Section 3. Therefore, the data have been sorted in a manner designed to consider data quality and to reduce the effects of the method sensitivities on the evaluation of the relationship between TSS and the potential surrogate parameters to the extent possible. The approach to culling the datasets is summarized in Table 4-2. Duplicate samples were collected at a rate of 5% during the study. The results of the duplicate analyses have been included in the development of the TSS surrogate relationships.

4.3.1 Settling Column Test Data

The most significant sources of analytical and method variability in the settling column test data are the high TSS concentration and presence of large particles during the early portions of the tests. Figures 4-3a through 4-3i illustrate the high initial TSS concentrations followed by a rapid decrease. These figures also demonstrate that after the first 20 minutes of each test, there is little variability between sampling ports in the column. Figure 4-4 shows cross plots of TSS and turbidity data collected during the first 20 minutes of the settling column test for each core. The regression equations and the R^2 coefficients noted at the bottom of each panel suggest that erratic settling processes lead to significant variability in the relationship between TSS and turbidity within and among cores.

An effective way to normalize the data between the three analytical methods is to compare samples that are as representative of actual field conditions as possible. Conditions in the settling column are not fully representative of conditions in the river due to the inability to simulate in-river dynamics. However, resuspended coarse grained particles are expected to settle rapidly in the river (as was observed during the settling column test) and are not expected to be in the water column by the time a sediment plume reaches the near-field monitoring stations. Therefore, to lessen the effect of the variability in particle sizes observed during the initial stages of the settling column tests, and to provide more comparable samples, data from the first 20 minutes was excluded during the development of correlations between TSS and the surrogates. Additionally, as there is little variability in the data between sample ports after 20 minutes, the data from all the ports has been used without regard to their position in the column.

The 24-hour sample data for all three analytical methods was also excluded from use for correlation development based on the presence of large particles (as measured by the LISST). As discussed in Section 4.2.3.4, large inorganic particles with normal densities should not have remained in suspension until the end of the tests. These large particles are likely an artifact of the experiment which facilitated flocculation as the water sat stagnant between the 6-hour and 24-hour sampling times. The LISST data reported for the last four bins (Bins 29 through 32) were also excluded from use due to irregularities identified in the field blank analyses (Section 3.1.3).

4.3.2 Serial Dilution Test Data

Due to the high degree of variability observed in the TSS data for the serial dilution testing (Section 3.1.1); the data are not considered to be useable. Therefore, correlations between TSS and the surrogates could not be developed using these data.

5 TSS SURROGATE REGRESSION ANALYSIS

5.1 Objective of the Analysis

The primary objective of the TSS surrogate study is to establish a suitable relationship(s) between TSS and a surrogate parameter to estimate TSS in the Hudson River and monitor compliance with the EPS during Phase 1 dredging. The surrogate parameters that have been evaluated (turbidity and particle volume) can be measured continuously and provide data in real-time.

As discussed in Section 2, the laboratory testing was conducted using nine sediment cores that encompass three sediment types. Variability among the cores in the relationship between the surrogate parameters and TSS is expected due to differences in sediment type. In the development of the TSS surrogate relationship, a primary objective is to minimize the number of regressions that may be needed for use in the field. Having more than one relationship adds complexity to the monitoring program because a method to select which regression is appropriate for use (based on field conditions) must be developed and implemented. To achieve the objective of minimizing the number of relationships, the following approach was adopted:

- Pool all data to examine the behavior of a single relationship
- Pool data based on similarity of sediment type.

5.2 Identification of a Regression Model

As discussed in Section 4, the data have been sorted in a manner designed to consider data quality and reduce the effects of the method sensitivities on the evaluation of the relationship between TSS and the potential surrogate parameters. The approach to normalizing the datasets is summarized in Table 4-2. Most notably, the serial dilution test data and the data collected during the first 20 minutes and at the end of the settling column tests have not been used in the development of the regression models.

5.2.1 Preliminary Analysis of Turbidity Data

Figure 5-1 presents a scatter plot of TSS versus turbidity for the combined data from all nine cores. The figure demonstrates a clear positive correlation (correlation coefficient of 0.967)

between the TSS and turbidity data. A large range of TSS and turbidity values are available for the development of a surrogate relationship. This range encompasses the concentrations that will likely be encountered in both near- (higher concentrations) and far-field (lower concentrations) stations. It can also be noted that the TSS and turbidity for Core 2 data is substantially higher when compared to the rest of the data. When Core 2 data is removed the correlation coefficient between TSS and turbidity drops only slightly suggesting that despite the somewhat different relationship, core 2 data contributes to explaining the correlation between TSS and turbidity.

Figure 5-2 presents core-wise scatter plots along with the core specific correlation coefficient for TSS versus turbidity. The relationship between TSS and turbidity is linear for most cores with some curvilinear tendency at high turbidity and TSS levels. Core 2 has substantially higher TSS and turbidity levels, as pointed out earlier. Cores 5 and 8 have substantially lower TSS concentrations and turbidities. The wide scatter of points exhibited by Cores 5 and 7 suggests substantial variability in the measurements.

The scatter plots suggest that a linear model may be adequate. Linear models are common (e.g., Suk et al. 1998; Grayson et al. 1995; Buchanan and Schoellhamer 1999), although power law models (i.e., linear model of log transformed data) are also used to account for non-linear behavior at high TSS (e.g., Packman et al. 1999; Christensen et al. 2002), as are other models (e.g., Lewis 1996).

The appropriateness of linear and power models was evaluated by examining the residuals. The estimation of model parameters is discussed in Section 5.3.

5.2.2 Preliminary Analysis of Particle Volume Data

Figure 5-3 presents a scatter plot of TSS vs. particle volumes for the combined data set. The LISST data in general exhibit a substantially larger scatter than the turbidity data. This is evident from the somewhat lower correlation coefficient (of 0.918) compared to the TSS-turbidity data set (see Figure 5-1). It can be noted that at higher measured particle volumes, the TSS appears to flatten out. If the data from Core 2 is excluded, then the scatter of points in the TSS vs. particle volumes plot shows a slight improvement in the correlation coefficient and suggests that a linear relationship will be appropriate.

Figure 5-4 presents core-wise scatter plots of TSS vs. particle volume. In comparison to the TSS-turbidity plots in Figure 5-2, the correlations of TSS with LISST volume for several cores are not as high as the correlations between TSS and turbidity. As in the case of the TSS-turbidity plots, Cores 5 and 7 exhibit considerable noise. In addition, the TSS-LISST particle volume data for Core 3 is particularly variable. Despite these differences, a linear relationship still appears to be appropriate for the majority of the cores.

5.3 Surrogate Relationship based on Turbidity

The evaluation of all regression models constructed herein will be based on the following: (a) The ability of the model to describe the data as indicated by statistical measures (R^2 and f-test) and visual inspection of the goodness of fit. R^2 indicates the ability of the model to explain the variability in the data, with a value of 1 signifying a perfect fit. The f-test evaluates the statistical significance of the proposed regression model as opposed to a model which uses just the mean of the data to describe the relationship between TSS and its surrogate. This is achieved by comparing the f-statistic (calculated based on the errors in the predictions of the two models) to a standardized value (which is a function of the desired level of confidence, number of data points available and the number of parameters estimated in the regression model). If the f-statistic is substantially larger than the standardized value, then it provides strong evidence that the regression model is successful in describing the relationship;

(b) An analysis of the regression residuals to confirm whether the assumptions used in the construction of the regression model have been met. Residuals are defined as the difference between the observed TSS and the model predicted value (i.e. the error in estimating the observations). Regression models are constructed based on the assumptions that the errors are normally distributed with a zero mean and a constant variance. A plot of residuals versus predictor (i.e. turbidity or LISST volumes) should show an even scatter of points on either side of zero. Any systematic deviations or patterns indicate a bias in the model predictions (non-zero mean), and a lack of constancy in error variance (heteroscedasticity). A normal probability of the residuals should be roughly linear. Substantial deviations from normality of the residuals can lead to inaccurate estimations of confidence and prediction intervals.

5.3.1 Models for the Combined Data from All Cores

As a first step in the analysis of the TSS-turbidity data, all data were pooled and a single regression model was developed. Pooling data implicitly assumes that the data for pooled cores can be described by a common relationship, the error variance is constant, and the slopes of the relationships pooled are similar.

5.3.1.1 Linear Model

A simple linear model was constructed to study the linear association between TSS and turbidity over all the cores. From Figure 5-1 it is evident that the TSS-turbidity data covers a wide range of concentrations. It is likely that the some of the high concentration data may have a higher influence on the estimated parameters. To avoid over-emphasis of high concentration data, a "damped-leveraged" weighted least squares regression (QEA 2004) was carried out.

Figure 5-5 shows the model fit and regression diagnostics. Table 5-1 summarizes the regression parameters. It can be noted from the scatter of residuals versus turbidity that the residuals exhibit considerable heteroscedasticity (non-constant variance) despite the weighting. Further, the residuals also show moderate departure from normality. The diagnostics suggest that the assumptions for regression are violated. The model fit plot indicates that a linear model reasonably captures the relationship however bands of data specific to each core appear to have a different slope than the pooled model (see Figure 5-5).

Table 5-1
Estimated Regression Parameters For Linear and Log-Log Models Based On Data from All Cores Pooled Together*

Model	Intercept	Slope	SE of Intercept	SE of Slope	R^2	F-Stat	No. of Samples	% of Samples	
								RDP<20	RPD<30
Linear	15.107	0.853	8.104	0.024	0.87	1270	195	49.74	67.69
Log-log	-0.026	0.983	0.038	0.016	0.95	3620	195	50.26	75.38

* Duplicates were retained. Non-detects were excluded. Data measured between 30 to 360 minutes. Parameters for linear model were estimated using damped-leveraged regression.

5.3.1.2 Logarithmic Model

It is likely that the large range in the magnitude of the data caused the heteroscedastic behavior observed for the linear model. The Box-Cox family of power transformations was studied to identify a suitable re-expression that would possibly eliminate the heteroscedasticity. A logarithmic transformation of both the TSS and turbidity was determined to be the optimal choice. Least squares regression was performed on the transformed TSS and turbidity data. The parameters of the log-log model are summarized in Table 5-1.

Figure 5-6 shows the model fit and regression diagnostics for the log-log model. The error variance has stabilized appreciably following the transformation. The violation in normality is minimal. Therefore, the log-log model for the pooled data appears to be meeting the assumptions for regression.

The data are plotted using the corresponding core number in the model fit plot in Figure 5-6 (bottom panel). As in the case of the pooled linear model, the log-log model appears to be capturing the trend of entire pooled data set but some strong core-to-core differences are still evident. The data from each core plot as distinct bands above or below the model fit thereby indicating that the model may, at a local scale, under- or over- predict the data. Moreover, the model consistently under predicts TSS at turbidities less than 100 NTU.

5.3.2 Models Based on Silt to Clay Fraction

Examination of Figures 5-5 and 5-6 indicates that the core-to-core differences noted above are not ascribable to core primary sediment type (i.e., silt [Cores 1 through 3], fine sand [Cores 4 through 6], and medium sand [Cores 7 through 9]). Cores of the same type fall both above and below the predictions of the pooled models. Moreover, we found that differences in slope among cores within a primary sediment type were as large as differences between sediment types (based on linear regressions of individual cores, the results of which are not presented here). Regardless of the original composition of the sediment used in a test, all samples were primarily composed of silt and clay sized particles (sand and gravel particles generally are not present in the post-20 minute data used for the regressions) and the differences among cores are likely due to differences in the nature of these sized particles.

Previous studies have indicated that turbidity measurements are sensitive to the size distribution of particles (see discussion in Section 4.2.2.). To investigate whether the turbidity data were impacted by such sensitivity, an approach to assess the effects of grain size distribution of particles within samples on turbidity measurements was developed. Based on the particle sizes measured by the LISST instrument, the suspended sediments were sub-divided as clay, silt, fine, and medium sands. The samples beyond 20 minutes predominantly contain silt and clay because the large-grained sand particles settle out rapidly. A simple means to identify the grain size characteristics of samples is to calculate the ratio of silt to clay particles obtained from the LISST measurements. This ratio was used to pool the data selectively from multiple cores. This approach is sensitive to the inherent granular characteristics of the core and is thus capable of capturing the lateral and vertical variability in sedimentology.

The relationship between the turbidity to TSS and silt to clay ratios is presented in Figure 5-7 as a scatter plot. Figure 5-8 shows the average ratio of turbidity to TSS calculated in bins of silt to clay ratio. In general, the turbidity to TSS ratio is high at lower silt to clay ratios and decreases as the proportion of silt increases. Based on the behavior exhibited by the data in Figures 5-7 and 5-8 roughly three groups can be discerned: below a silt to clay ratio of 1.5 a sharp decline in the turbidity to TSS ratio is displayed; between silt to clay ratios of approximately 1.5 to 3.0 the rate of decline in the turbidity to TSS ratio is shallower; beyond silt to clay ratios of 3.0 the turbidity to TSS ratio appears to flatten out. As evident from Figure 5-7, silt to clay ratios greater than 4 are obtained predominantly for Core 5, which had very low TSS concentrations (typically below 20 mg/L).

Based on the characteristics observed in Figures 5-7 and 5-8, the silt to clay ratio was used to divide the TSS-turbidity data into three groups: those with a silt to clay ratio less than or equal to 1.5; those with a silt to clay ratio above 1.5 but less than or equal to 3.0; those with a silt to clay ratio above 3.

As in the case of the pooled models presented earlier, a linear model with parameters estimated using damped-leveraged weighted least squares regression and a log-log model were fitted for the data in each group. The earlier analysis of TSS-turbidity correlation suggests that at high TSS values the relationship with turbidity tends to become non-linear

(see Figures 5-1 and 5-2). Given that the highest resuspension performance standard for TSS is 700 mg/L, samples with TSS greater than 1000 mg/L were not used in this analysis.

Table 5-2
Linear Models for Data Classified Using Silt to Clay Ratio*

Silt to Clay Ratio	Intercept	Slope	SE of Intercept	p-Value for Intercept	SE of Slope	R^2	F-Stat	No. of Samples	% of Samples	
									RDP< 20	RPD <30
<1.5	4.00	0.70	12.48	0.75	0.02	0.96	1003	46	73.91	93.48
1.5-3.0	-0.28	0.92	9.50	0.98	0.03	0.91	859	87	64.37	86.21
>=3	-0.25	1.18	8.93	0.98	0.03	0.97	1193	41	58.54	73.17

* Data points with TSS > 1000 mg/L, TSS non-detects and LISST transmission less than 10% were not used. Data measured between 30 to 360 minutes.

Table 5-3
Log-Log Models for Data Classified Using Silt to Clay Ratio*

Silt to Clay Ratio	Intercept	Slope	SE of Intercept	p-Value for Intercept	SE of Slope	R^2	F-Stat	No. of Samples	% of Samples	
									RDP <20	RPD <30
<1.5	-0.26	1.04	0.08	0.00	0.03	0.96	1190	46	73.91	93.48
1.5-3.0	-0.19	1.06	0.07	0.00	0.03	0.94	1400	87	59.77	78.16
>=3	-0.04	1.04	0.06	0.46	0.03	0.97	1229	41	51.22	78.05

* Data points with TSS > 1000 mg/L, TSS non-detects and LISST transmission less than 10% were not used. Data measured between 30 to 360 minutes.

The parameters for the linear models are summarized in Table 5-2 and regression diagnostics and model fit plots are shown in Figure 5-9. The residuals appear to be non-constant and non-normal for the first group (silt to clay < 1.5); while they appear to be reasonably stable and somewhat non-normal for the other two groups. The slopes vary between the groups suggesting that the data in each group exhibit different TSS-turbidity relationships. The model fit plots for all three groups appear to be capturing the trend reasonably for the data in each group. The intercepts for all three groups are not statistically different from zero. While the first group exhibits the most prominent violations in regression assumptions, it also produces the highest percentage of samples with RPDs below 20% and 30%, respectively.

Logarithmic transformation of the TSS and turbidity data is successful in stabilizing the residuals and also in making their distribution in each group more normal (see Figure 5-10). The slopes (exponent in real space) do not differ much between the groups; however the intercepts (coefficient in real space) vary considerably between the groups (see Table 5-3). Note also that the exponent is close to one for all three groups, suggesting that a linear model is likely sufficient in capturing the trend (as the linear models proved in the previous paragraph). The transformation appears to be over-correcting in group three (silt to clay ratio > 3) as evident from the decreasing magnitude of the residuals with increasing turbidity values (compare bottom panel plots in Figures 5-9 and 5-10). As in the case of the linear model, the percentage of samples with low RPDs are higher for the first group.

5.4 Surrogate Relationship based on Particle Volume

As in all previous analyses, linear and log-log models were fitted to the TSS-LISST data. The estimates of regression parameters of the linear model for the TSS-particle volume data is shown in Table 5-4 and the regression diagnostics are shown in Figure 5-11. The particle volume data, like the turbidity data, exhibits a positive (though weaker) correlation with TSS. As pointed out earlier, the particle volume data is substantially noisier and plots well beyond the confidence bands of the model. The scatter of residuals indicates that the error variance is not constant and the normal probability plot shows a mild departure from normality.

Figure 5-12 shows the diagnostics for the log-log model. Here, the departure from normality is more severe and the error variance also appears to be more heteroscedastic (as evidenced by the slight curvilinear trend of the residuals). This suggests that a logarithmic transformation is not required for the LISST-volume data since the residuals for the linear model behaves better than the logarithmic model.

Table 5-4
Estimated Regression Parameters For Linear and Log-Log Models for TSS-LISST Data from All Cores Pooled Together*

Model	Intercept	Slope	SE of Intercept	SE of Slope	R2	F-Stat	No. of Samples	% of Samples	
								RDP<20	RPD<30
Linear	36.10	0.55	8.35	0.020	0.82	792	179	48.60	58.66
Log-log	-0.12	0.97	0.06	0.027	0.88	1340	179	36.87	54.75

*Data measured between 30 to 360 minutes. Data points with TSS>1000mg/L were excluded. Parameters for linear model were estimated using damped-leveraged regression.

The particle volume relationships to TSS are weaker than the turbidity relationships, and the models are less defensible. The percentage of samples with RPDs less than 20% or less than 30% is lower (for linear and log-log models) when compared to the all previously developed TSS-turbidity models. Based on these results it is concluded that the particle volume data alone are not sufficient as a surrogate for TSS measurement.

5.5 Performance on Baseline Monitoring Data

The performances of the top five pooled models presented earlier were evaluated using the TSS and turbidity data from the Hudson River baseline monitoring program (BMP; QEA and ESI 2004). As part of the BMP, TSS, and turbidity data have been collected along four transects across the upper Hudson River since June 2004. Data measured through the end of 2006 was used in the analysis below.

Turbidity is measured at mid-depth at multiple stations along each transect, while a single TSS composite sample is formed from depth integrated aliquots collected at these same stations for each transect. The turbidity data and the aliquot for the TSS composite are obtained concurrently. To facilitate comparing the data, the turbidity data was averaged at each transect and the average value was used in the comparisons presented here.

Based on the behavior of the residuals and the model fit statistics, the linear models for silt-to-clay ratios between 1.5 and 3, and above 3, and the log-log model for silt to clay ratios below 1.5 and between 1.5 and 3 were selected for evaluation. For comparison, the log-log model of all data was also evaluated.

Figure 5-13 compares the performance of these models on the BMP TSS-turbidity data. Table 5-5 compares the performance statistics for the five models. In these predictions, the intercept for the linear silt to clay ratio models were set to zero since they were not statistically different from zero (see Table 5-2).

Interestingly, the data seem to indicate two relationships between TSS and turbidity that are roughly consistent with the range of regression models. The linear silt to clay model with ratios above 3 exhibits a relatively steep slope that is verified by the majority of the BMP data. The linear silt-to-clay model with ratios in the range 1.5 to 3 and the pooled log-log model are in-between the upper and lower clouds while the log-log silt to clay models have a shallower slope than all other models. Since particle size information was not available for the BMP data, it was not possible to classify the data based on the silt-to-clay ratio to verify whether the bi-modal behavior of the data is explainable by particle size differences.

Table 5-5
Performance of Models on Hudson River Baseline Monitoring Program Data

Model	% Samples	
	RPD < 20%	RPD < 30%
Pooled log-log (all cores)	17.38	29.39
Silt-to-Clay Ratio = 1.5-3 (Linear)	17.03	29.03
Silt-to-Clay Ratio > 3 (Linear)	29.75	42.83
Silt-to-Clay Ratio < 1.5 (log-log)	8.42	10.22
Silt-to-Clay Ratio = 1.5-3 (log-log)	10.22	16.49

5.6 Additional Regression Analysis in Response to Agency Comments

In response to agency comments 44, and 245 through 271 (USEPA, 2008), additional regression analyses were performed to evaluate the recommendation of using a linear model constructed with lab data with silt-to-clay ratio greater than 3. The following paragraphs present the details of these analyses.

5.6.1 Pooled Models Developed with Lab Data Only

5.6.1.1 Models with All Lab Data with TSS below 1000 mg/L

In comments 249 and 268 (USEPA, 2008), the agency has suggested removing data points with TSS higher than 1000 mg/L. In response to this request, the pooled linear and log-log regressions presented in Section 5.3.1 were repeated using only TSS data below 1000 mg/L. The model fits for the linear and the log-log models are shown in Figures 5-14 and 5-15 respectively. The parameters for the models are summarized in Table 5-6.

The pooled linear model in Figure 5-14 with the reduced data set (TSS < 1000 mg/L) is not appreciably different from the model presented in Figure 5-1 with the entire data set. The new model shows a slightly higher slope albeit with a lower intercept. The RPD's in Table 5-6 represent a marginal improvement over the model fitted with the entire data set (see Table 5-1) although the R^2 suggests that the older model was slightly better at explaining the variability in the data. The residual patterns (top panel) and the deviations from normality (middle panel) in Figure 5-14 are similar to Figure 5-1 with the exception of the high TSS data which have now been removed. As in the case of the old model, the new model over predicts TSS values at high turbidities (> 700 NTU) represented in core 2. This can be observed in the cluster of negative residuals at higher turbidity in the top panel of Figure 5-14.

Removing data with TSS > 1000 mg/L produces a negligible difference in the log-log model fit as evidence by the slopes and the intercepts in Tables 5-6 and 5-1. The R^2 and RPD values in these tables, and the model fits and residuals patterns in Figures 5-15 and 5-2 confirm this conclusion.

Table 5-6
Model Parameters Estimated with Lab TSS Data < 1000 mg/L

Model	Intercept	Slope	SE of Intercept	SE of Slope	R^2	F-Stat	No. of Samples	% of Samples	
								RDP<20	RPD<30
Linear	7.203	0.890	8.392	0.029	0.833	919	186	48.92	70.97
Log-log	-0.023	0.981	0.041	0.018	0.942	3001	186	47.85	74.19

5.6.1.2 Models with Lab Data Set Split into Two Groups

In comments 44 and 252 (USEPA, 2008) the agency has suggested developing two separate regressions, one using data with TSS below 100 mg/L and another for data above 100 mg/L but less than 1000 mg/L. Two approaches, one using lab data alone and another using data from the baseline monitoring program (BMP) in addition to lab data were adopted as discussed below. For each approach linear and log-log models were developed.

The linear models fitted for data with TSS less than100 mg/L and between 100 and 1000 mg/L are shown in Figures 5-16 and 5-17. Both models provide a reasonable fit to the data. The distinctly different slopes between the models (see Table 5-7) provide some justification for analyzing the data in two groups. Figure 5-16 suggests that the residuals of the TSS < 100 mg/L model are evenly scattered around the zero line suggesting no bias (see top panel) and are nearly linear on the normal probability plot (middle panel) suggesting that the assumptions of regressions are not violated. The residuals of the model with 100<TSS<1000 mg/L (see Figure 5-17) shows a similar pattern compared to the pooled linear model in Figure 5-14: an even scattering of residuals above and below 0 for turbidities less than about 600 NTU; and a cloud of points below 0 at higher turbidities. The tails of the residuals for this model shows some deviations from normality.

The log-log model provides a somewhat better fit for the TSS < 100 mg/L data compared to the linear model (see Figure 5-18). However, the residuals suggest a greater departure from normality (middle panel of Figure 5-18). The log-log model for TSS data between 100 to 1000 mg/L is nearly identical to the linear model (Figure 5-19). This near linearity of the log-log fit is evident from its slope which is very close to 1.0 (exponent in real space – see Table 5-7). The residuals of this model do not show any appreciable departure from normality (Figure 5-19, middle panel) and are scattered nearly uniformly on either side of the zero line with the exception of the high turbidity values greater than bout 700 NTU (Figure 5-19, top panel).

Table 5-7
Parameters Estimated for Two Regression Models with Lab Data

Model	TSS Data Filter (mg/L)	Intercept	Slope	SE of Intercept	SE of Slope	R^2	F-Stat	No. of Samples	% of Samples	
									RDP <20	RPD <30
Linear	< 100	12.516	0.535	2.384	0.034	0.782	208	60	52.69	71.51
	100 to 1000	49.226	0.794	16.221	0.043	0.751	375	126		
Log-log	< 100	0.242	0.791	0.075	0.044	0.845	316	60	58.60	76.88
	100 to 1000	0.146	0.923	0.085	0.034	0.856	738	126		

5.6.2 Pooled Models Developed with Lab Data and BMP Data Through 2007

In Comment 252 (USEPA, 2008), the agency has suggested the use of field data to update the regression models. With the availability of BMP data through 2008, refinement to the surrogate model is now potentially feasible. Previously the 2006 BMP data were used for validation of the regression models recommended in the draft report. If all BMP data were to be used to refine the model, then there is no potential for validation should this model be the final choice. To overcome this, BMP data collected through 2007 were used in developing candidate surrogate relationships for comparison with those developed in Section 5.6.1. As before, two approaches were adopted: a single model approach with TSS below 1000 mg/L; and a two model approach with the pooled (lab and BMP) data set split into TSS<100 mg/L and 100<TSS <1000 mg/L groups. The details are presented below.

5.6.2.1 Model with TSS below 1000 mg/L

The results of the linear regression of the pooled TSS/turbidity data set are presented in Figure 5-20. It can be noted that much of the BMP data have been measured with a TSS value below 100 mg/L with a few data points interspersed with the lab data above this value. There is a heavy concentration of points very close to the origin. The BMP data seems to suggest a steeper relationship between TSS and turbidity than what the lab data suggests. The regression model in the bottom panel of Figure 5-20 tends to under-predict the field data and also most of the lab data with a tendency to over-predict TSS for turbidity above 700 (predominantly core 2 data). This trend was observed previously in all the pooled linear models that were evaluated. The normal probability plot shows a clear departure from normality suggesting a violation of regression assumptions. The scatter pattern of residuals

(top panel) is similar to the linear models presented earlier. The model parameters are shown in Table 5-8. While the R^2 in Table 5-8 are still fairly high, the RPD's are substantially lower. This is partly because of the higher number of samples, and partly due to the fact when the magnitude of the TSS is small (predicted and observed) relative deviations appear amplified when expressed as a percentage.

Table 5-8

Model Parameters Estimated with Lab and BMP TSS Data < 1000 mg/L

Model	Intercept	Slope	SE of Intercept	SE of Slope	R^2	F-Stat	No. of Samples	% of Samples	
								RDP<20	RPD<30
Linear	1.505	0.923	0.719	0.010	0.886	7368	954	33.75	48.11
Log-log	0.264	0.815	0.011	0.009	0.895	8073	954	31.45	46.54

Figure 5-21 shows that a logarithmic model is not appropriate for the combined data set. The logarithmic transformation improves the normality of the residuals (middle panel) but produces a residual scatter (top panel) that is clearly indicative of non-constant error variance. The model parameters in Table 5-8 suggest a nearly linear relationship between (slope close to 1) between TSS and turbidity.

5.6.2.2 Models with Pooled Data Set Split into Two Groups

The linear models for TSS less than 100 mg/L and TSS between 100 and 1000 mg/L data are shown in Figures 5-22 and 5-23 respectively. For TSS below 100 mg/L, the data is dominated by BMP, which shows a distinctly different (steeper) relationship compared to the lab data. The regression model attempts to balance both and provides a fit that tends to predominantly under-predict TSS for the BMP data and over predict TSS for turbidities greater than 50 NTU. The residuals show substantial departure from normality. For TSS greater than 100 mg/L, lab data dominates the combined data set. The linear fit (Figure 5-23) appears to be quite appropriate for this range. Deviations from normality are minimal. The parameters for the two models are shown in Table 5-9. Unlike the lab data only model (see Table 5-7) the slopes of the two models for the combined data set do not differ substantially. In particular, it is interesting to note that the slope for the TSS less than 100 mg/L range is substantially higher for the combined data set model compared to the lab data model. This suggests that

this is likely to provide a more conservative estimate of TSS at lower turbidity. However, the clear violations in the regression assumptions (Figure 5-22) preclude the use of this model.

Table 5-9
Parameters Estimated for Two Regression Models with Lab and BMP Data Through 2007

Model	TSS Data Filter (mg/L)	Intercept	Slope	SE of Intercept	SE of Slope	R2	F-Stat	No. of Samples	% of Samples	
									RDP <20	RPD <30
Linear	< 100	1.322	0.846	0.164	0.015	0.764	2596	806	33.54	49.06
	100 to 1000	58.354	0.782	13.440	0.039	0.736	407	148		
Log-log	< 100	0.292	0.671	0.011	0.014	0.750	2408	806	33.65	48.32
	100 to 1000	0.649	0.730	0.081	0.033	0.770	489	148		

The log-log model fits for the two groups of data are shown in Figures 5-24 and 5-25. For the less than 100 mg/L range, the log-log model tends to under predict nearly all the data. This is likely influenced by the few outliers present in BMP data set (very low TSS at turbidities of approximately 120 and 160 NTU's respectively – see Figure 5-24 bottom panel). While the residuals do not show any substantial deviations from normality, the scatter plot in the top panel of Figure 5-24 suggests that the error variance is not constant. For the 100 to 1000 mg/L TSS range, the slope (exponent in real space) differs substantially for the combined data set when compared to the model for the lab data alone (compare log-log models in Tables 5-7 and 5-9). This is evident in the fairly non-linear fit in Figure 5-25. With the exception of one outlier, the residuals are fairly normal and do not display significant deviations from normality.

5.6.2.3 Discussion on Models Derived from Pooling Lab and BMP Data

It is clear from the results in Section 5.6.2 that inclusion of BMP data did not produce an improvement to the models that were obtained with the lab data alone. In most cases, the cluster of BMP data close to the zero degraded the fit, and the residuals clearly displayed violations in regression assumptions. Logarithmic transformations did not produce appreciable improvements both in terms of the quality of the fit and the stabilization of the residuals. Given these limitations, and the lack of substantive improvement in predictions the models evaluated in Section 5.6.2 are not recommended for use during Phase 1 dredging.

These models were not considered in the validation and false positive analysis to be presented in the subsequent sections.

5.6.3 Validation with Baseline Monitoring Program data through 2008

The performance of the candidate models from Section 5.6.1 (i.e. those derived with lab data only) on the BMP data (through 2008) was evaluated against the recommendation in the December 2006 version of this report which is the linear model derived from the lab data with silt to clay ratio greater than 3 (see Table 5-2 and discussion in Section 5.3.2). For the two model approach in Section 5.6.1.2, turbidity breaks of 113.73 NTU and 130.49 NTU were used for the linear and log-log models to classify the BMP data. The break values for each (i.e. linear and log-log) group of models were determined by back calculating the turbidities by substituting a TSS value of 100 mg/L in the two model equations (i.e. TSS<100 mg/L and 100 < TSS < 1000 mg/L) and then calculating the average value.

Figure 5-26 shows the performance of the model in predicting the BMP data. There is substantial scatter in the BMP data, but the density of the points slightly above an imaginary 1:1 line suggests a clear linear relationship. None of the new candidate models (single or two models, linear or log-linear) appear to capture this dominant linear trend accurately. The best description of this trend is obtained using the linear model derived using data with silt-to-clay ratio >3. Moreover, this model is also the most conservative among all candidate models because it predicts the largest TSS increase for a given increase in turbidity.

The RPD's in Table 5-10 confirm the superior performance of the linear model derived using the data with silt-to-clay ratio >3. Even though the fit of the log-log pooled single and split data models are relatively poor, their RPDs are comparable to the silt to clay ratio based model. This can be explained on the basis of the high density of BMP data at TSS < 10 mg/L where the log-log models provide a better fit. The new linear single and split data set models tend to predominantly over estimate TSS at turbidities less than about 20 NTU. This causes a large difference in the RPD calculations. Thus, relative to the log-log models, even though visually the newer linear models fit the data better the RPDs calculated in Table 5-10 are lower. Thus, in this case the RPD's are not an accurate metric for evaluating model performance.

Data Set	Model	% of Samples	
		RDP<20	RPD<30
Silt to clay ratio > 3	Linear	29.01	41.19
TSS < 1000 mg/L	Linear	6.41	9.86
	Log-log	18.51	30.77
2 Models: one for TSS < 100 mg/L and another for 100<=TSS <1000 mg/L	Linear	4.01	6.33
	Log-log	30.37	44.31

The detailed analysis performed herein subsequent to the evaluations presented in the December 2006 version of this report has shown that the linear model derived using laboratory data with silt-to-clay ratio greater than three remains a robust option. The linear models based on split data sets (TSS<100 mg/L and 100<TSS<1000 mg/L) holds some promise because it also provides conservative estimates of TSS similar to the older recommendation, in addition to providing reasonable fits to the laboratory data.

6 SUMMARY, CONCLUSIONS AND RECOMMENDATIONS

6.1 Summary

A detailed analysis of the turbidity and particle volume data was performed to identify suitable TSS surrogate relationships for use during the RAMP. Analysis of the TSS-turbidity and TSS-particle volume data were carried out by pooling the data from multiple cores. The following approaches were considered for developing the surrogate relationships:

- Using the data from all the cores in a common pool (TSS-turbidity and TSS-particle volume data).
- Using silt to clay ratio to classify data based on sediment type (for TSS-turbidity data only).
- Combining baseline monitoring program data with the laboratory data (TSS-turbidity data only).

6.1.1 Common Pool Approach

In this approach, data from all cores were pooled and analyzed. Linear and log-log models were fitted for the common pool of data. While both models captured the trend of the TSS-turbidity relationship, the linear model violated several assumptions for regression. The log-log model was successful in stabilizing the error variance. The model exhibited organized deviations from the data, tending to consistently over-predict or under-predict TSS data for individual cores.

A suite of linear and log-log models were developed with a reduced dataset that excluded TSS greater than 1000 mg/L data. Single linear and log-log models that used all data within this data set indicated no substantial improvements from those presented in the previous paragraph. Subsequently the data set was further divided into two groups, one with TSS less than 100 mg/L data to represent a relationship for low TSS levels and one with TSS between 100 to 1000 mg/L data to represent a relationship for high TSS levels. Linear models for the split data set were more successful in capturing the observed TSS-turbidity dynamics than the log-log models.

6.1.2 Models Based on Silt to Clay Ratio

Silt to clay ratio was used to classify the TSS-Turbidity data into three groups: silt to clay ratio less than 1.5; silt to clay ratio above 1.5 but below 3; and silt to clay ratio above 3. Linear and log-log models were fitted to each group. Upon analysis of the residuals and comparing the model performance statistics, four candidate models had comparable performance. These were linear models for silt to clay ratios above 1.5 but below 3 and above 3, and the log-log models for silt-to-clay ratios below 1.5 and above 1.5 but below 3. Pooling of data on the basis of silt to clay ratio appeared to account for much of the core to core differences in the TSS-turbidity relationship.

6.1.3 Particle Volume Data

The particle volume data exhibited considerably higher core-to-core variability than the turbidity data. The model fit plots for linear as well log-log pooled models exhibited weaker correlations and indicated that the substantial core to core variability of the particle volume-TSS relationship will likely require distinctly different models for the type of sediment in each core. The identification of distinct sediment types and deployment of multiple relationships would be complex and likely problematic to implement in the field.

6.1.4 Models Based on Laboratory and BMP Data

The BMP data were included with the laboratory data with TSS less than 1000 mg/L to investigate possible refinements to the suite of pooled linear and log-log models that were developed with the lab data alone. Since the BMP data consisted predominantly of low TSS/turbidity values, the regression models in general were influenced by the lower range of data (particularly < 10 mg/L). Violations to regression assumptions for the linear and log-log models were substantial and the predictive abilities of these models were generally poor compared to those developed with the lab data alone.

6.2 Conclusions and Recommendations

The TSS surrogate relationships developed during this study indicate that both turbidity and particle volume can be used to estimate TSS in the field. However, both methods have limitations and are sensitive to different suspended sediment characteristics. The use of

turbidity as a TSS surrogate is desirable from the standpoint of ease of installation and operation of the monitoring equipment. However, to achieve reasonable accuracy, multiple relationships may be required to account for particle size variability (as expressed by silt to clay ratio). The use of multiple models will be complex, and will likely introduce additional variability due to the need to select the appropriate model to use on a real time basis.

The relationships developed using particle volume data did not perform as well as those developed using turbidity data. The particle volume data obtained during this study were quite variable. While the source of this variability is not fully understood, at least a portion of it appears to be related to the design of the study and sample handling and analysis procedures that were followed. The use of the LISST to select which model to use on a real time basis using the silt-to-clay ratio appears to be promising; however, operation and maintenance of the LISST instruments is complex.

Two primary considerations were identified in this study for maximizing the accuracy of a TSS surrogate relationship:

- obtain samples that contain the most uniform grain size possible
- obtain samples that are well within the operating ranges of the instrumentation

Turbidity was found to be superior to particle volume as a correlate to TSS. The relationship between turbidity and TSS differed among the nine cores tested and showed little coherence by core primary sediment type. The commonality of primary sediment type was lost early in the experiment as sand and gravel sized particles rapidly settled to the column bottom. The primary determinant of the turbidity-TSS relationship appears to be particle size distribution among the silt and clay sized particles that remained in the columns after the first 20 to 30 minutes of settling. This fact is evidenced by the dependency of the turbidity to TSS ratio on the ratio of silt to clay sized particles (as determined by the LISST). This dependency is expected due to the variation in sensitivity of the turbidity meter with particle size.

The option exists to measure both turbidity and particle size distribution in the field and to estimate TSS from the regression equation appropriate to the silt-to-clay ratio determined from the particle size distribution. This option requires the use of LISST particle size analyzers in tandem with turbidity meters at all near-field and far-field stations. Its

practicality is questionable, given the requirements for continuous monitoring, real-time data acquisition, and processing and simultaneous measurements at 40 or more locations.

Based on the analysis presented in Section 5 and the summary in Section 6.1, two options become evident. One option is to use the linear regression equation developed using samples with silt-to-clay ratios greater than three regardless of the actual silt-to-clay ratio. Another option is to use two linear models one for turbidity less than 113.73 NTU (i.e., TSS less than 100 mg/L) and another for turbidities greater than this value. From the comparison of performance on baseline monitoring program data it was clear that these two approaches were the most conservative of the developed equations, i.e., they yielded the highest TSS at a given turbidity.

6.2.1 Analysis of False Negatives to Determine Final Recommendation

A conservative TSS-turbidity regression equation will minimize the likelihood of false negatives (i.e., estimating a TSS less than a performance standard threshold when the TSS is actually greater than the threshold) but will tend to produce false positives (i.e., estimating a TSS greater than a performance standard threshold when the TSS is actually less than the threshold). To assess the likelihood of false negatives and false positives, the two candidate surrogate approaches identified earlier were tested using the combined data from the settling column experiments and the 2004 - 2008 BMP data.

TSS values were computed using the two candidate approaches from turbidity values associated with measured TSS values within the range of 50 to 150 percent of the performance standard thresholds of 12, 24, and 100 mg/L (the 700 mg/L standard was not included because of limited data for testing). The frequency of correct (true negatives or true positives) and incorrect (false negatives or false positives) predictions were compiled and are shown in Table 6-1. The model predictions are also compared graphically to the data in quadrants of true and false predictions in Figure 6-1. If the model is accurate all the time then the percentage of true positives and true negatives will be 100 and the percentage of false positive and false negative will be 0 (i.e., in Figure 6-1 points will fall only on the top-right and the bottom-left quadrants). Moreover, the density of points in the vicinity of the one-to-one line in Figure 6-1 demonstrates the accuracy and bias in model estimations. The

farther away the points are to the one-to-one line, the less accurate the model is. Similarly if the points are concentrated predominantly on one side or the other then it suggests a bias in the model estimate. It is clear from the concentration of points close to the one-to-one line in Figure 6-1, that the silt-to-clay ratio based model is relatively more accurate (particularly for 100 mg/L threshold) and significantly unbiased (for all thresholds) compared to the two model approach.

The silt to clay ratio based model correctly predicted the threshold exceedances (i.e. true positives) in 69, 66, and 76 percent of the cases for the 12, 24, and 100 mg/L. The corresponding predictions of the two model approach are 100, 59, and 62 percent respectively. From this standpoint it appears that the two model approach performs well at lower TSS levels, whereas the silt-to-clay ratio based model does well at moderate to high TSS concentrations. Upon comparing the false positives (declaring an exceedance when there is not) it becomes clear that the two model approach nearly always declares a sample as a positive (100 percent of the time for the samples evaluated) for the lowest TSS threshold of 12 mg/L whereas the silt-to-clay ratio based model predicts false positives at a frequency of just 20 percent (i.e. 1 in 5).

The results above suggest that the silt-to-clay ratio based model provides optimal performance both in terms of minimizing false positives and maximizing the true positives. The two model approach is overly conservative and nearly always declares a false positive for the lowest TSS thresholds (12 mg/L). At moderate to high thresholds both approaches are about equally conservative in terms of declaring a false positive. The two model approach is somewhat more complicated to implement and introduces more uncertainty than the single slit-to-clay ratio based model, because additional analysis is required to identify the appropriate model component.

The above analysis suggests that the use of the TSS-turbidity equation derived from data with silt to clay ratios greater than three is a reasonable means of providing a conservative real-time prediction of TSS and it is recommended for use at the commencement of Phase 1 dredging. Paired TSS-turbidity data collected during Phase 1 dredging will be used to further assess this equation. GE will perform weekly reviews of the paired data, and make recommendations to EPA regarding updating the TSS-turbidity relationship.

Table 6-1

Frequency of Correct and Incorrect Model Predictions At Different TSS standards

TSS Standard (mg/L)	Single Linear Model from Silt to Clay Ratio > 3 Data				Two Linear Models from Split Data Set (TSS<100 mg/L and 100<TSS<1000 mg/L)			
	False Positive	True Positive	False Negative	True Negative	False Positive	True Positive	False Negative	True Negative
12	20.4	69.0	31.0	79.6	100	100	0	0
24	21.5	65.6	34.4	78.5	18.5	59.4	40.6	81.5
100	39.3	75.7	24.3	60.7	24.6	62.2	37.8	75.4

Based on 2004 – 2008 BMP data.

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Table 1-1. Core sample data summary.

CORE ID	FIELD SAMPLE ID	TARGETED RESULTS	FINAL RESULTS												
		PRIMARY USCS SEDIMENT TYPE *(Median Diameter)*	GEOTECHNICAL ANALYSIS (%)						APROXIMATE MEDIAN DIAMETER (µm)	CALCULATED DRY SEDIMENT WEIGHT (kg)	DRY BULK DENSITY (g/cm3)	MOISTURE CONTENT (%)	TOC %	WET SEDIMENT WEIGHT (kg)	GENERAL SAMPLE DESCRIPTION
			GRAVEL	COARSE SAND	MEDIUM SAND	FINE SAND	SILT	CLAY							
RS1-9392-TS022*	RS1-9392-TS022-000060	**MS** (425-2000 µm)	27.8	16.5	35.05	16.2	3.3	1.15	1500	10.8	1.45	9.8	0.33	11.9	BLACK, GRAVEL, SOME CS, TRACE MS
RS1-9392-TS024*	RS1-9392-TS024-000024		18.9	13.2	30.7	33.8	1.3	2.2	850	4.6	1.57	15	0.28	5.4	DARK BROWN, CS, SOME GR, TRACE CL.
RS1-9392-TS020*	RS1-9392-TS020-000013		45.7	8.9	29.6	14.8	1	0	**3000**	2.0	1.23	19	0.28	2.5	SATURATED, DARK BROWN, GR, SOME CS, LITTLE WOOD, TRACE SHALE
RS1-9493-TS005	RS1-9493-TS005-000036		25.8	10.4	27.9	28.8	3.7	3.4	850	5.9	1.32	9.3	0.56	6.5	DARK BROWN, MS, SOME SI, TRACE COBBLES
RS1-9594-TS002	RS1-9594-TS002-000024		18	12	23.8	36.2	9.3	0.6	450	3.4	1.12	22	0.53	4.3	DARK BROWN, MS, LITTLE GR, TRACE WOOD, SULPHUR ODOR
RS1-9493-TS002	RS1-9493-TS002-000024		28	10.5	20.2	25.8	11.2	4.2	850	2.7	0.85	26	0.32	3.6	6 INCH VOID AT 12 IN. BLACK, SATURATED, MS, SOME SI, LITTLE WOOD TRACE GR. SULPHUR ODOR.
RS1-9594-TS020*	RS1-9594-TS020-000024		37.2	13.9	18.1	13.2	10.8	6.8	2000	3.2	1.09	30	0.38	4.6	BROWN, GR, SOME CL
RS1-9493-TS028*	RS1-9493-TS028-000039		9.1	6.3	10.1	10.7	17.8	45.9	**8**	5.3	1.09	25	0.34	7.1	GRAY, CL, SOME GR, LITTLE CS
Average Sediment Type (%)			26	13	26	26	7	3							
RS1-9190-TS001	RS1-9190-TS001-000024	**FS** (74-425 µm)	1.1	1.9	8.2	79.1	8	1.7	200	3.6	1.16	8.3	0.42	3.9	LIGHT BROWN, MS, TRACE SI,
RS1-9594-TS003	RS1-9594-TS003-000030		2.1	3	9.7	76.7	7.2	1.3	200	3.2	0.81	23	1.10	4.2	DARK BROWN, FS, SOME WOOD.
RS1-9392-TS003	RS1-9392-TS003-000024		3.5	1.6	11.6	68.5	10.6	4.2	180	2.4	0.79	35	2.50	3.7	DARK BROWN, SILT, SOME FS, TRACE WOOD
RS1-9493-TS001	RS1-9493-TS001-000030		16.4	8.9	19.2	48	5.1	2.4	425	3.8	1.02	29	12.00	5.4	DARK BROWN, MS, LITTLE SI, TRACE CS, AND WOOD
RS1-9190-TS003	RS1-9190-TS003-000024		6	4	7.8	46.8	32.4	3	160	2.1	0.69	42	3.90	3.7	DARK BROWN, SILT AND FINE SAND
RS1-9190-TS002	RS1-9190-TS002-000024		0.1	0.2	3	31.5	45.9	19.4	**50**	4.0	1.33	9	0.16	4.4	BROWN FS TRACE GR AND CLAY
RS1-9392-TS002	RS1-9392-TS002-000024		23.3	11.5	34.1	27.4	2.5	1.3	**850**	3.6	1.20	18	0.25	4.4	LIGHT BROWN TO BLACK ANGULAR GRAVEL, MS, TRACE WOOD
RS1-9493-TS008	RS1-9493-TS008-000042		8.3	6.6	17.5	24	18.8	24.9	130	5.7	1.08	24	1.90	7.5	MOIST, DARK BROWN SILT, SOME WOOD, LITTLE MS, TRACE CL
Average Sediment Type (%)			6	4	12	57	14	6							
RS1-9493-TS010	RS1-9493-TS010-000066	**SI** (5-74 µm)	0	0	2.7	13.6	70	13.8	40	2.8	0.31	64	7.20	7.9	DARK GRAY, CL, SOME SI, TRACE ORGANICS
RS1-9392-TS001	RS1-9392-TS001-000018		0	0	2.2	31.5	55	11.3	60	**0.9**	0.36	61	4.70	2.3	MOIST, DARK BROWN SILT, TRACE WOOD
RS1-9493-TS009	RS1-9493-TS009-000048		0	0.5	3.8	35.2	46.7	13.75	75	2.9	0.53	55	5.35	6.5	BLACK, MOIST, SILT, SOME CL, TRACE WOOD
RS1-9392-TS005	RS1-9392-TS005-000024		2.1	0.5	3.9	48.6	39.6	5.3	75	2.7	0.88	38	2.20	4.3	DARK BROWN SI, TRACE WOOD
RS1-9392-TS006	RS1-9392-TS006-000030		3.3	2.4	14	35.9	34.2	10.2	75	**1.9**	0.48	55	9.40	4.2	DARK BROWN, MOIST CLAY, TRACE MS, TRACE WOOD.
RS1-9594-TS001	RS1-9594-TS001-000036		0	0	11.9	45.9	32	10.2	**150**	3.6	0.79	36	5.00	5.7	LIGHT GRAY, FS, LITTLE ORGANIC, TRACE CL
RS1-9493-TS011	RS1-9493-TS011-000036		0	1.2	8.1	55	30.5	5.1	**100**	3.1	0.67	43	4.70	5.5	DARK BROWN, SILT, SOME CL, TRACE WOOD
RS1-9190-TS020*	RS1-9190-TS020-000030		13.3	9.8	19.3	50.6	5.5	1.5	**400**	**1.2**	0.30	67	7.90	3.7	DARK GRAY, MOIST, SI,
Average Sediment Type (%)			1	1	5	33	49	11							

Notes:

1) *Median diameters of cores considered for the TSS surrogate study are in black (outliers - cores with median diameter outsider the targeted sediment type, are in red)*
2) *Records highlighted in blue are cores recommended for the study.*
3) *Numbers highlighted in gray are average sediment compositions calculated from cores with median diameter consistent with targeted primary sediment type.*
4) *Cores with dry sediment weight <2 kg not selected due to insufficient sample volume (in red)*
5) *Core IDs with asterisk identify cores that were targeted in a second round of assignments*

Table 2-1. Sediment sample test volumes.

Primary USCS sediment type	Name used in text	Core id	Field sample id	Aproximate median diameter (μm)	Moisture content (%)	Amount of sediment added to the settling column (Kg)	Amount of sediment added to the dilution vessel (Kg)
Silt	Core 1	RS1-9493-TS010	RS1-9493-TS010-000066	40	64	4.253	28
	Core 2	RS1-9493-TS009	RS1-9493-TS009-000048	75	51.5	3.157	21
	Core 3	RS1-9392-TS005	RS1-9392-TS005-000024	75	38	2.470	16
Fine sand	Core 4	RS1-9190-TS001	RS1-9190-TS001-000024	200	8.3	1.670	11
	Core 5	RS1-9392-TS003	RS1-9392-TS003-000024	180	35	2.356	15
	Core 6	RS1-9190-TS003	RS1-9190-TS003-000024	160	42	2.640	17
Medium sand	Core 7	RS1-9392-TS022*	RS1-9392-TS022-000060	1500	10.4	1.709	11
	Core 8	RS1-9493-TS005	RS1-9493-TS005-000036	850	9.3	1.688	11
	Core 9	RS1-9594-TS002	RS1-9594-TS002-000024	450	22	1.963	13

Table 3-1. Data quality summary.

Data set	Settling Test		Dilution Test	
	Duplicate RPD	Average FB Contamination	Duplicate RPD	Average FB Contamination
TSS	14.24%	-	62.72%	-
Turbidity	4.77%	0.14 NTU	12.32%	0.13 NTU
Particle Volume	20.73%	4.57 uL/L	24.70%	2.26 uL/L

Table 4-1. Factors potentially contributing to sensitivity of analytical methods.

Data set type	Concentration	Particle size			Shape	Color	Refractive index	Entrained Air (bubbles)
		Small particles (<0.45 um; colloids)	Large particles diameter > 500 um	Primary range (>0.45 um - 500 um)				
TSS	None	Yes, low	Yes (due to variability in samples)	None	None	None	None	None
Turbidity	No, unless instrument range exceeded	Yes, high	Yes (difficult to keep particles uniformly distributed in sample)	Yes, high (inversly proportional)	Yes	Yes	Yes	None
Particle volume	No, unless instrument range exceeded	Minimal	Minimal	None	Yes, unless particles are perfect spheres	None	Yes, if particles are small	Yes

Table 4-2. Datasets excluded from TSS Surrogate correlation development.

Test	Data excluded	Reason
Dilution test	All TSS, turbidity and particle volume data	Poor data quality - TSS RPD > 60%
Settling column test	All TSS, turbidity and particle volume data collected in the first 20 min of the test	High concentrations, rapid settling of large particles, high degree of particle size variability
	All TSS, turbidity and particle volume data of final samples (collected at 24 hours)	Detection of large particles assumed to be result of flocculation
	Four last bins of the particle volume data collected after 20 min	Field blank analysis indicated presence of large particles; assumed to be related to entrained air (bubbles) created by stirrer in sample cell
	Particle volume data w/transmission <10% in samples collected after 20 min. (6 samples)	Poor data quality; samples not reanalyzed due to scheduling error

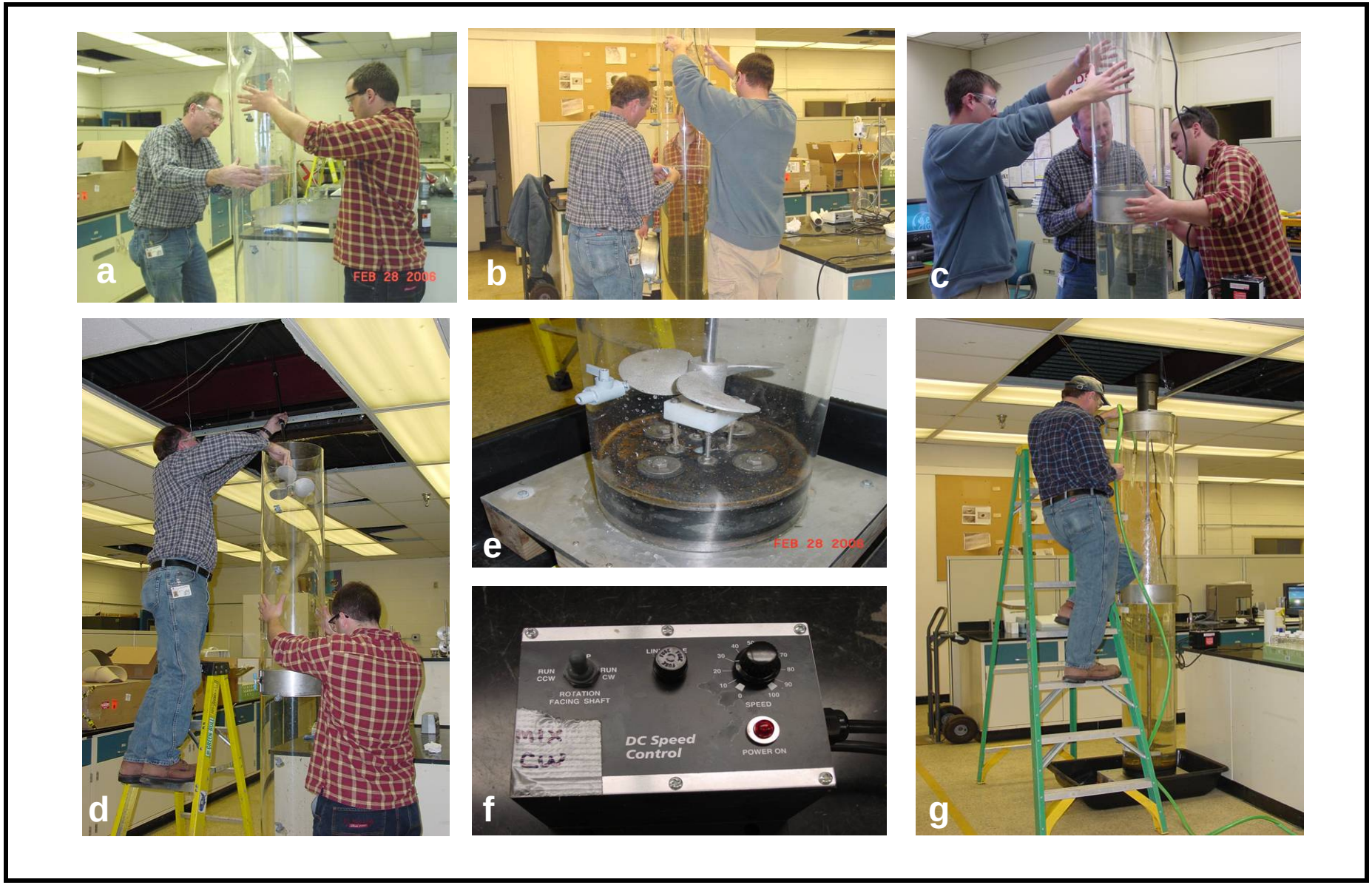

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Figure 2-1. Settling column test apparatus.

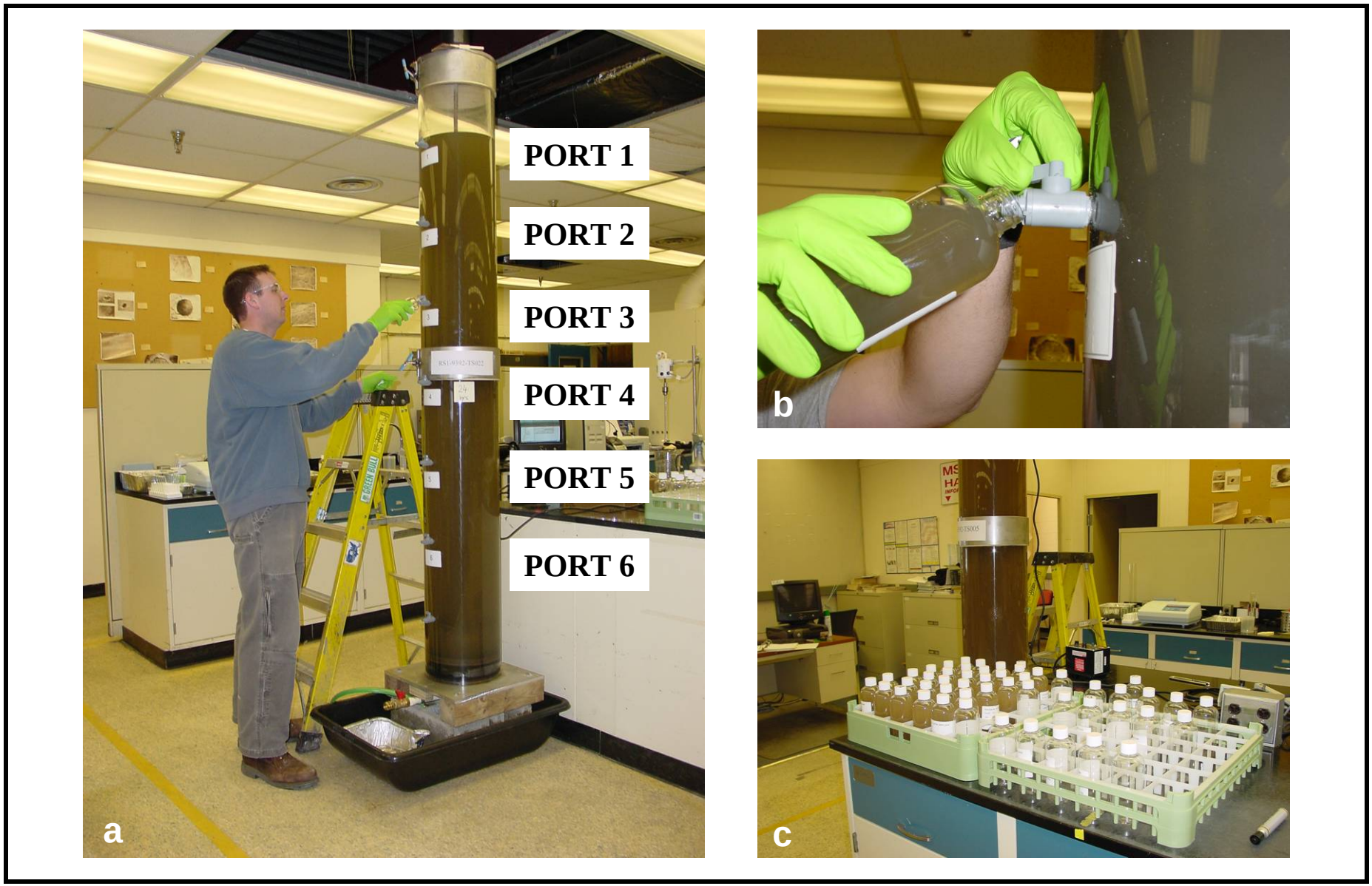

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Figure 2-2. Port identification, sample withdrawal, and storage.

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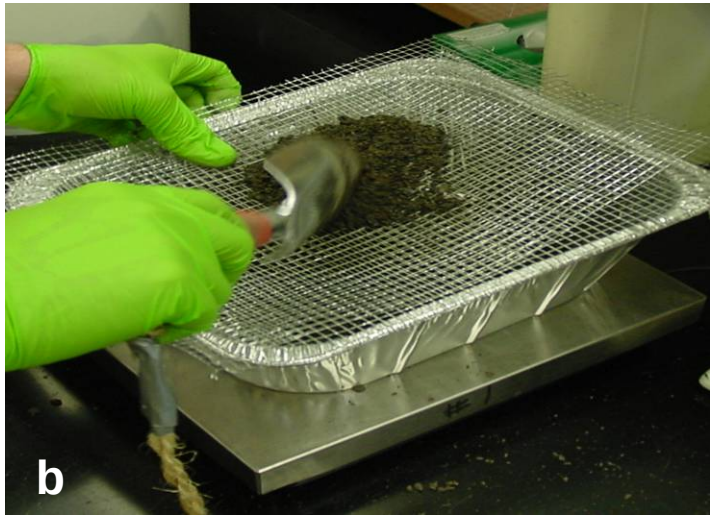
Figure 2-3. Sediment addition.



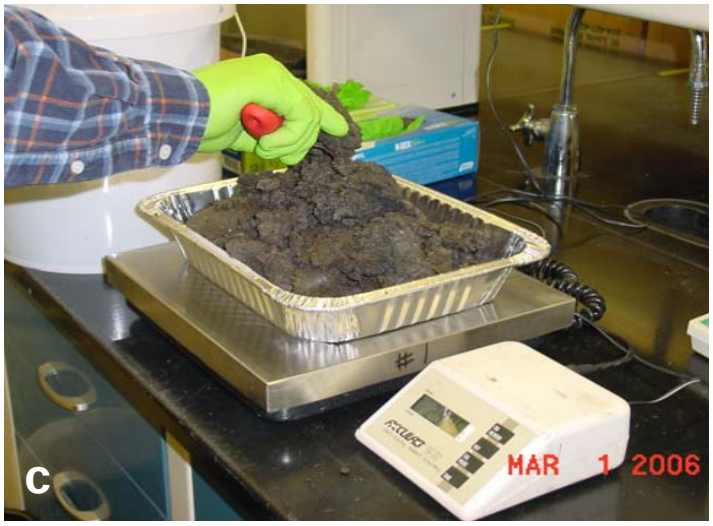


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Figure 2-4. Water collection and sample preparation for testing.

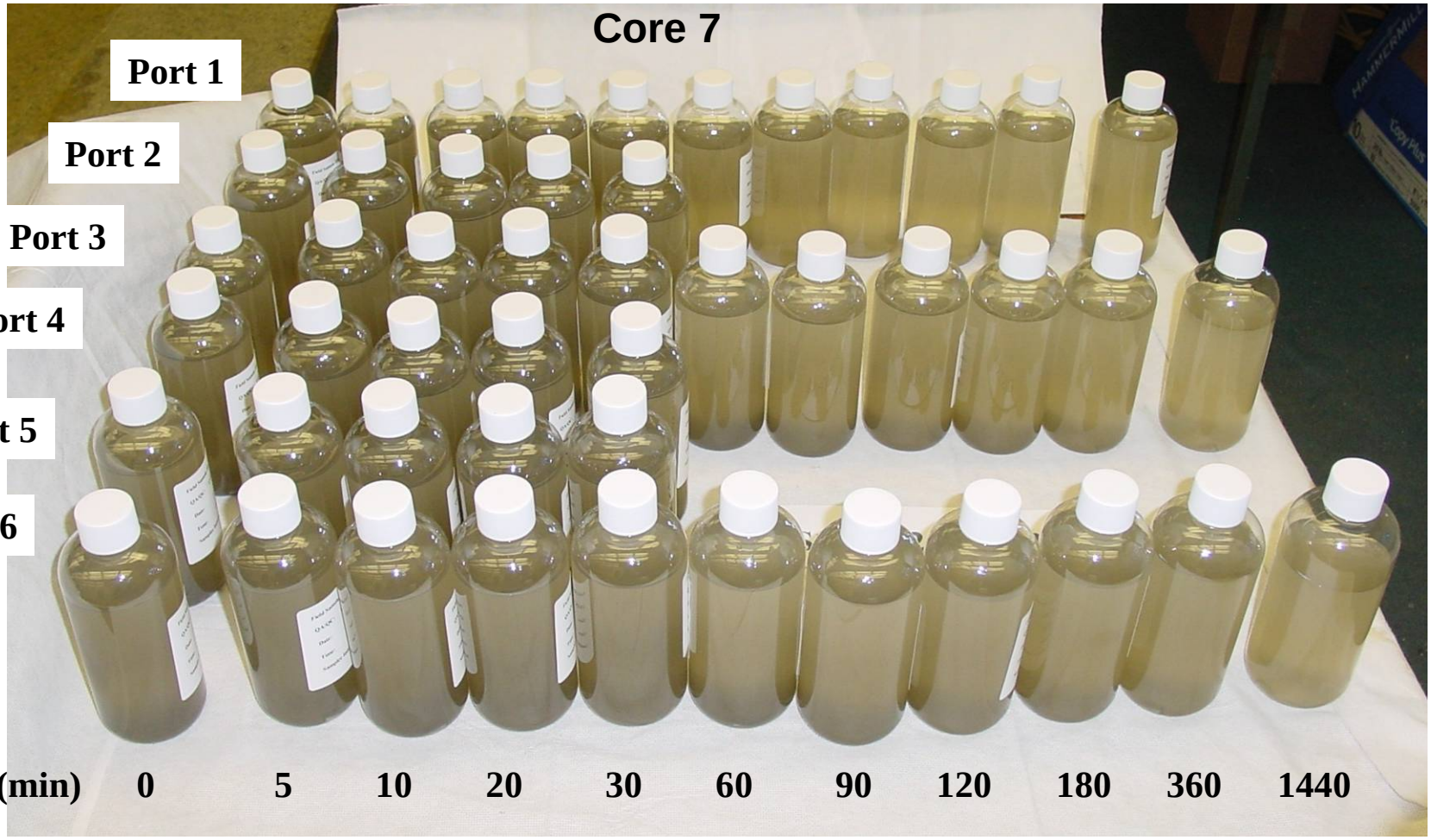

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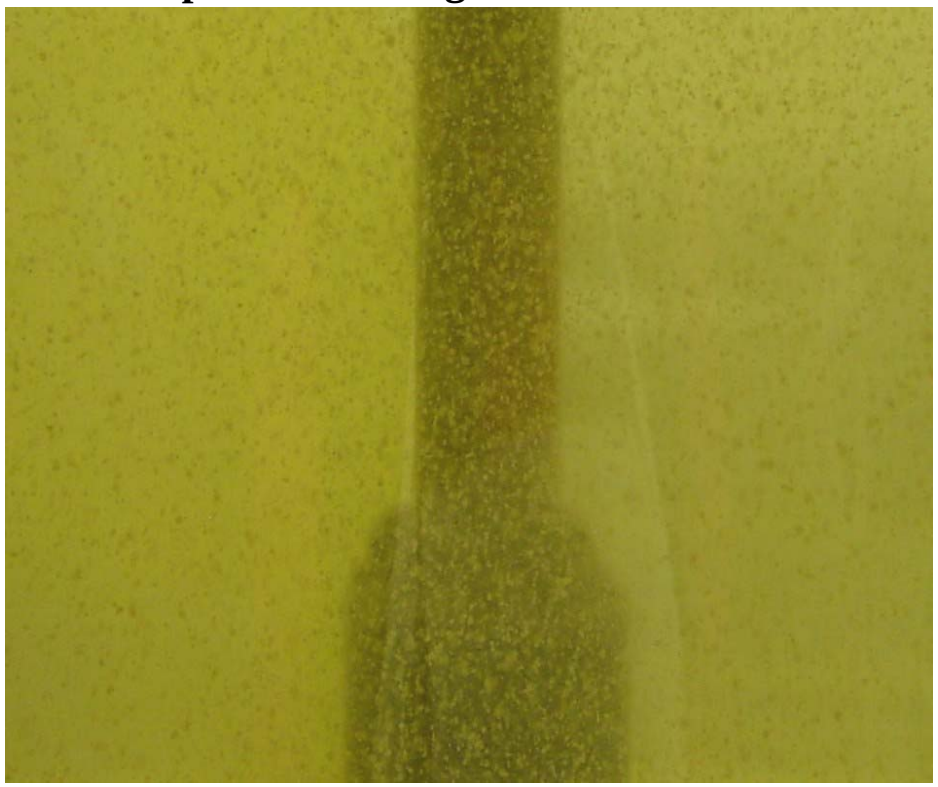
Figure 2-5. Sample organization.

Core 5 - particle settling 20 min into the test



Core 5 - particle settling 50 min into the test

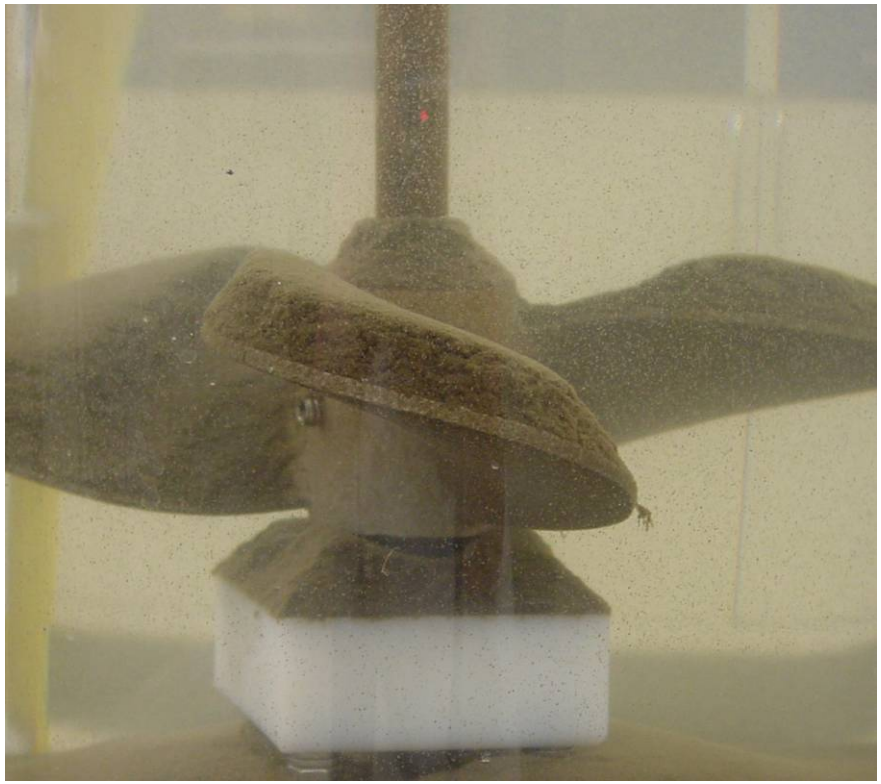


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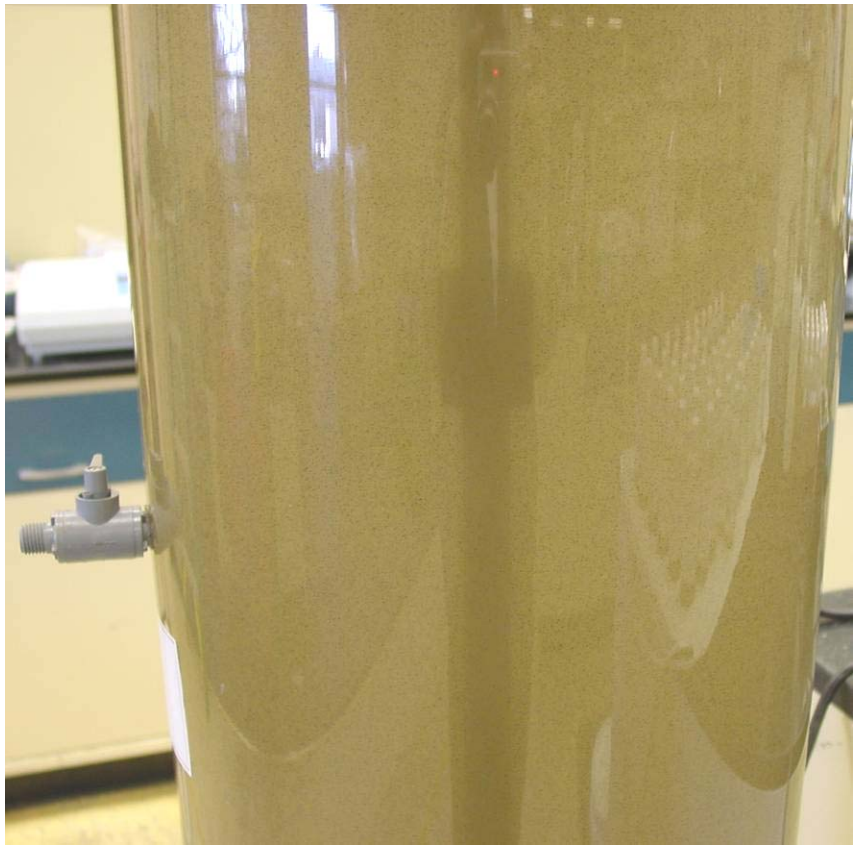
Figure 2-6. Core 5 short term settling characteristics.

Core 8 - particle settling 10 min into the test



Core 8 - particle settling 20 min into the test

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Figure 2-7. Core 8 short term settling characteristics.

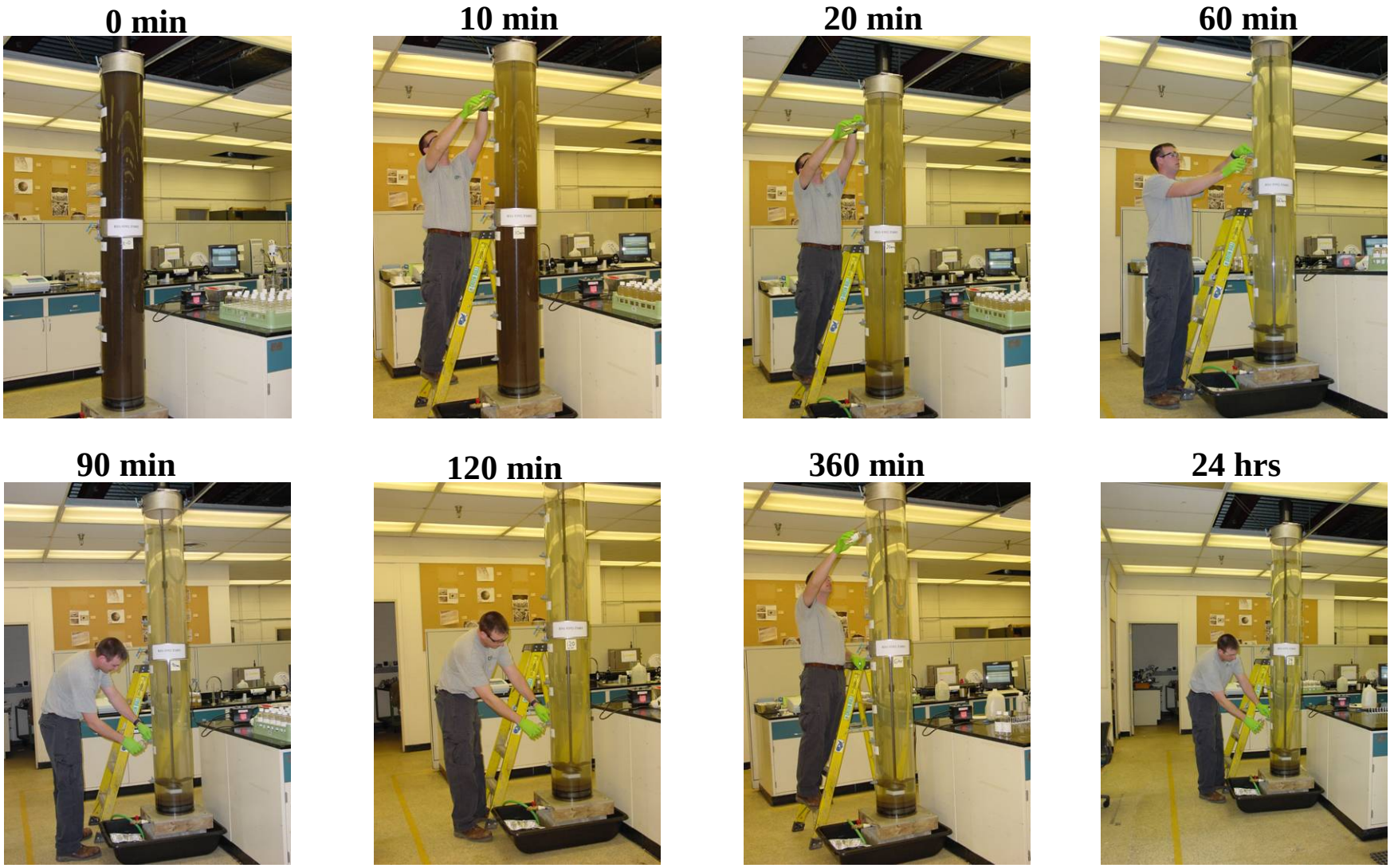

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Figure 2-8. Core 5 settling time series.

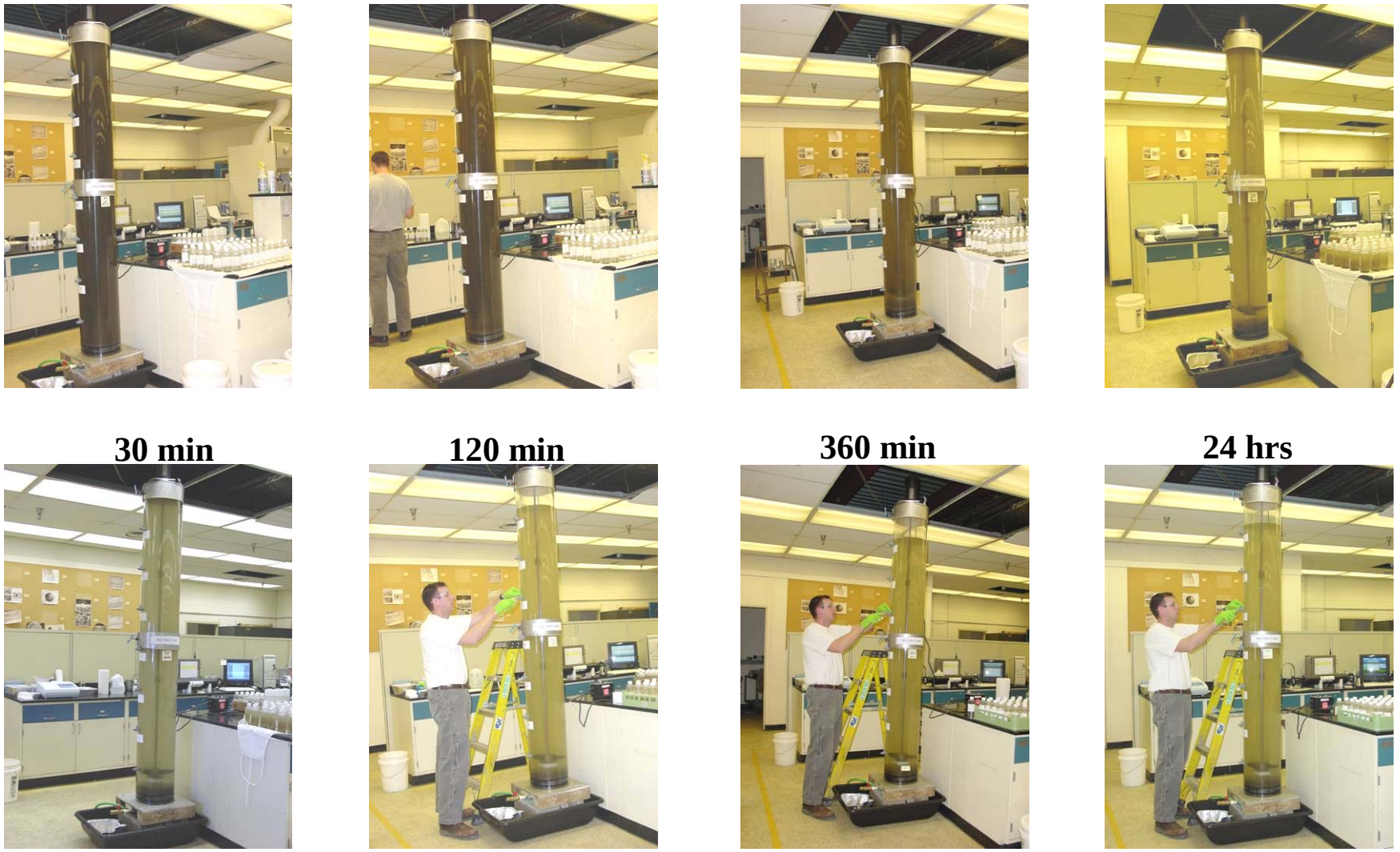

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Figure 2-9. Core 8 settling time series.

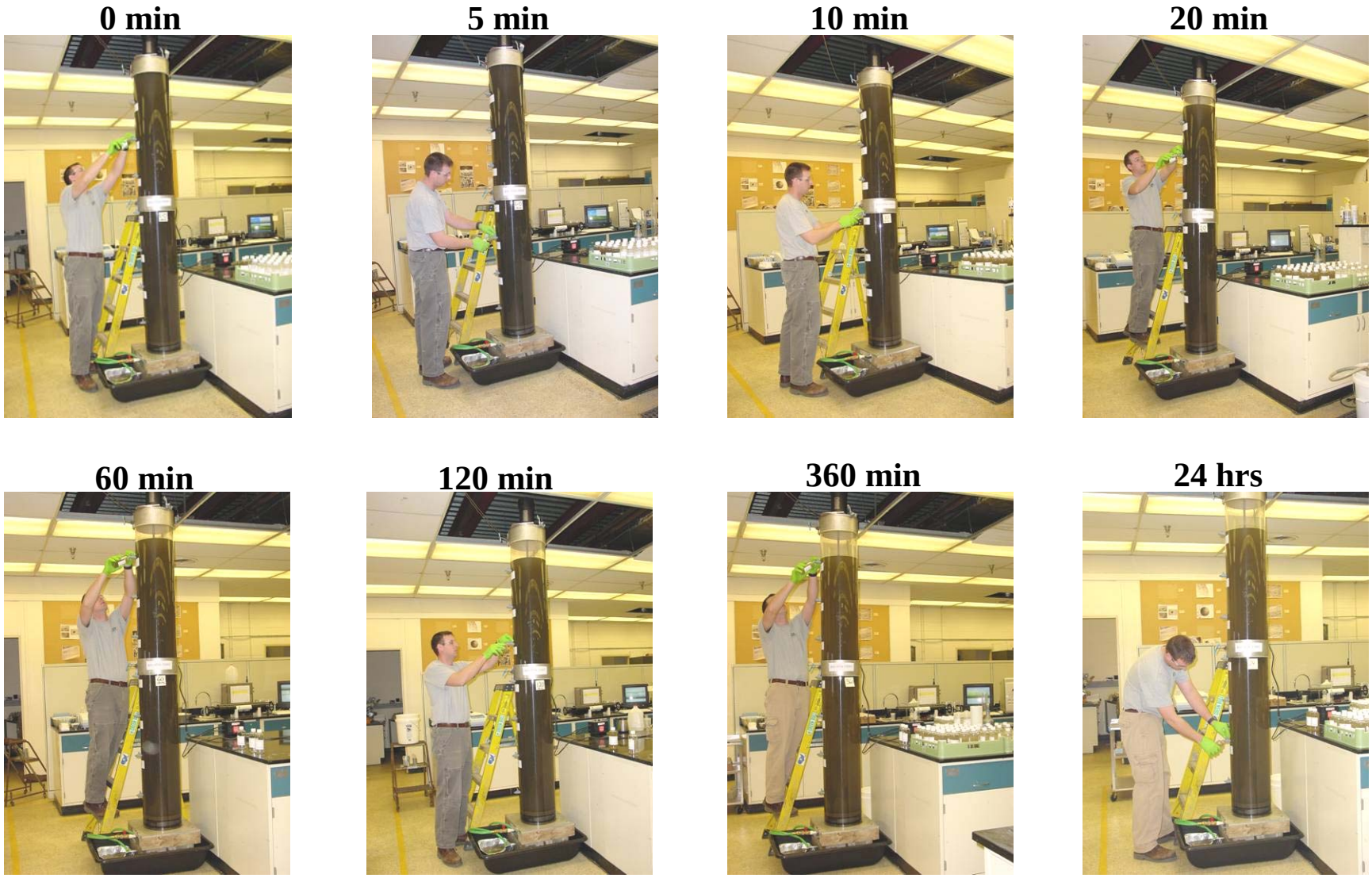

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Figure 2-10. Core 9 settling time series.

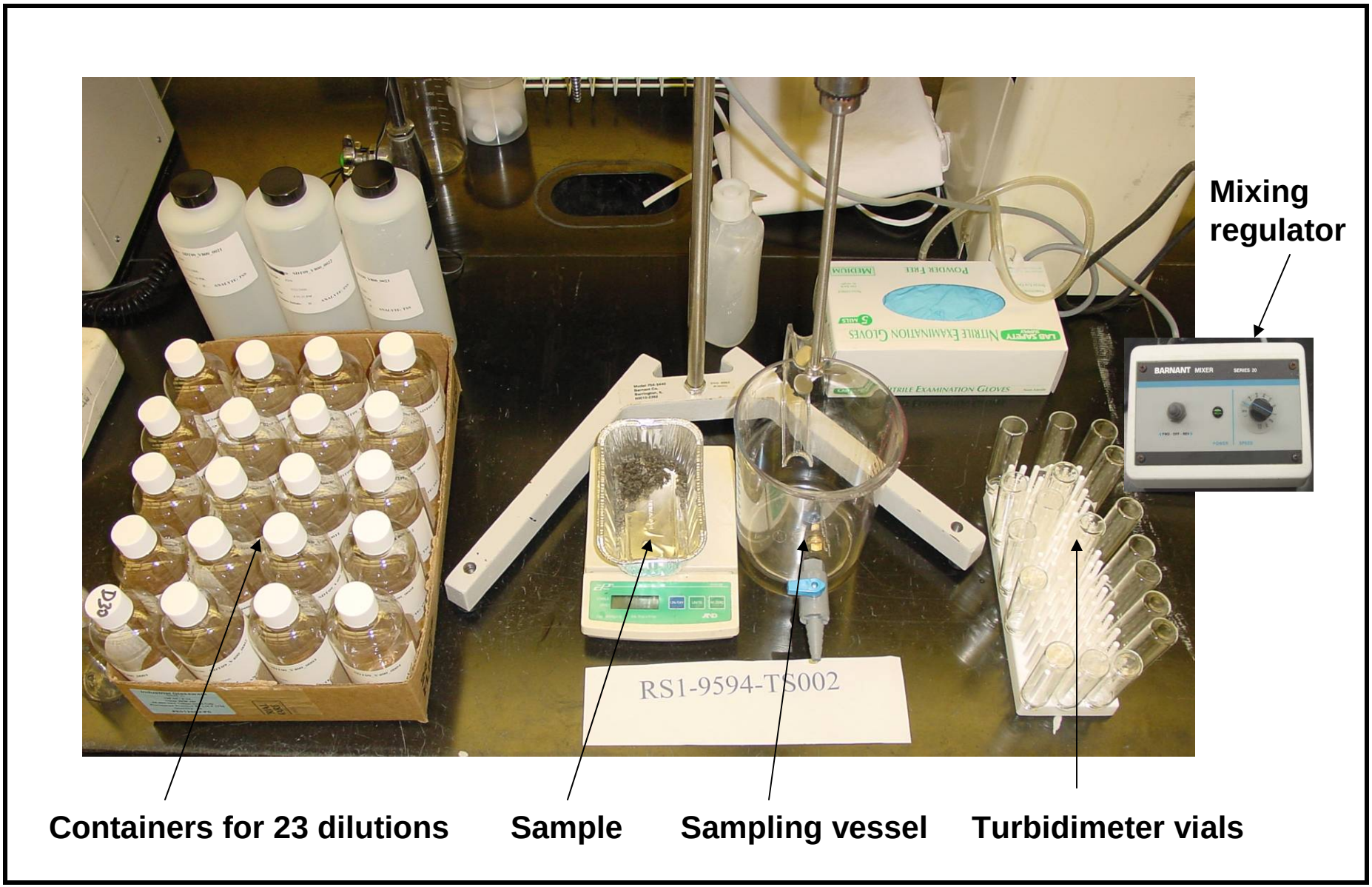

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Figure 2-11. Serial dilution test apparatus.

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Figure 2-12. Serial dilution test procedures.

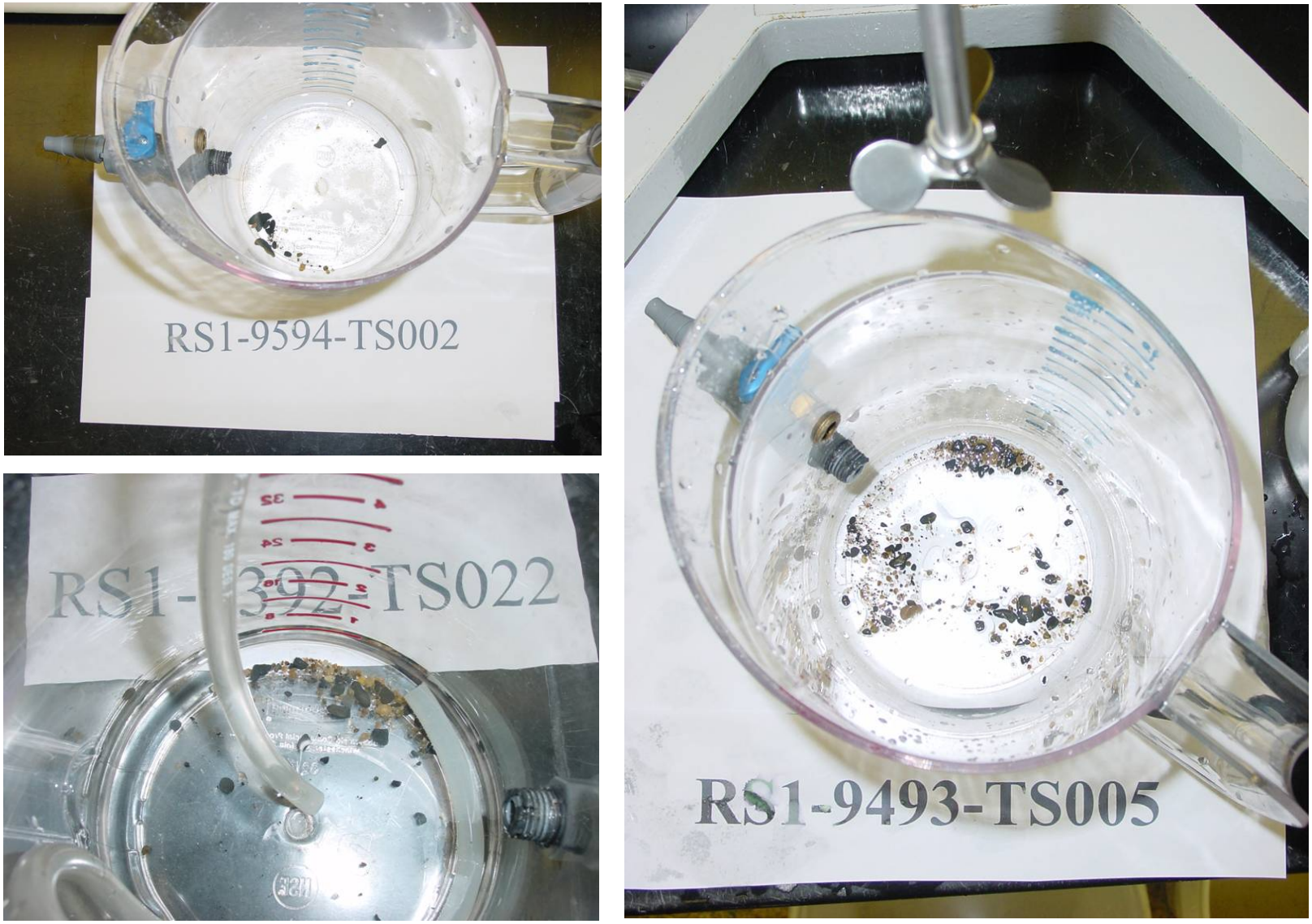

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Figure 2-13. Residual sediment in serial dilution test.

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Figure 2-14. Hach turbidity meter.

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Figure 2-15. YSI turbidity meter.

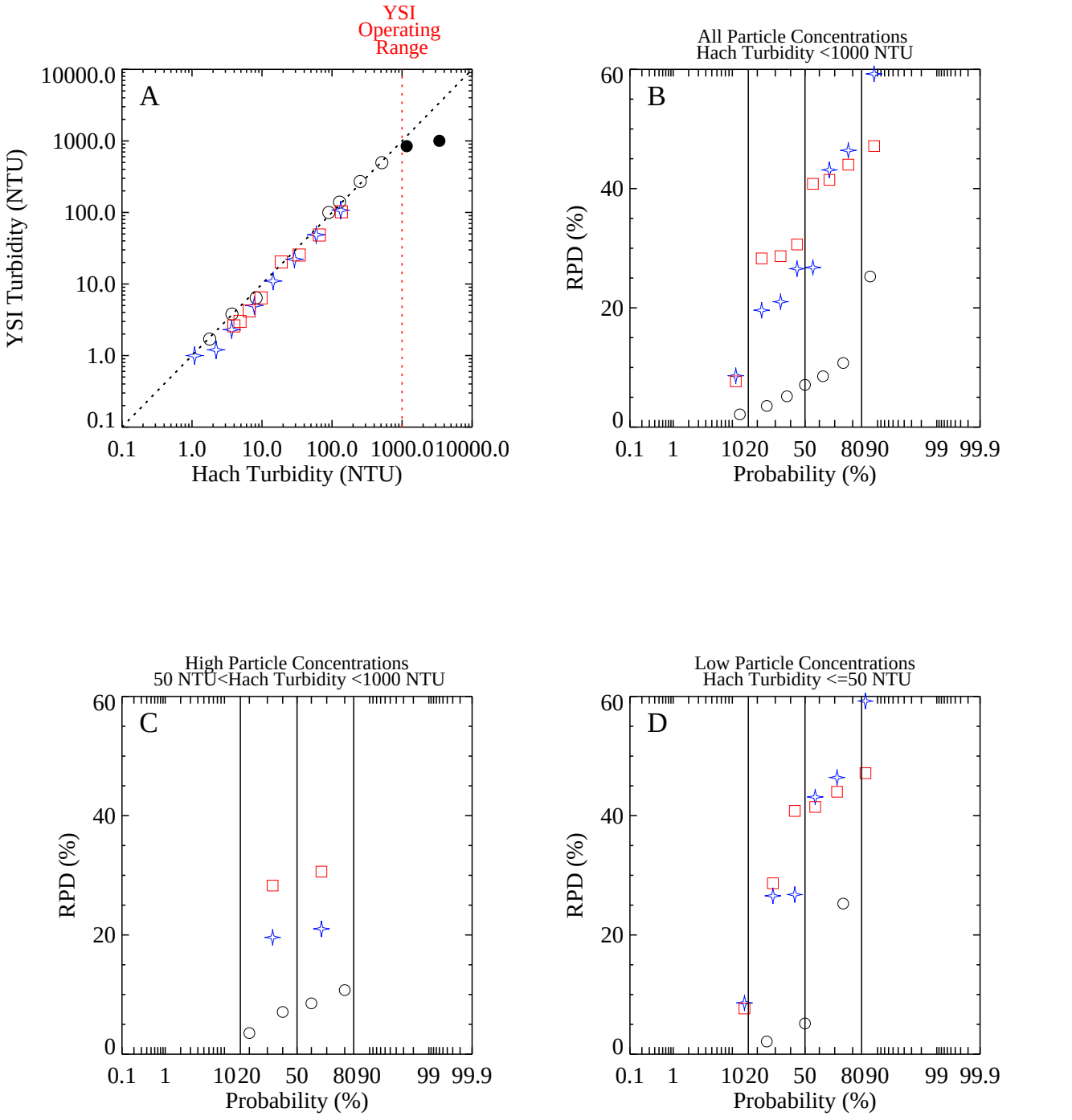

Figure 2-16. Turbidity meter performance comparison.

Average RPDs were 8.9 % (Core 1), 31.4 % (Core 4), and 33.6 % (Core 9).

Two Core 1 samples that exceeded YSI operating range were excluded from RPD analysis.

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Figure 2-17. LISST instrument set-up.

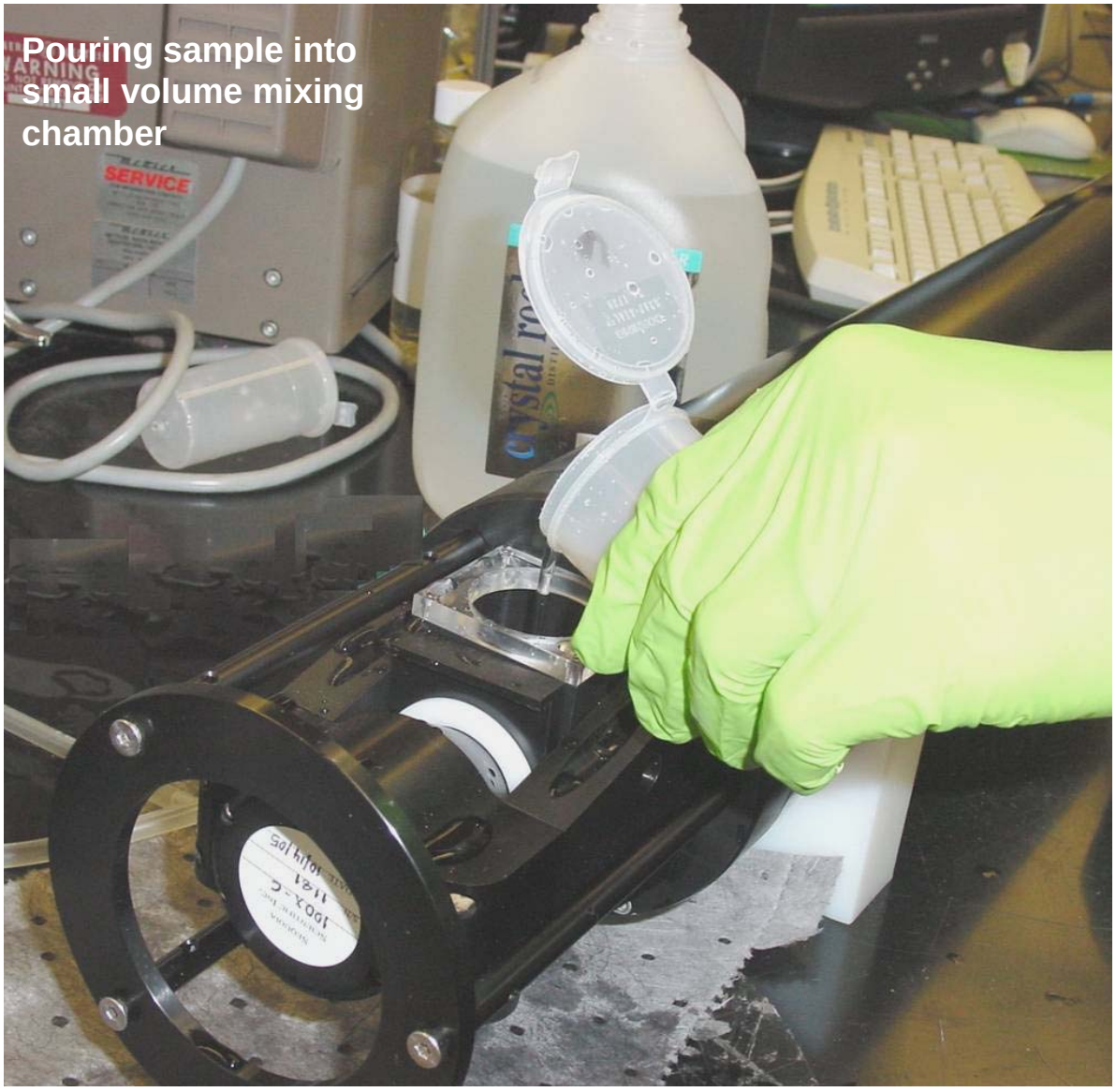

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Figure 2-18. Sample analysis using LISST.

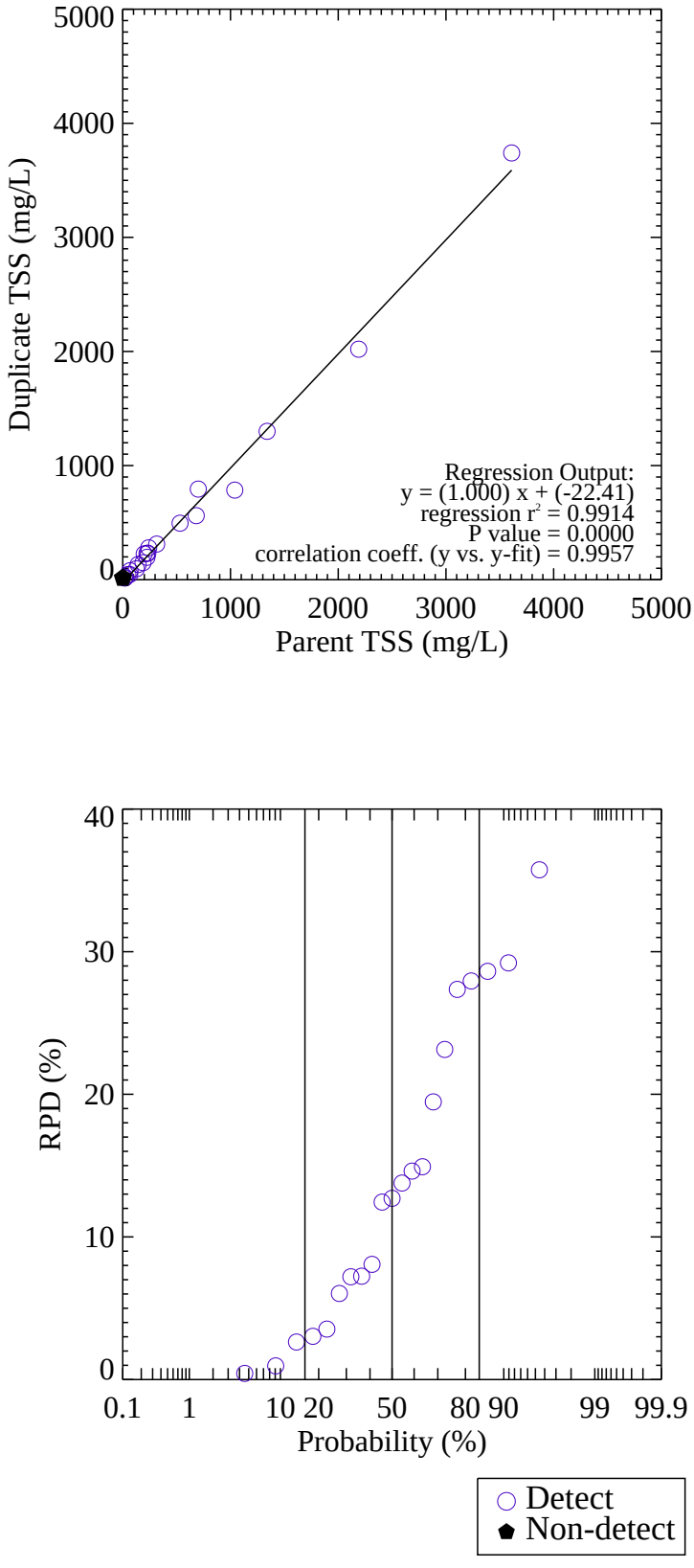
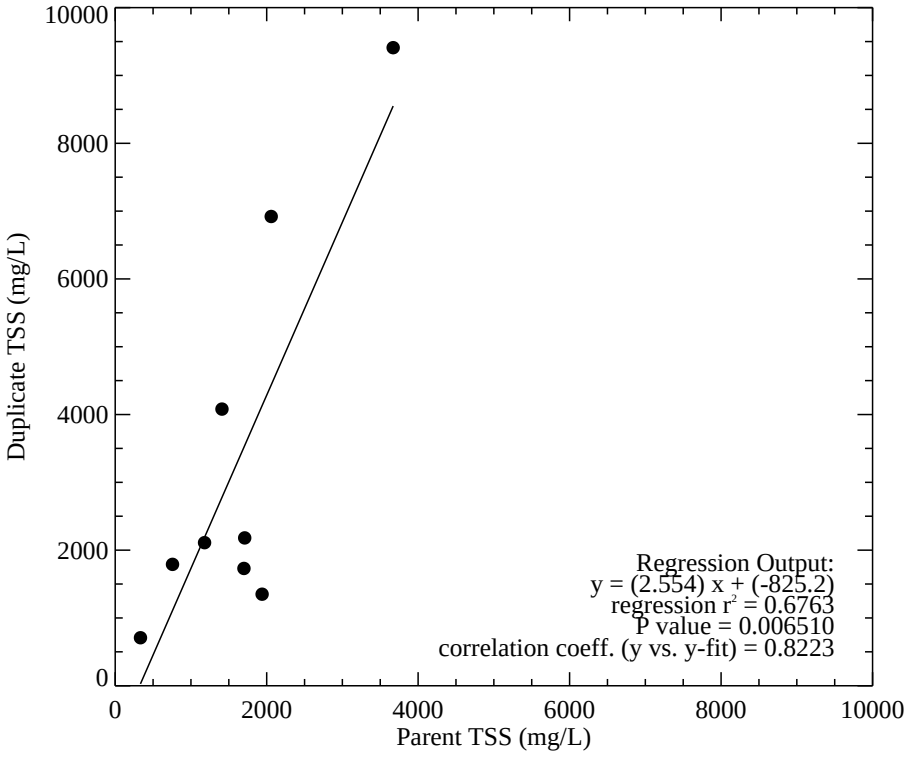


Figure 3-1. TSS duplicate results for settling column study.

Overall RPD calculated from detect values is 14.24 %.



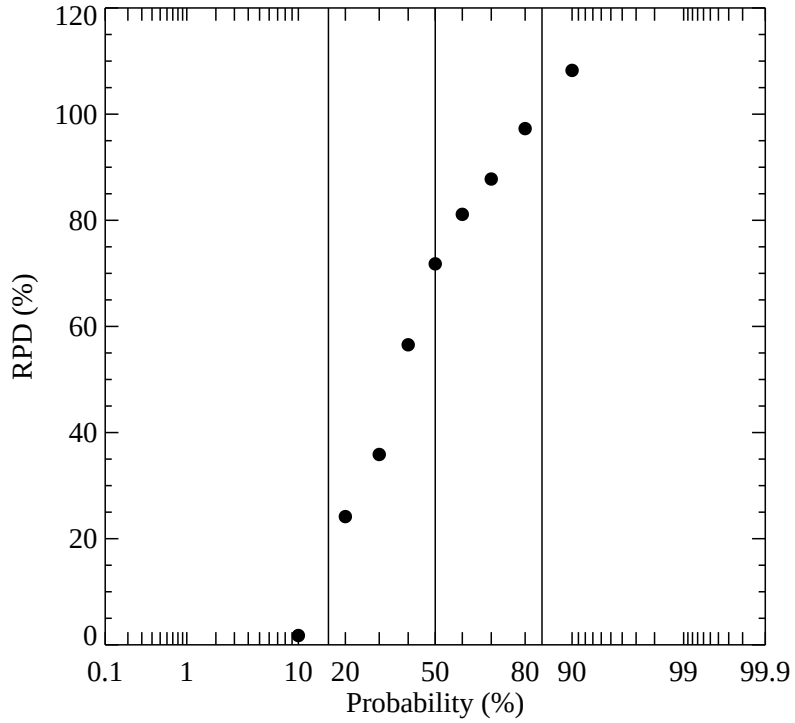
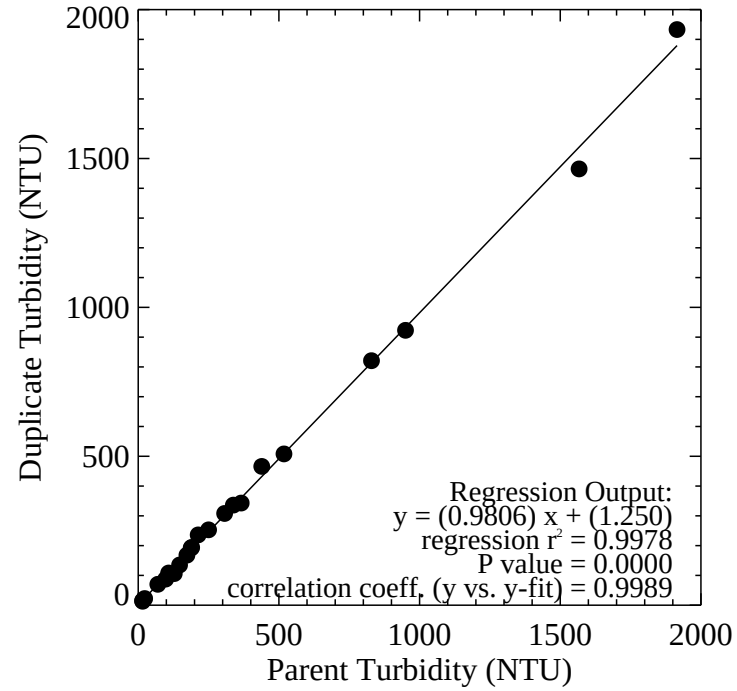


Figure 3-2. TSS duplicate results for serial dilution study.

Overall RPD for the dilution study data is 62.72 %



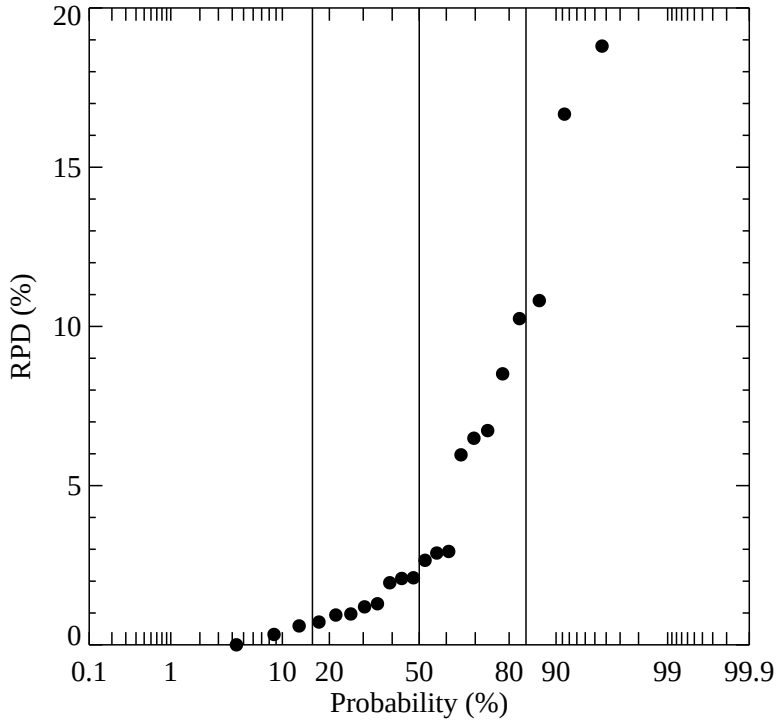
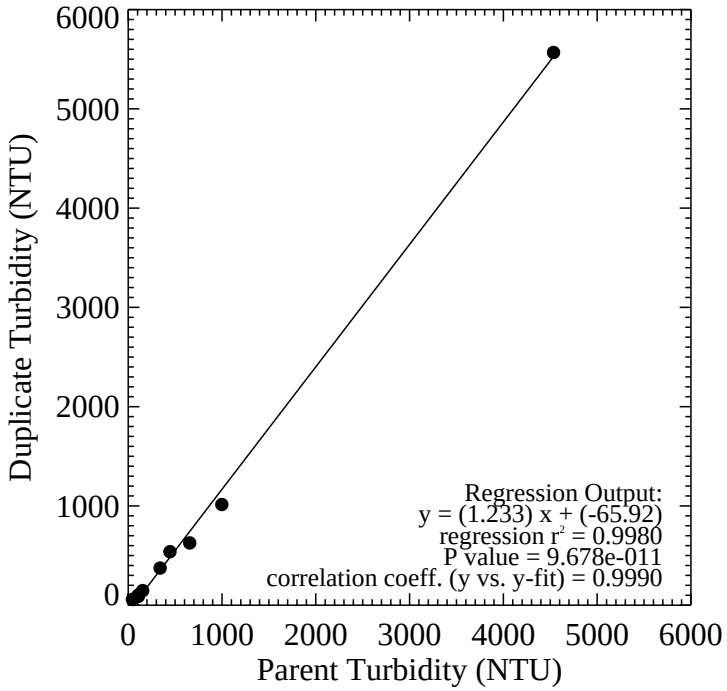


Figure 3-3. Turbidity duplicate results for settling column study.

Overall calculated RPD is 4.77 %.



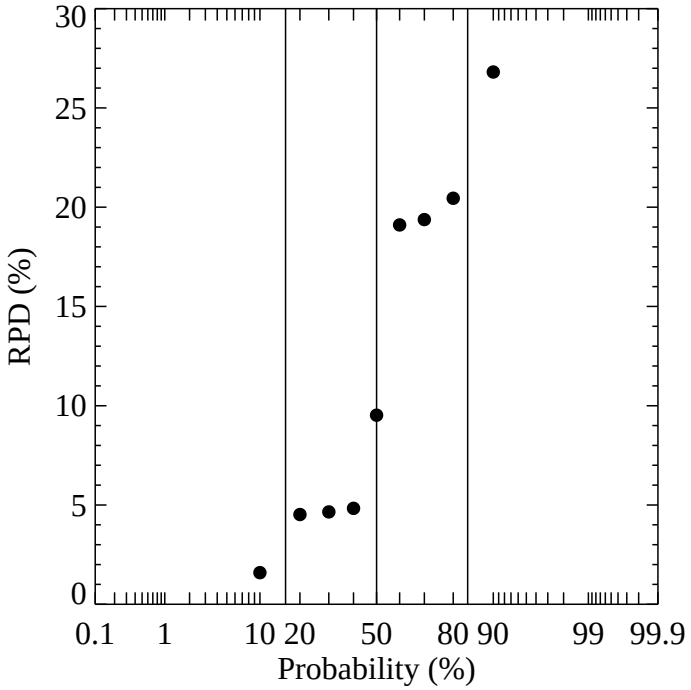


Figure 3-4. Turbidity duplicate results for serial dilution study.

Overall average RPD is 12.32 %.

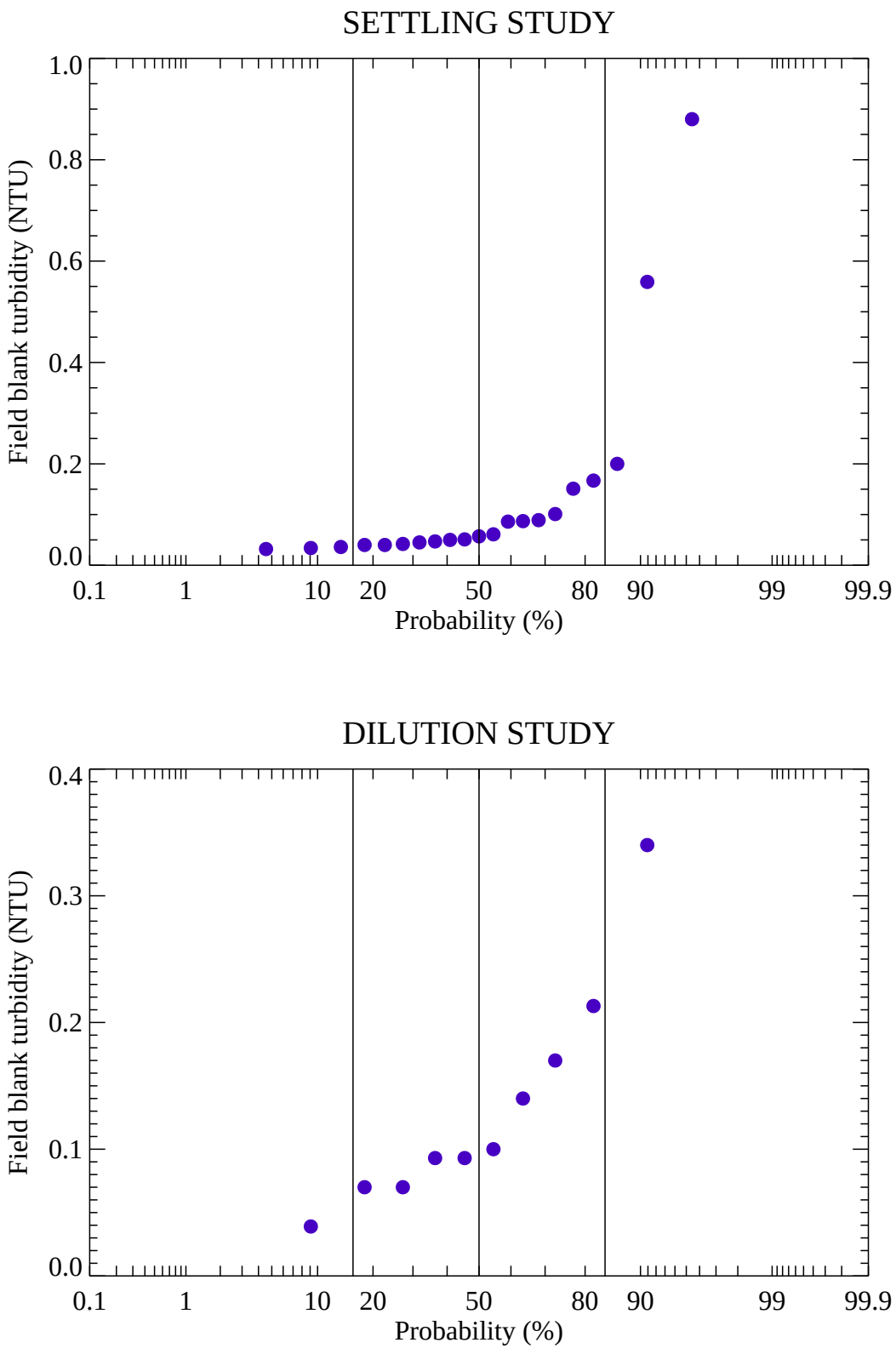


Figure 3-5. Field blank turbidity results for settling column and serial dilution study.

.

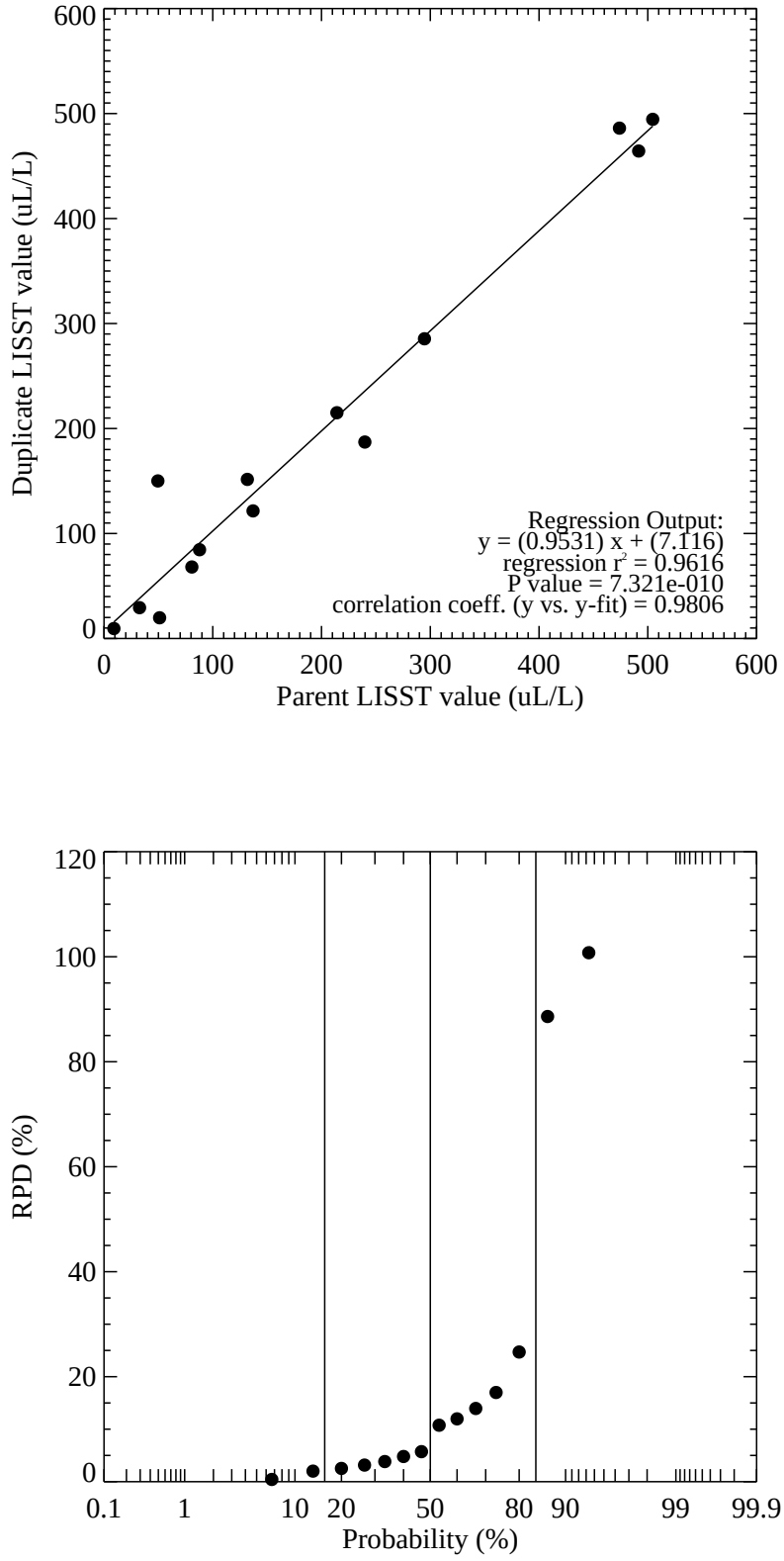
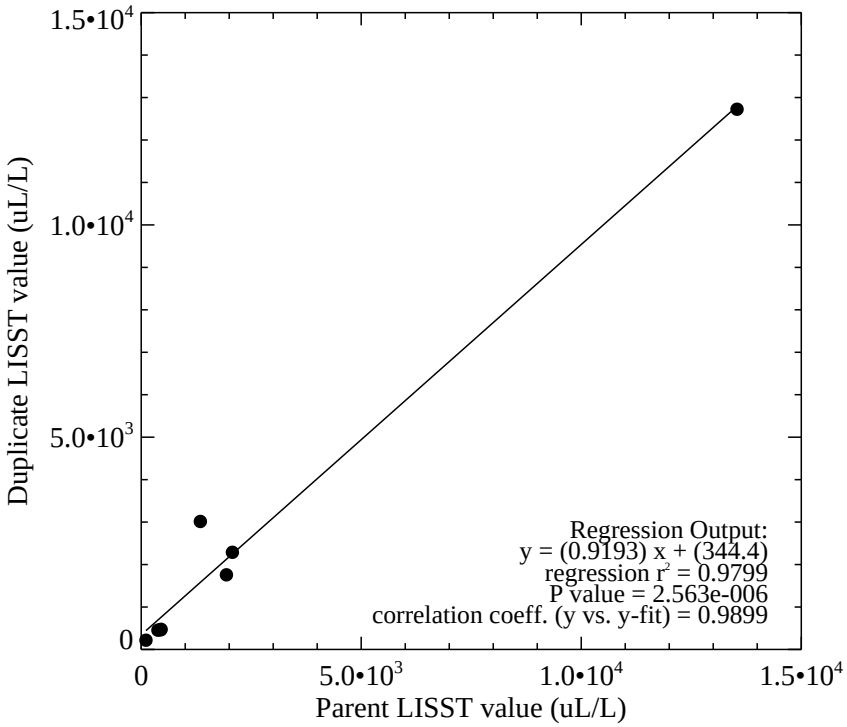


Figure 3-6. Particle volume duplicate results for settling column study.

Overall RPD calculated from duplicate volume data is 20.73 %.



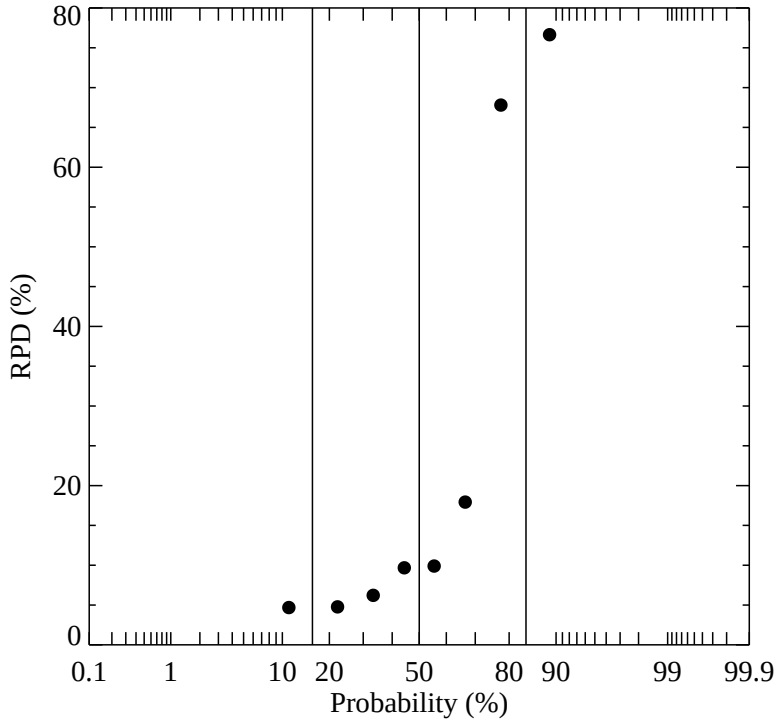


Figure 3-7. Particle volume duplicate results for serial dilution study.

Overall RPD for the dilution study data is 24.70 %

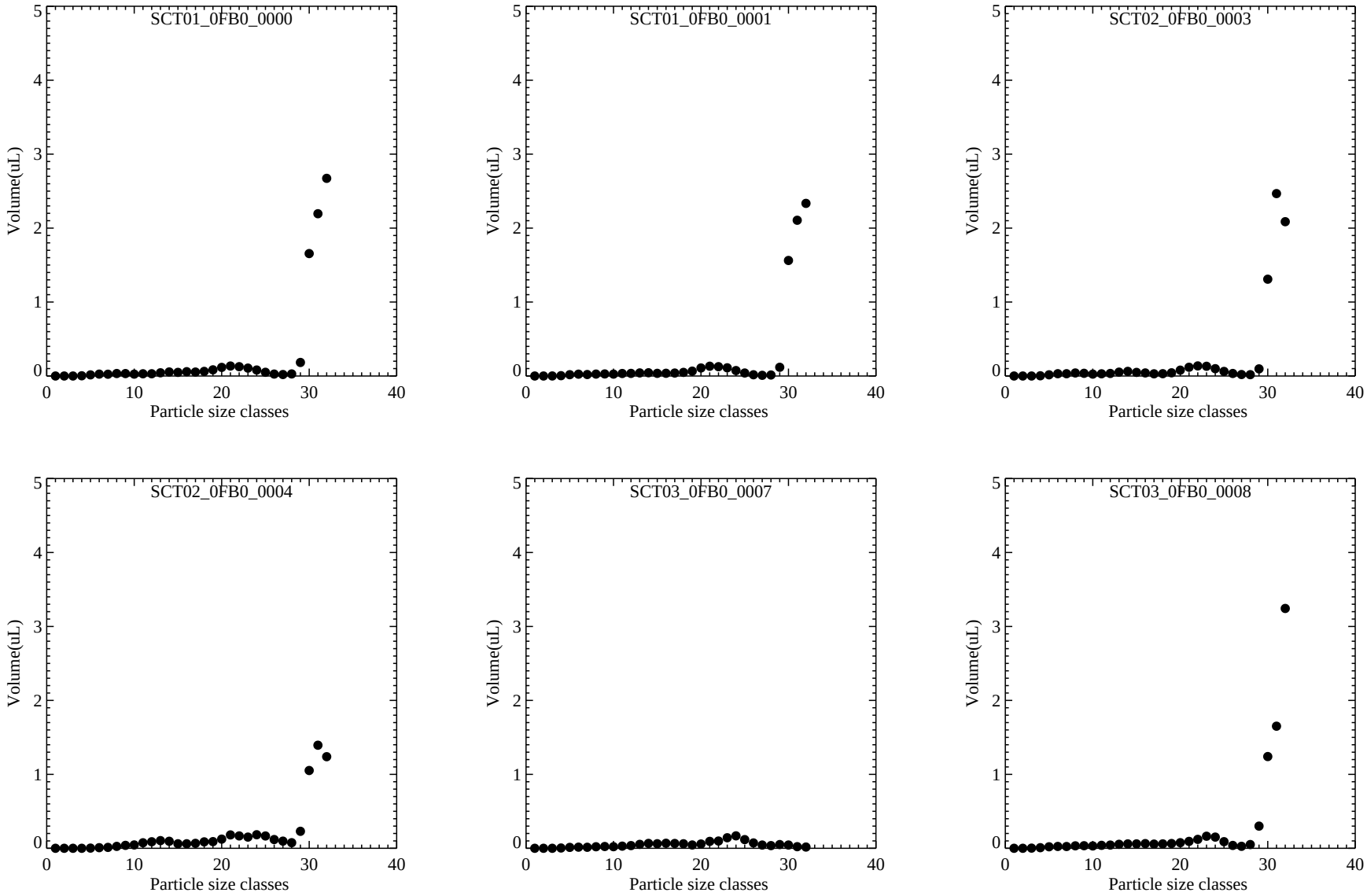


Figure 3-8a. Particle volume distribution in field blanks.

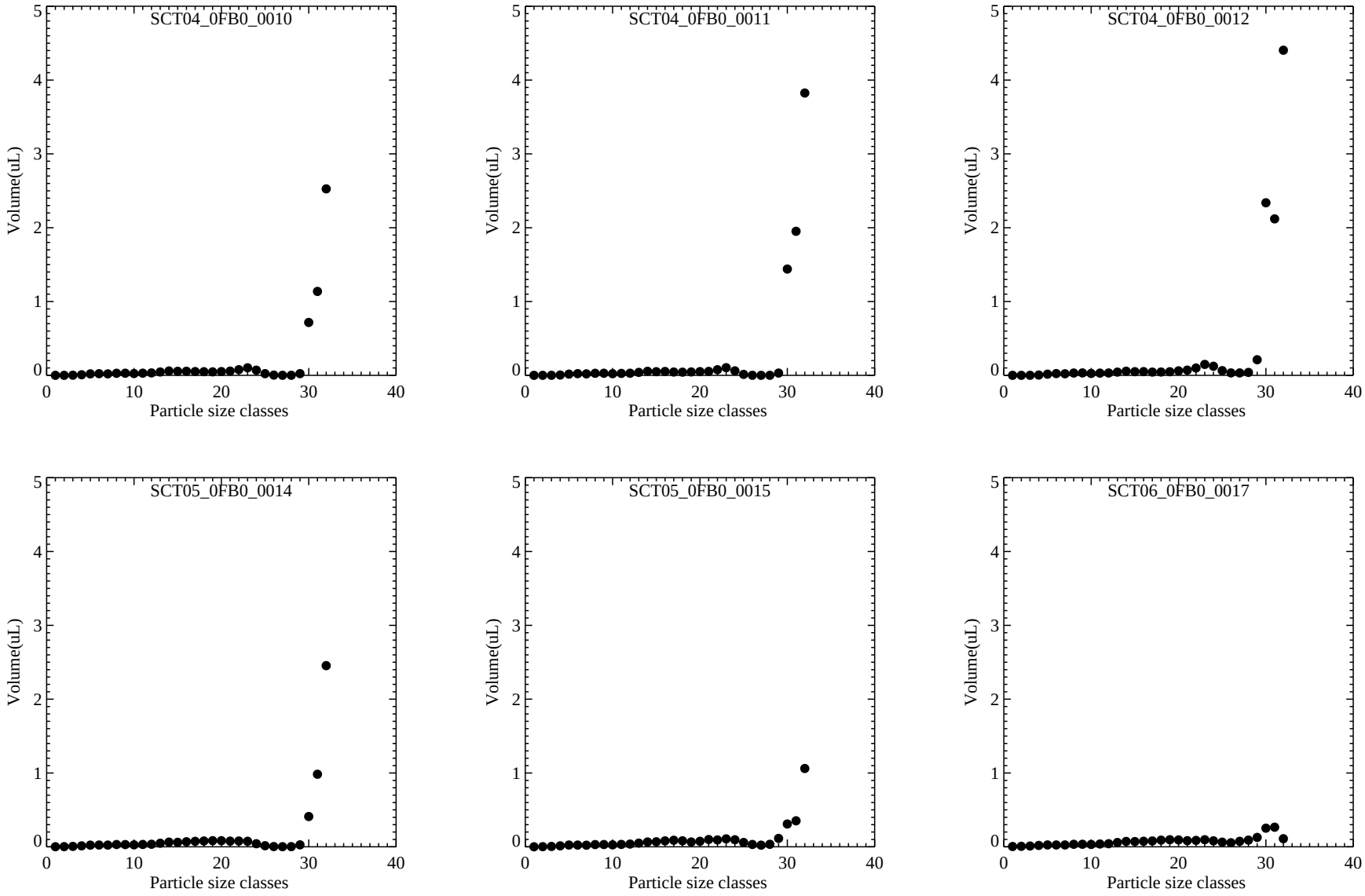


Figure 3-8b. Particle volume distribution in field blanks.

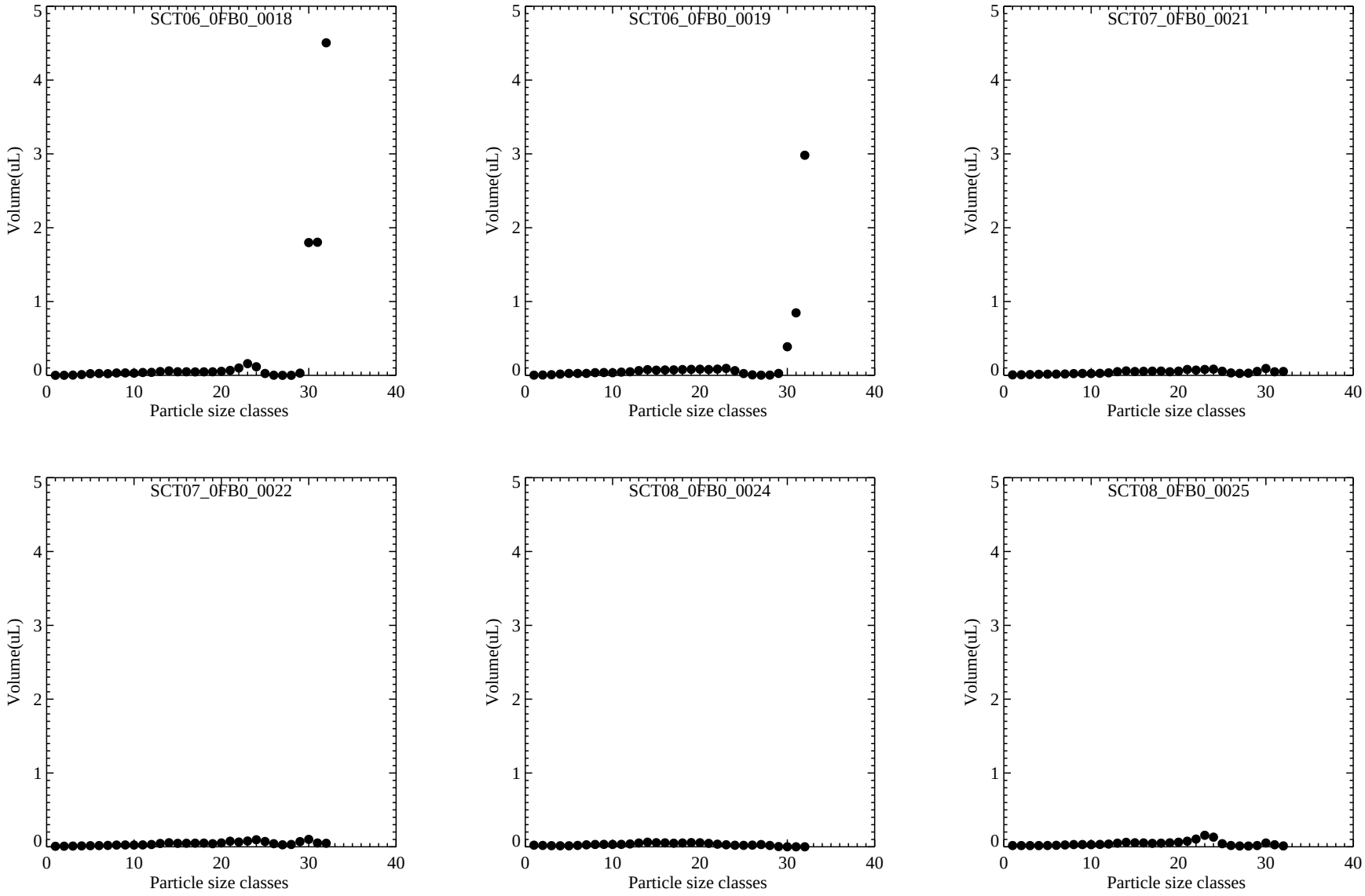


Figure 3-8c. Particle volume distribution in field blanks.

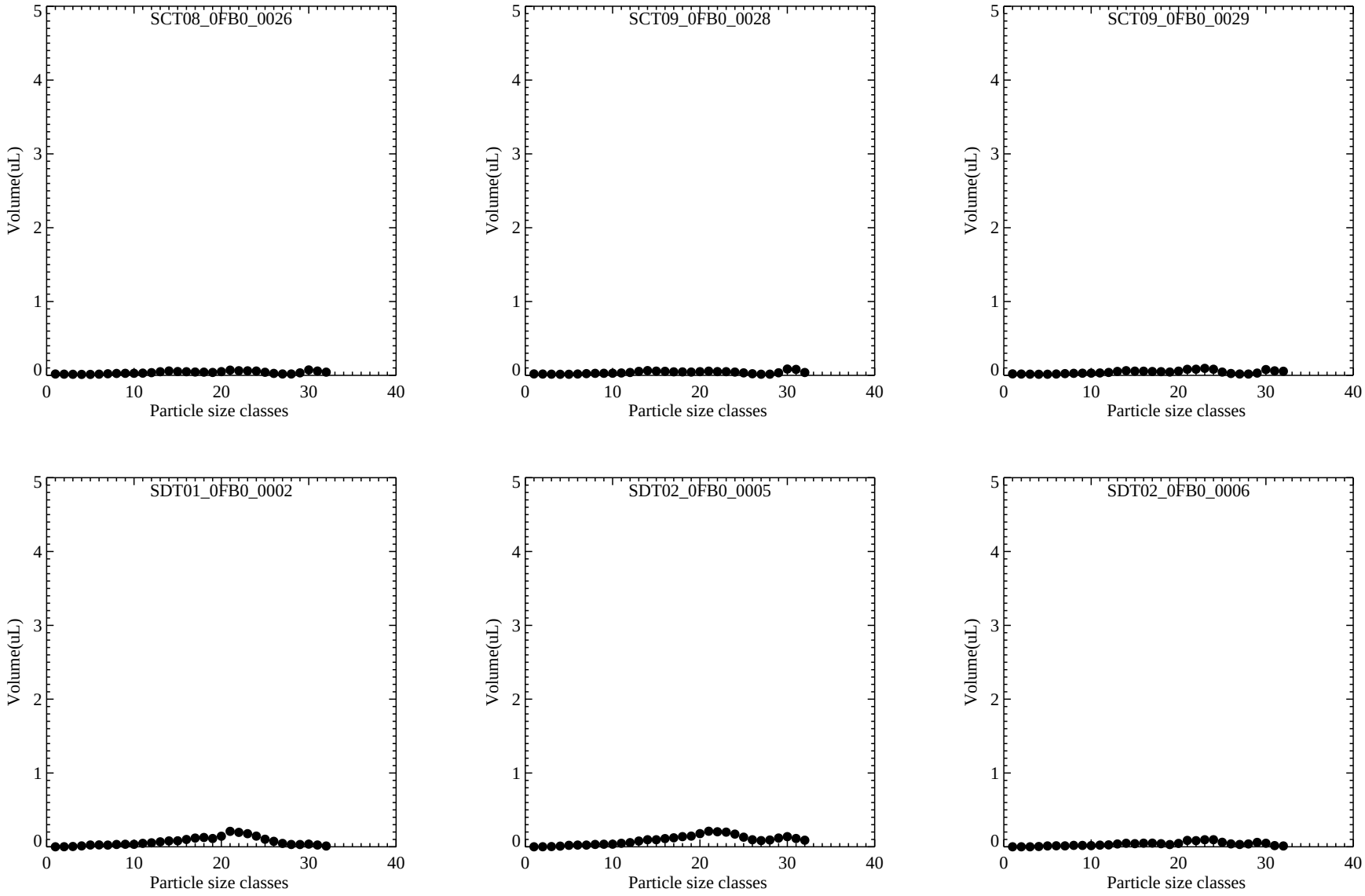


Figure 3-8d. Particle volume distribution in field blanks.

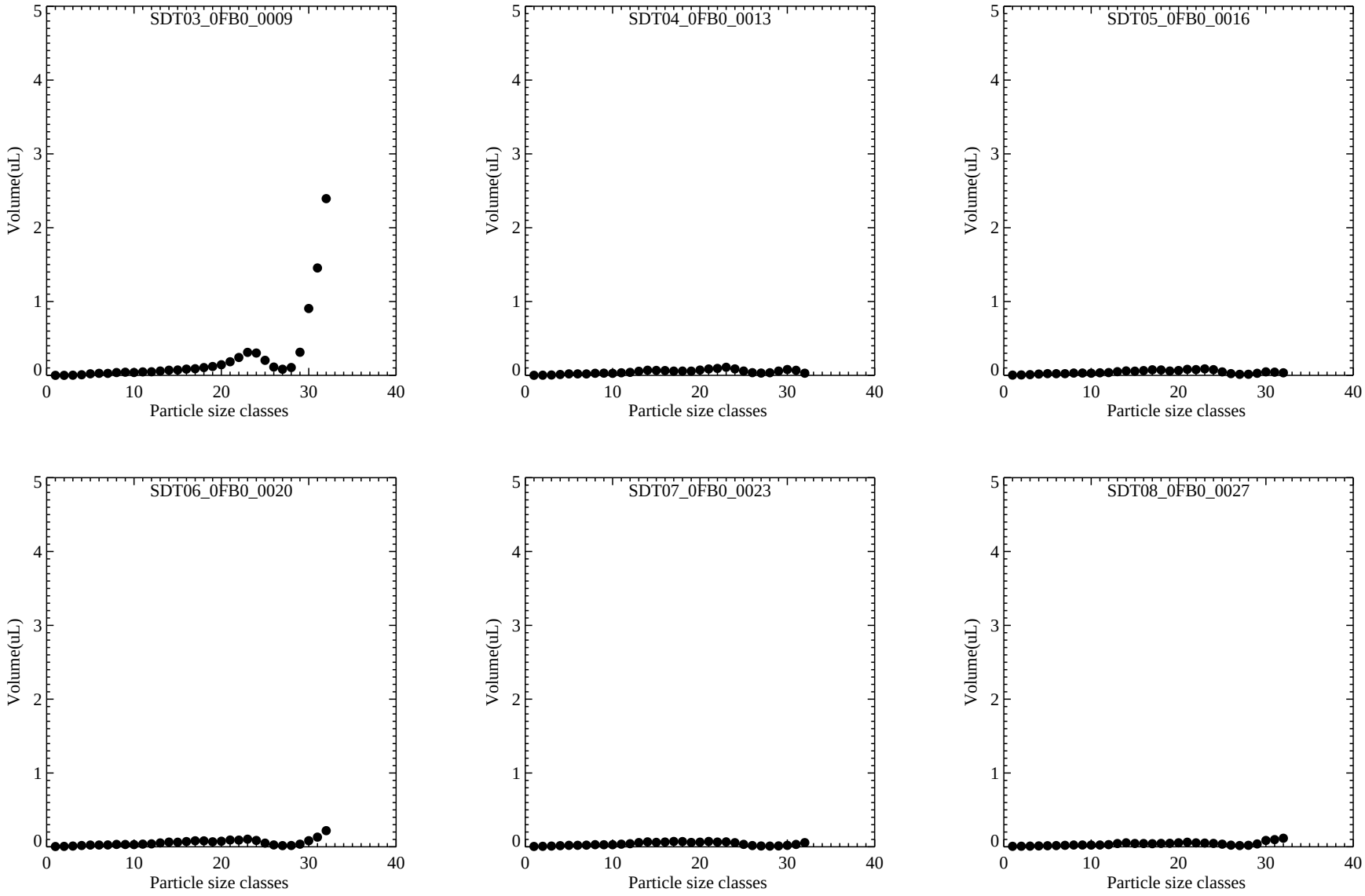


Figure 3-8e. Particle volume distribution in field blanks.

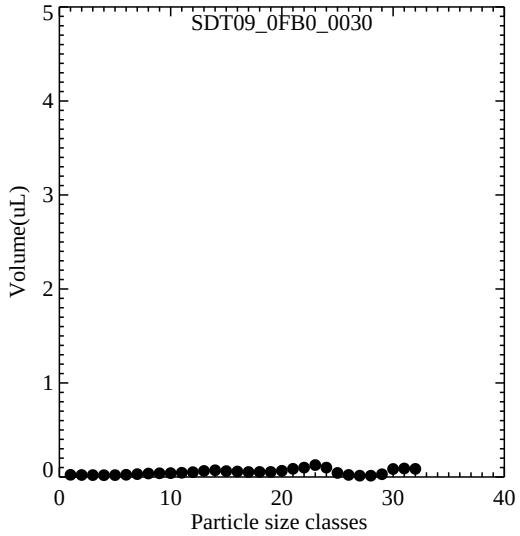


Figure 3-8f. Particle volume distribution in field blanks.

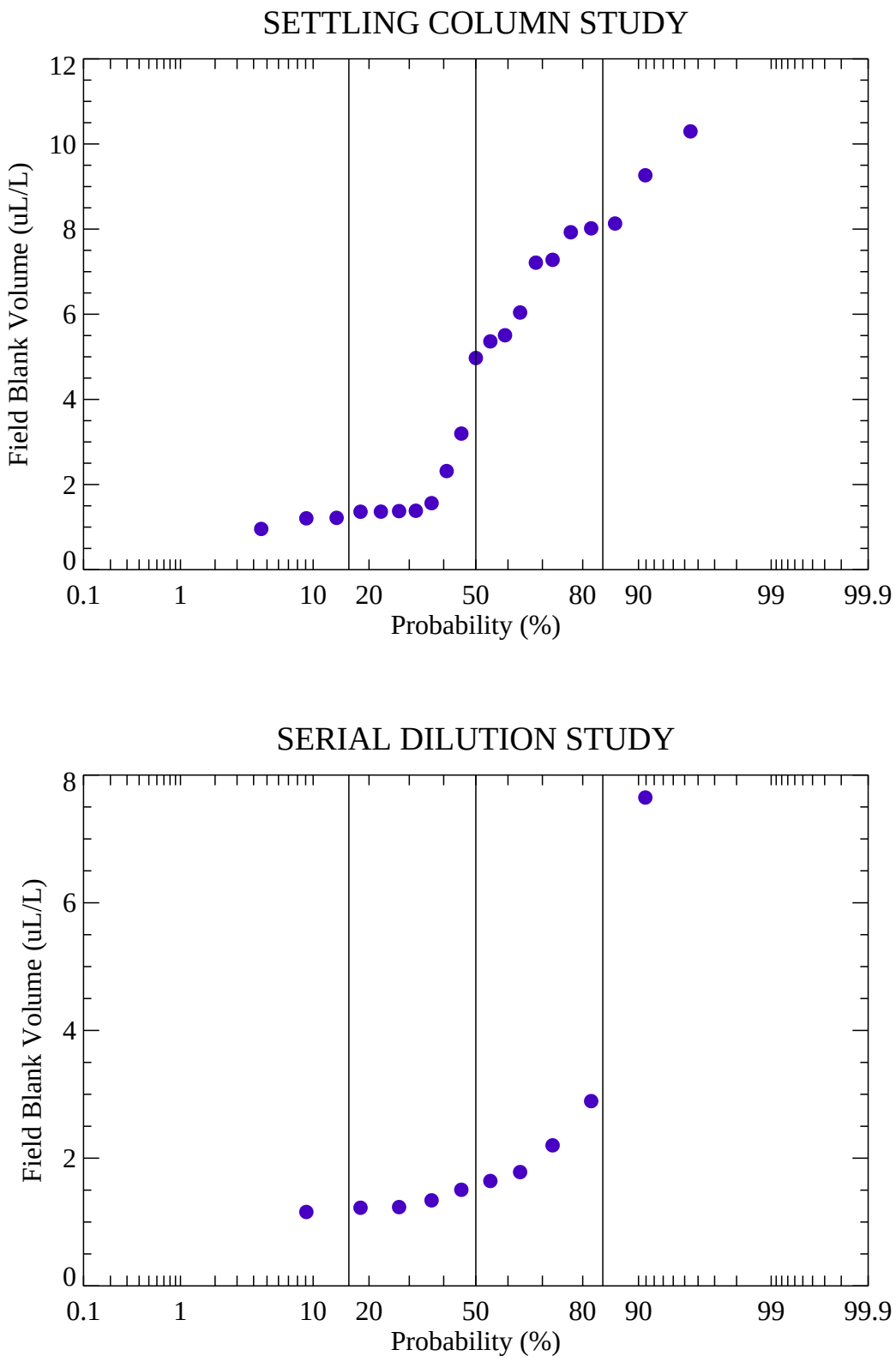


Figure 3-9. Particle volume probability plots for field blanks.

Field blank analysis.

.

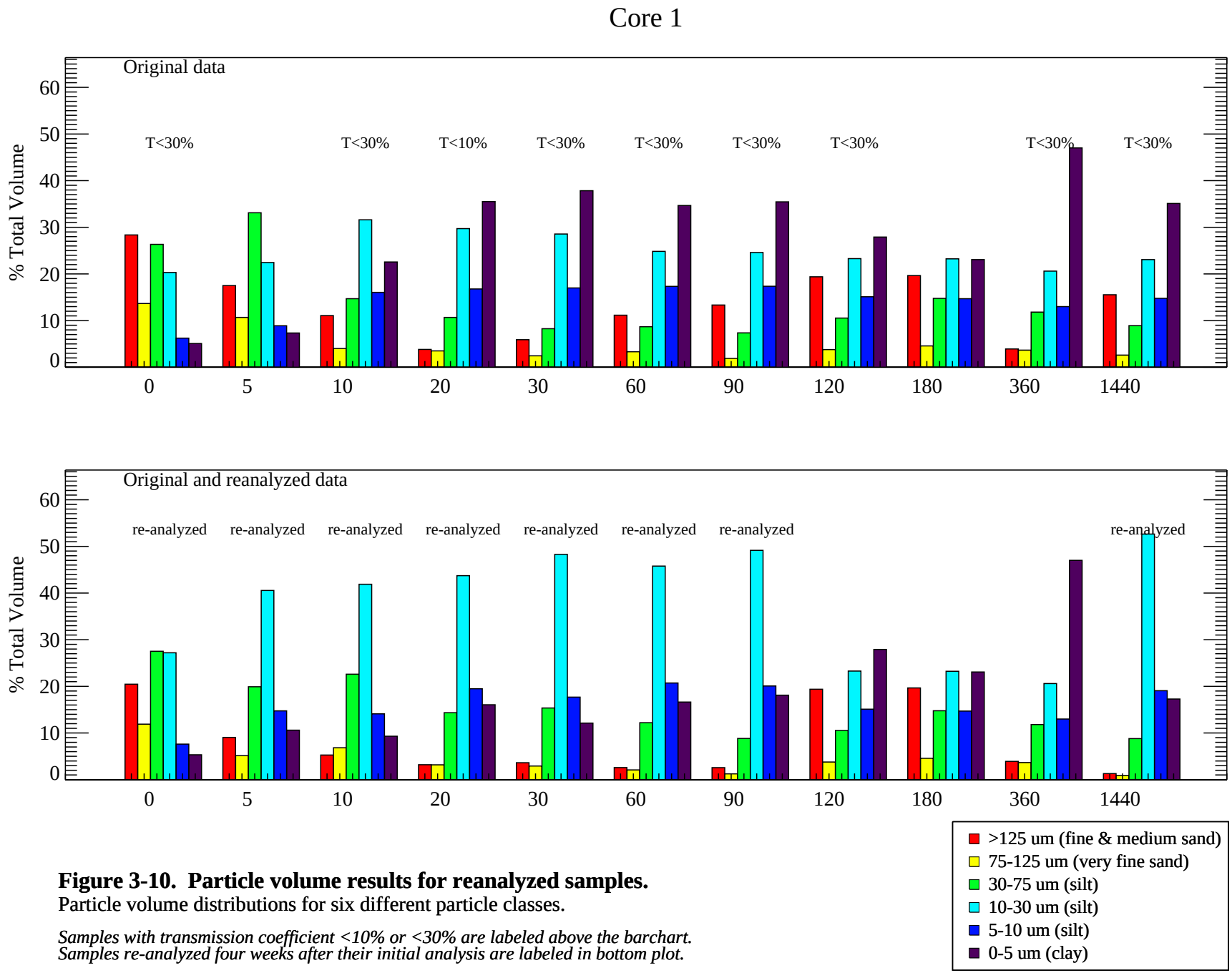


Figure 3-10. Particle volume results for reanalyzed samples.
Particle volume distributions for six different particle classes.

Samples with transmission coefficient <10% or <30% are labeled above the barchart.
Samples re-analyzed four weeks after their initial analysis are labeled in bottom plot.

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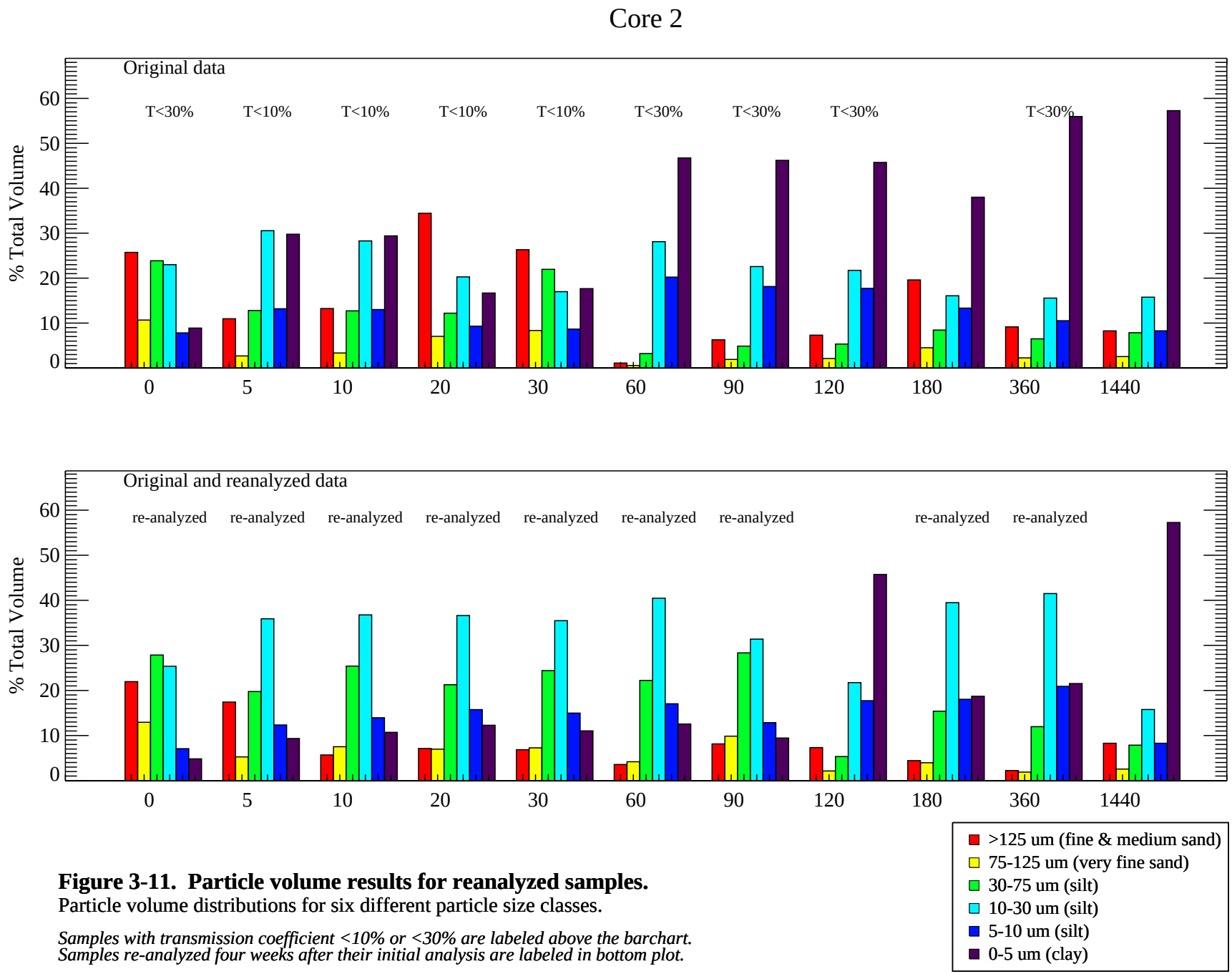

Figure 3-11. Particle volume results for reanalyzed samples.
Particle volume distributions for six different particle size classes.

Samples with transmission coefficient <10% or <30% are labeled above the barchart.
Samples re-analyzed four weeks after their initial analysis are labeled in bottom plot.

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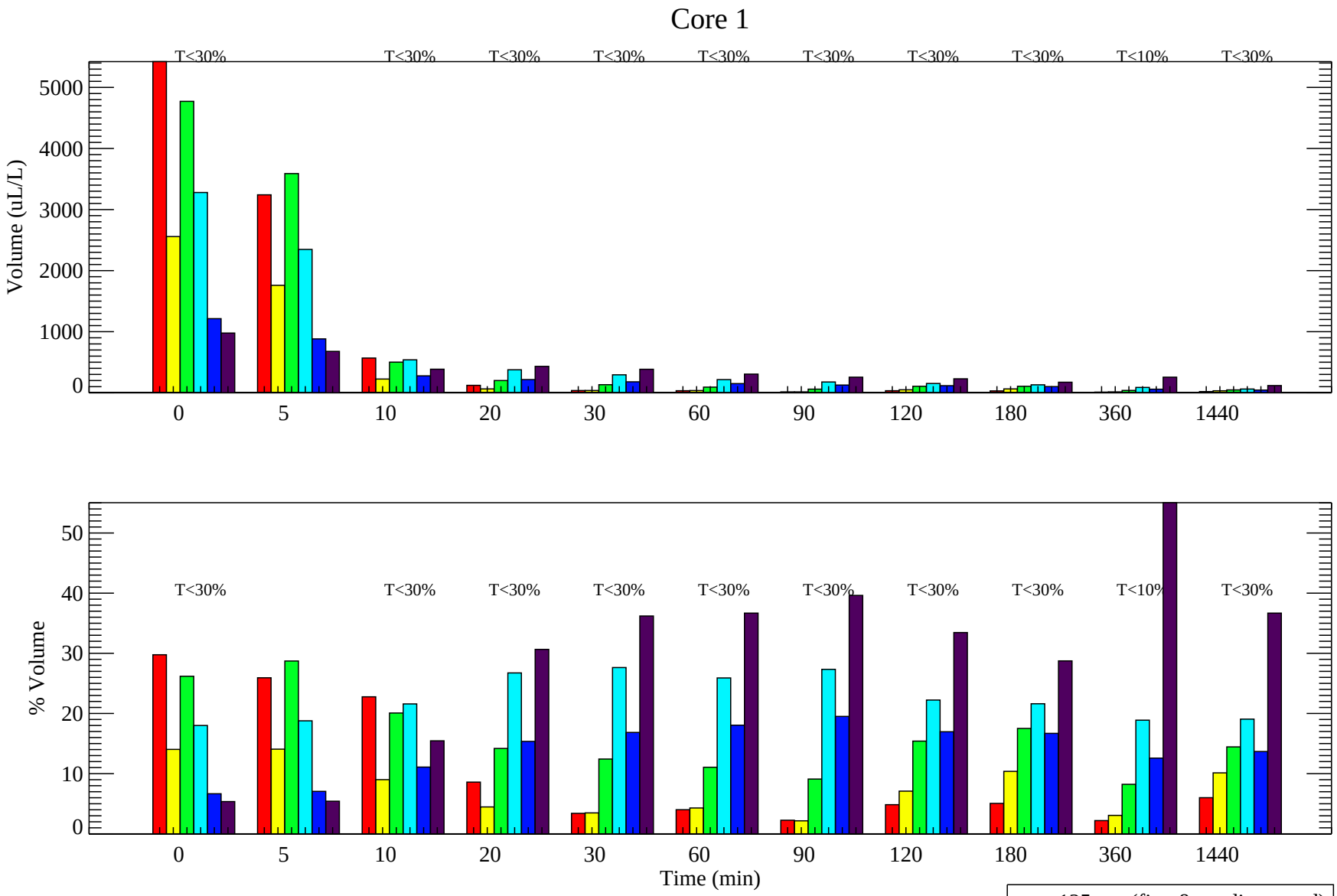

Figure 4-1a. Particle volume distributions in column settling tests.
Port averaged LISST data is shown on volume bases (top) and in % of sample volume (bottom).

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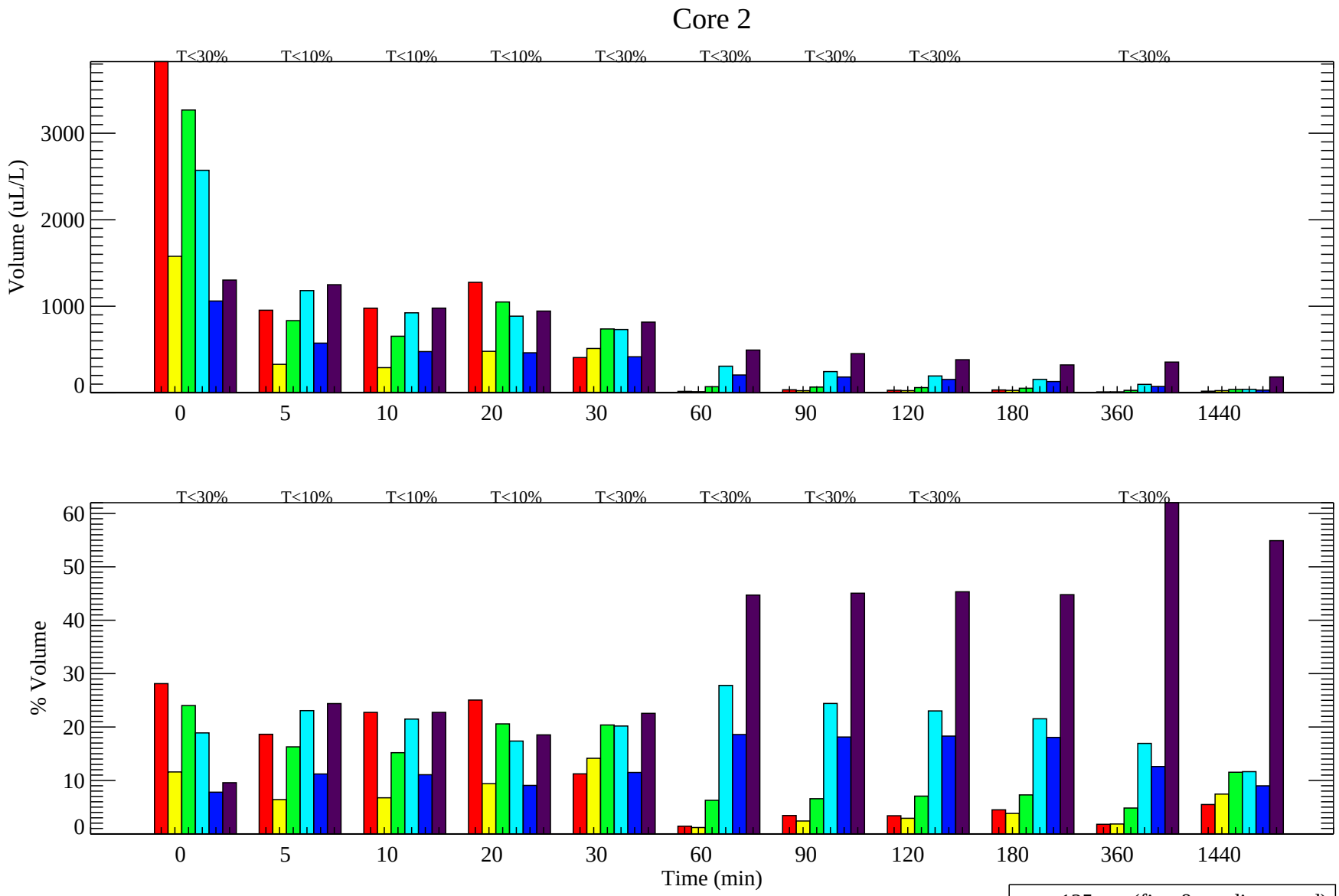

Figure 4-1b. Particle volume distributions in column settling tests.
Port averaged LISST data is shown on volume bases (top) and in % of sample volume (bottom).

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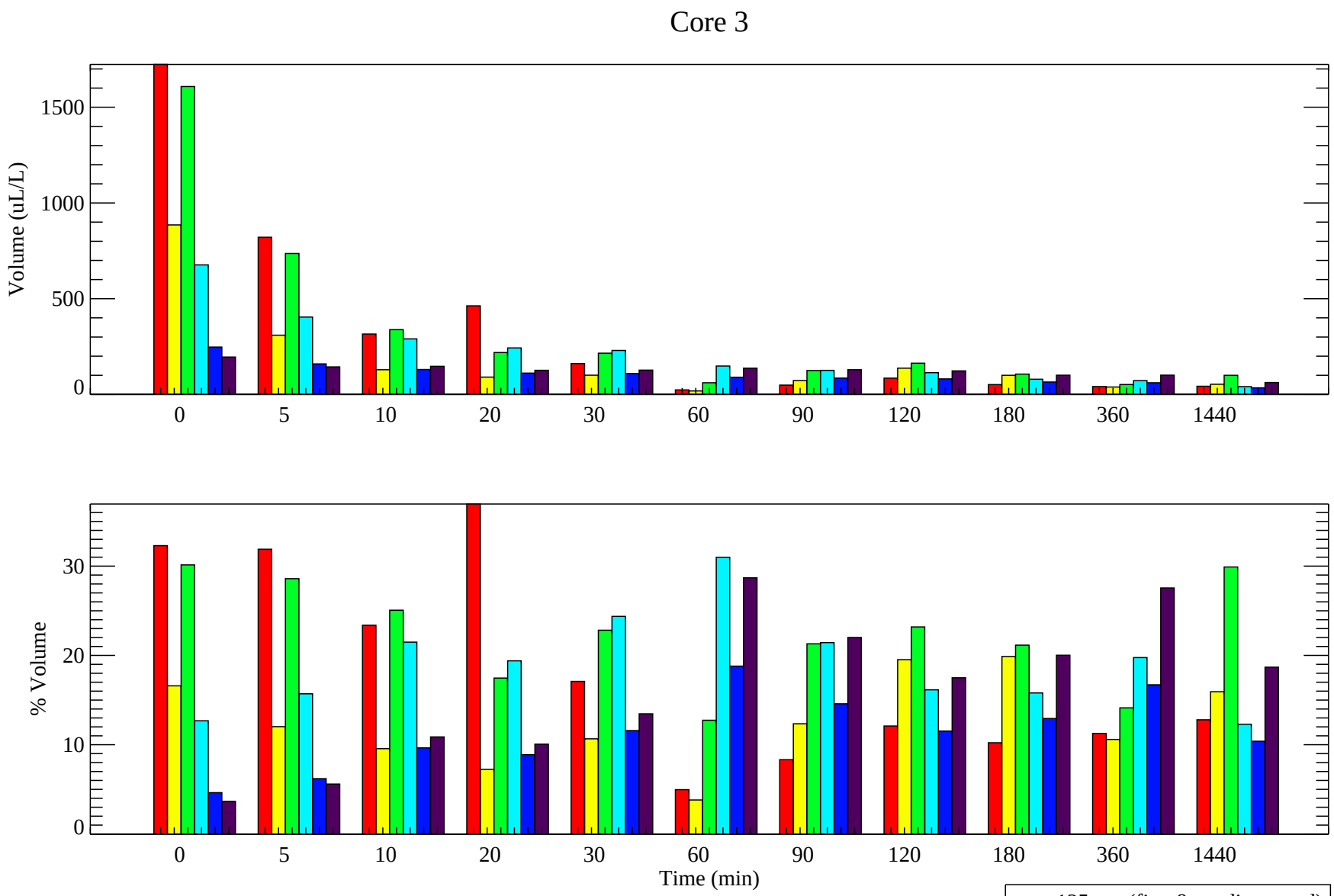

Figure 4-1c. Particle volume distributions in column settling tests.
Port averaged LISST data is shown on volume bases (top) and in % of sample volume (bottom).

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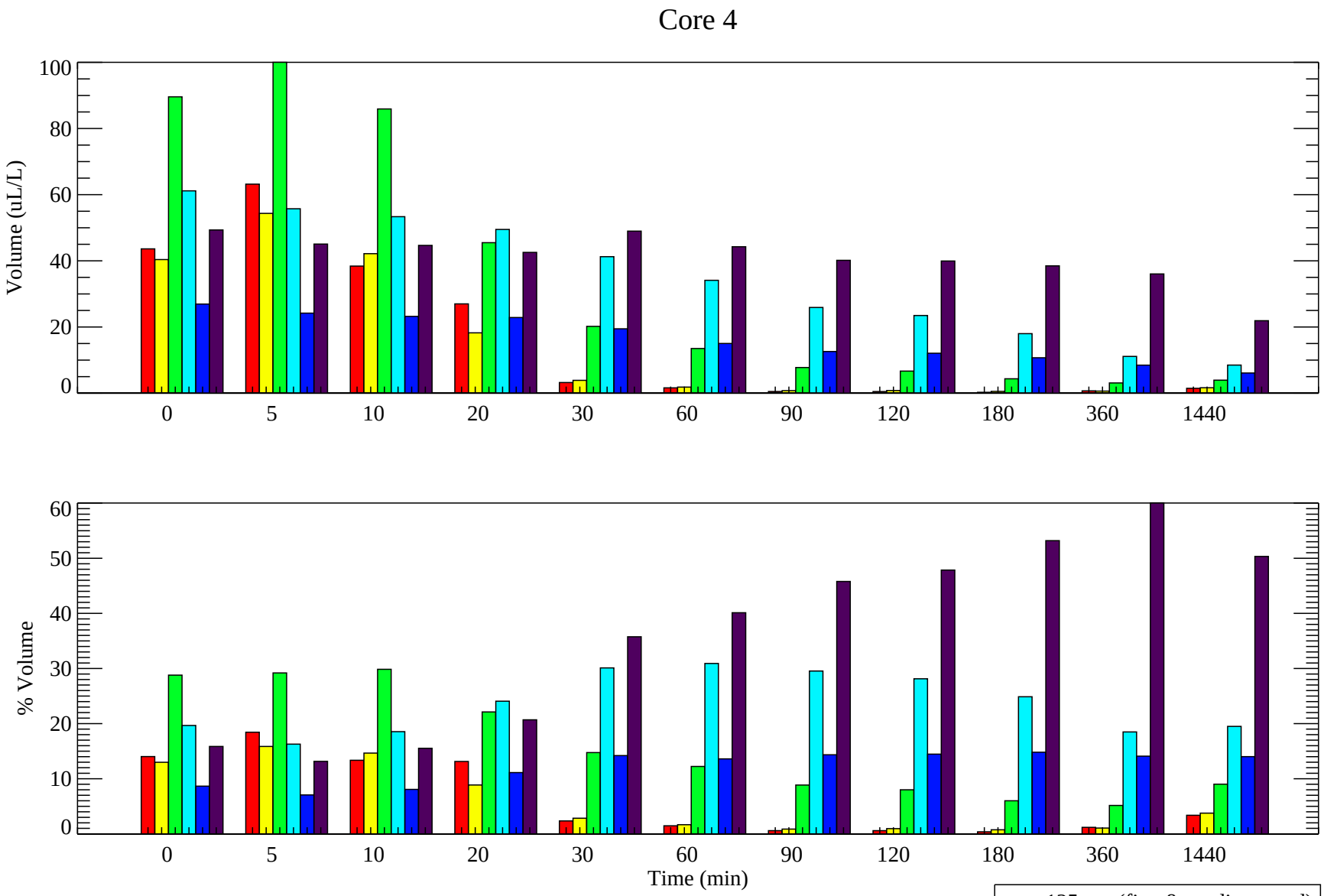

Figure 4-1d. Particle volume distributions in column settling tests.
Port averaged LISST data is shown on volume bases (top) and in % of sample volume (bottom).

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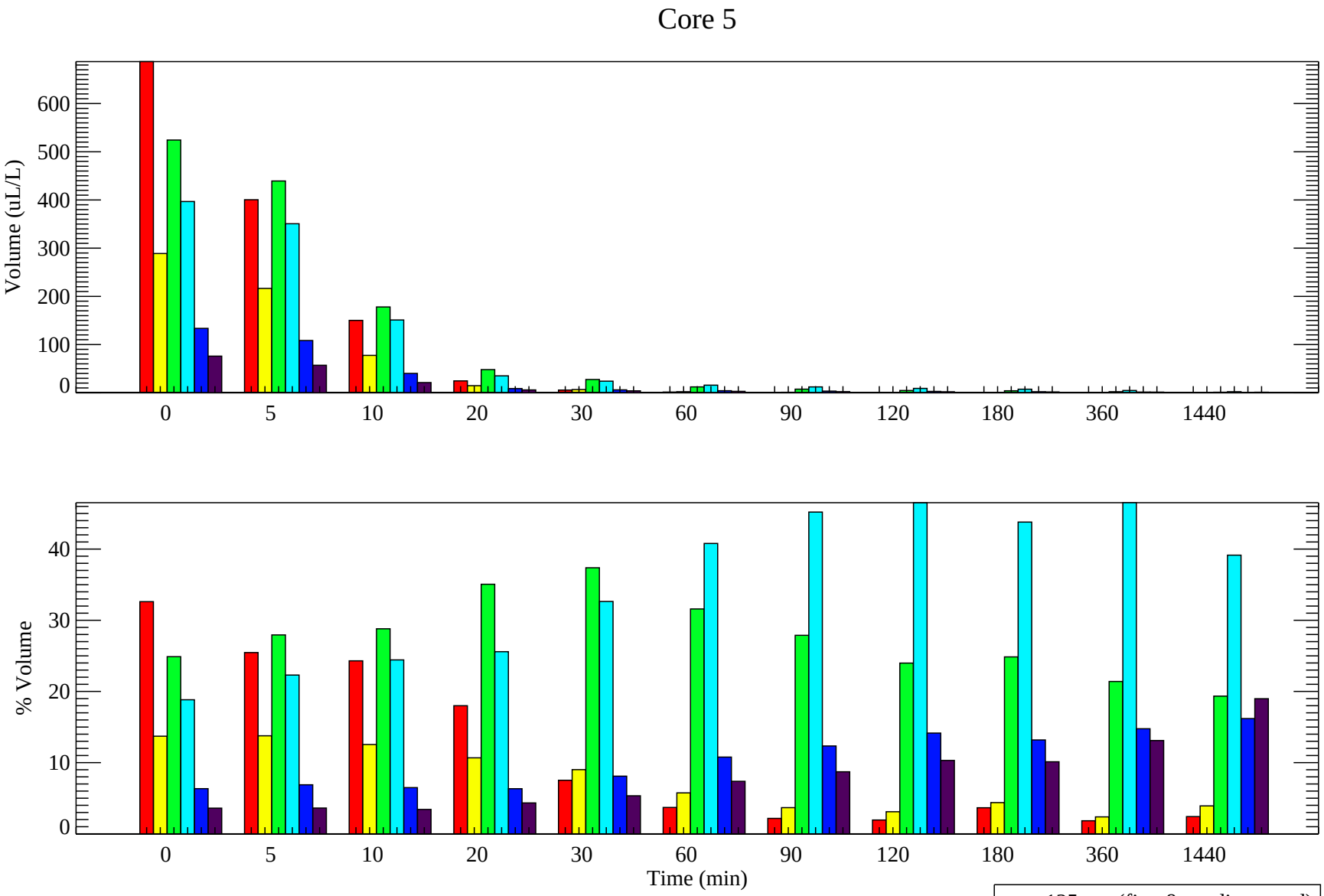

Figure 4-1e. Particle volume distributions in column settling tests.
Port averaged LISST data is shown on volume bases (top) and in % of sample volume (bottom).

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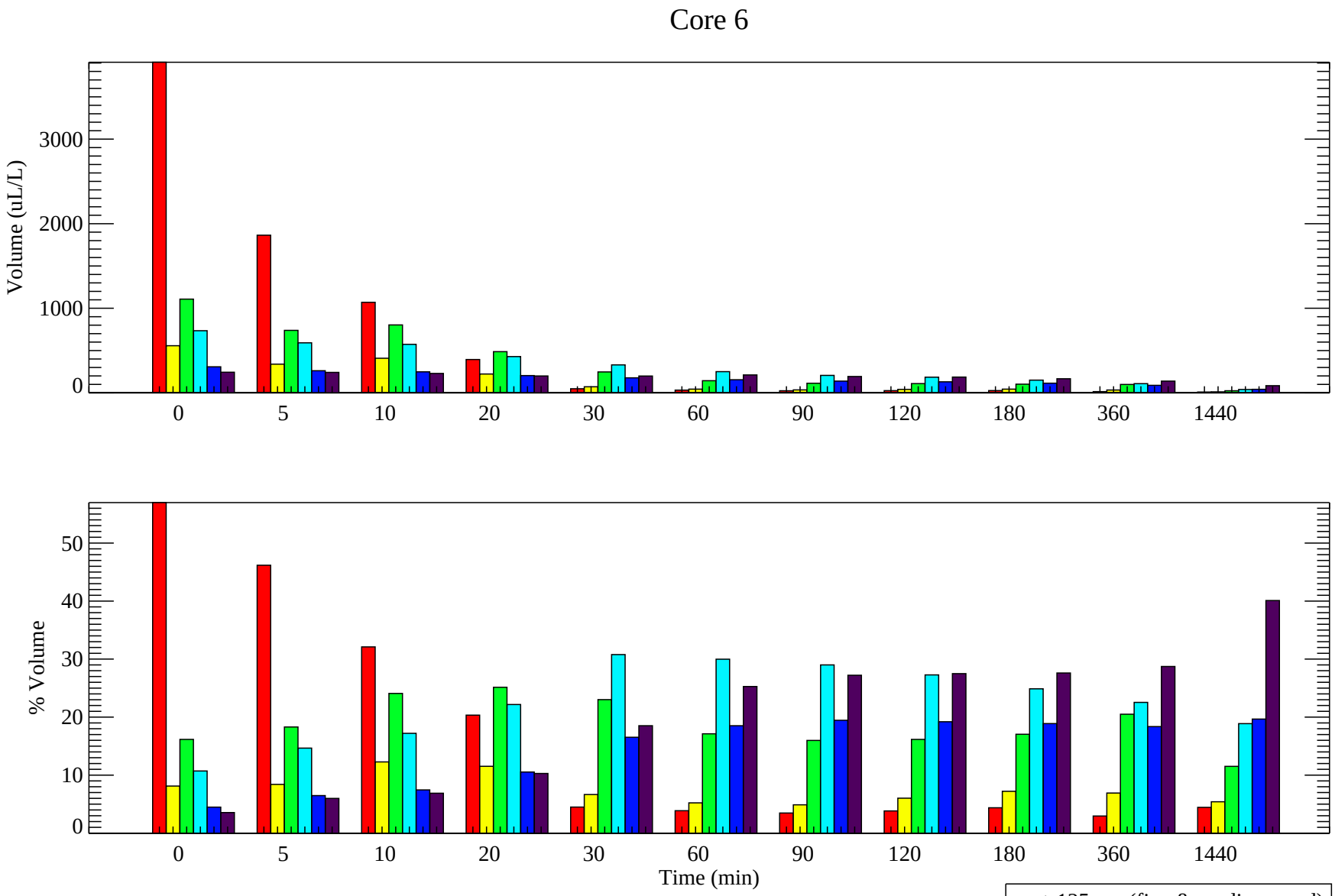

Figure 4-1f. Particle volume distributions in column settling tests.
Port averaged LISST data is shown on volume bases (top) and in % of sample volume (bottom).

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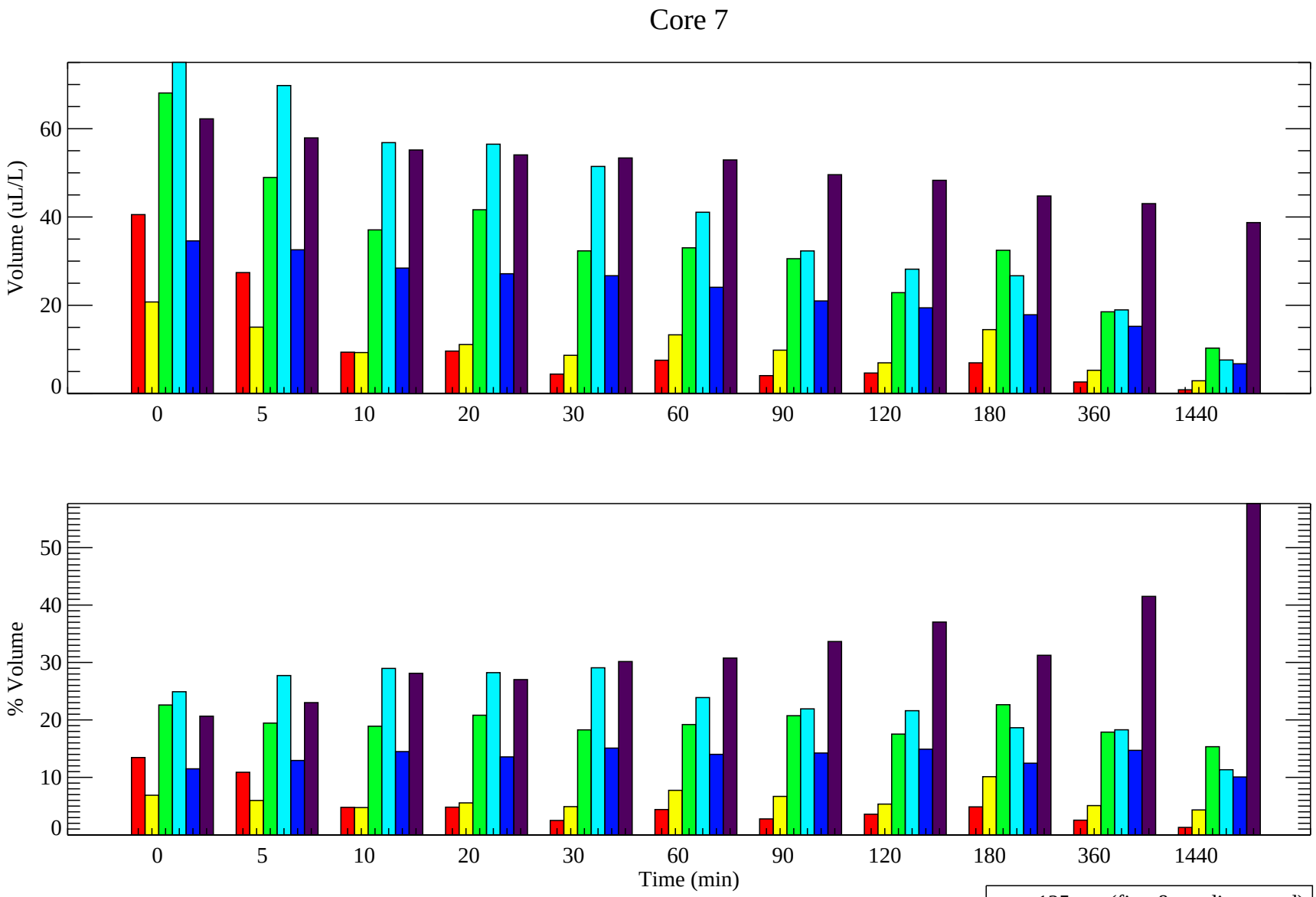

Figure 4-1g. Particle volume distributions in column settling tests.
Port averaged LISST data is shown on volume bases (top) and in % of sample volume (bottom).

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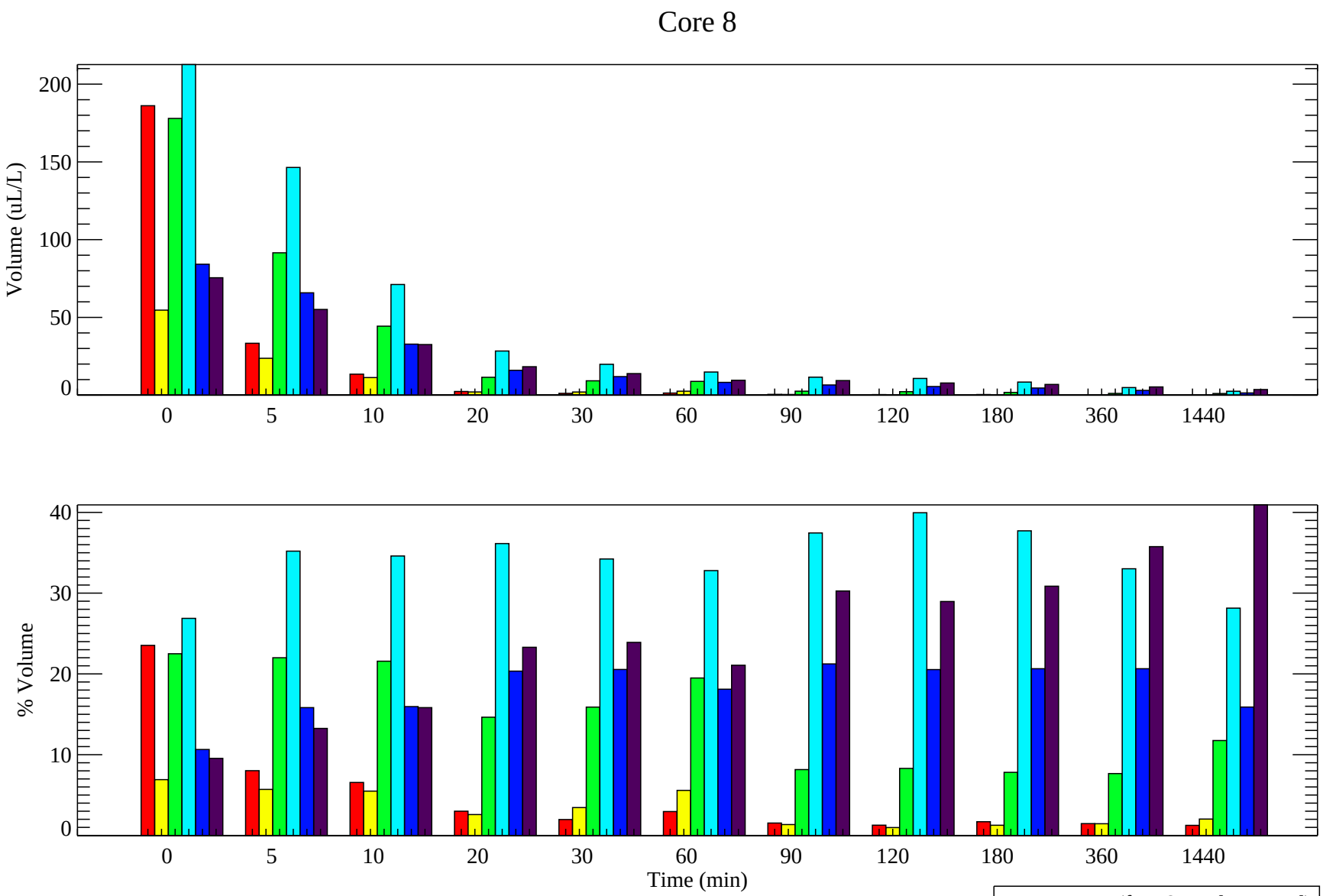

Figure 4-1h. Particle volume distributions in column settling tests.
Port averaged LISST data is shown on volume bases (top) and in % of sample volume (bottom).

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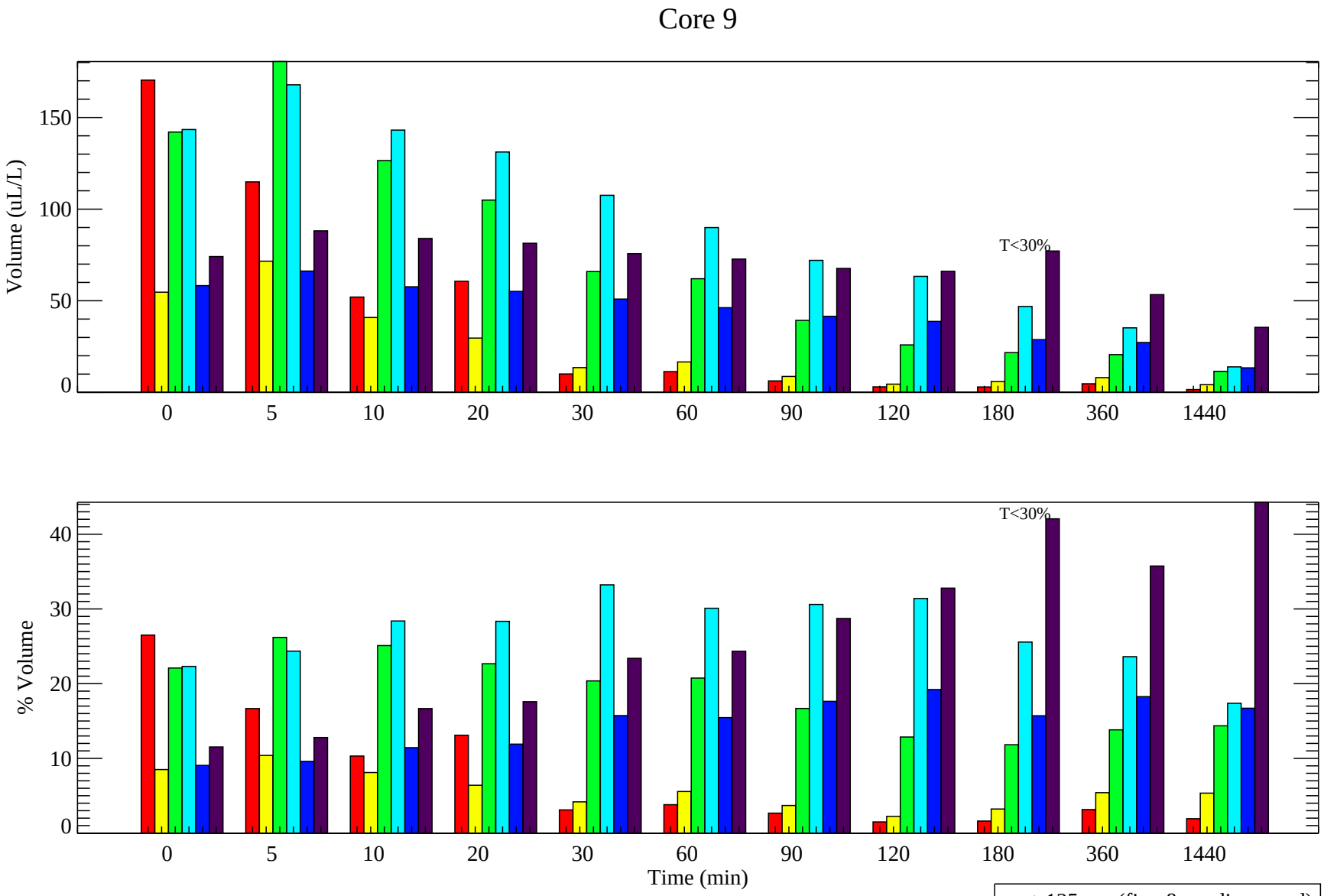

Figure 4-1i. Particle volume distributions in column settling tests.
Port averaged LISST data is shown on volume bases (top) and in % of sample volume (bottom).

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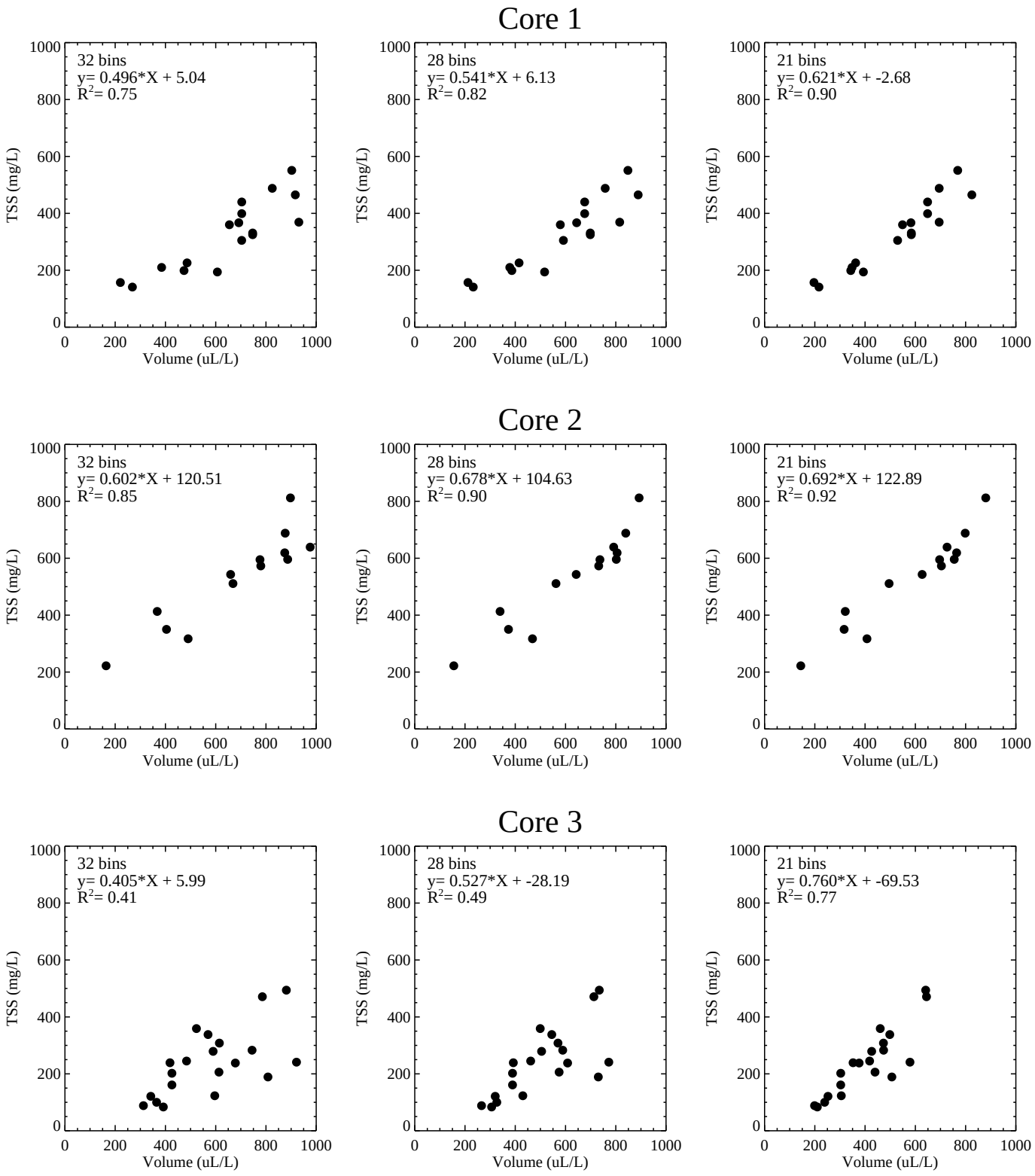

Figure 4-2a. TSS correlation with particle volume by sorted bins.

Volume data shown was collected after 20 minutes of settling.

Posted is the number of bins used to calculate particle volumes and regression output. Volumes > 1000 uL/L not shown.

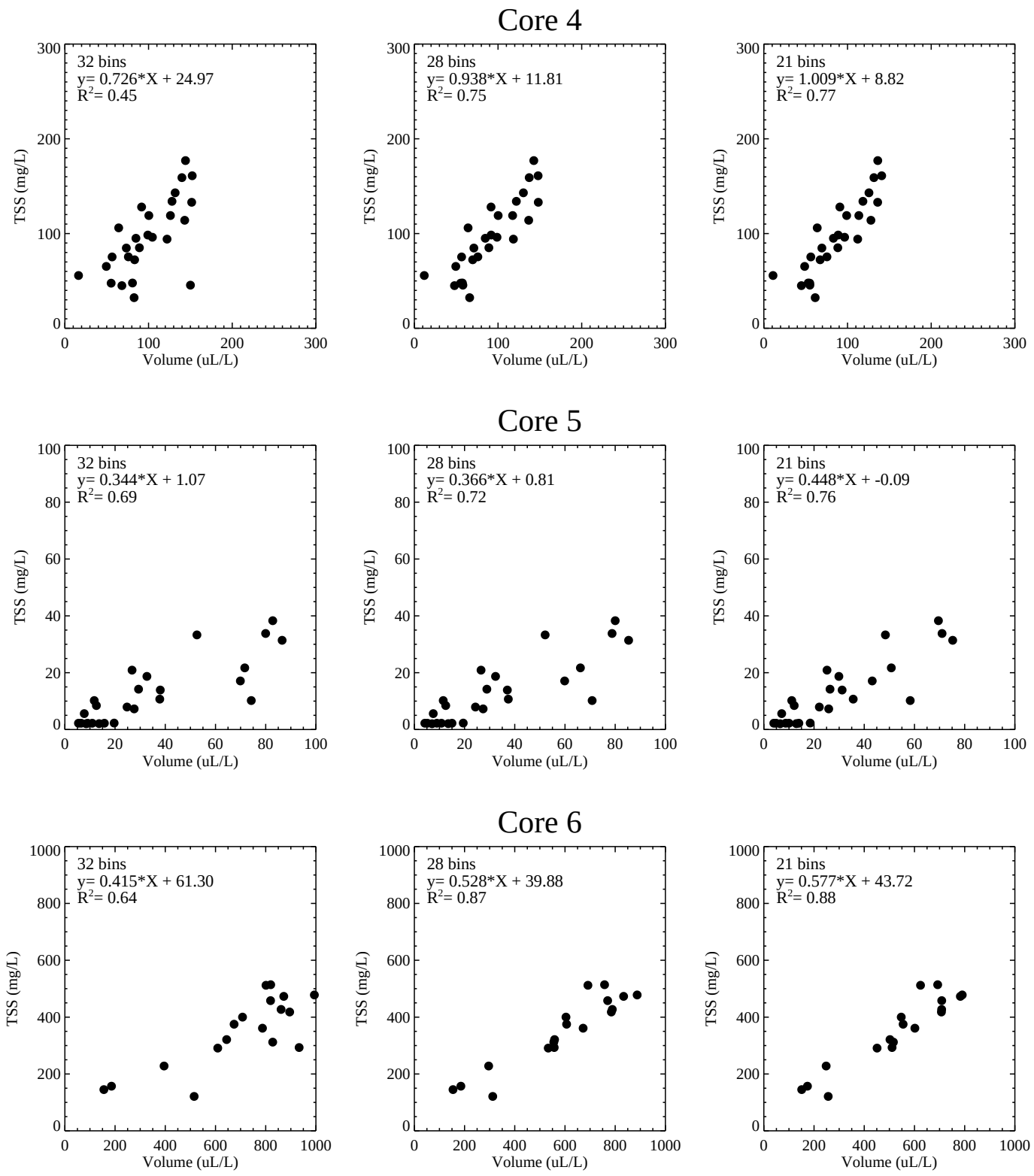

Figure 4-2b. TSS correlation with particle volume by sorted bins.

Volume data shown was collected after 20 minutes of settling.

Posted is the number of bins used to calculate particle volumes and regression output. Volumes > 1000 uL/L not shown.

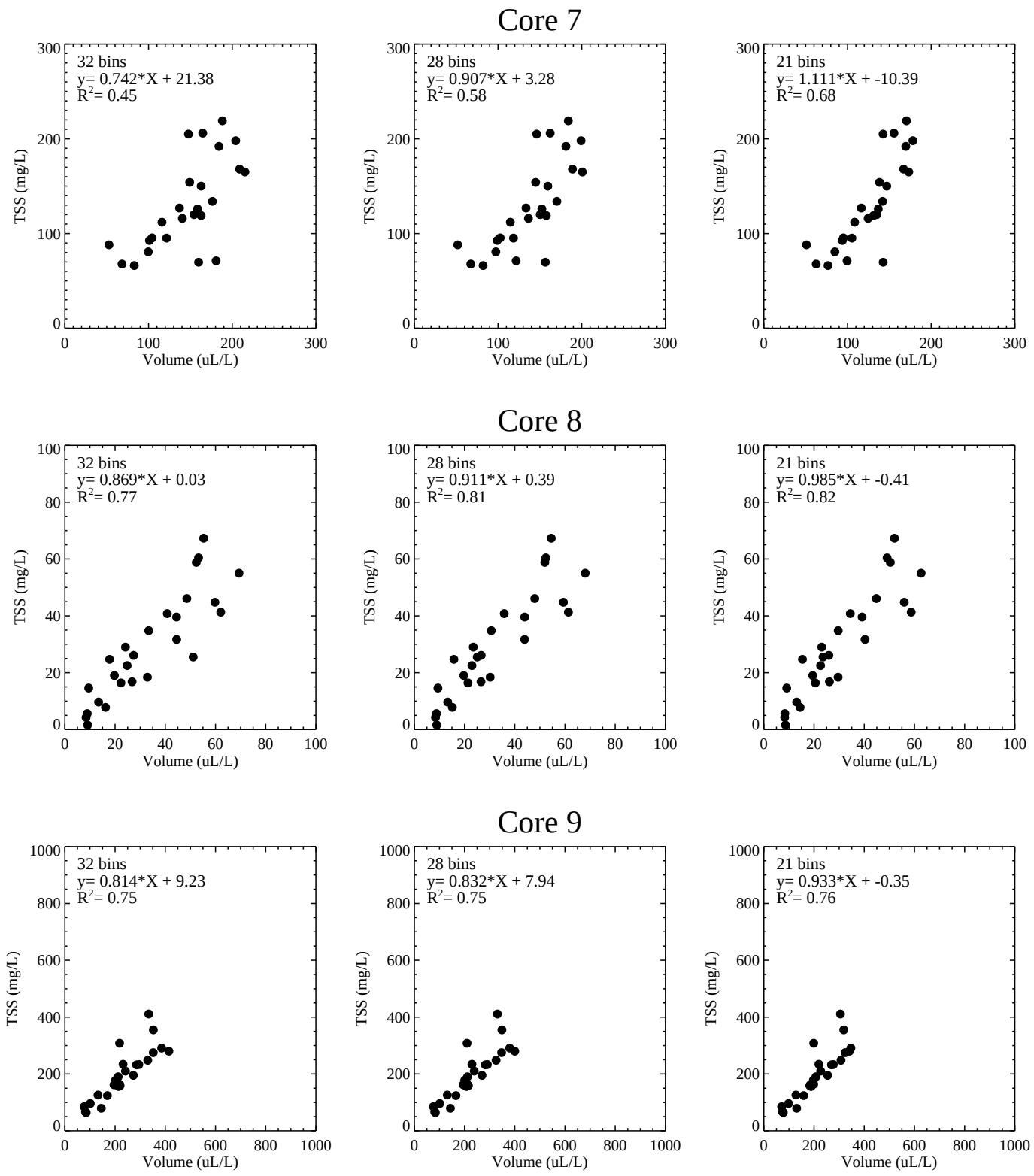

Figure 4-2c. TSS correlation with particle volume by sorted bins.

Volume data shown was collected after 20 minutes of settling.

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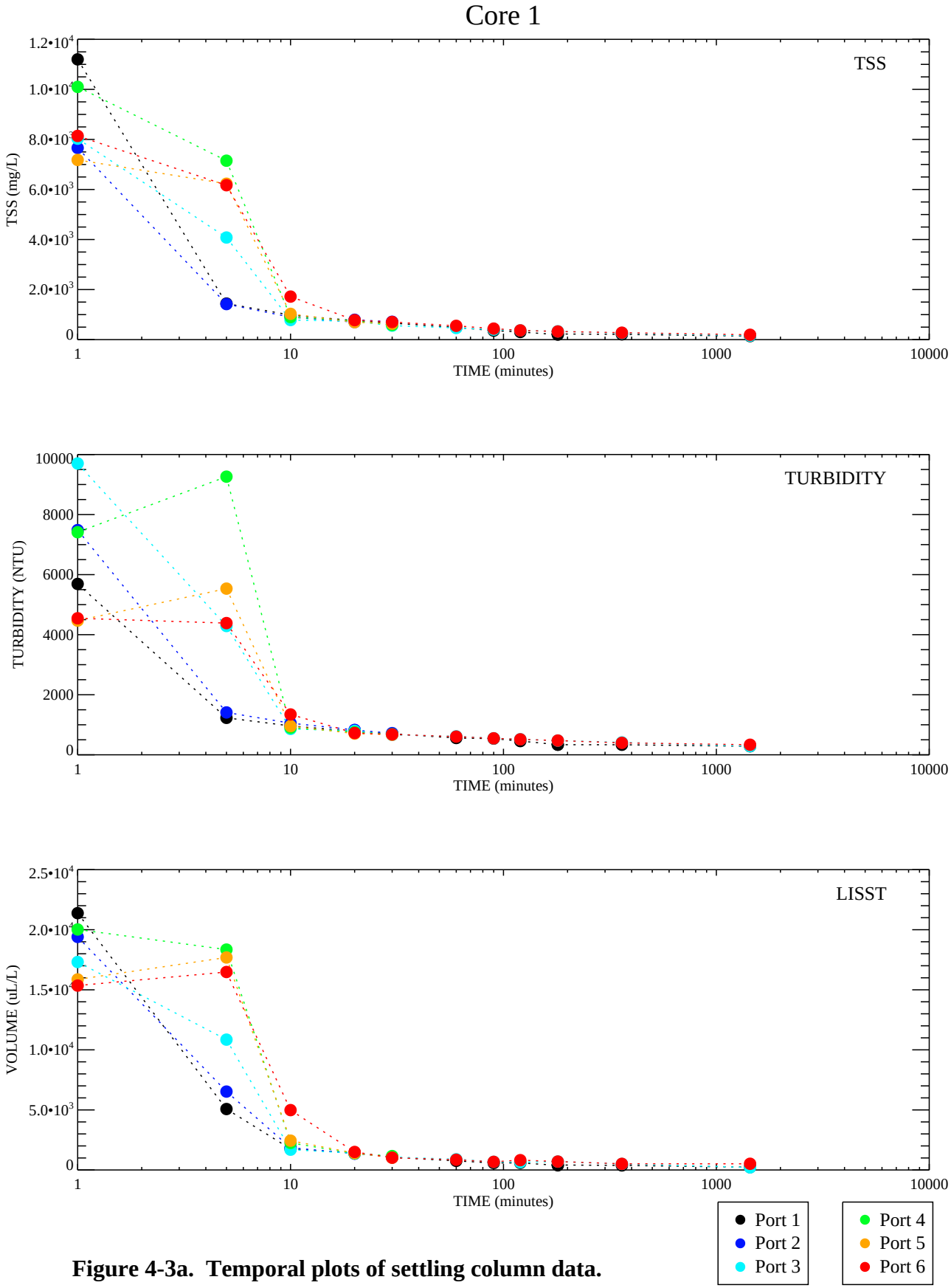

Figure 4-3a. Temporal plots of settling column data.

Temporal plots of settling test data.

For simplicity, data shown at proposed (not actual) sampling times.
Innitial sampling time was set to 1 minute after the beginning of the study.

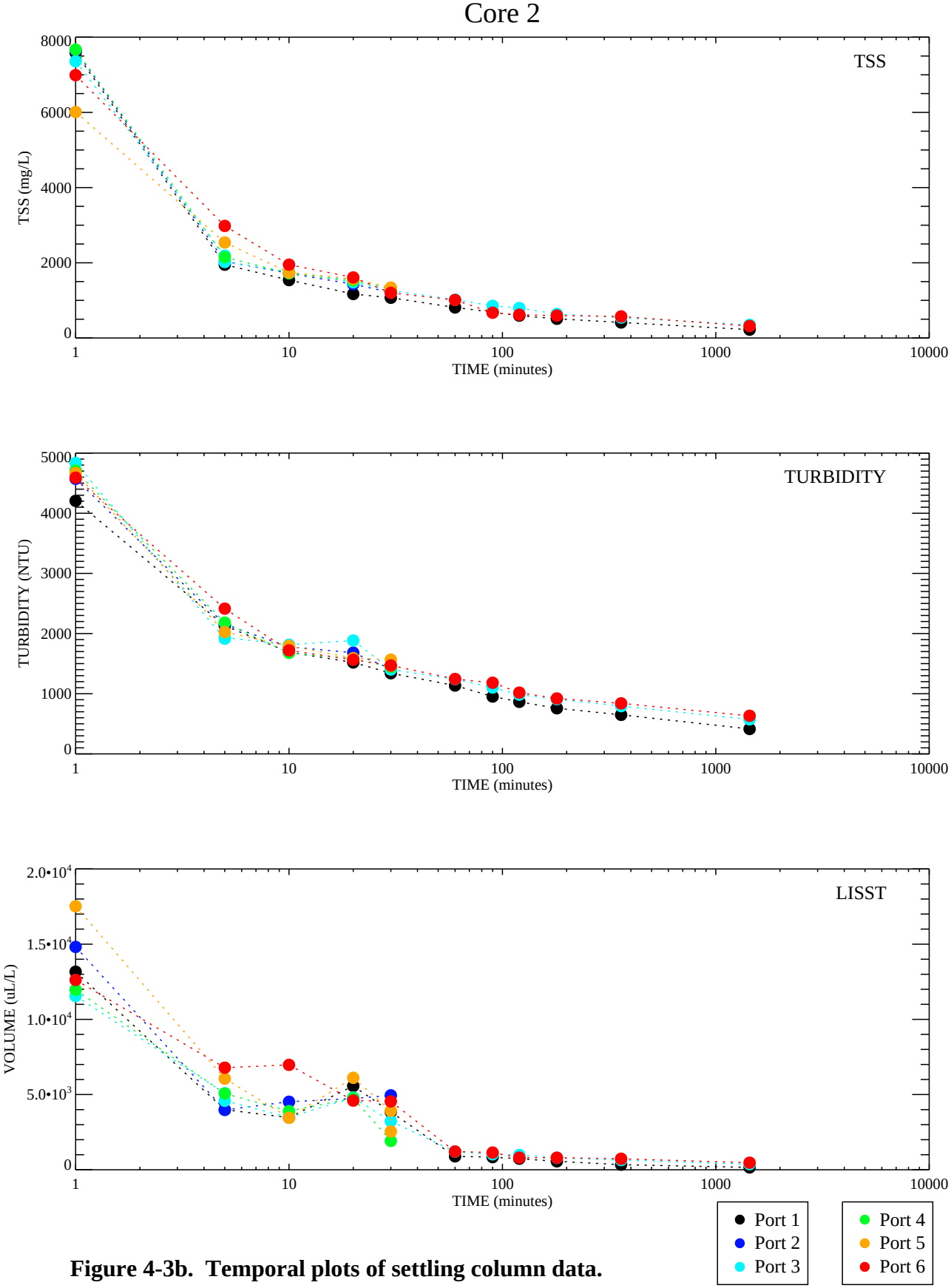

Figure 4-3b. Temporal plots of settling column data.

Temporal plots of settling test data.

For simplicity, data shown at proposed (not actual) sampling times.
Innitial sampling time was set to 1 minute after the beginning of the study.

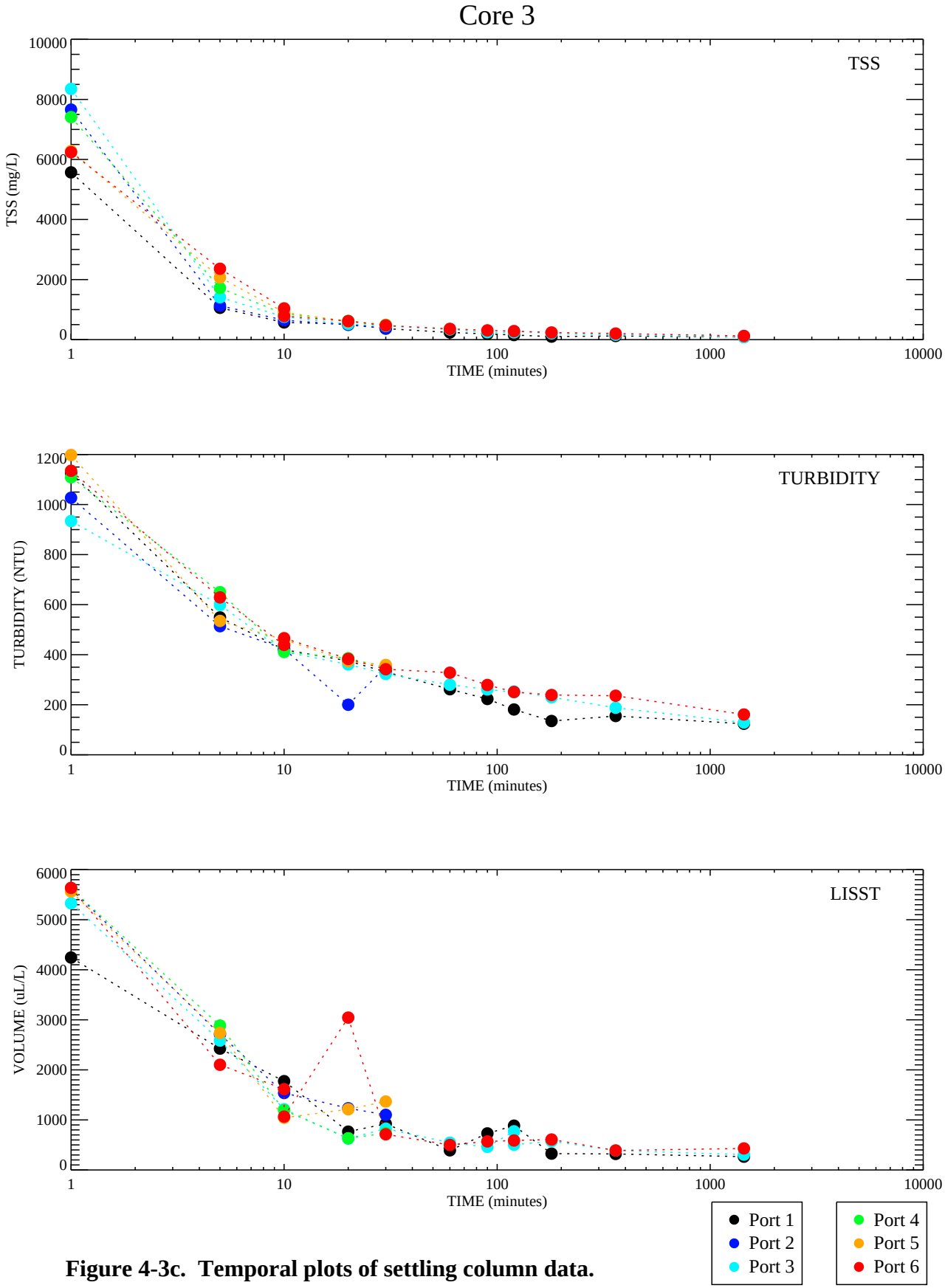

Figure 4-3c. Temporal plots of settling column data.

Temporal plots of settling test data.

For simplicity, data shown at proposed (not actual) sampling times.
Innitial sampling time was set to 1 minute after the beginning of the study.

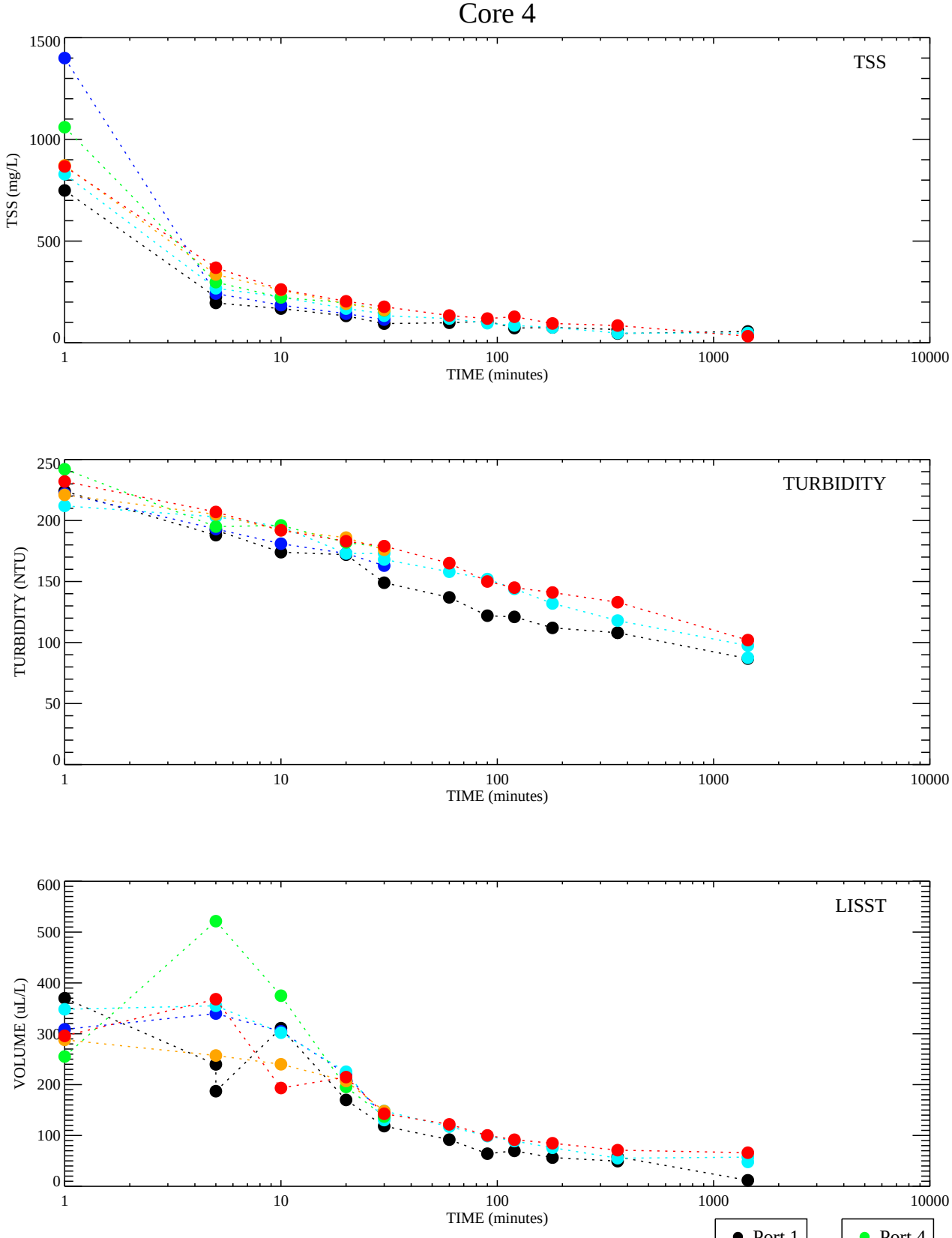

Figure 4-3d. Temporal plots of settling column data.

Temporal plots of settling test data.

For simplicity, data shown at proposed (not actual) sampling times.
Innitial sampling time was set to 1 minute after the beginning of the study.

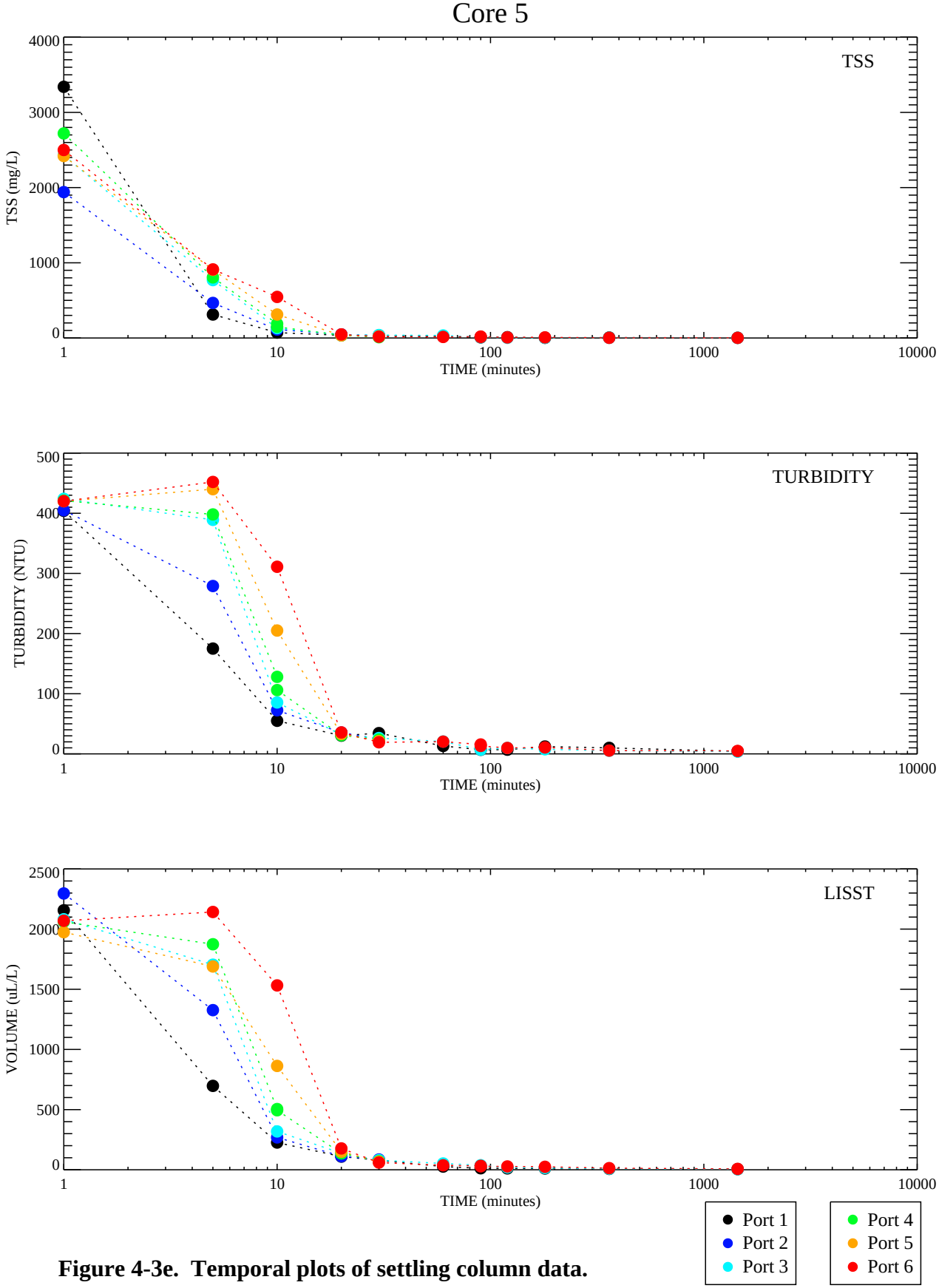

Figure 4-3e. Temporal plots of settling column data.

Temporal plots of settling test data.

For simplicity, data shown at proposed (not actual) sampling times.
Innitial sampling time was set to 1 minute after the beginning of the study.

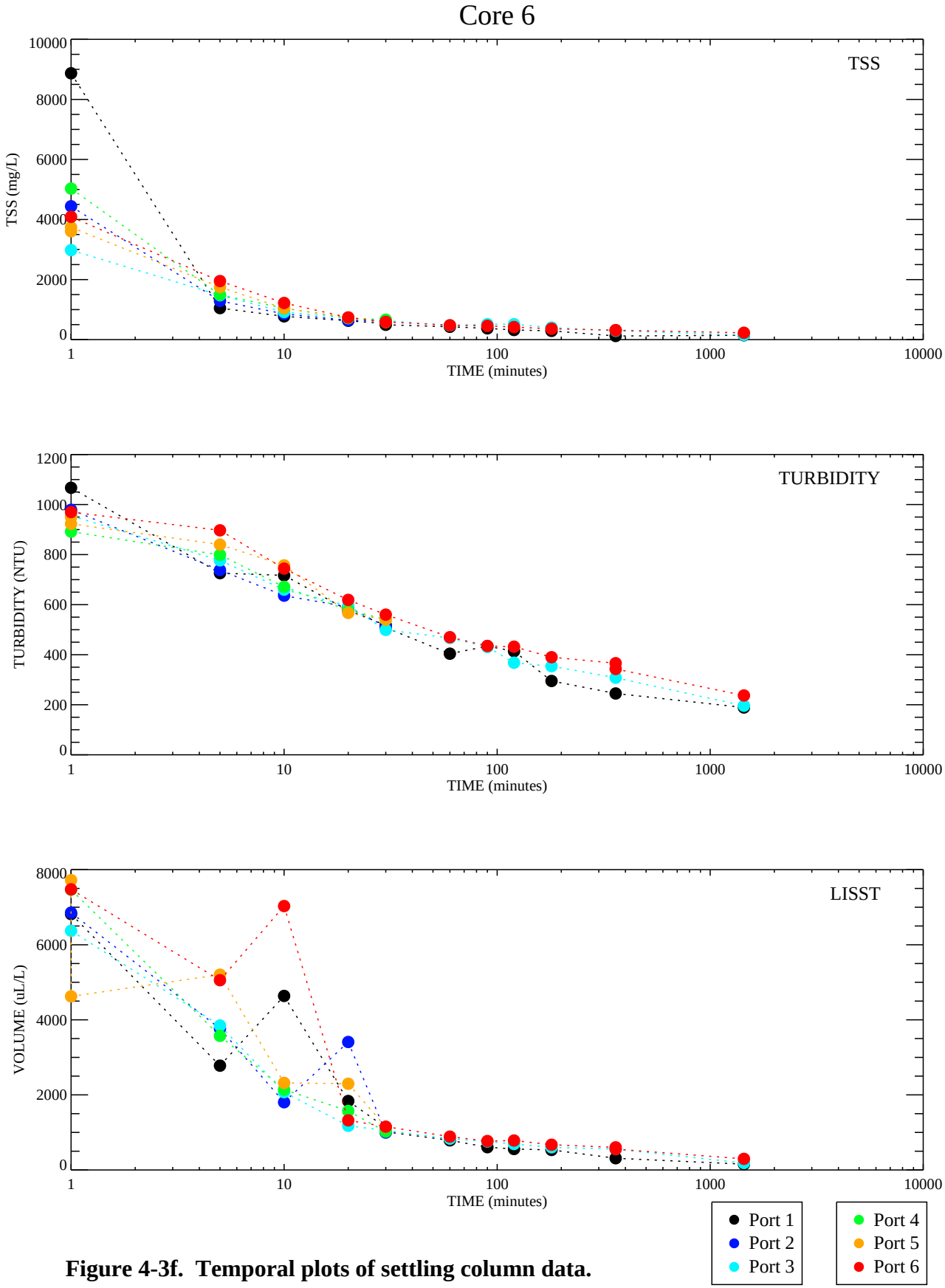

Figure 4-3f. Temporal plots of settling column data.

Temporal plots of settling test data.

For simplicity, data shown at proposed (not actual) sampling times.
Innitial sampling time was set to 1 minute after the beginning of the study.

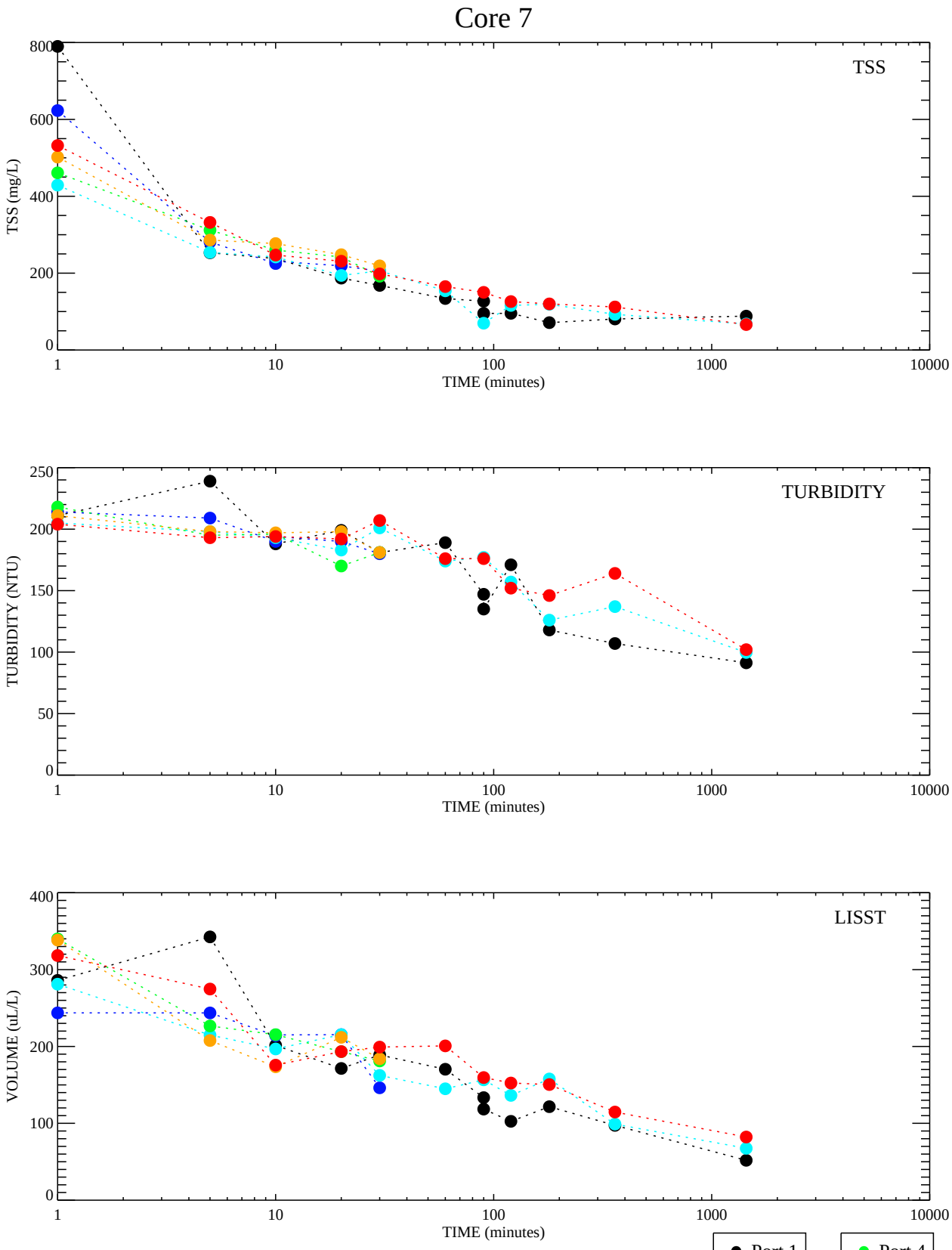

Figure 4-3g. Temporal plots of settling column data.

Temporal plots of settling test data.

For simplicity, data shown at proposed (not actual) sampling times.
Innitial sampling time was set to 1 minute after the beginning of the study.

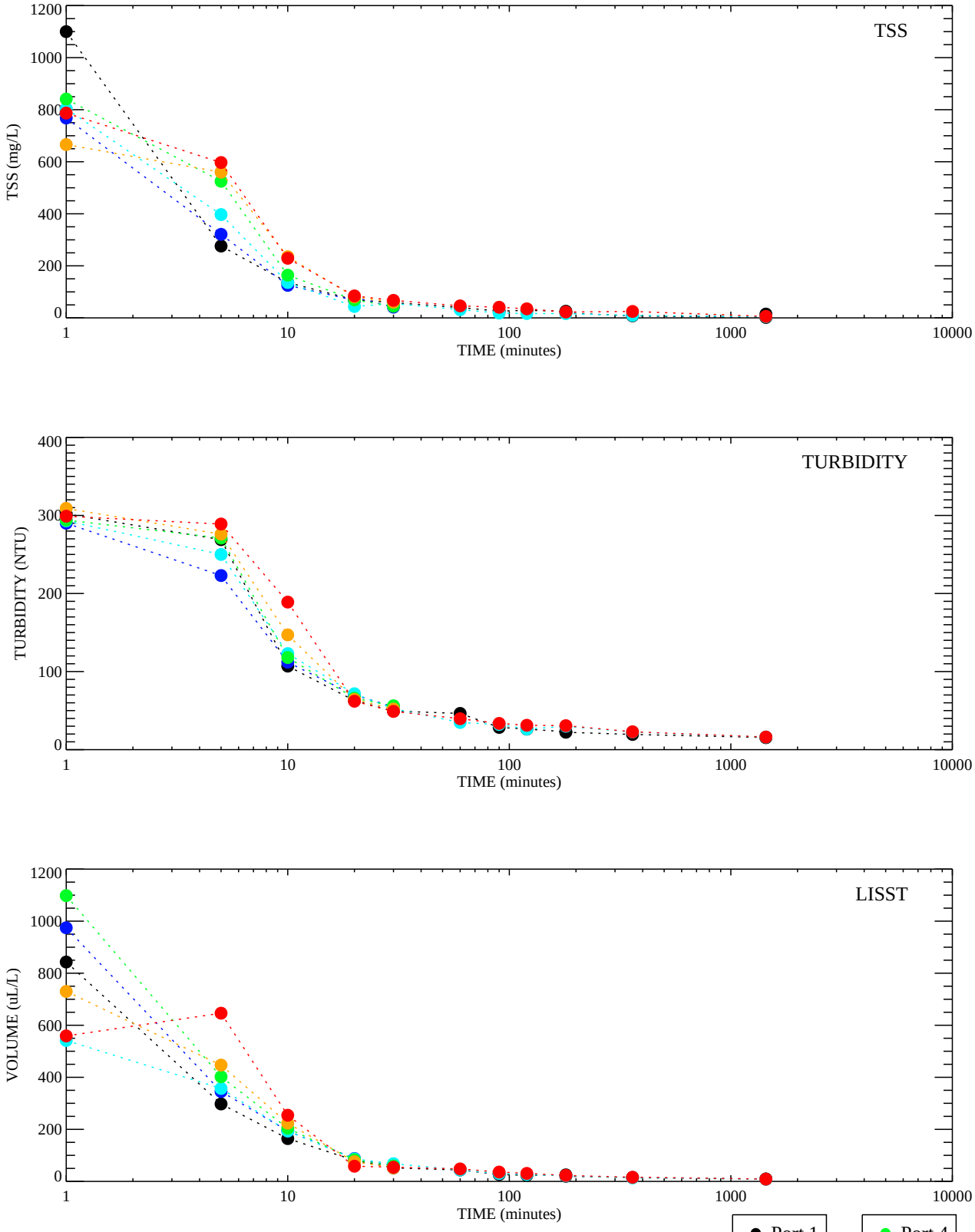

Figure 4-3h. Temporal plots of settling column data.

Temporal plots of settling test data.

For simplicity, data shown at proposed (not actual) sampling times.
Innitial sampling time was set to 1 minute after the beginning of the study.

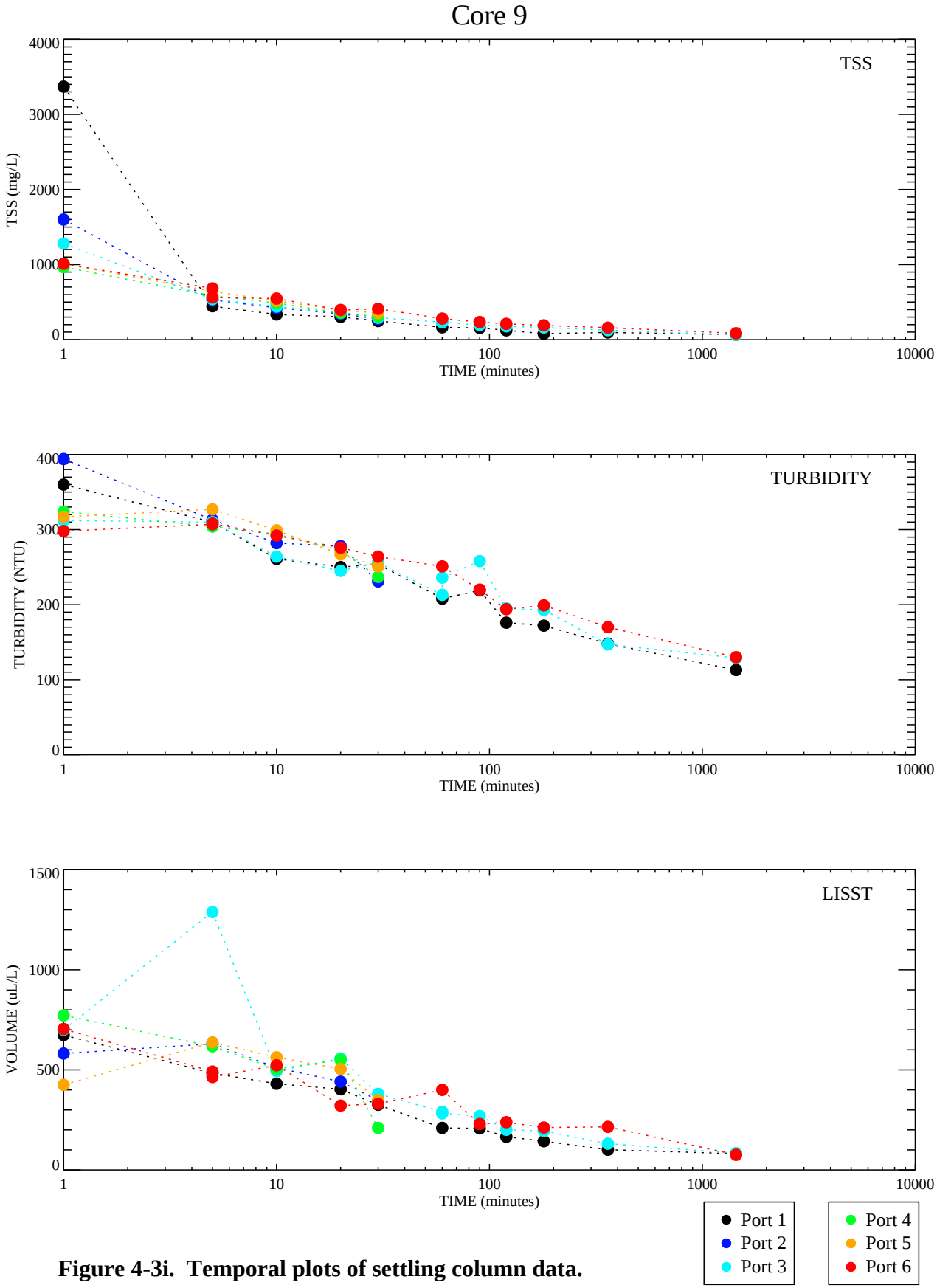

Figure 4-3i. Temporal plots of settling column data.

Temporal plots of settling test data.

For simplicity, data shown at proposed (not actual) sampling times.
Innitial sampling time was set to 1 minute after the beginning of the study.

IF - Q:\GENra1\DOCUMENTS\Reports\TSS Surrogate Study\Report\Figures\Feltyindividual_figures\NoPrivConf_Draft\Figure4_3.pro
Mon Nov 20 11:18:29 2006

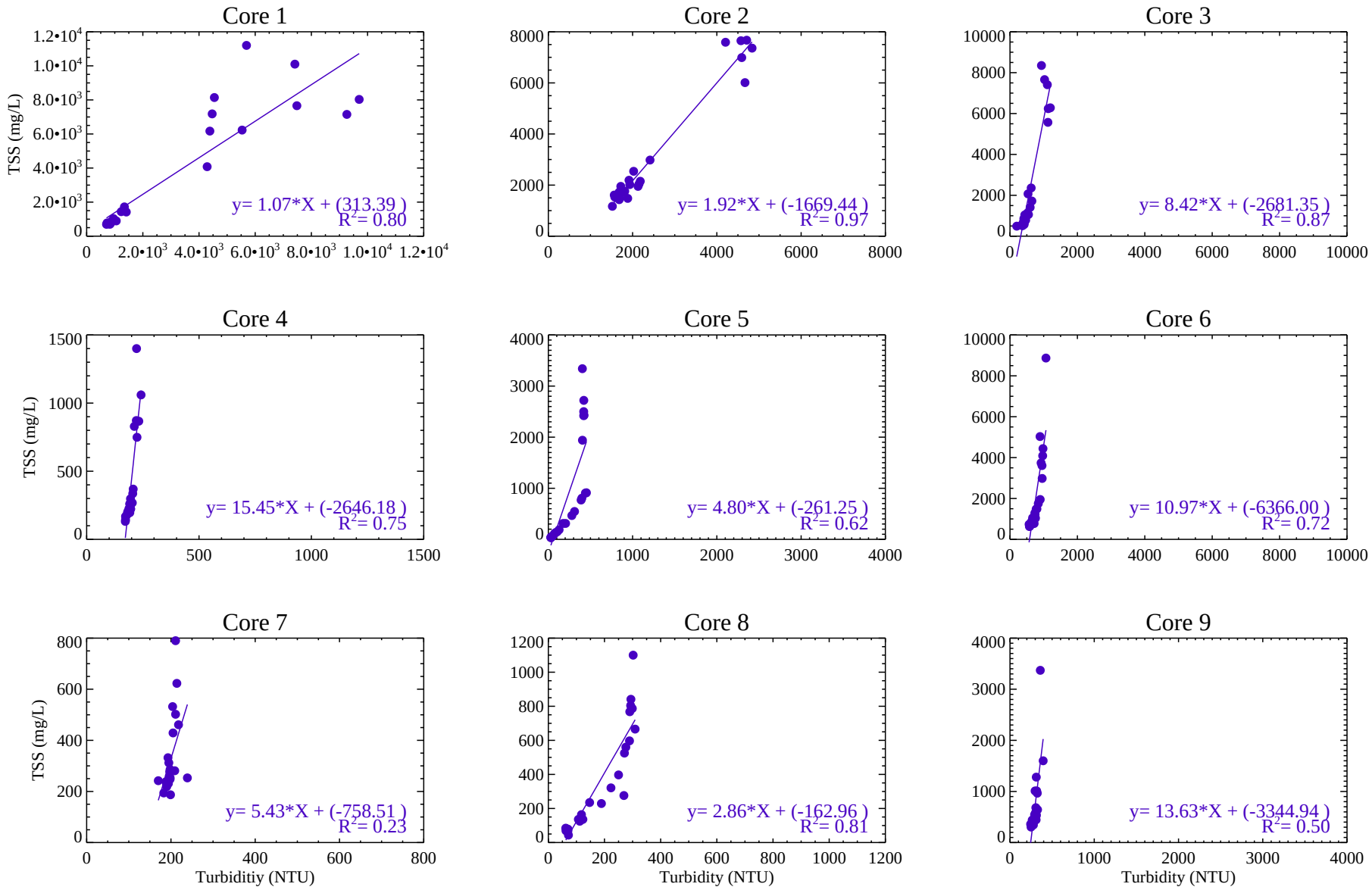

Figure 4-4. Crossplots of TSS and Turbidity data collected during the first 20 minutes of the settling column study.

IF - Q:\GENra1\DOCUMENTS\Reports\TSS Surrogate Study\Report\Figures\Feltyindividual_figures\NoPrivConf_Draft\Figure4_4.pro
Mon Nov 20 11:18:43 2006

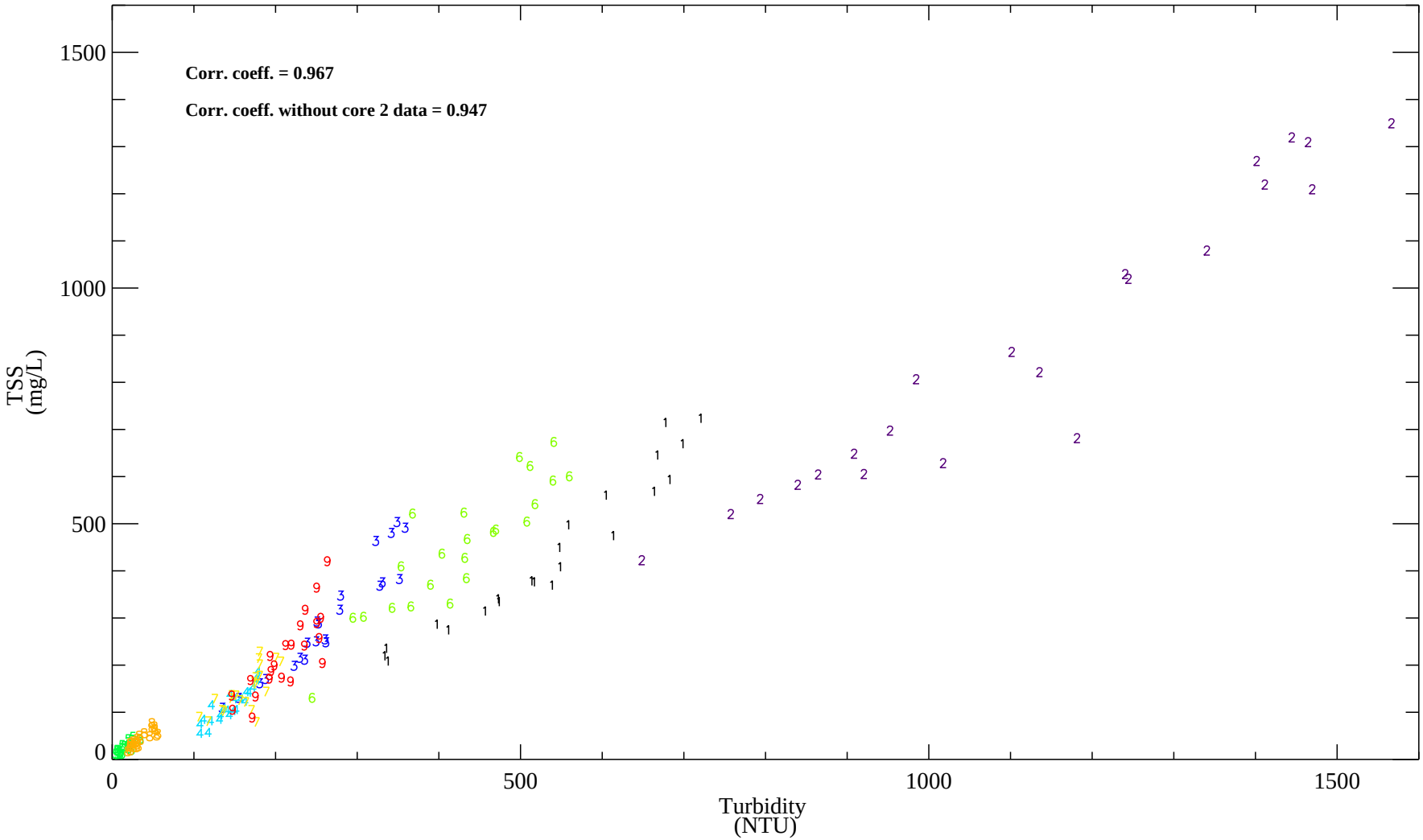

Figure 5-1. Comparative scatter plot of TSS vs. turbidity for the combined data set. The numbers in the plot represent the core number.
Only data measured between 30 mins and 360 minutes are plotted. Duplicates have been included.

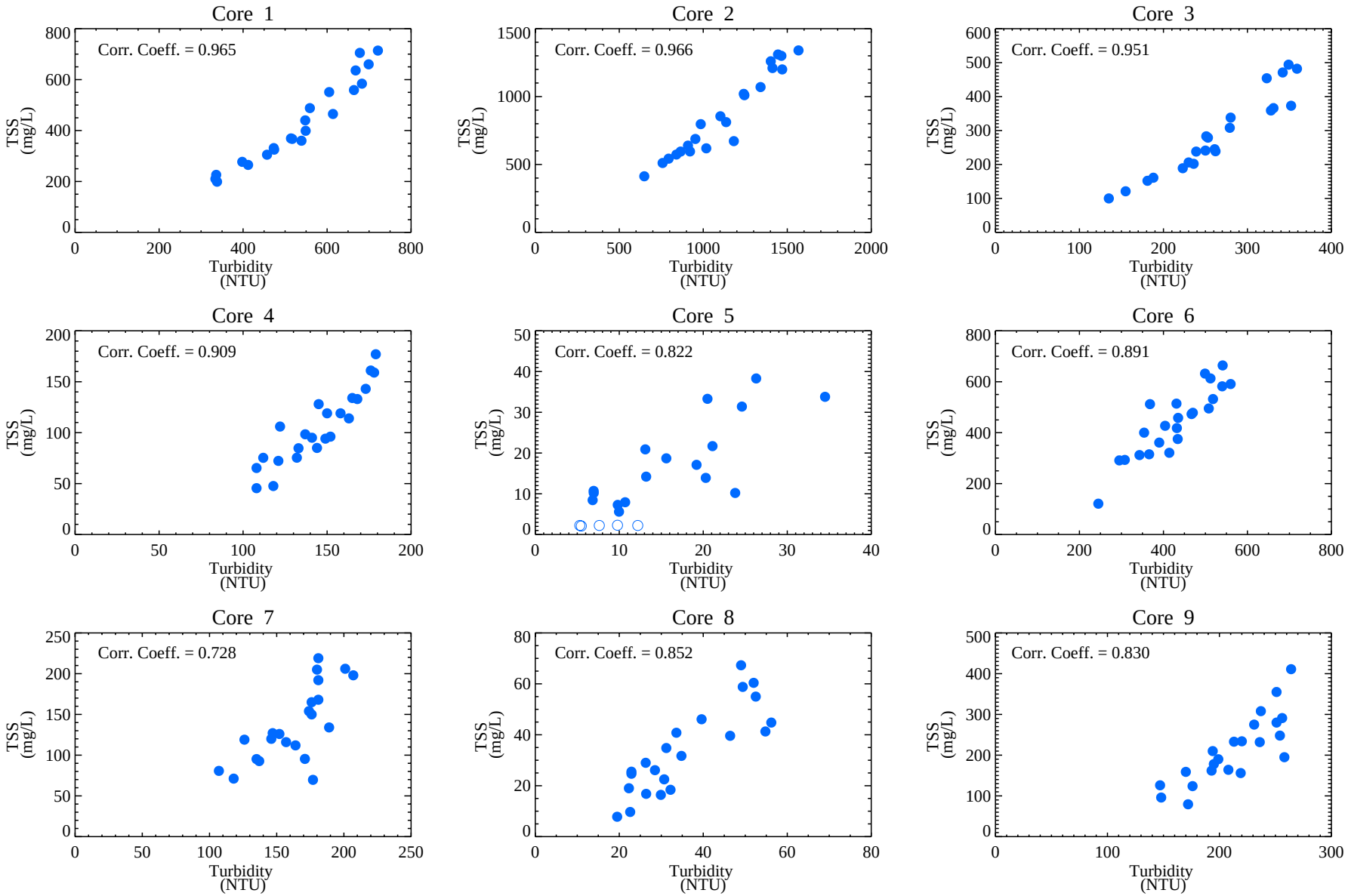

Figure 5-2. Scatter plots of TSS vs turbidity measured in settling column experiments between 30 mins and 360 minutes.

Non-detects are plotted at half the detection limit with open symbols. Duplicates have been included.

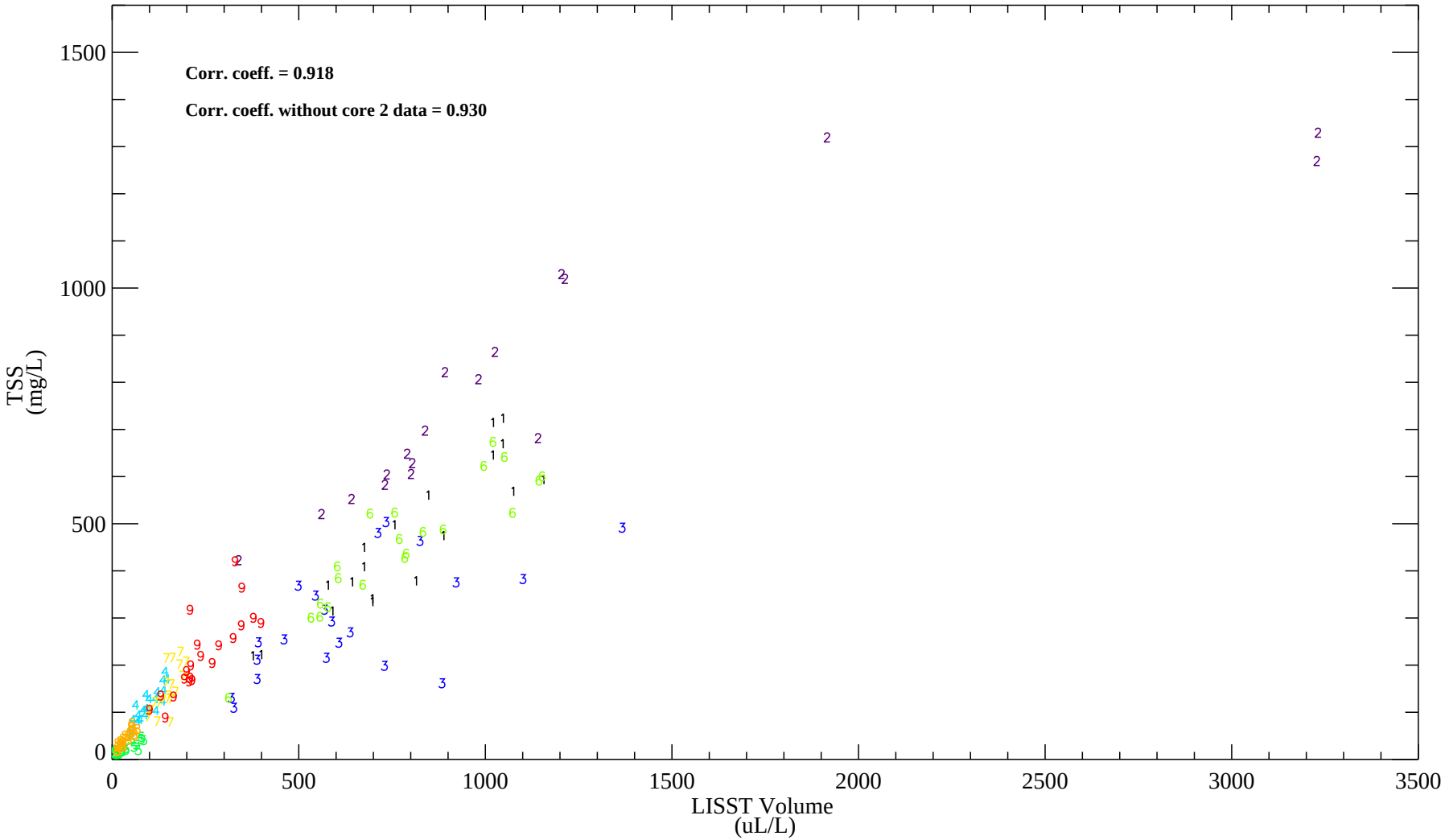

Figure 5-3. Comparative scatter plot of TSS vs. LISST volume for the combined data set. The numbers in the plot represent the core number.

Only data measured between 30 mins and 360 minutes with LISST transmission above 10% are plotted.

PM - D:\GENra1\Analysis\plots_for_report_lisst.pro
Fri Feb 20 17:54:21 2009

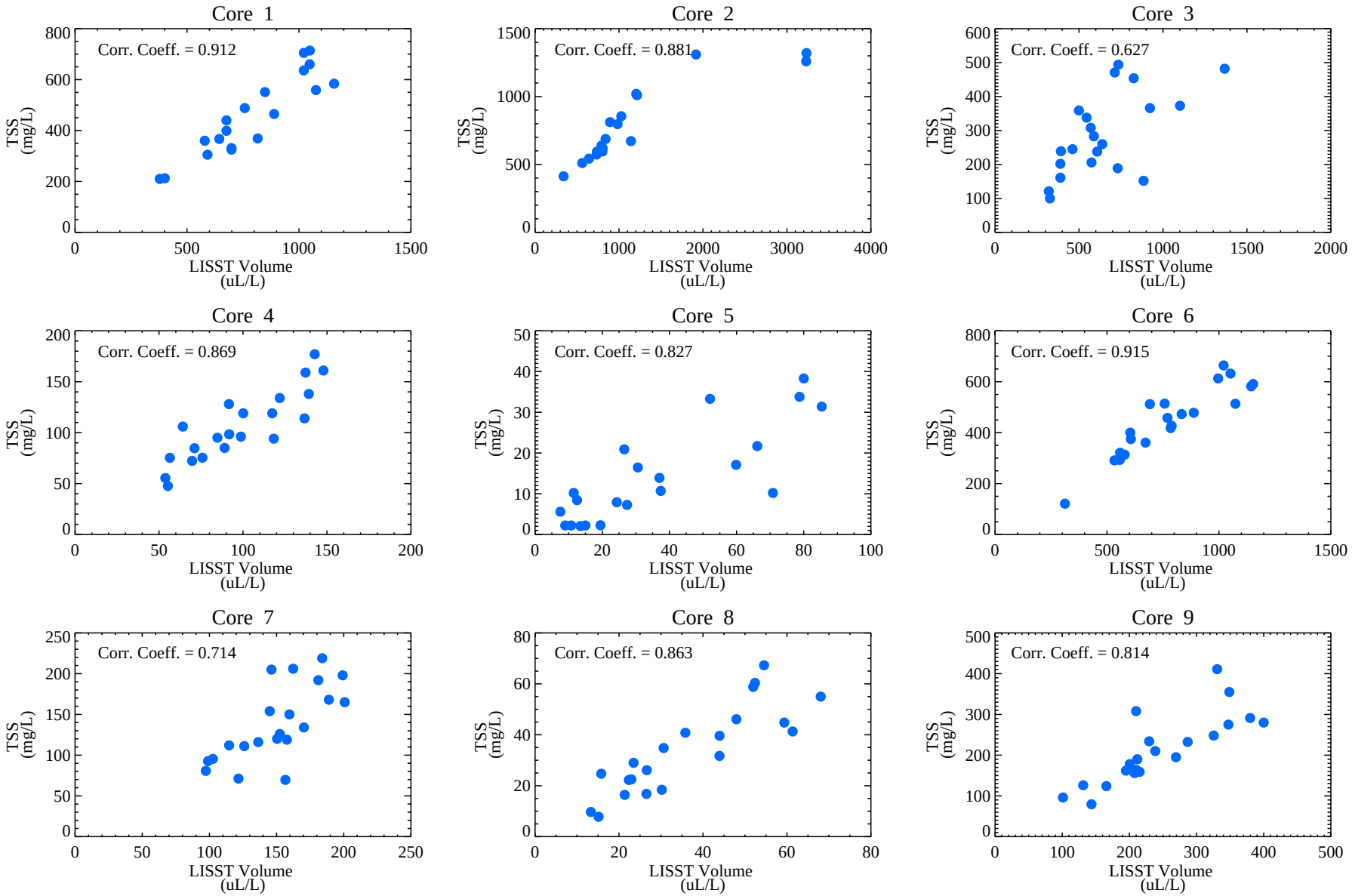

Figure 5-4. Scatter plots of TSS vs LISST Volume measured in settling column experiments between 30 mins and 360 minutes.

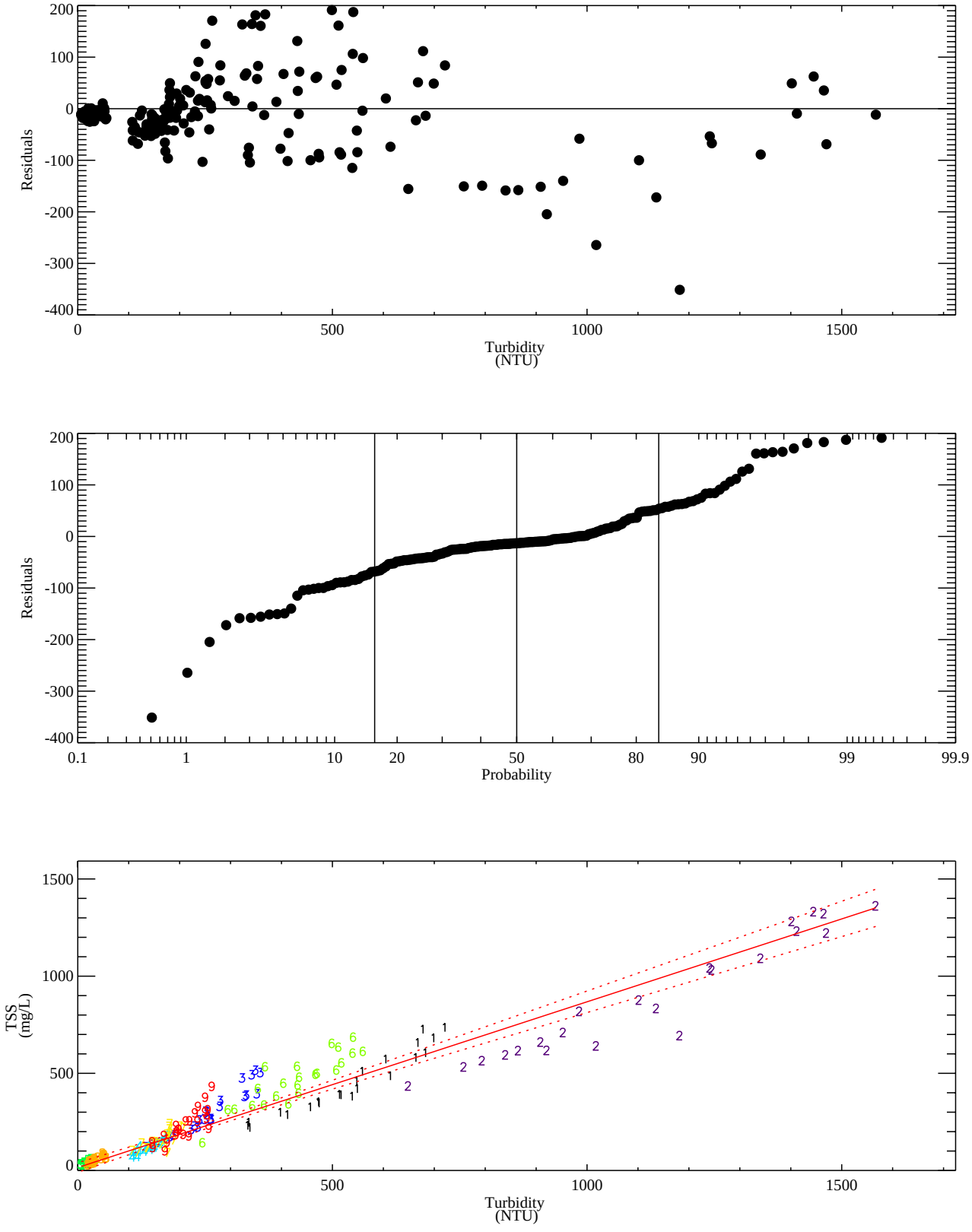

Figure 5-5. Linear model obtained using data from all cores.

Only data measured between 30 and 360 minutes are plotted. TSS non-detects were excluded.

Parameters estimated using damped-leveraged regression.

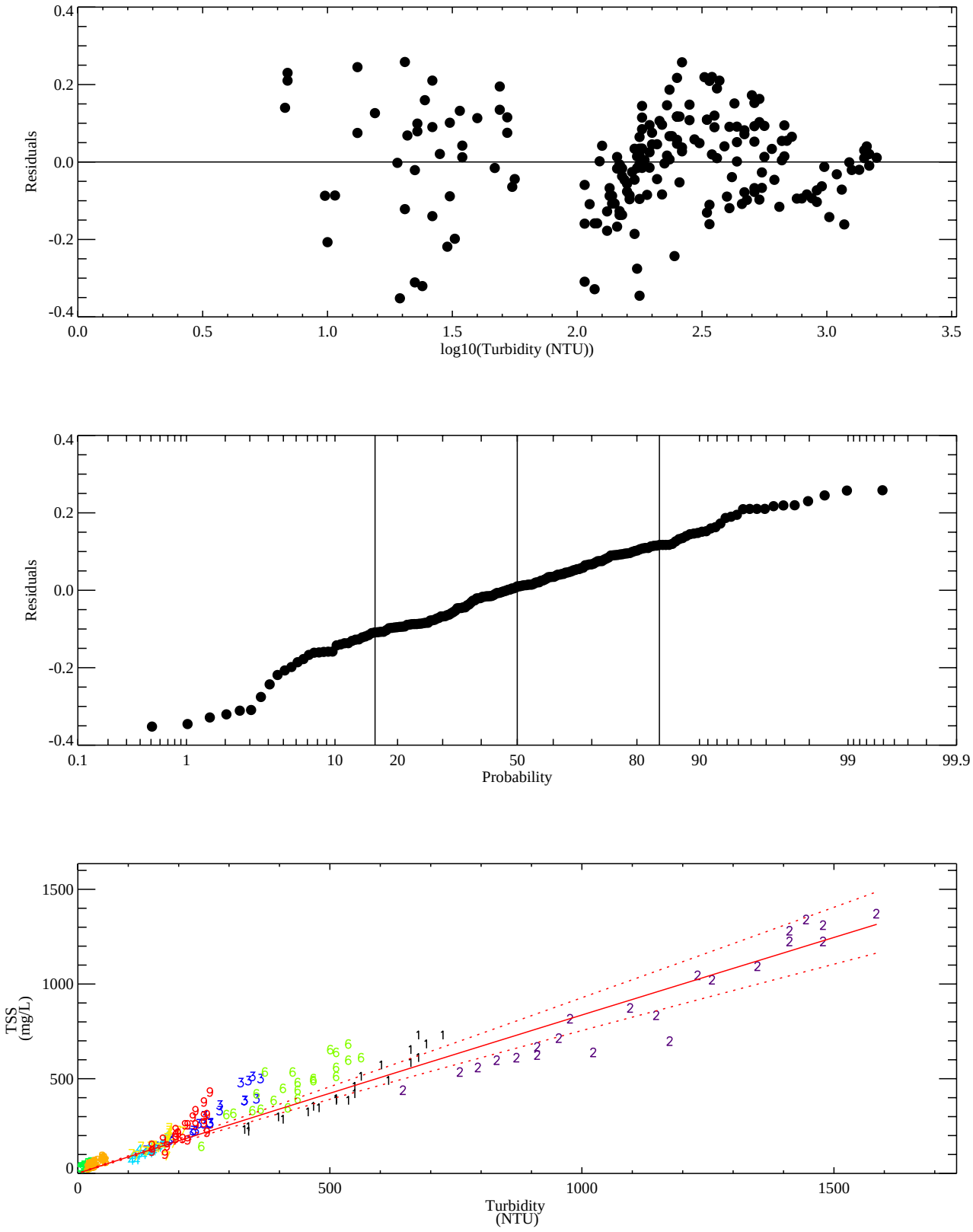

Figure 5-6. Log-log model obtained using data from all cores.

Only data measured between 30 and 360 minutes are plotted. TSS non-detects were excluded.

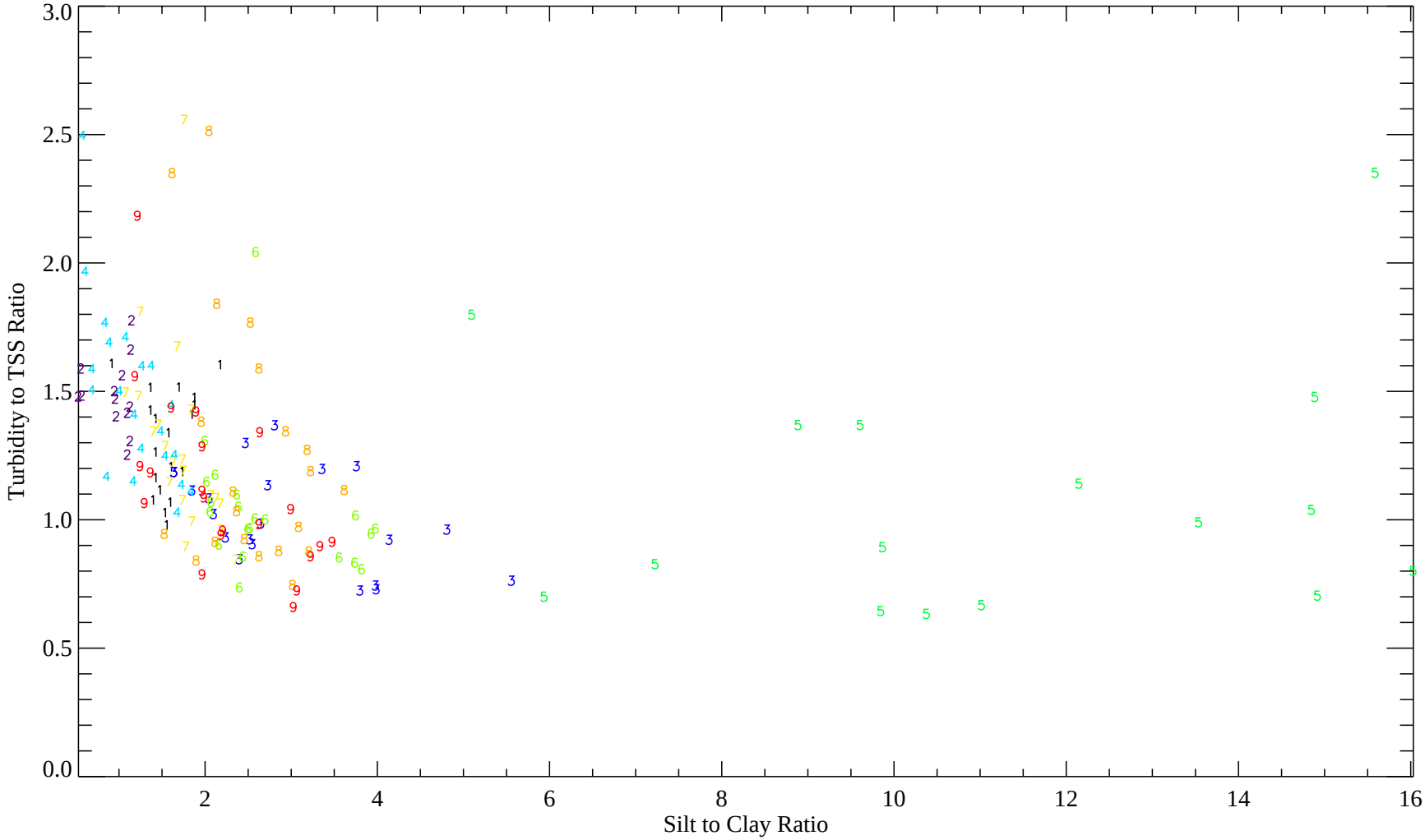

Figure 5-7. Relationship between turbidity to TSS and silt to clay ratios.

Data measured between 30 and 360 minutes was used in the analysis. The plotting symbol for each datum represents the core number. Non-detects were excluded.

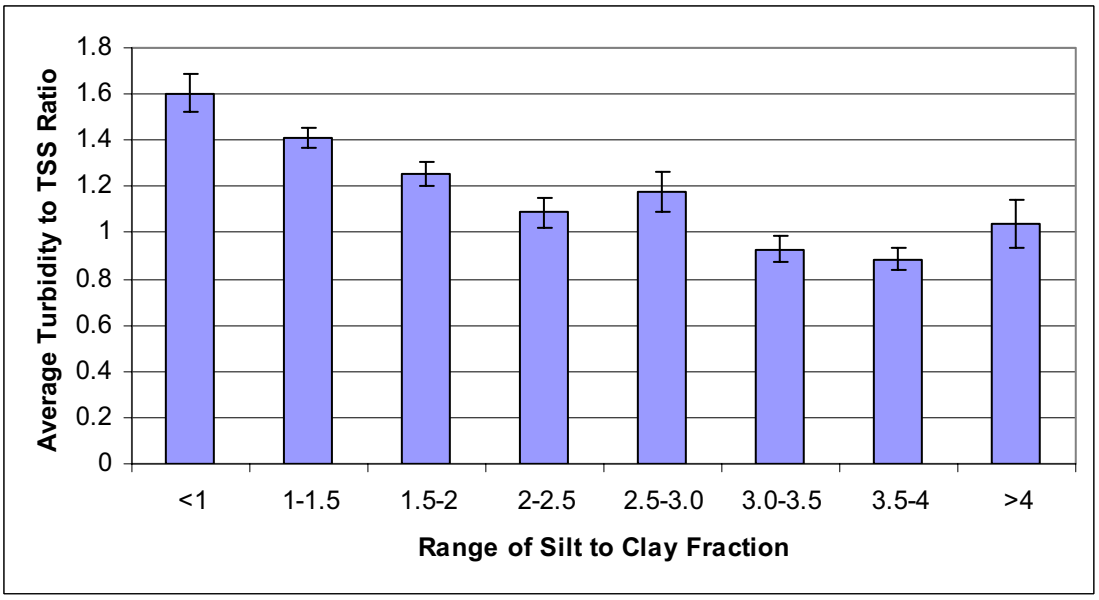

Figure 5-8. Average turbidity to TSS ratio in the silt to clay ratio bins specified.
TSS non-detects were not used in the estimation of average turbidity to TSS ratio. Error bars represent one standard error.

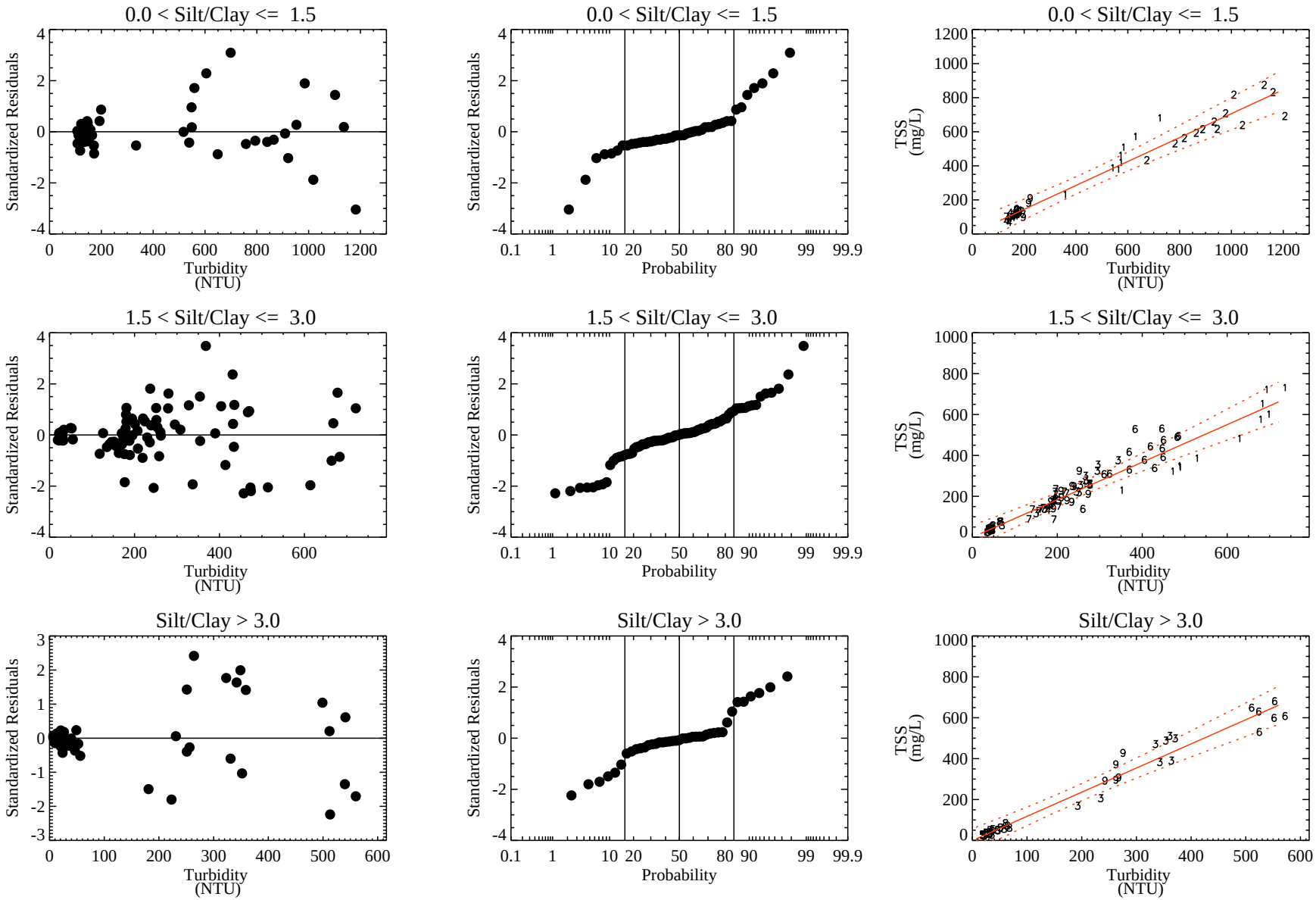

Figure 5-9. Model fits and diagnostics for TSS and turbidity data grouped by silt to clay ratios specified - linear model.

Data measured between 30 to 360 minutes were used in the analysis. Data points with TSS > 1000 mg/L and TSS non-detects were excluded. Data symbols in the model-fit plots represent core numbers.

Model
95% CI for Model

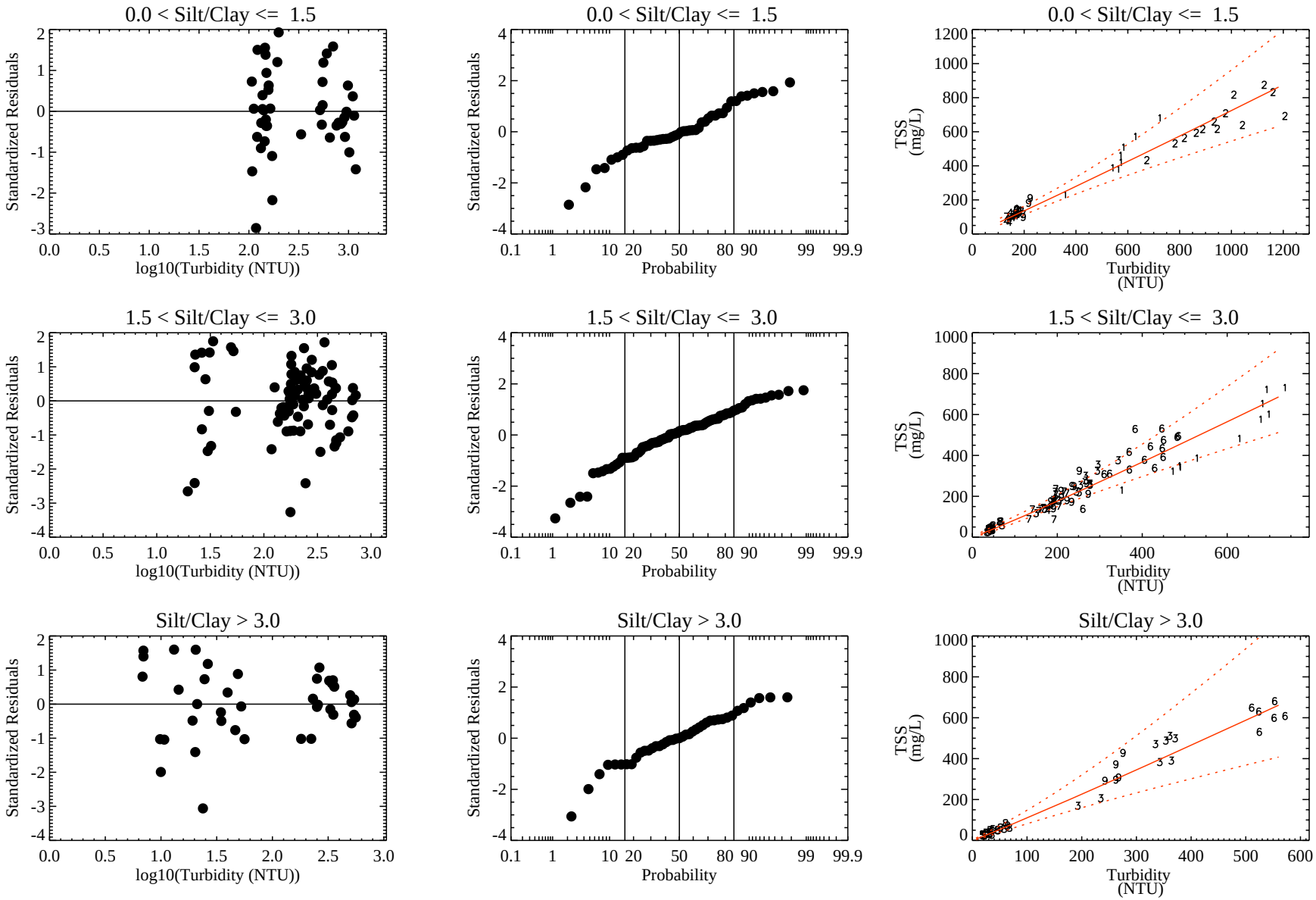

Figure 5-10. Model fits and diagnostics for TSS and turbidity data grouped by silt to clay ratios specified - log-log model.

Data measured between 30 to 360 minutes were used in the analysis. Data points with TSS > 1000 mg/L and TSS non-detects were excluded. Data symbols in the model-fit plots represent core numbers.

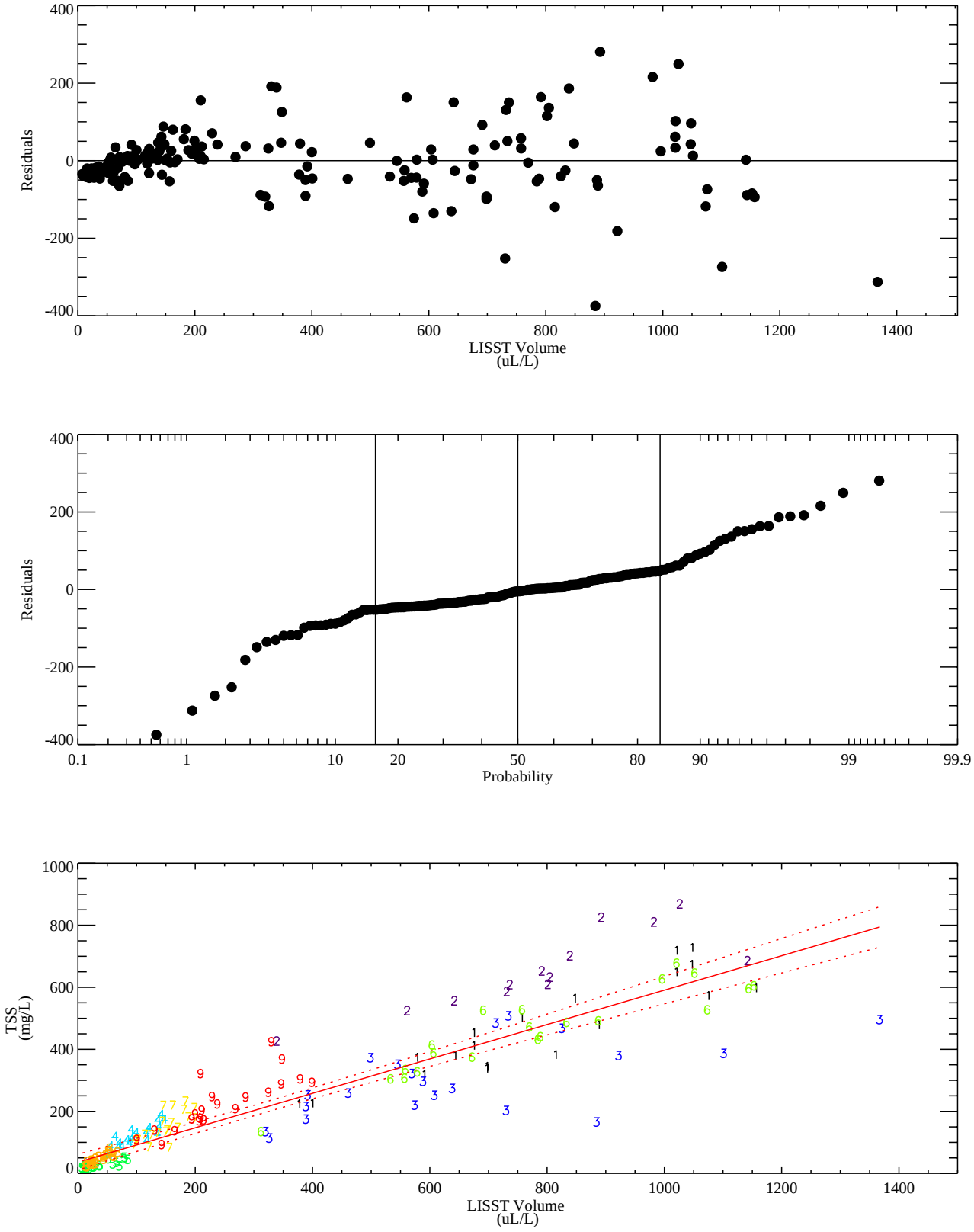

Figure 5-11. Linear TSS-particle volume model obtained using data from all cores.

Only data measured between 30 and 360 minutes are plotted. Data points with TSS greater than 1000 mg/L were excluded.
Parameters estimated using damped-leveraged regression.

PM - D:\GENra1\Analysis\TSS_lab_Study\LISST_data_Analysis\Pooled Model\create_r_model_plots.pro
Thu Sep 07 12:37:56 2006

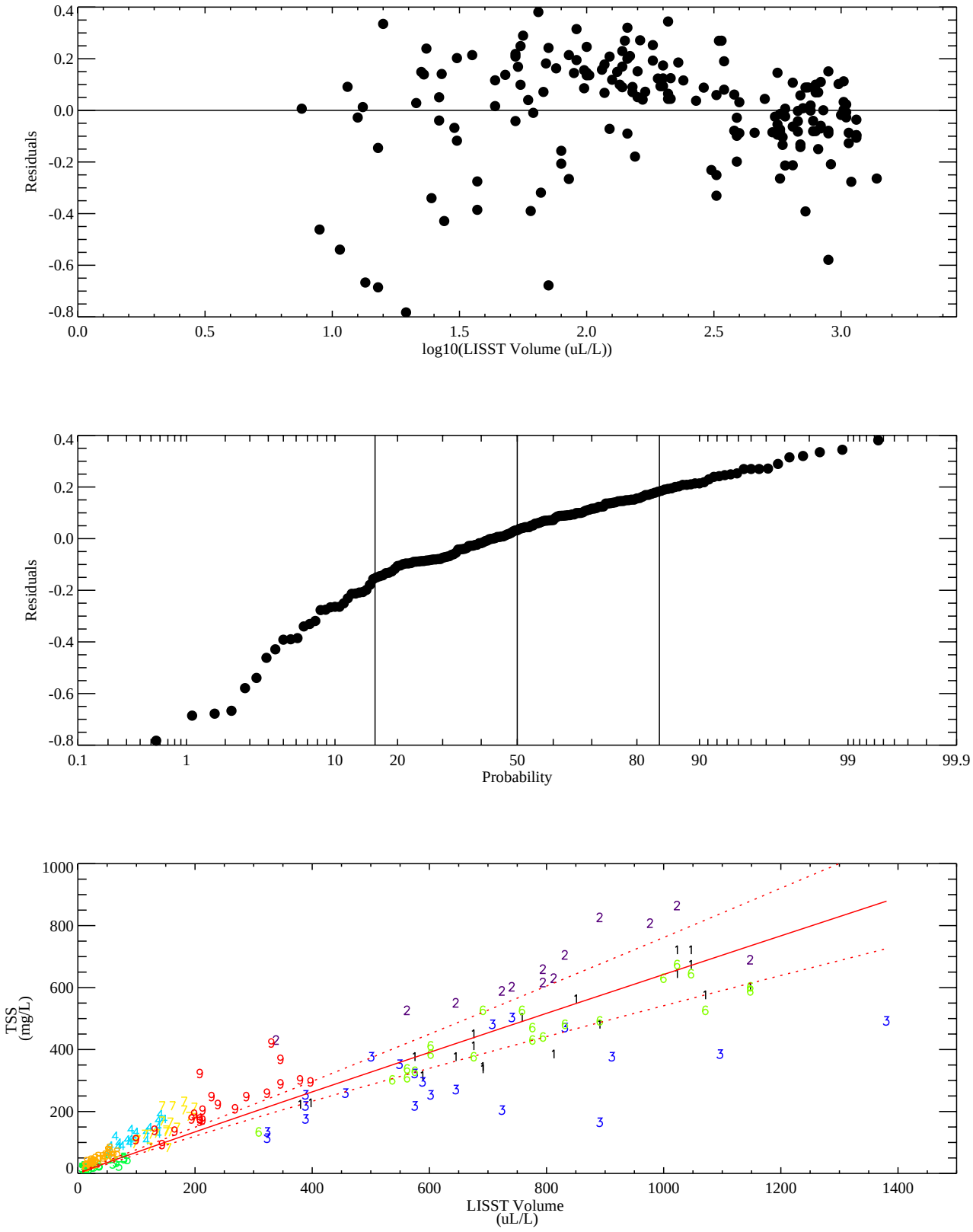

Figure 5-12. Log-log TSS-particle volume model obtained using data from all cores.

Only data measured between 30 and 360 minutes are plotted. Data points with TSS greater than 1000 mg/L were excluded.

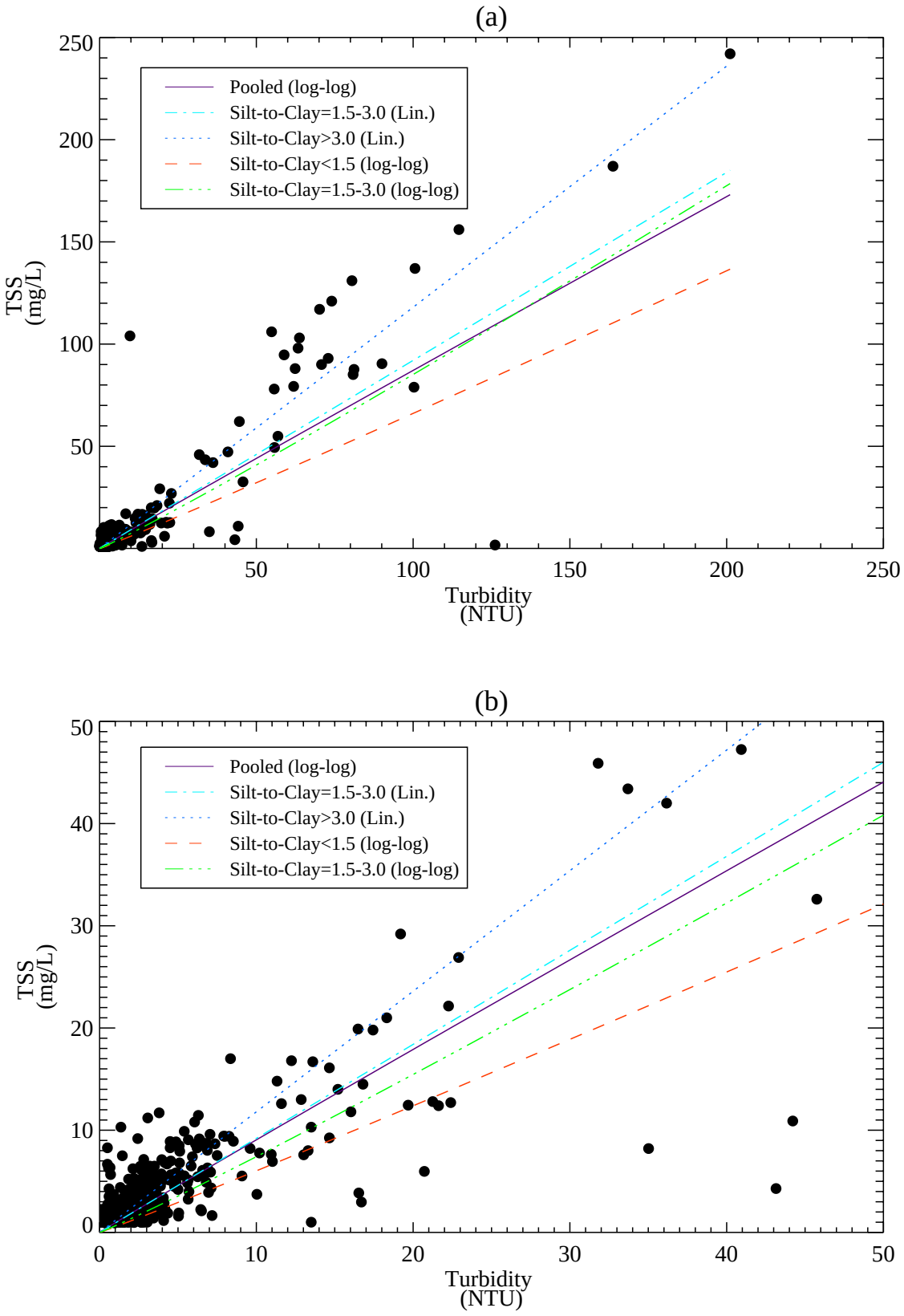

Figure 5-13. Comparison of model performance on baseline monitoring program data: (a) All data; (b) TSS data in the range of 0-50 mg/L.

Turbidity measurements were taken over a transect, while TSS measurements are based on composite samples over the same transect. TSS model estimates are based on the average turbidity value measured at each transect.

A data point with a very high standard error for turbidity was removed. Another data point with unusually high TSS value at zero measured turbidity was removed.

PM - D:\GENra1\Analysis\validation_w_bmp_data.pro
Thu Sep 07 14:24:36 2006

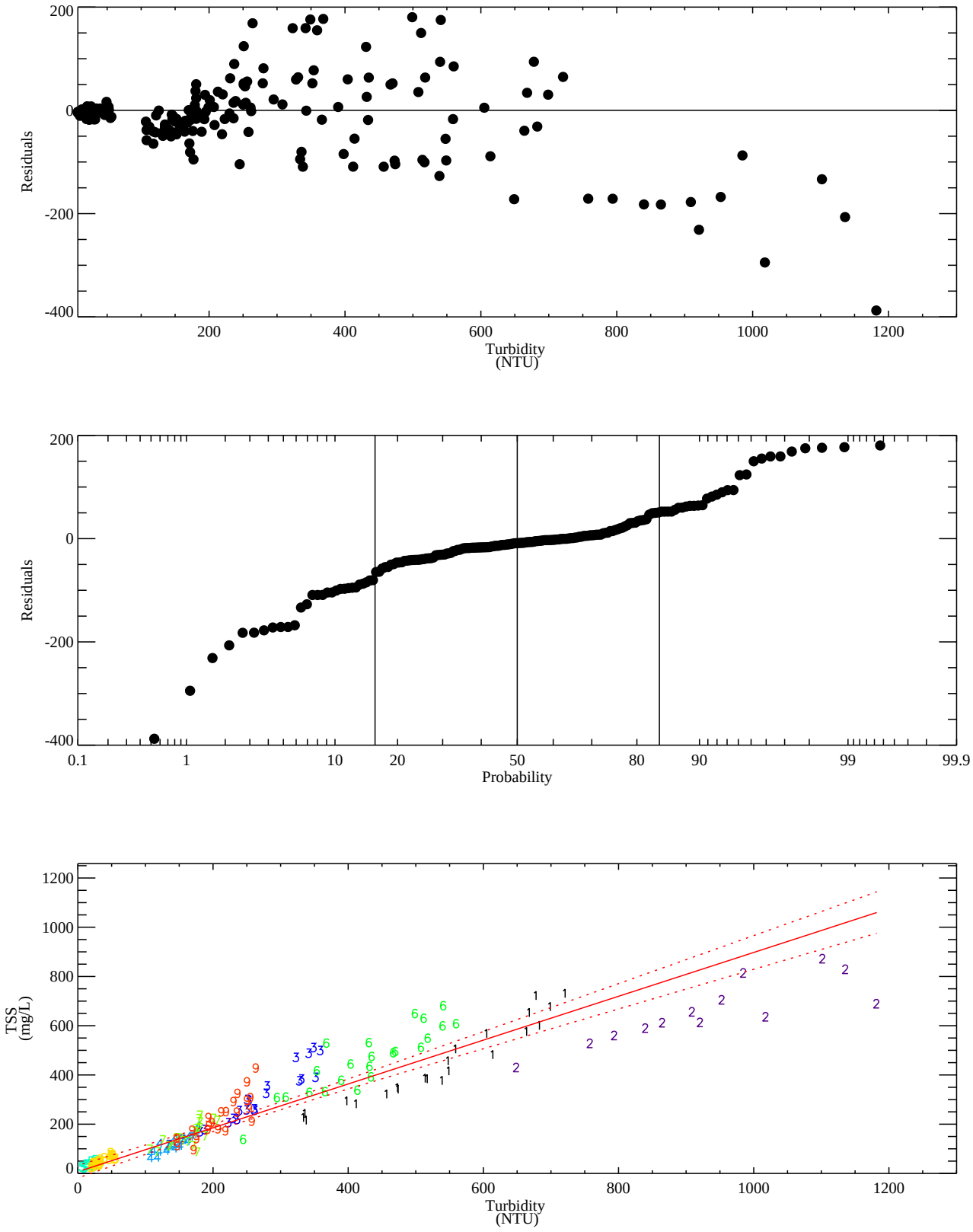

Figure 5-14. Linear model for pooled lab data with TSS less than 1000 mg/L.

Data treatment: no TSS non-detects or TSS>1000 mg/L; lab data measured between 30 and 360 mins.

Numbers in bottom panel represent laboratory core number.

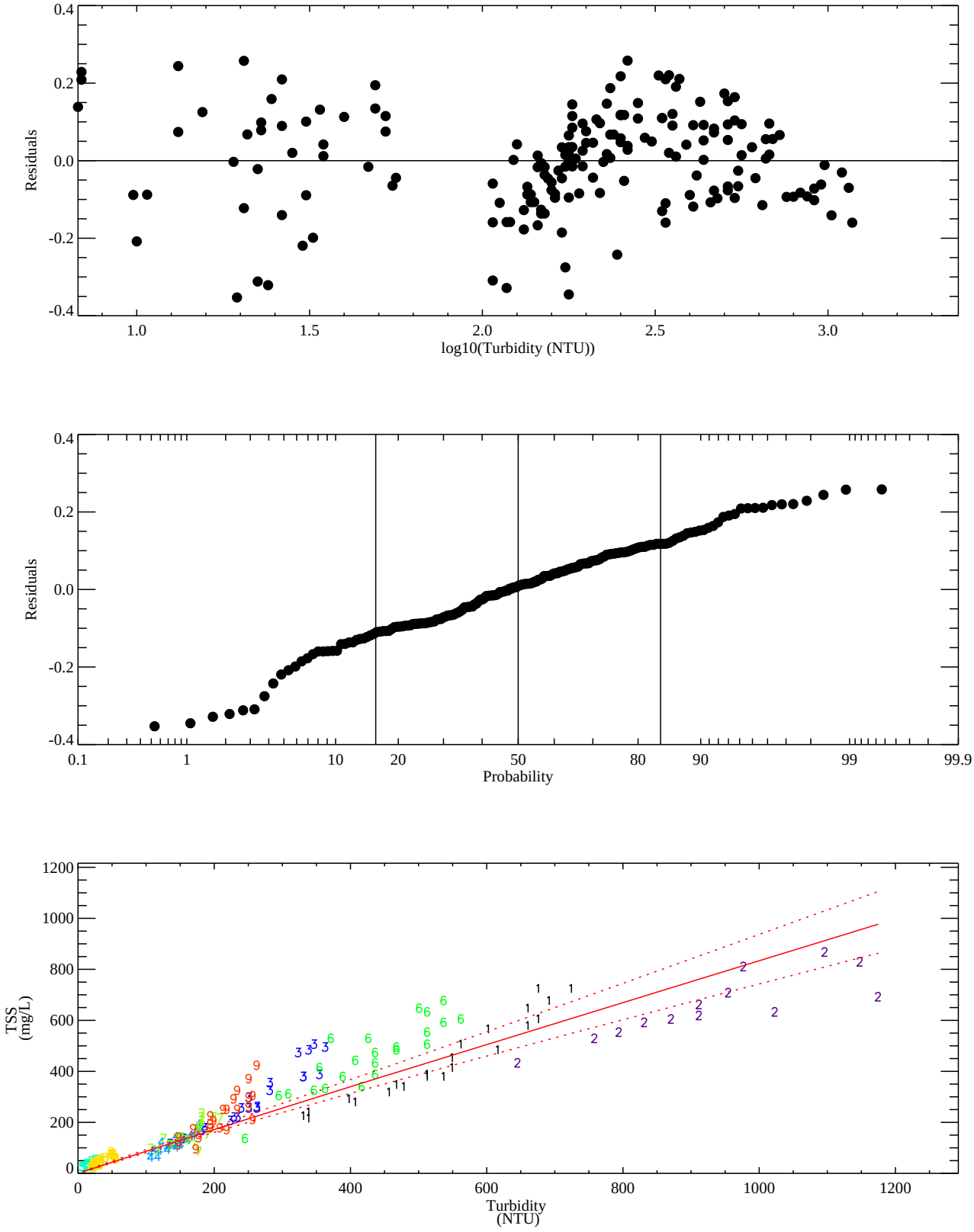

Figure 5-15. Log-log model for pooled lab data with TSS less than 1000 mg/L.

Data treatment: no TSS non-detects or TSS>1000 mg/L; lab data measured between 30 and 360 mins.

Numbers in bottom panel represent laboratory core number.

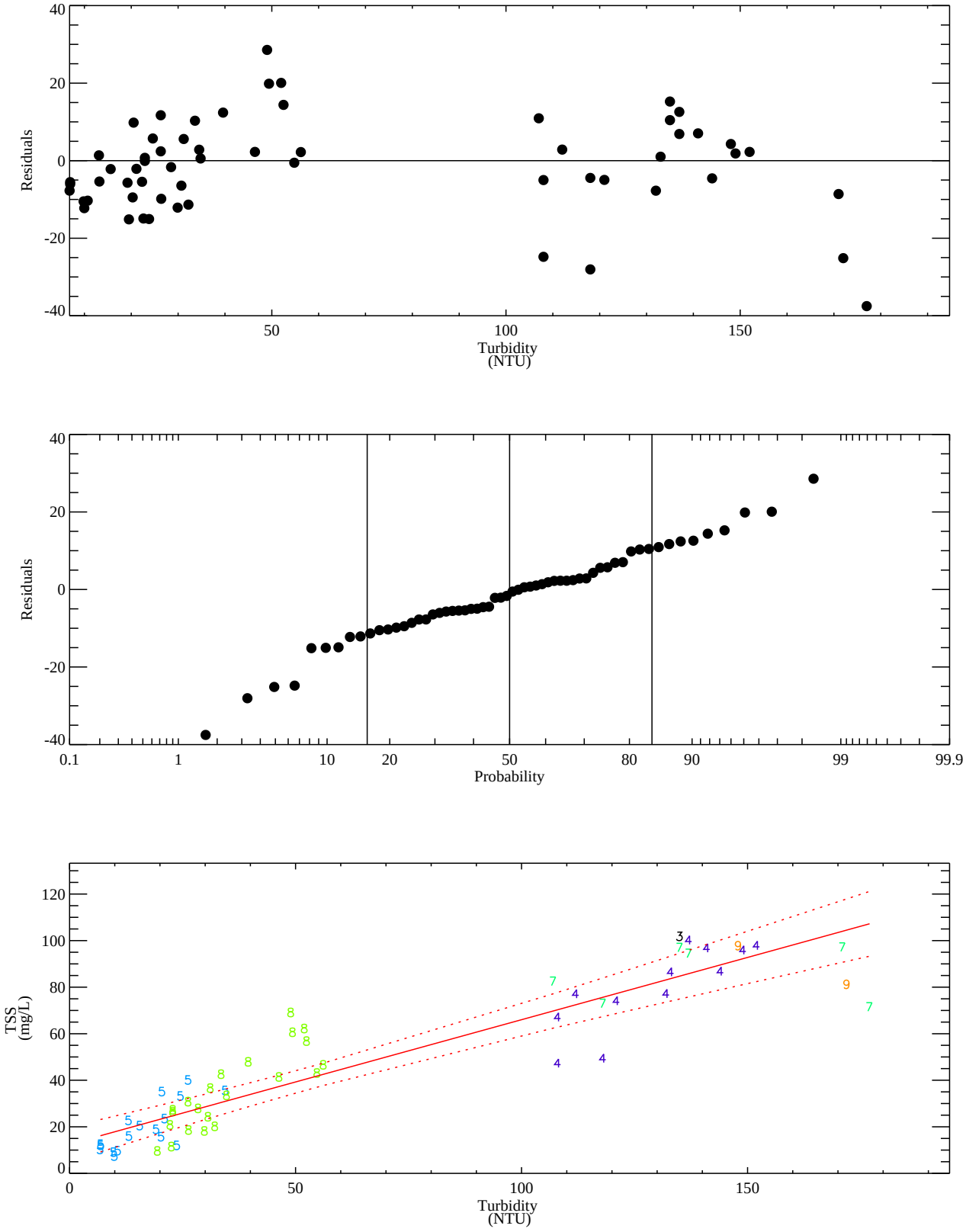

Figure 5-16. Linear model for pooled lab data with TSS less than 100 mg/L.

Data treatment: no TSS non-detects or TSS>100 mg/L; lab data measured between 30 and 360 mins.

Numbers in bottom panel represent laboratory core number.

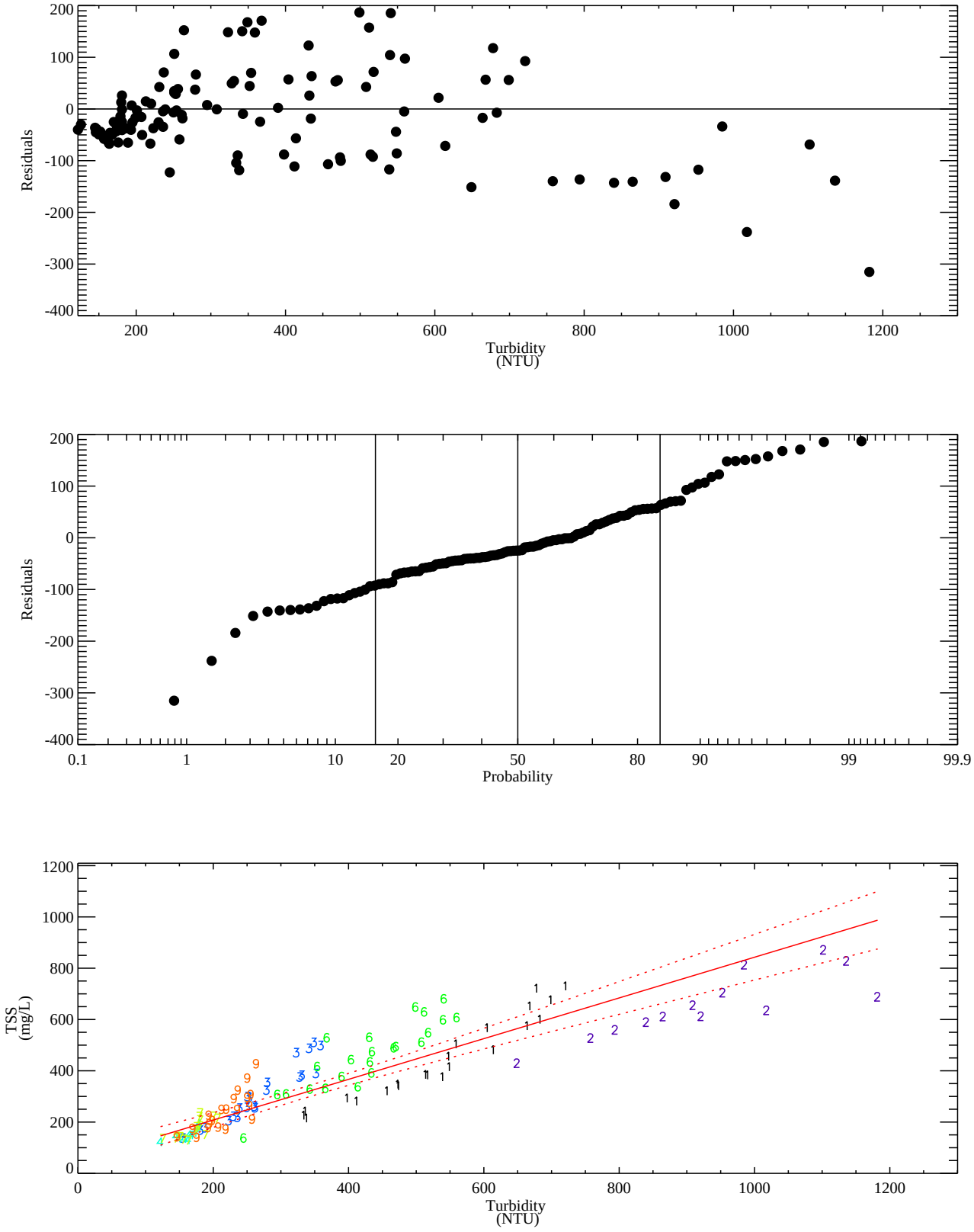

Figure 5-17. Linear model for pooled lab data with TSS between 100 and 1000 mg/L.

Data treatment: no TSS non-detects or TSS<100 mg/L or TSS > 1000 mg/L; lab data measured between 30 and 360 mins.

Numbers in bottom panel represent laboratory core number.

Model
95% CI for Model

PM - D:\GENra1\Analysis\TSS_lab_Study\Log-Log Models - Possolo\R_runs\create_r_model_plots.pro
Fri Feb 20 18:22:52 2009

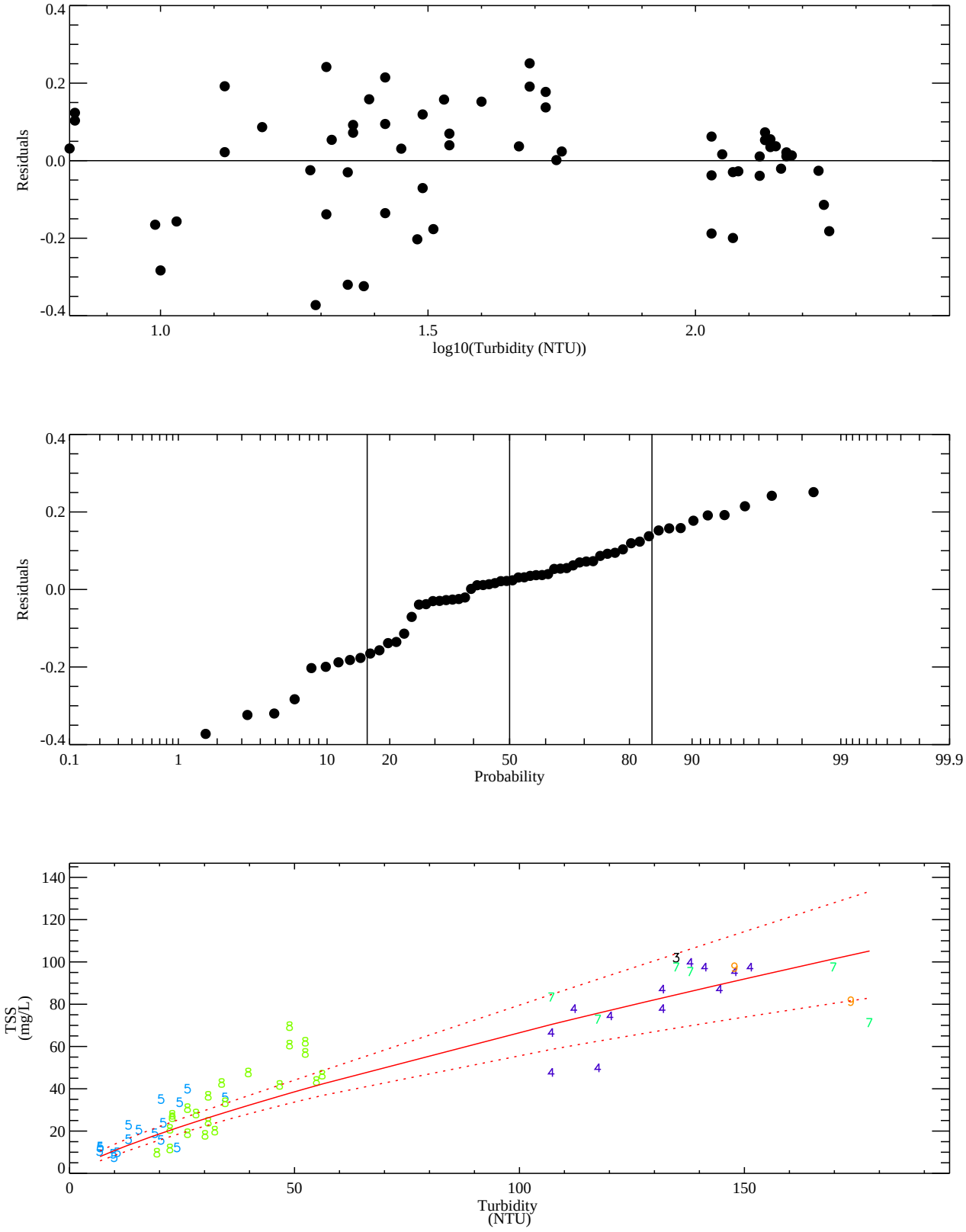

Figure 5-18. Log-log model for pooled lab data with TSS less than 100 mg/L.

Data treatment: no TSS non-detects or TSS>100 mg/L; lab data measured between 30 and 360 mins.

Numbers in bottom panel represent laboratory core number.

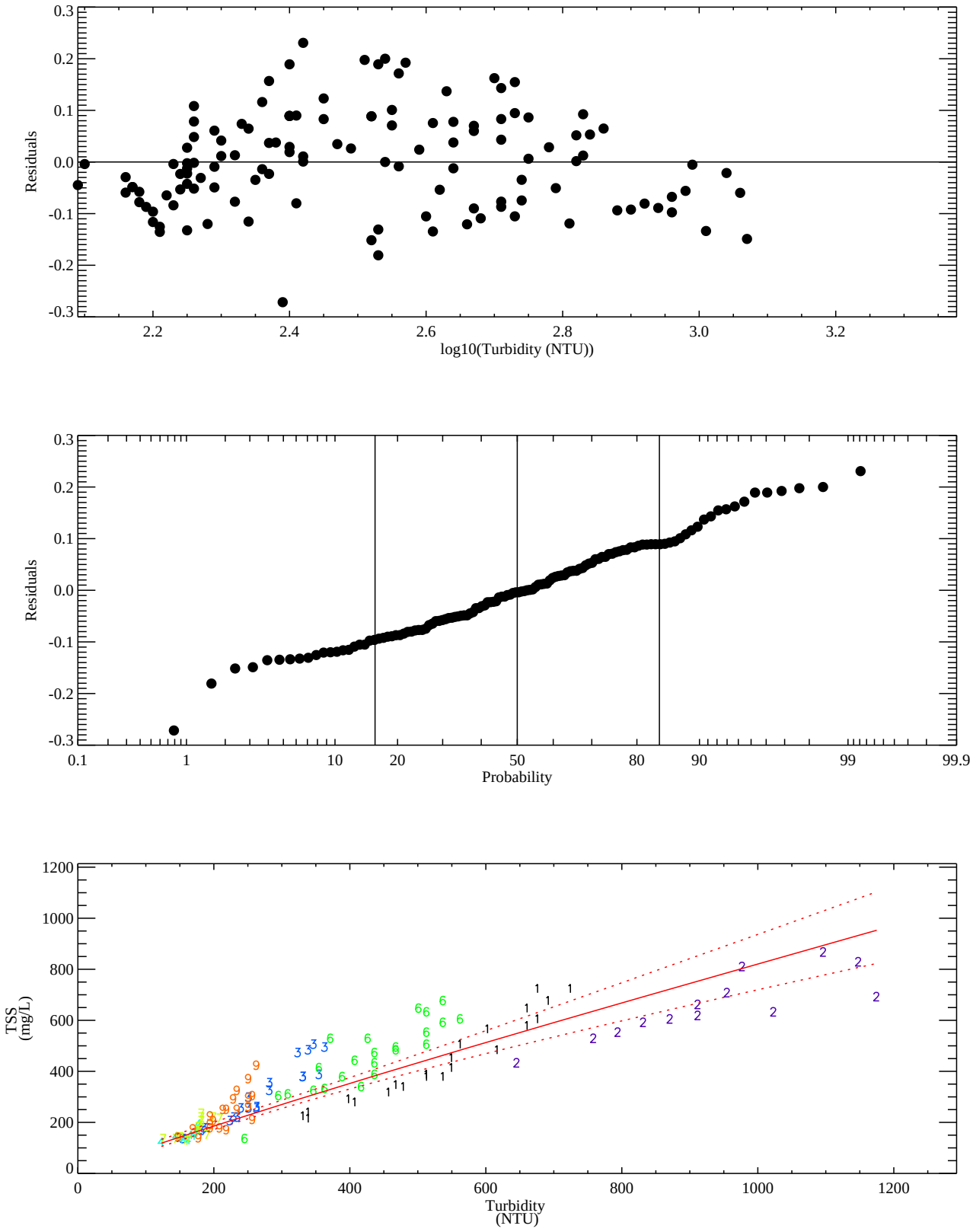

Figure 5-19. Log-log model for pooled lab data with TSS between 100 and 1000 mg/L.

Data treatment: no TSS non-detects or TSS<100 mg/L or TSS > 1000 mg/L; lab data measured between 30 and 360 mins.

Numbers in bottom panel represent laboratory core number.

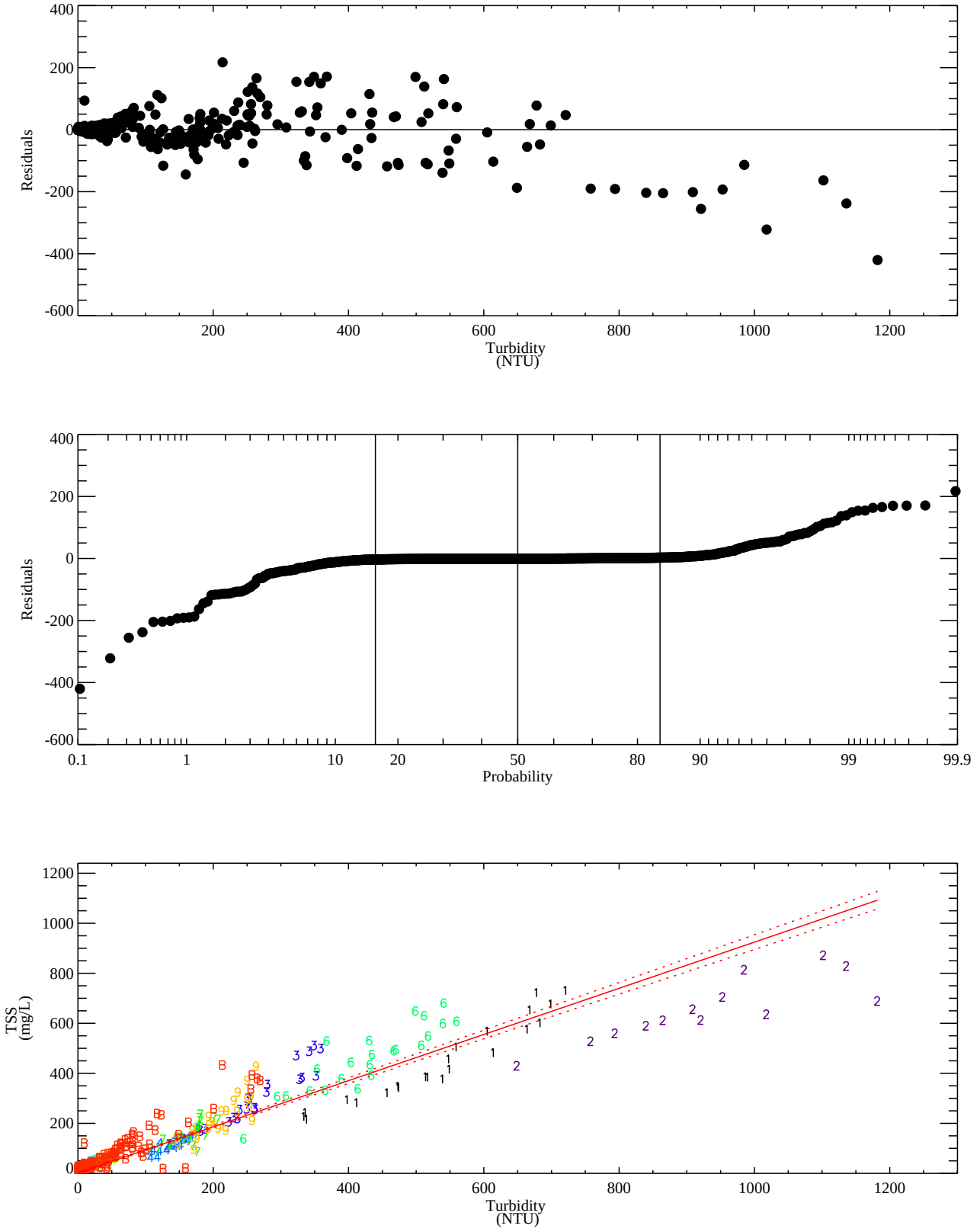

Figure 5-20. Linear model for pooled lab and BMP data with TSS less than 1000 mg/L.

Lab and BMP data (through 2007): no TSS non-detects or TSS>1000 mg/L; lab data measured between 30 and 360 mins.

Numbers in bottom panel represent laboratory core number. "B" indicates BMP data.

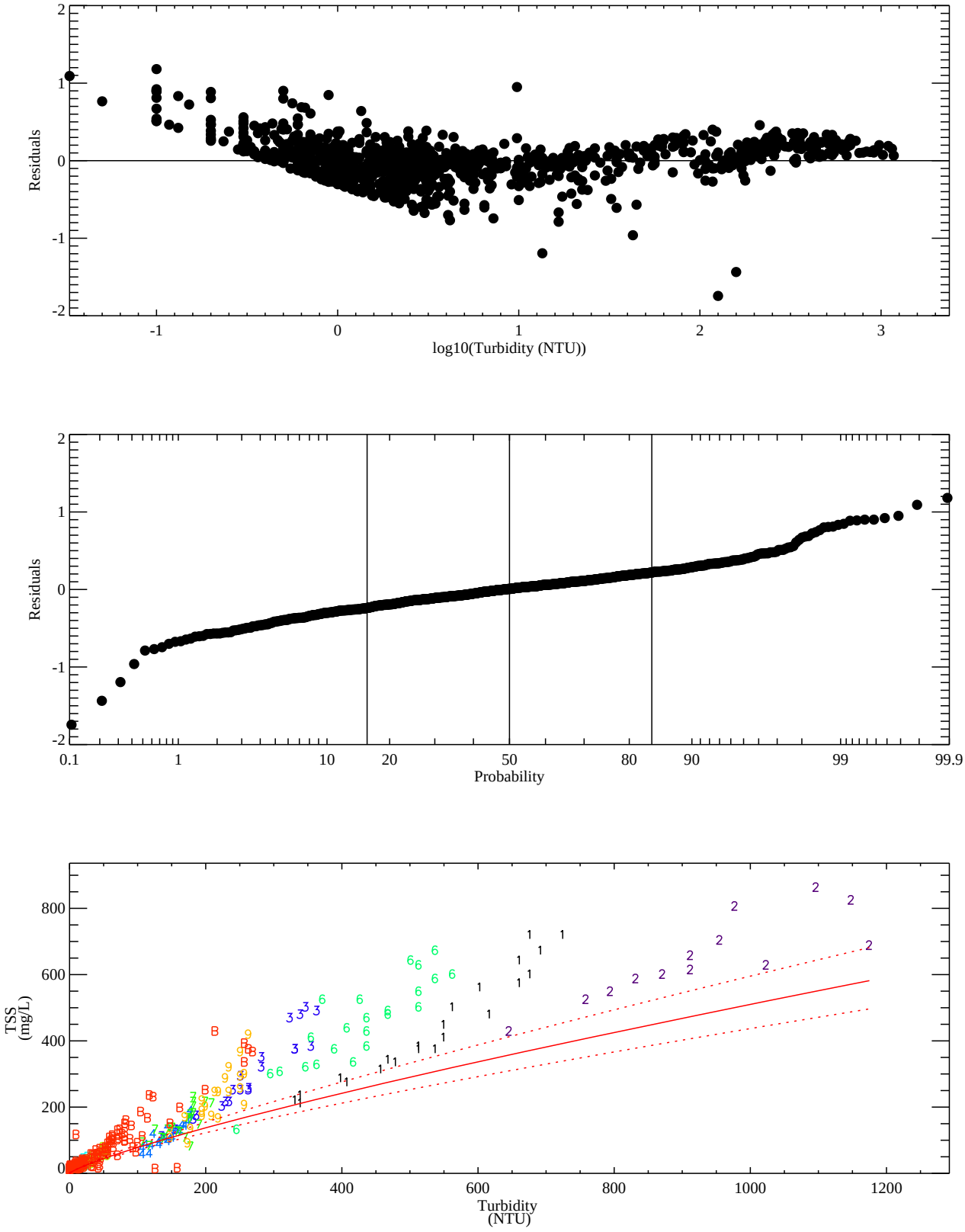

Figure 5-21. Log-log model for pooled lab and BMP data with TSS less than 1000 mg/L.

Lab and BMP data (through 2007): no TSS non-detects or TSS>1000 mg/L; lab data measured between 30 and 360 mins.

Numbers in bottom panel represent laboratory core number. "B" indicates BMP data.

Model
95% CI for Model

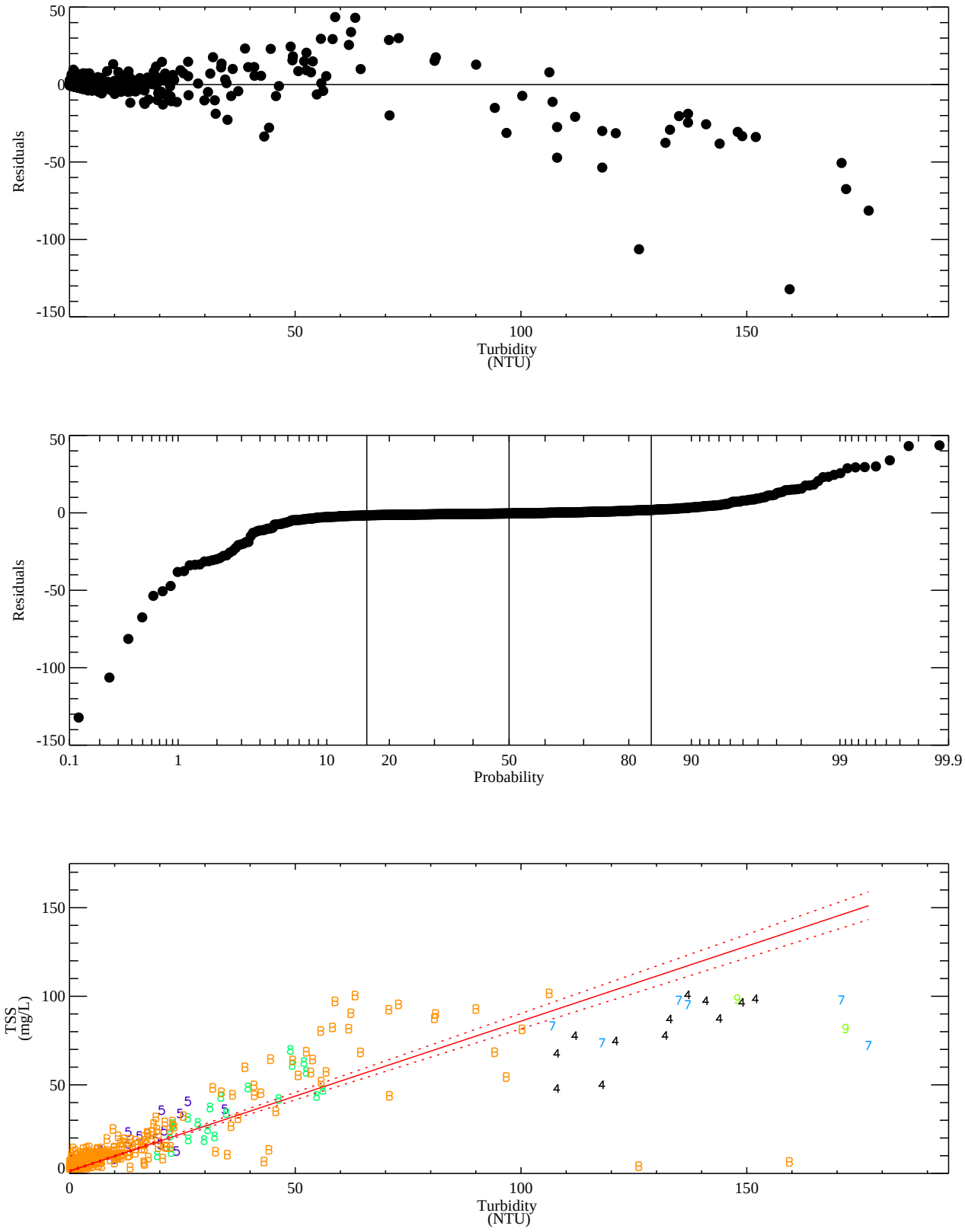

Figure 5-22. Linear model for pooled lab and BMP data with TSS less than 100 mg/L.

Lab and BMP data (through 2007): no TSS non-detects or TSS>100 mg/L; lab data measured between 30 and 360 mins.

Numbers in bottom panel represent laboratory core number. "B" indicates BMP data.

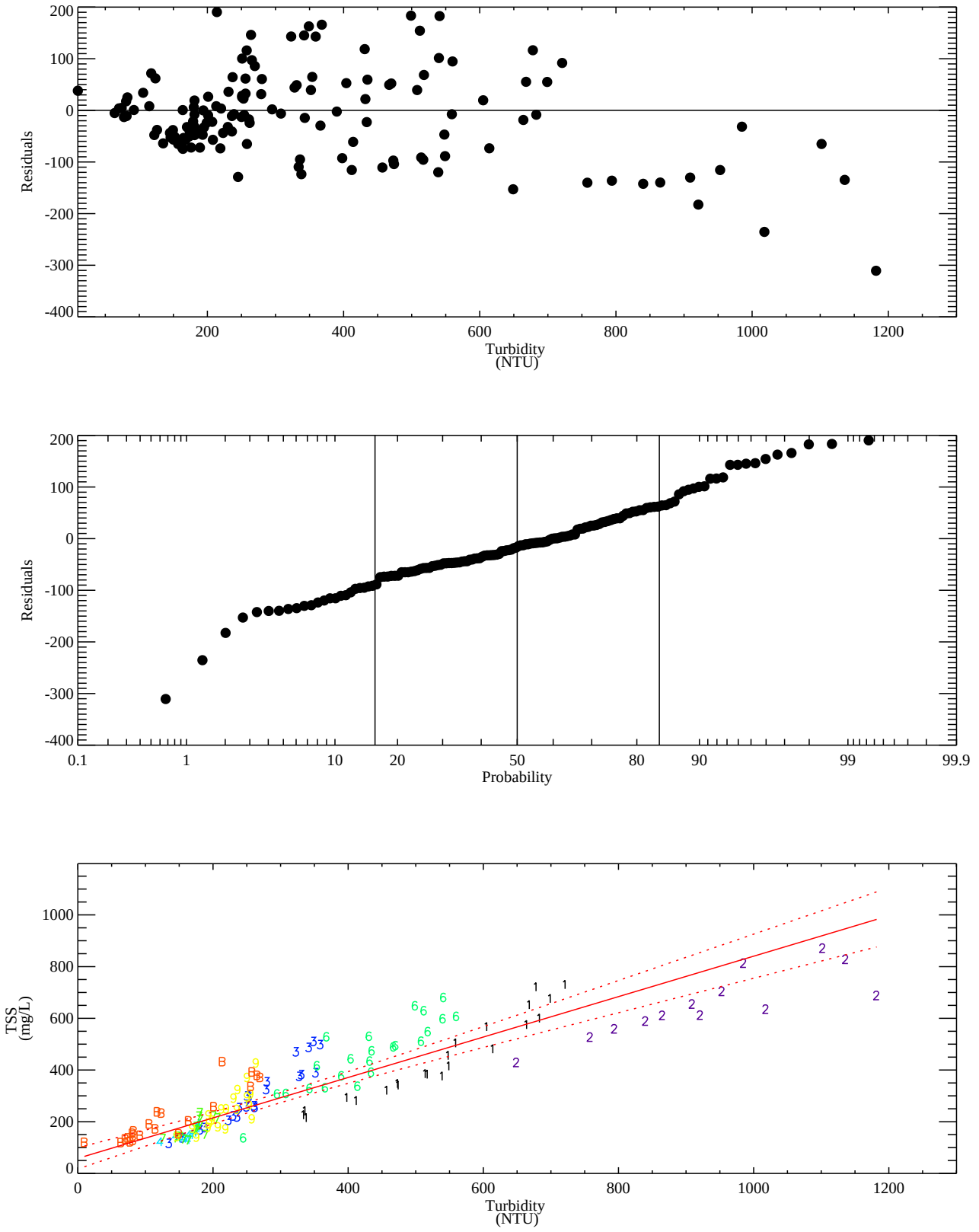

Figure 5-23. Linear model for pooled lab and BMP data with TSS between 100 and 1000 mg/L.

Lab and BMP data (through 2007): no TSS non-detects or TSS<100 mg/L or TSS>1000 mg/L; lab data measured between 30 and 360 mins.

Numbers in bottom panel represent laboratory core number. "B" indicates BMP data.

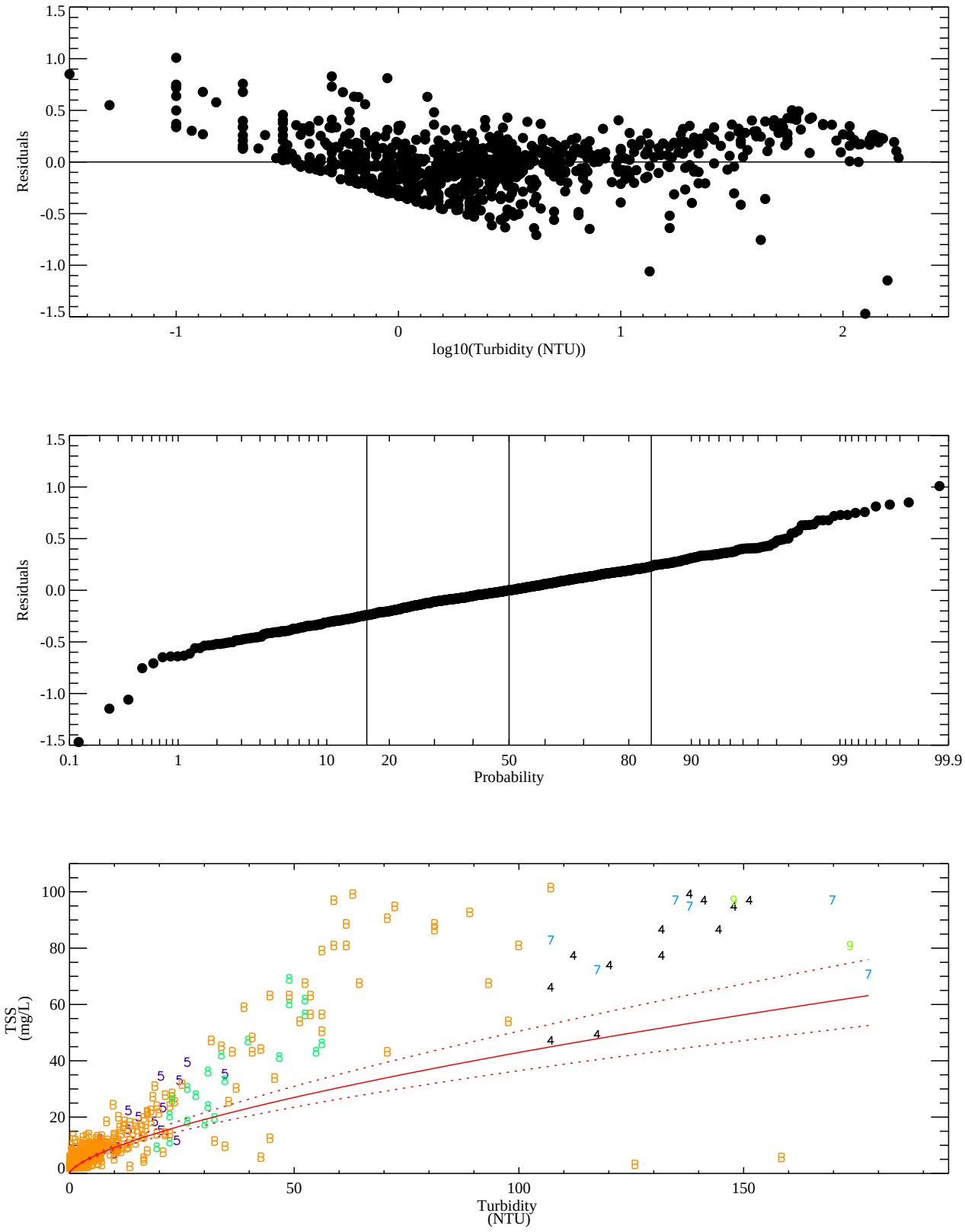

Figure 5-24. Log-log model for pooled lab and BMP data with TSS less than 100 mg/L.

Lab and BMP data (through 2007): no TSS non-detects or TSS>100 mg/L; lab data measured between 30 and 360 mins.

Numbers in bottom panel represent laboratory core number. "B" indicates BMP data.

Model
95% CI for Model

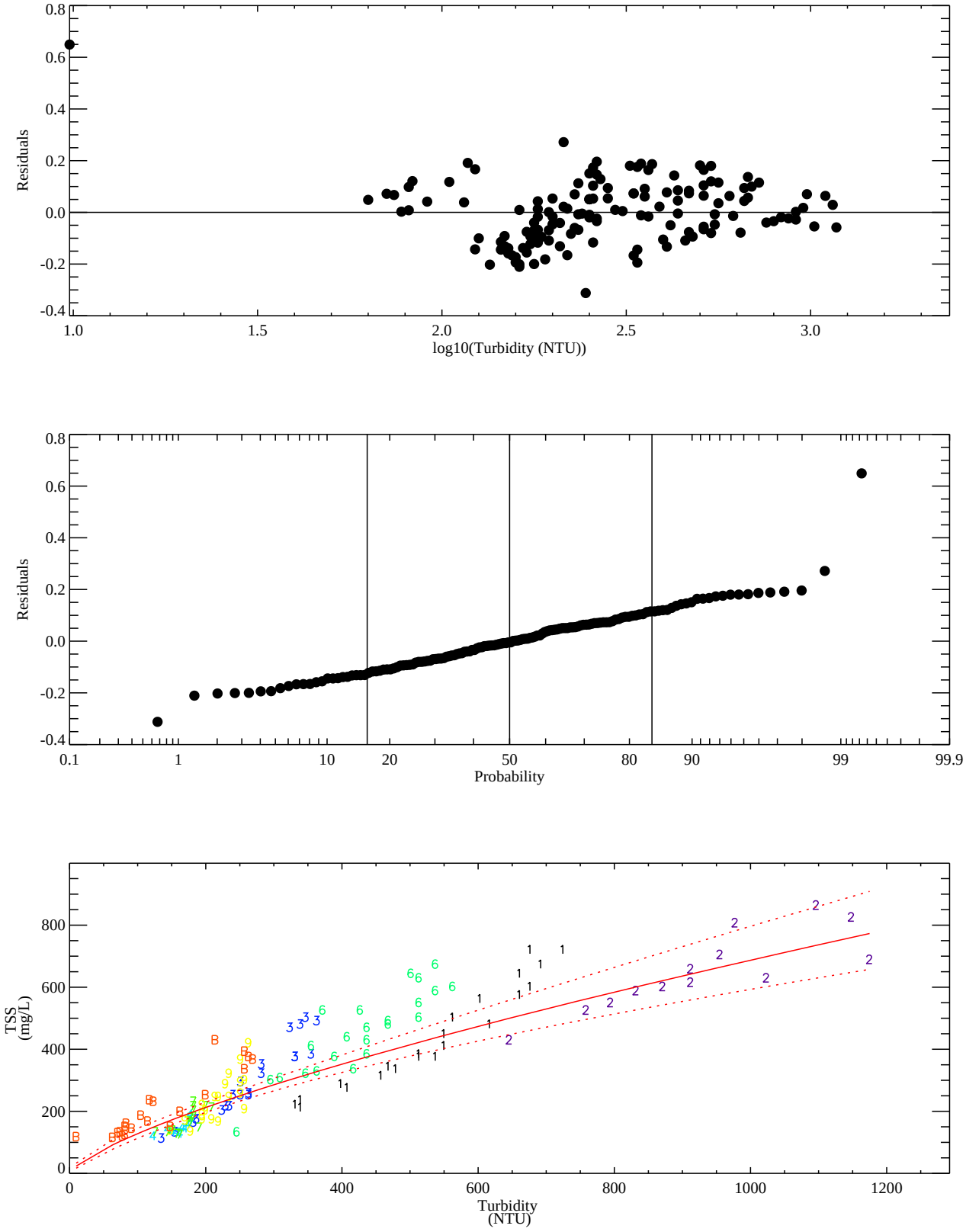

Figure 5-25. Log-log model for pooled lab and BMP data with TSS between 100 and 1000 mg/L.

Lab and BMP data (through 2007): no TSS non-detects or TSS<100 mg/L or TSS>1000 mg/L; lab data measured between 30 and 360 mins.

Numbers in bottom panel represent laboratory core number. "B" indicates BMP data.

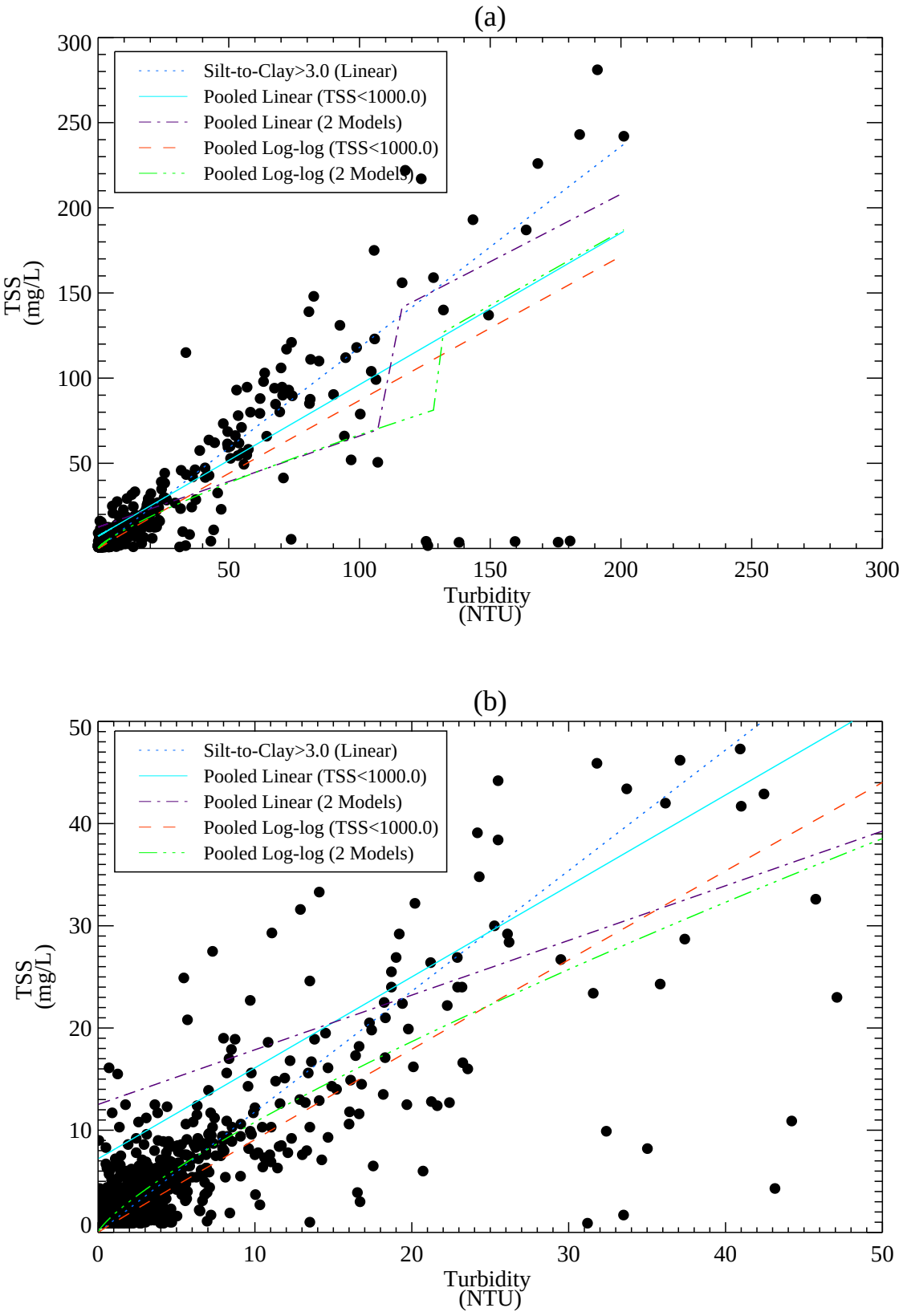

Figure 5-26. Comparison of model performance on baseline monitoring program data measured through 2008: (a) All data; (b) TSS data in the range of 0-50 mg/L.

Turbidity measurements were taken over a transect, while TSS measurements are based on composite samples over the same transect. TSS model estimates are based on the average turbidity value measured at each transect.

A data point with a very high standard error for turbidity was removed. Another data point with unusually high TSS value at zero measured turbidity was removed.

PM - D:\GENra1\Analysis\validation_w_bmp_data_ver2.pro
Fri Feb 20 18:54:25 2009

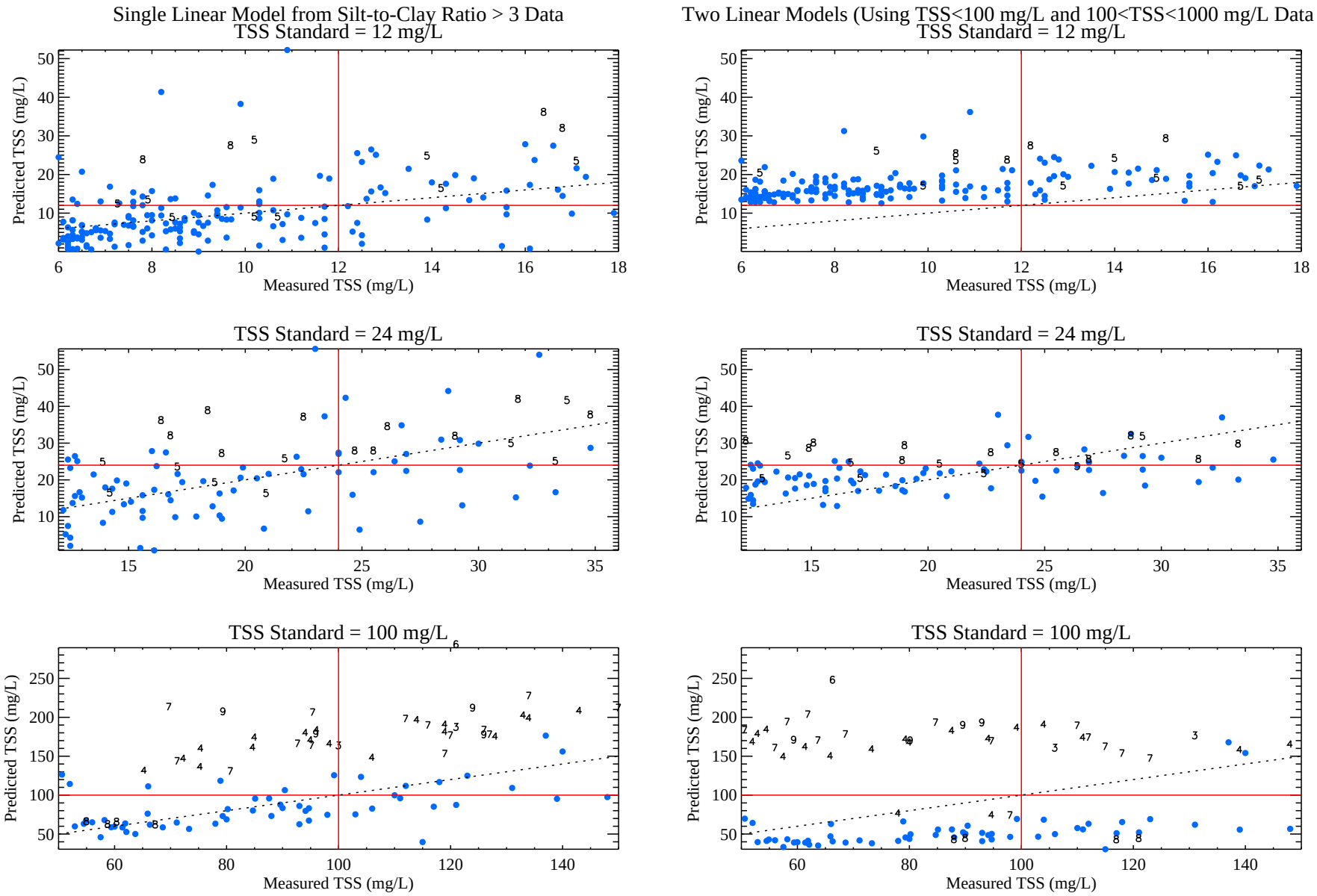

Figure 6-1. Comparison of TSS predictions of top two models to TSS measurements from lab study and the baseline monitoring program.

Solid red lines represent TSS standard. Top left quadrant shows false positives and bottom right quadrant shows false negatives. Dotted line is the one-to-one line. BMP data collected through 2008 are shown as solid circles. Lab data are plotted by core numbers.

Quantitative Environmental Analysis, LLC
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TECHNICAL MEMORANDUM

TO:	Bob Gibson – General Electric Company	**DATE:**	October 28, 2005
FROM:	Margaret Murphy, Ph.D.	**RE:**	TSS/Turbidity Bench Scale Test Sample Collection
CC:	Files	**JOB#:**	GENbmp

Background

The work plan titled *Development of a Semi-Quantitative Surrogate Relationship for Suspended Solids Work Plan* (TSS Work Plan) describes the scope of bench scale laboratory studies and additional field studies to be performed to develop a semi-quantitative relationship between total suspended solids (TSS) and a surrogate parameter (e.g., turbidity or particle size and volumetric concentration) that can be monitored in real-time during near- and far-field compliance monitoring. This monitoring will be performed by General Electric Company (GE) as part of a comprehensive Remedial Action Monitoring Plan (RAMP) for Phase 1 dredging. The TSS Work Plan states that sediment samples will be collected from Phase 1 dredge areas for use in the laboratory studies, in accordance with the Engineering Performance Standards for Resuspension (RPS; USEPA 2004). The objectives of the laboratory studies are to:

- Compare the semi-quantitative relationships of TSS and real-time surrogate parameters for different sediment types to evaluate the sufficiency of using a single near-field surrogate relationship.
- Compare the surrogate relationship(s) for near-field TSS and turbidity with the initial far-field relationship(s) developed using paired data collected under the BMP.
- Evaluate the particles size distribution of suspended sediments under baseline conditions.

The sediment used for the bench scale studies will be selected in a manner that is consistent with the RPS, and will include up to eight separate samples from each of three primary sediment classifications (silt, fine sand, and medium sand; USEPA 2004). According to the RPS: "Samples must have median diameters consistent with their intended class (e.g., silt must fall between 5 and 75 um median diameter (and have that class as the major fraction in the sample." (USEPA 2004; page 122). The samples will be obtained from locations selected based on a review of the data obtained from cores collected from Phase 1 dredge areas.

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The TSS surrogate, turbidity, is affected by particle size and color. Hence, an assessment of grain size and color was conducted on sediment samples collected from October 2002 through August 2005 as part of the Sediment Sampling and Analysis Plan (SSAP) and Supplemental Engineering Data Collection (SEDC) sampling programs. The range in variability of these parameters within Phase 1 and Phase 2 areas, as well as River Sections 1, 2, and 3, provided a means of assessing the need for more site specific TSS-turbidity relationships. Based on these analyses, specific locations within Phase 1 areas were identified to collect the samples necessary for the bench-scale laboratory studies within the required sediment types.

Core selection in Phase 1 areas

The SSAP/SEDC sediment database was queried to assess the variability in grain size and color within the Upper Hudson River. Two separate queries were conducted to assess these parameters. First the database was queried for grain size characteristics in Phase 1 areas and then for each river section and Phase 2 areas. Phase 1 areas were queried to identify potential locations for collection of samples for the bench scale test, while Phase 2 areas were queried for representativeness of the Phase 1 samples to the rest of the river.

The SSAP/SEDC sediment database consists of cores collected during the 2002, 2003, 2004, and 2005 field programs (SSAP, Supplemental Delineation, and Data Gap Programs). Core locations for use in the TSS study and for comparison of grain size in Phase 2 areas were selected based on the following criteria:

1. the primary visual classification of each core segment;
2. core segments with geotechnical data that matched the visual description; and
3. the majority of the core segments above the depth of contamination matched the desired sediment types (silt, fine sand, or medium sand).

In addition, the locations were separated by river section as well as dredge area (Phase 1 or Phase 2) and by the primary visual texture type of the core segments for comparison of variability between both river sections and Phase 1 and 2 dredge areas.

The color analysis was more difficult than the grain size analysis due to the variety of ways that color was recorded in the database. This was not standardized in the database or programmed as a searchable field; therefore, there are many unique records of color descriptions (over 100). Colors were combined into one of three categories: dark color, medium color, and light color. Samples were selected for each category based on the assessment of the primary color type with “very dark”, “dark”, and “black” sediment types falling into the dark color category; “brown”, “gray” combinations, “olive”, “green”, or “red” were placed into the medium color category; and “pink”, “tan”, “light”, “yellow”, “orange”, or “gray” were placed into the light category.

Comparison of samples

Core locations in Phase 1 areas that met the grain size criteria (silt, fine sand, or medium sand) were selected as locations to be sampled for the TSS study. Tables 1 through 3 list the eight cores within each of the three sediment types (24 total) whose locations are recommended for sampling in this study (Table 1 - silt; Table 2 – fine sand; Table 3 – medium sand; Figure 1). It should be noted that at the start of the SSAP program in 2002, there was not a classification for medium sand in the database (only coarse sand and fine sand). This category was added to the program in 2003 to better match the results of the quantitative grain size analysis provided by the geotechnical laboratory (Corrective Action Memo QEA 007; May 2003). There were a limited number of cores collected in the Phase 1 areas after 2002 that met the medium sand sampling criteria. As such, five of the eight selected cores do not have a medium sand classification. Evaluation of the data indicates that samples designated as primarily coarse sand in the processing laboratory in 2002 were actually classified as medium sand when submitted for grain size analysis (see Table 3). Therefore, for samples collected in 2002, a coarse sand description was considered to represent a medium sand composition.

An analysis of the primary texture type in Phase 1 versus Phase 2 dredge areas resulted in slightly different mixtures (Figure 2). Phase 2 has a higher percentage of silt in core segments compared to Phase 1 areas. Fine sand percentages were similar in Phase 1 and Phase 2 areas; therefore, cores selected for the TSS study should be representative of Phase 2 areas as well. There is a slightly higher percentage of coarse sand in Phase 1 areas compared to Phase 2 areas (Figure 2). Comparing sediment types in River Sections 1, 2, and 3 we found a general trend of increasing silt content and decreasing coarse sand content moving downstream (Figure 3).

The color of each core segment was used to assess turbidity conditions during dredging (turbidity measurements can be influenced by color of particles). Brown and grey brown (both classified as medium color) are the predominant colors that are located within the segments above the depth of contamination (Tables 1, 2, 3). There did not appear to be a relationship between grain size and color. Within Phase 1 and 2 areas combined, medium color is dominant with very little light colored sediments. Fine sand was the only sediment type that contained light colored sediment, while silt and medium sand had a similar composition of almost evenly spread medium and dark color (Table 4).

Conclusion

Overall, the locations selected for the TSS surrogate study are representative of conditions throughout the Upper Hudson River. The eight selected cores within each of the three sediment types were the most homogeneous with respect to desired grain size from the surface to the depth of contamination. These locations should allow for samples that will test the range of conditions expected during both Phase 1 and Phase 2 dredging.

Table 1. Silt proposed sampling locations.

CORE ID	FIELD SAMPLE ID	START DEPTH	END DEPTH	FIELD DESCRIPTION	SILT	COARSE SAND	MEDIUM SAND	GRAVEL	CLAY	FINE SAND	DOC (IN)	SELECT	YEAR	DESCRIPTION
RS1-9392-WT032	RS1-9392-WT032-000002	00	02	SI/FS/--/--	53.5	0	2.1	0	11.5	32.9	18		2002	DARK GRAY-BROWN
	RS1-9392-WT032-002012	02	12	SI/--/OR/--										DARK GRAY; SMALL PIECES OF WOOD
	RS1-9392-WT032-012018	12	18	SI/OR/--/--										BROWN; SOME WOOD PULP
	RS1-9392-WT032-018024	18	24	SI/OR/FS/--										BROWN; SOME WOOD PULP
	RS1-9392-WT032-024030	24	30	FS/SI/--/--										GRAY-BROWN
	RS1-9392-WT032-030032	30	32	SI/OR/FS/--										GRAY-BROWN; SOME WOOD PULP
RS1-9392-WT150	RS1-9392-WT150-000002	00	02	SI/--/OR/FS	49.1	0.1	1.4	0	8.5	40.9	24		2002	DARK BROWN. OR= WOOD & ROOTS
	RS1-9392-WT150-002024	02	24	SI/OR/--/FS										DARK BROWN. OR= WOOD, WOOD PULP, TWIGS AND ROOTS
	RS1-9392-WT150-024030	24	30	SI/FS/OR/--										GREY BROWN. OR= WOOD PULP
	RS1-9392-WT150-030036	30	36	SI/FS/--/OR										BROWN. OR= ROOTS
	RS1-9392-WT150-036042	36	42	FS/SI/--/OR										BROWN, OR= WOOD, ROOTS
	RS1-9392-WT150-042048	42	48	FS/SI/--/OR										BROWN, OR = TRACE ROOTS
	RS1-9392-WT150-048051	48	51	FS/SI/--/OR										BROWN, OR= ROOTS
RS1-9493-IN110	RS1-9493-IN110-000002	00	02	FS/SI/--/OR	48.7	0	3.6	0	19.1	28.6	36		2004	GR BR, OR=ROOTS AND VEG
	RS1-9493-IN110-002012	02	12	FS/--/SI/OR										DK BR, OR=ROOTS
	RS1-9493-IN110-012024	12	24	SI/FS/--/OR										DK GR BR, OR=LVS, ROOTS, VEG, ODOR
	RS1-9493-IN110-024030	24	30	SI/FS/--/OR										DK BR, OR=WOOD CHIPS, VEG, SLIGHT ODOR
	RS1-9493-IN110-030036	30	36	SI/--/FS/OR										DK BR, OR=WOOD CHIPS, WOOD PULP, VEG, TWIGS
	RS1-9493-IN110-036042	36	42	SI/FS/OR/--										GR BR, OR=VEG
	RS1-9493-IN110-042048	42	48	FS/--/--/OR										GR BR, OR=VEG, TR SI
	RS1-9493-IN110-048050	48	50	SI/OR/FS/--										GR BR, OR=WOOD AND WOOD PULP
RS1-9493-WS602	RS1-9493-WS602-000002	00	02	CS/GR/FS/OR	33.7	9.6	14.8	11.7	17.4	12.9	24		2003	DARK GRAY BROWN, ORGANICS-WOOD
	RS1-9493-WS602-002024	02	24	SI/CS/GR/CL										2-10 INCHES SAND AND GRAVEL, 10-24 INCHES SILT, LITTLE CLAY
	RS1-9493-WS602-024030	24	30	SI/--/CL/--										GRAY
	RS1-9493-WS602-030036	30	36	SI/--/CL/--										GRAY
	RS1-9493-WS602-036042	36	42	SI/--/CL/--										GRAY
	RS1-9493-WS602-048054	48	54	SI/--/CL/FS										GRAY
	RS1-9493-WS602-054060	54	60	SI/--/CL/FS										GRAY
	RS1-9493-WS602-060066	60	66	SI/--/CL/FS										GRAY
RS1-9493-WT206	RS1-9493-WT206-000002	00	02	SI/--/--/OR	46.7	0.2	3.7	0	22	27.5	48		2003	DARK GRAY BROWN, ORGANICS/ROOTS
	RS1-9493-WT206-002024	02	24	SI/CL/--/OR										DARK GRAY BROWN, SLIGHT ODOR, ORGANICS/WOOD & ROOTS
	RS1-9493-WT206-024030	24	30	SI/--/CL/OR										DARK GRAY BROWN, SLIGHT ODOR, ORGANICS/ROOTS
	RS1-9493-WT206-030036	30	36	SI/--/CL/FS										DARK GRAY BROWN, SLIGHT ODOR, TRACE ORGANICS/ROOTS & LEAVES
	RS1-9493-WT206-036042	36	42	SI/--/CL/FS										GRAY BROWN, SLIGHT ODOR, TRACE ORGANICS/ROOTS
	RS1-9493-WT206-042048	42	48	SI/--/CL/OR										GRAY BROWN, ORGANICS/ROOTS
	RS1-9493-WT206-048054	48	54	SI/--/CL/OR										GRAY BROWN, ORGANICS/ROOTS
	RS1-9493-WT206-054060	54	60	SI/FS/--/OR										GRAY BROWN, ORGANICS/ROOTS & WOOD
	RS1-9493-WT206-060064	60	64	FS/--/OR/MS										GRAY BROWN, ORGANICS/WOOD PULP
	RS1-9493-WT206-064066	64	66	OR/--/--/FS										ORGANICS/WOOD & WOOD PULP
RS1-9493-WT211	RS1-9493-WT211-000002	00	02	SI/--/--/--	60.3	0	1.5	0	24.8	13.4	66		2003	DARK BROWN
	RS1-9493-WT211-002024	02	24	SI/--/--/OR										DARK BROWN; OR-TRACE LEAVES & WOOD PULP; ODOR
	RS1-9493-WT211-024030	24	30	SI/--/--/OR										DARK GRAY-BROWN TO BROWN; OR-TRACE LEAVES; SOME SMALL PIECES OF PLASTIC; ODOR
	RS1-9493-WT211-030036	30	36	SI/--/--/OR										BROWN; OR-TRACE VEGETATION; SOME SMALL PIECES OF PLASTIC; ODOR
	RS1-9493-WT211-036042	36	42	SI/--/OR/--										BROWN; OR-LITTLE LEAVES; SOME SMALL PIECES OF PLASTIC; ODOR
	RS1-9493-WT211-042048	42	48	SI/--/OR/--										DARK BROWN; OR-LITTLE LEAVES & TWIGS; ODOR
	RS1-9493-WT211-048054	48	54	SI/--/OR/--										DARK BROWN; OR-LITTLE LEAVES & TWIGS; ODOR
	RS1-9493-WT211-054060	54	60	SI/--/OR/--										DARK BROWN; OR-LITTLE LEAVES & TWIGS
	RS1-9493-WT211-060066	60	66	SI/MS/FS/CL										DARK BROWN; OR-LITTLE LEAVES & TWIGS; SOME SMALL PIECES OF PLASTIC
	RS1-9493-WT211-066068	66	68	FS/MS/GR/--										BROWN; SOME SMALL PIECES OF PLASTIC
RS1-9594-AR071	RS1-9594-AR071-000002	00	02	SI/OR/--/--	54.2	0	2.5	0	30.4	12.8	36		2004	BROWN, OR-WOODPULP, WEEDS, AND ROOTS.
	RS1-9594-AR071-002012	02	12	SI/OR/--/FS										GRAY-BROWN, OR-LEAVES AND ROOTS, SLIGHT ODOR.
	RS1-9594-AR071-012024	12	24	SI/OR/--/--										GRAY-BROWN, OR-LEAVES, TWIGS AND ROOTS, ODOR.
	RS1-9594-AR071-024030	24	30	SI/--/OR/FS										GRAY-BROWN, OR-VEG, ODOR.
	RS1-9594-AR071-030036	30	36	SI/--/OR/FS										GRAY-BROWN, OR-ROOTS, VEGETATION, ODOR.
	RS1-9594-AR071-036042	36	42	SI/--/OR/FS										DARK GRAY-BROWN, OR-VEG, SLIGHT ODOR.
	RS1-9594-AR071-042048	42	48	SI/--/FS/OR										GRAY-BROWN, OR-VEG.
	RS1-9594-AR071-048054	48	54	SI/--/FS/OR										GRAY-BROWN, OR-VEG.
	RS1-9594-AR071-054059	54	59	SI/--/FS/OR										GRAY-BROWN, OR-LEAVES AND TWIGS.
	RS1-9594-AR071-059061	59	61	SI/--/FS/OR										GRAY-BROWN, OR-LEAVES AND TWIGS.
RS1-9392-WT182	RS1-9392-WT182-000002	00	02	SI/--/FS/OR	29	4.3	16.8	12.2	9.2	28.6	30		2002	DARK BROWN, OR=VEG
	RS1-9392-WT182-002024	02	24	SI/FS/CS/--										DARK BROWN, OR=VEG
	RS1-9392-WT182-024030	24	30	FS/CS/--/SI										DARK BROWN, SILT FS/CS INTERFACE AT 26in
	RS1-9392-WT182-030036	30	36	FS/--/CS/SI										DARK BROWN, SILT FS/CS INTERFACE AT 26in
	RS1-9392-WT182-036042	36	42	CS/--/FS/--										OLIVE BROWN, TRACE SLAG

Table 2. Fine sand proposed sampling locations.

CORE ID	FIELD SAMPLE ID	START DEPTH	END DEPTH	FIELD DESCRIPTION	FINE SAND	SILT	COARSE SAND	MEDIUM SAND	GRAVEL	CLAY	DOC (IN)	SELECT	YEAR	SEGMENT DESCRIPTION
	RS1-9190-CS318-000002	00	02	CS/--/--/FS										OLIVE BROWN, TRACE OR=WOOD CHIPS
	RS1-9190-CS318-002024	02	24	FS/--/CS/GR	79.7	1.6	1.6	9.5	5.7	2				OLIVE BROWN FS/-/-/CS AND GR TO 12, GRAY FS TO 24.
	RS1-9190-CS318-024030	24	30	FS/--/--/--										GRAY
	RS1-9190-CS318-030036	30	36	FS/--/--/SI										GRAY
RS1-9190-CS318	RS1-9190-CS318-036042	36	42	FS/--/--/--							24		2002	GRAY
	RS1-9190-CS318-042048	42	48	FS/--/SI/--										GRAY
	RS1-9190-CS318-048054	48	54	FS/SI/--/--										GRAY
	RS1-9190-CS318-054060	54	60	FS/--/SI/--										GRAY
	RS1-9190-CS318-060062	60	62	FS/--/--/SI										GRAY
	RS1-9190-ET358-000002	00	02	FS/SI/OR/--										BROWN-GREY; O-VEGETATION, BIOTA-CLAM
	RS1-9190-ET358-002024	02	24	FS/SI/GR/OR	71.7	2.5	4.8	11.6	6.4	3				BROWN; O-ROOTS, WOOD
	RS1-9190-ET358-024030	24	30	CS/FS/GR/--										DARK GREY
	RS1-9190-ET358-030036	30	36	CS/FS/GR/--										DARK GREY
RS1-9190-ET358	RS1-9190-ET358-036042	36	42	CS/FS/GR/--							24		2002	DARK GREY
	RS1-9190-ET358-042048	42	48	CS/FS/GR/SI										DARK GREY
	RS1-9190-ET358-048054	48	54	CS/FS/GR/SI										DARK GREY
	RS1-9190-ET358-054060	54	60	CS/FS/GR/SI										DARK GREY
	RS1-9190-ET358-060062	60	62	CS/FS/GR/SI										DARK GREY
	RS1-9190-ET426-000002	00	02	FS/SI/OR/--										GRAY-BROWN
	RS1-9190-ET426-002024	02	24	FS/SI/OR/--	54.9	13.5	0	9.3	0	22.2				2-8 IN - GRAY-BROWN SI, ODOR; 8-14 IN - BROWN, OR-WOOD & WOOD PULP; 14-24 IN - GRAY-BROWN FS
	RS1-9190-ET426-024030	24	30	FS/OR/GR/--										GRAY-BROWN; OR-WOOD PULP
	RS1-9190-ET426-030036	30	36	FS/MS/CS/--										GRAY-BROWN; SOME MS TO CS
RS1-9190-ET426	RS1-9190-ET426-036042	36	42	FS/MS/CS/--							24		2003	GRAY-BROWN; SOME MS TO CS
	RS1-9190-ET426-042048	42	48	FS/MS/CS/OR										GRAY-BROWN; SOME MS TO CS; OR-LITTLE WOOD
	RS1-9190-ET426-048054	48	54	FS/MS/CS/CL										GRAY-BROWN; SOME MS TO CS; TRANSITION TO GRAY-BROWN CLAY AT 53 IN MARK
	RS1-9190-ET426-054060	54	60	CL/--/--/--										GRAY-BROWN
	RS1-9190-ET426-060062	60	62	CL/--/--/--										GRAY-BROWN
	RS1-9392-AB013-000002	00	02	FS/--/MS/OR										GREY BROWN, SOME SLAG, OR=WOOD
	RS1-9392-AB013-002012	02	12	FS/--/--/GR										GREY BROWN, LITTLE SLAG
	RS1-9392-AB013-012024	12	24	FS/GR/OR/MS										DARK GREY BROWN, OR=WOOD
	RS1-9392-AB013-024030	24	30	FS/GR/--/--										GREY BROWN
RS1-9392-AB013	RS1-9392-AB013-030036	30	36	FS/--/--/CS	87	4.3	1.3	3.1	0.9	3.4	24		2004	GREY BROWN
	RS1-9392-AB013-036042	36	42	FS/--/--/--										GREY BROWN
	RS1-9392-AB013-042048	42	48	FS/--/--/--										GREY BROWN
	RS1-9392-AB013-048054	48	54	FS/--/--/--										GREY BROWN
	RS1-9392-AB013-054056	54	56	FS/--/--/--										GREY BROWN
	RS1-9392-AB013-056058	56	58	FS/--/--/--										GREY BROWN
	RS1-9392-WT072-000002	00	02	SI/--/FS/OR										DARK BROWN; O-ROOTS VEGETATION
	RS1-9392-WT072-002024	02	24	FS/SI/OR/--	75.2	9.9	2	11.9	0.4	0.6				DARK GREY-BROWN; O-WOOD PULP, WOOD, VEGETATION, ROOTS
RS1-9392-WT072	RS1-9392-WT072-024030	24	30	FS/OR/CS/SI							24		2002	DARK GREY; O-WOOD PULP, WOOD
	RS1-9392-WT072-030036	30	36	FS/CS/GR/SI										DARK GREY
	RS1-9392-WT072-036042	36	42	FS/--/CS/GR										GREY-BROWN
	RS1-9392-WT072-042047	42	47	FS/--/--/OR										GREY; O-WOOD, TWIGS
	RS1-9493-WT004-000002	00	02	OR/--/--/--										BROWN WOOD CHIPS
	RS1-9493-WT004-002024	02	24	FS/--/CS/CL	56.2	10.8	6.6	14.9	8.2	3.4				DARK BROWN, TRACE SLAG, DARK BROWN CLAY LAYER 22-24in.
	RS1-9493-WT004-024030	24	30	FS/--/CS/--										OLIVE BROWN, TRACE SLAG (CS)
RS1-9493-WT004	RS1-9493-WT004-030036	30	36	FS/--/--/OR							30		2002	GRAY, OR=VEG
	RS1-9493-WT004-036042	36	42	CL/SI/--/--										GRAY VARVED CLAY WITH SILT
	RS1-9493-WT004-042048	42	48	CL/SI/--/--										GRAY VARVED CLAY WITH SILT
	RS1-9493-WT004-048054	48	54	CL/SI/--/--										GRAY VARVED CLAY WITH SILT
	RS1-9493-WT718-000002	00	02	FS/SI/--/MS										DARK GREY BROWN. TRACE OR= ROOTS, TWIGS.
	RS1-9493-WT718-002024	02	24	FS/SI/--/MS	68.8	5.8	3.7	8.7	3.3	9.7				DARK GREY BROWN. TRACE OR= ROOTS, TWIGS.
	RS1-9493-WT718-024030	24	30	FS/SI/CS/OR										DARK GREY BROWN. OR= TWIGS, WOOD CHUNKS
RS1-9493-WT718	RS1-9493-WT718-030036	30	36	FS/SI/CS/OR							42		2003	DARK GREY BROWN. OR= TWIGS, WOOD CHUNKS
	RS1-9493-WT718-036042	36	42	FS/SI/CS/OR										DARK GREY BROWN. OR= WOOD CHUNKS, TWIGS, TRACE WOOD PULP.
	RS1-9493-WT718-042045	42	45	FS/SI/CS/OR										DARK GREY BROWN. OR=TWIGS. TRACE WOOD PULP.
	RS1-9493-WT718-045047	45	47	CS/GR/MS/FS										DARK GREY BROWN. TRACE OR= TWIGS.
	RS1-9594-WS175-000002	00	02	SI/FS/CS/OR										DARK BROWN; O-ROOTS, VEGETATION
	RS1-9594-WS175-002024	02	24	FS/--/SI/OR										GREY; O-WOOD PULP
RS1-9594-WS175	RS1-9594-WS175-024030	24	30	FS/--/SI/OR	78.2	11.8	0	6.2	0	3.8	30		2002	GREY BROWN; O-WOOD PULP; SLIGHT ODOR.
	RS1-9594-WS175-030036	30	36	FS/CS/SI/OR										BROWN;O-WOOD PULP; SLIGHT ODOR
	RS1-9594-WS175-036040	36	40	CS/FS/GR/OR										DARK GREY; O-WOOD

Table 3. Medium Sand proposed sampling locations.

CORE ID	FIELD SAMPLE ID	START DEPTH	END DEPTH	FIELD DESCRIPTION	MEDIUM SAND	SILT	COARSE SAND	GRAVEL	CLAY	FINE SAND	DOC (IN)	SELECT	YEAR	DESCRIPTION
RS1-9392-CT121	RS1-9392-CT121-000002	00	02	CS/GR/--/FS							18		2002	BROWN, TR SLAG(CS)
	RS1-9392-CT121-002006	02	06	CS/GR/--/--										BROWN, TR SLAG (CS)
	RS1-9392-CT121-006012	06	12	CS/FS/GR/OR										BROWN, TR ORG=WOOD, L SLAG, TR POTTERY
	RS1-9392-CT121-012018	12	18	CS/FS/GR/OR	35.1	4.2	17.2	26.1	1.3	15.9				OLIVEBROWN, TR ORG=WOOD, L SLAG
	RS1-9392-CT121-018022	18	22	FS/OR/--/GR										OLIVEBROWN, ORG=WOODCHIPS AND PULP
RS1-9392-CT633	RS1-9392-CT633-000002	00	02	MS/FS/CS/GR							34		2003	GRAY BROWN, TRACE ORGANICS/WOOD
	RS1-9392-CT633-002012	02	12	CS/MS/FS/GR	36.3	5.2	23.1	16.3	0.9	18.2				GRAY BROWN, TRACE SLAG
	RS1-9392-CT633-012018	12	18	CS/MS/FS/GR										GRAY BROWN, TRACE SLAG
	RS1-9392-CT633-018024	18	24	CS/MS/FS/GR										GRAY BROWN, LITTLE SLAG, TRACE ORGANICS/WOOD
	RS1-9392-CT633-024030	24	30	CS/MS/FS/GR										GRAY BROWN, LITTLE SLAG, TRACE ORGANICS/WOOD
	RS1-9392-CT633-030034	30	34	FS/MS/CS/OR										GRAY BROWN, ORGANICS/WOOD, TRACE SLAG
	RS1-9392-CT633-034036	34	36	FS/--/--/GR										GRAY BROWN
RS1-9493-WS091	RS1-9493-WS091-000002	00	02	GR/CS/FS/SI							30		2002	DARK GREY
	RS1-9493-WS091-002024	02	24	CS/FS/GR/SI										DARK GREY
	RS1-9493-WS091-024030	24	30	CS/FS/GR/SI	33.1	9.4	15.5	16.1	9.2	16.7				DARK GREY; AT 29in GREY CLAY CONTACT; TRACE
	RS1-9493-WS091-030036	30	36	CL/--/--/--										GREY;TRACE SILT SEAM AT 33in
RS1-9493-WS617	RS1-9493-WS617-000002	00	02	GR/CS/MS/FS							36		2003	DARK GRAY BROWN, TRACE SILT
	RS1-9493-WS617-002024	02	24	CS/MS/GR/FS	35	3.1	13.6	16.5	1.9	29.9				DARK GRAY BROWN, TRACE SILT
	RS1-9493-WS617-024030	24	30	MS/FS/CS/GR										DARK GRAY BROWN
	RS1-9493-WS617-030036	30	36	MS/FS/CS/GR										DARK GRAY BROWN
	RS1-9493-WS617-036038	36	38	MS/FS/CS/GR										DARK GRAY BROWN
RS1-9493-WS626	RS1-9493-WS626-000002	00	02	OR/GR/FS/--							24		2003	BROWN: OR- PRIMARY WOOD AND WOOD CHIPS
	RS1-9493-WS626-002024	02	24	MS/GR/OR/--	47.2	4.8	15.5	9.4	3.4	19.8				DARK GRAY-BROWN; SOME SLAG; OR-SOME WOOD
	RS1-9493-WS626-024030	24	30	MS/CS/GR/--										DARK GRAY-BROWN; LITTLE SLAG
	RS1-9493-WS626-030036	30	36	CS/MS/GR/--										DARK GRAY-BROWN
	RS1-9493-WS626-036042	36	42	CS/GR/MS/--										DARK GRAY-BROWN
	RS1-9493-WS626-042044	42	44	CS/GR/MS/--										DARK GRAY-BROWN
RS1-9493-WT009	RS1-9493-WT009-000002	00	02	FS/--/SI/OR							24		2002	DARK BROWN; O-VEGETATION, ROOTS
	RS1-9493-WT009-002024	02	24	CS/FS/GR/SI	32.1	7.1	14.1	22.8	0.3	23.7				DARK GREY
	RS1-9493-WT009-024030	24	30	CS/FS/GR/SI										DARK GREY
	RS1-9493-WT009-030036	30	36	CS/FS/GR/SI										DARK GREY
	RS1-9493-WT009-036042	36	42	FS/CS/GR/SI										DARK GREY
	RS1-9493-WT009-042048	42	48	CS/FS/GR/SI										DARK GREY
	RS1-9493-WT009-048054	48	54	SI/--/--/CL										48in-51in - SAME AS ABOVE,GREY BROWN, TRACE CLAY LAMINATIONS
	RS1-9493-WT009-054058	54	58	SI/--/FS/CL										GREY; TRACE F-SAND AND CLAY LAYERS
RS1-9493-WT051	RS1-9493-WT051-000002	00	02	OR/FS/SI/CS							36		2002	DARK BROWN; O-WOOD; TRACE SLAG
	RS1-9493-WT051-002024	02	24	CS/FS/--/OR	43.2	3.5	12.7	4.6	0.4	35.6				DARK BROWN; TRACE SILT; O-WOOD
	RS1-9493-WT051-024030	24	30	CS/FS/OR/--										DARK BROWN; O-WOOD
	RS1-9493-WT051-030036	30	36	CS/FS/GR/OR										DARK GREY; O- WOOD
	RS1-9493-WT051-036042	36	42	CL/--/--/SI										GREY
	RS1-9493-WT051-042048	42	48	CL/--/--/SI										GREY; DISCARDED FROM 48in-86in DUE TO CLAY.
RS1-9594-WS169	RS1-9594-WS169-000002	00	02	CS/FS/OR/SI							24		2002	BROWN; O-WOOD
	RS1-9594-WS169-002024	02	24	CS/FS/GR/OR	30.3	2.3	14	26.4	0.9	26.1				BROWN; O-WOOD
	RS1-9594-WS169-024030	24	30	GR/CS/FS/SI										DARK GREY
	RS1-9594-WS169-030036	30	36	CS/FS/GR/SI										DARKM GREY

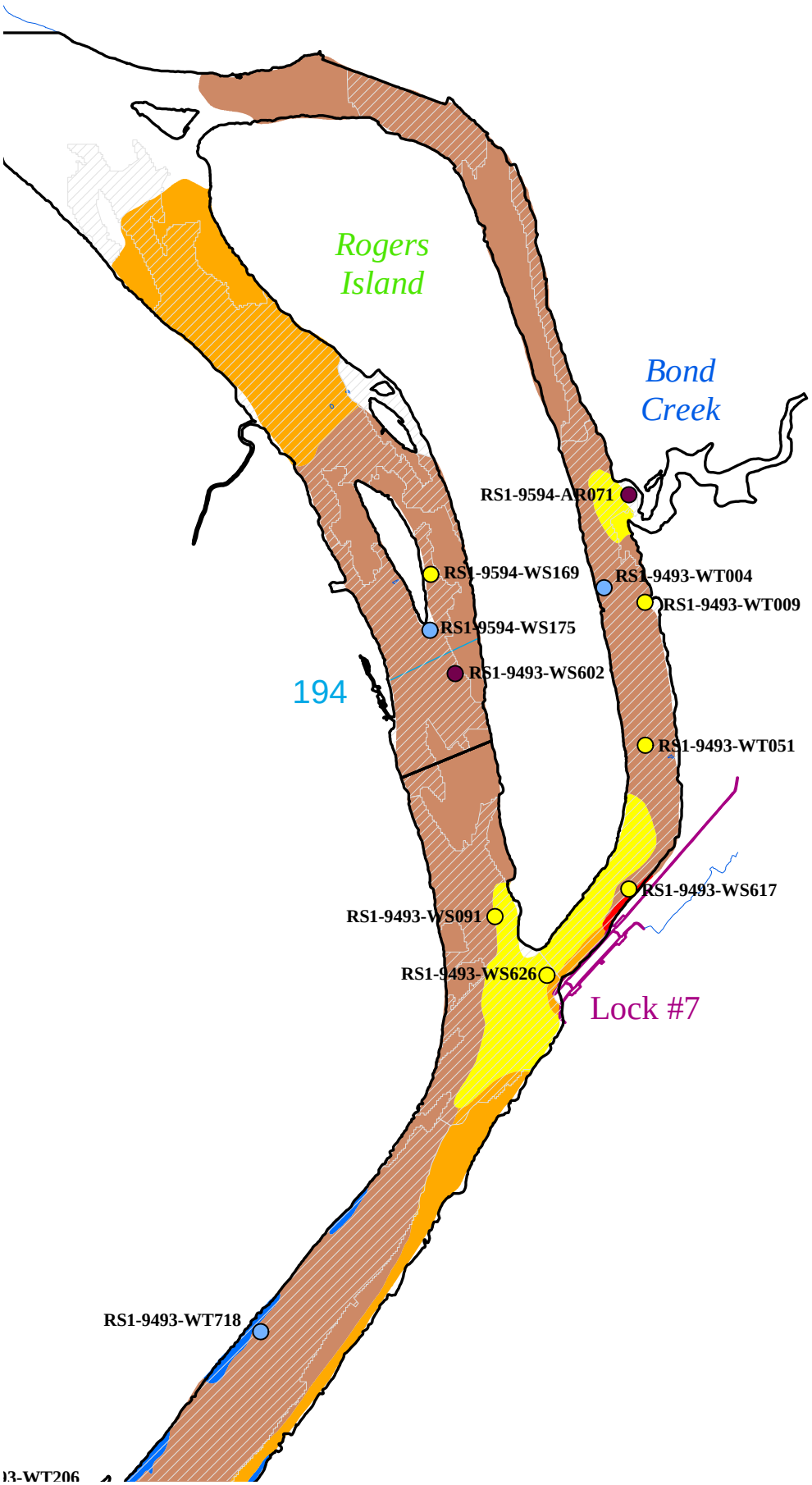
Table 4. Percentage of color types within core segments.

		Light Color	Medium Color	Dark Color
Phase 1, 2		9.9	59.4	30.7
Phase 1	**FS**	4.5	50.0	45.5
	SI	0	50	50
	MS	0	48.1	51.9

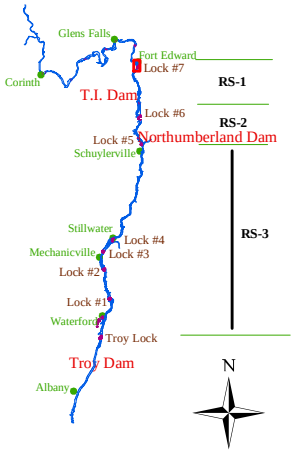
Notes:

Phase 1,2 - color shown for all core segments

Phase 1- color shown for cores from segments in proposed locations only



LOCATOR MAP OF THE UPPER HUDSON RIVER



GRAPHIC SCALE

0 250 500 Feet

LEGEND

Proposed TSS Locations

- FS
- MS
- SI

OSI Side Scan Sonar

- Fine grained / silty
- Sandy
- Gravel / Cobbles
- Variable / Transitional
- Rocky

Background data

- Phase I Area
- Proposed Dredge Areas
- Dams and Locks
- Shore Line

Notes:
Proposed Dredge Areas file issued on 3/3/05.
Phase I Area file updated on 9/26/05.

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Figure 1a.

Proposed TSS Study Locations
(Primary sediment type shown)

QEA Quantitative Environmental Analysis, LLC

GENbmp Oct 28, 2005

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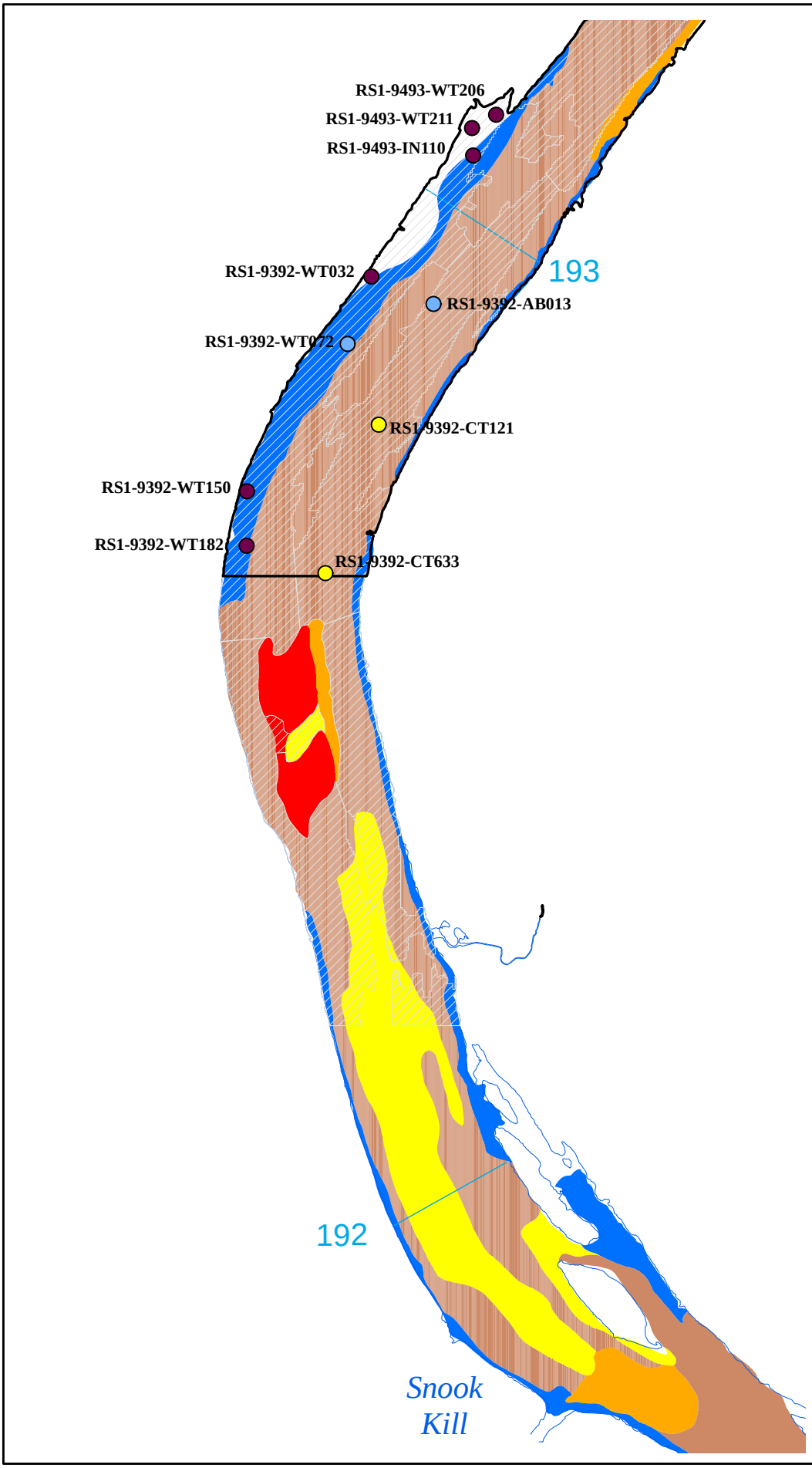
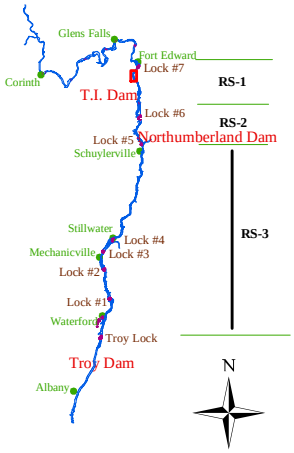


LOCATOR MAP OF THE UPPER HUDSON RIVER



GRAPHIC SCALE

0 250 500 Feet

LEGEND

Proposed TSS Locations

- FS
- MS
- SI

OSI Side Scan Sonar

- Fine grained / silty
- Sandy
- Gravel / Cobbles
- Variable / Transitional
- Rocky

Background data

- Phase I Area
- Proposed Dredge Areas
- Dams and Locks
- Shore Line

Notes:
Proposed Dredge Areas file issued on 3/3/05.
Phase I Area file updated on 9/26/05.

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Hudson River Project

Figure 1b.

Proposed TSS Study Locations
(Primary sediment type shown)

QEA Quantitative Environmental Analysis, LLC

GENbmp Oct 28, 2005

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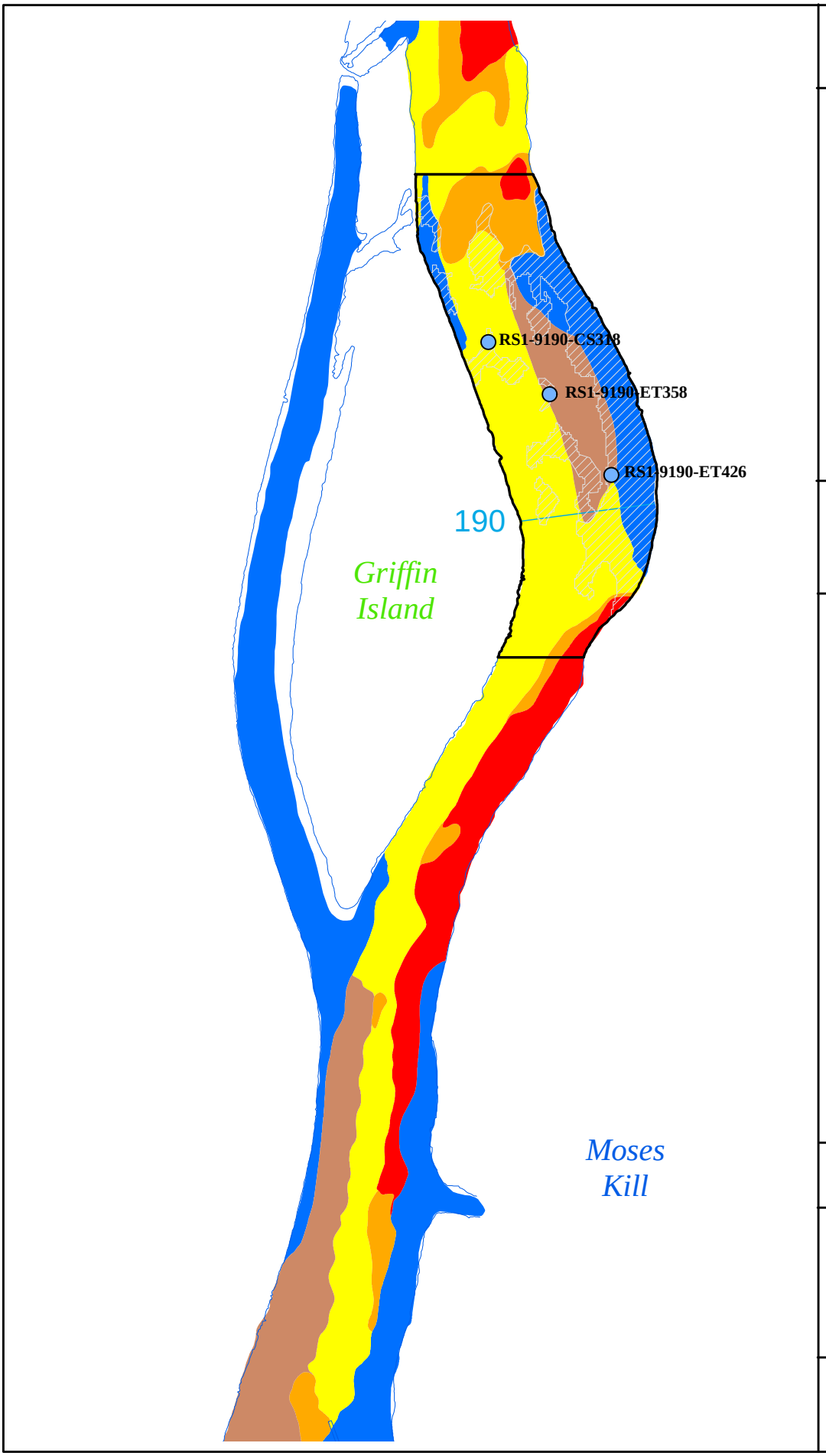
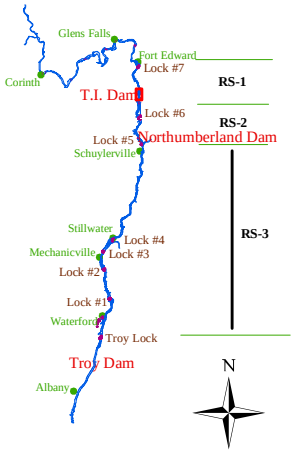


LOCATOR MAP OF THE UPPER HUDSON RIVER



GRAPHIC SCALE

0 250 500 Feet

LEGEND

Proposed TSS Locations

- FS
- MS
- SI

OSI Side Scan Sonar

- Fine grained / silty
- Sandy
- Gravel / Cobbles
- Variable / Transitional
- Rocky

Background data

- Phase I Area
- Proposed Dredge Areas
- Dams and Locks
- Shore Line

Notes:
Proposed Dredge Areas file issued on 3/3/05.
Phase I Area file updated on 9/26/05.

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Figure 1c.

Proposed TSS Study Locations
(Primary sediment type shown)

QEA Quantitative Environmental Analysis, LLC

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IF - Q:\GENrem\GIS\maps\ArcGIS8_maps\IF_TSS_select_cores05\TSS_study_05.mxd

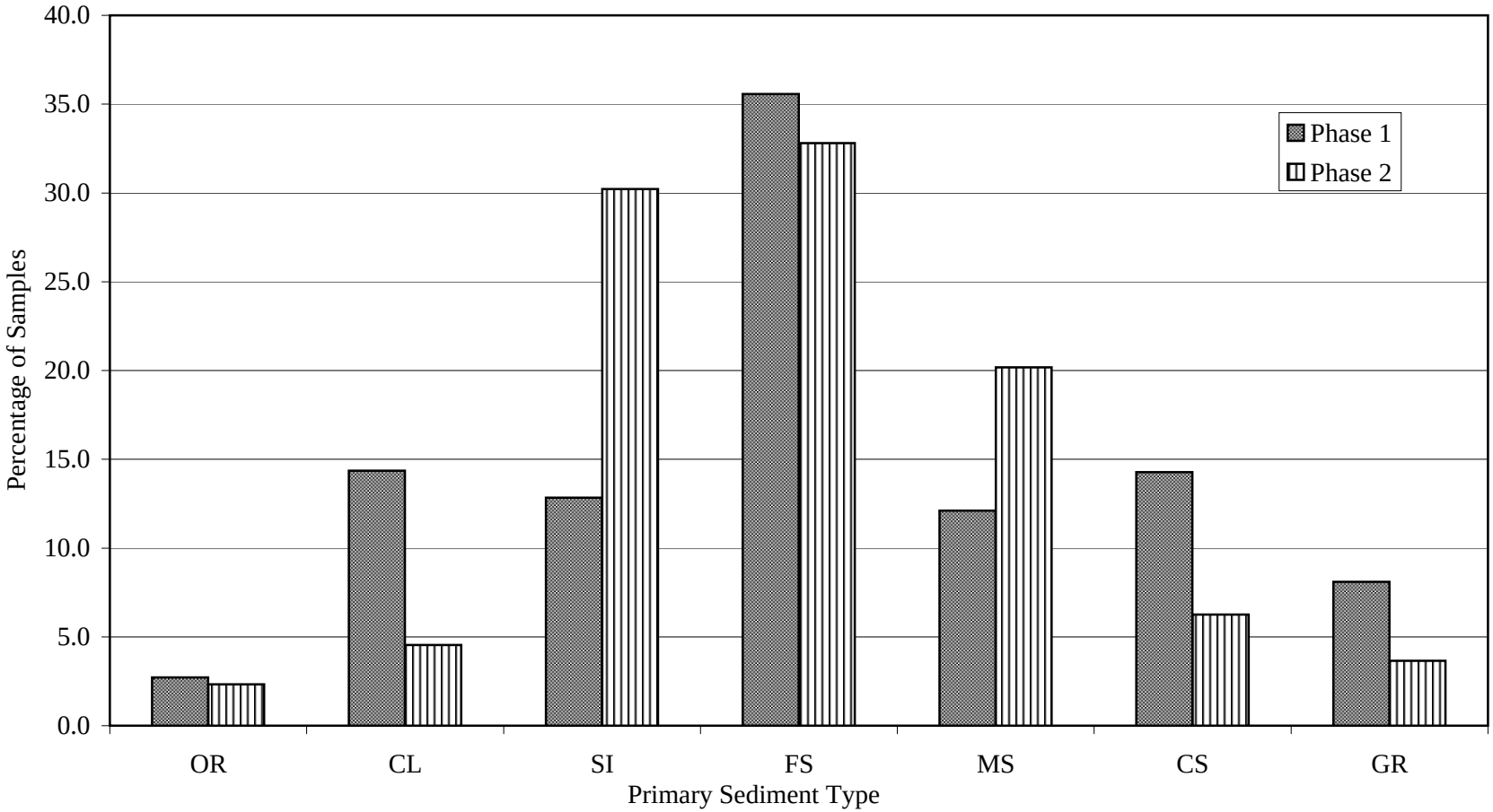

Figure 2. Comparison of primary sediment type in Phase 1 and Phase 2 dredge areas.

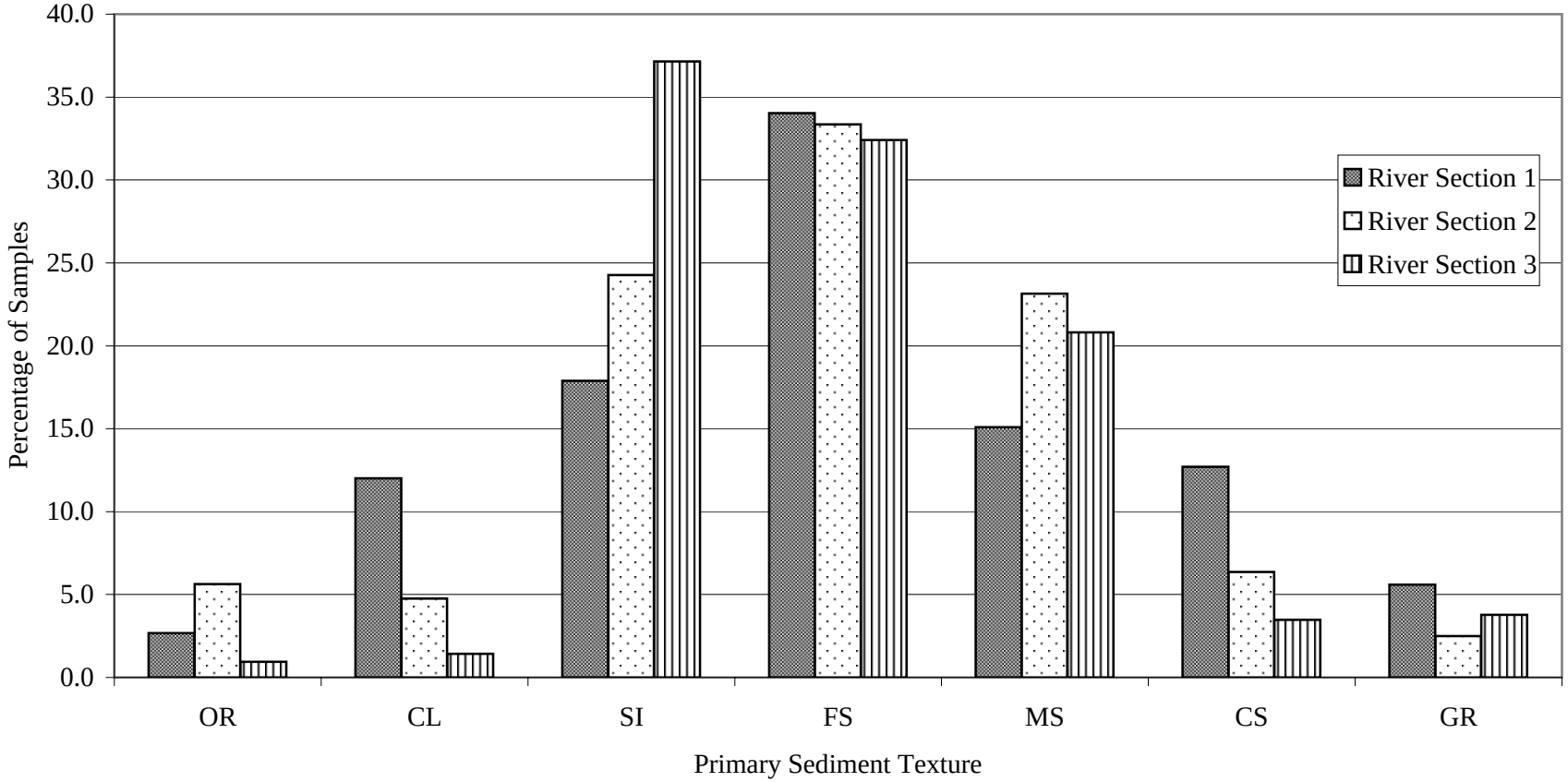

Figure 3. Comparison of primary sediment type in River Sections 1, 2, and 3.

Quantitative Environmental Analysis, LLC
∂c/∂t

MEMORANDUM

TO: Bob Gibson (GE)

DATE: February 7, 2006

FROM: Irena Felty

RE: Core Selection for the TSS laboratory study

CC:
John Connolly (QEA)
Jim Rhea (QEA)
Mark LaRue (QEA)
Margaret Murphy (QEA)
Christopher Yates (QEA)

JOB #: GENra1: 156

The purpose of this memorandum is to summarize field and analytical information for cores that were collected in November 2005 for use in the Total Suspended Solids Surrogate Study (TSS Surrogate Study), and to present recommendations for proceeding with the study. This study will be performed in accordance with the revised TSS Surrogate Study Work Plan which was presented to EPA on 11/15/05. The results of the study will be used to develop initial correlations between TSS concentrations and a surrogate parameter for the upcoming Hudson River dredging operations. Cores targeted for the TSS surrogate study were selected to be representative of three sediment categories - silt, fine sand and medium sand – in the Hudson River. A total of 24 cores - eight cores in each sediment type category were targeted to be collected for the study, in accordance with the Technical Memorandum dated October 14, 2005.

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Initially, testing will be performed on nine out of the 24 cores available (three cores from each sediment type category). These cores were selected to provide information for a range of sediment characteristics, including median particle size and color, within each primary sediment type. The amount of sample available for each core was also evaluated; cores that do not have sufficient volume have not been recommended for testing. Additional testing using sediments from the remaining cores may be performed after the data from the initial series of tests have been evaluated. The remainder of this memorandum presents the data and identifies the cores that are recommended for use in the study.

Coring locations for the TSS study were selected based on an analysis of the QEA Export database which contains the sediment data collected during the SSAP since 2002. The criteria used to select the initial twenty four cores for the TSS study included:

- Sampling location
- Depth of PCB contamination
- Prevalent sediment type
- Color

Cores for the TSS study were selected from areas targeted for Phase 1 dredging. Their selection was based on analysis of geotechnical data, visual segment descriptions, and PCB data. The core locations were selected in a manner designed to obtain eight cores for each of three primary sediment type categories - Medium Sand, Fine Sand, or Silt. A range of colors for each sediment type (to the extent that significant variability exists) was also considered when selecting the core

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locations. The goal was to select cores that are representative of the Phase 1 dredge areas and have a high content of the targeted primary sediment type while considering the variability of the sediment matrix existing in each sediment type category.

Cores for the TSS study were assigned unique Core IDs containing the letters "TS". They were collected between November 16th and 28th, 2005 at the end of the 2005 data gap sampling season from twenty four locations. Due to high flow, some of the original proposed coring locations could not be occupied and were replaced by locations in shallower areas outside of the main channel. The replacement locations are denoted by an asterisk next to the Core ID in Table 1 and Appendix 1.

Upon collection, the cores were stored in the processing laboratory at the Ford Edward plant site until they were processed on December 19, 2005. The actual field recoveries of the "TS" cores exceeded the depths of contamination that were previously determined in these locations (Technical Memorandum from 10/14/05) in all cores but one. During processing, the cores were cut at the depth of contamination, homogenized, visually characterized, and photographed. Samples of the homogenized sediment were submitted to analytical laboratories for grain size analysis, total organic carbon analysis, and moisture content analysis. The cores were collected, described, and processed in accordance with the procedures used in the SSAP. Field observations, processing lab descriptions, and analytical results have been added to the QEA Data Export.

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Table 1 and Appendix 1 summarize the information that was evaluated in order to select the most suitable cores for the TSS surrogate study. Table 1 presents a list of core IDs sorted by targeted primary sediment type. The table also includes the results of grain size, TOC, moisture content, and bulk density analysis. Additionally, visual characterization results, wet and dry sediment weight, and approximate median particle size diameter is included. Records highlighted in blue identify cores that are recommended for the study. Appendix 1 presents photographs of the homogenized cores. Each photo is accompanied by the core ID, targeted primary sediment type, processing lab description, percentage of the targeted sediment type determined by the laboratory grain size analysis, and whether the core is recommended for use in the initial round of testing to be conducted for the TSS surrogate study.

The approach to selecting cores for the TSS surrogate study was as follows:

1. The range of median particle diameters for each sediment type category (Medium Sand, Fine Sand and Silt) was identified based on the Unified Soil Classification System (USCS; see 3rd column in Table 1).
2. A median particle diameter was then estimated for each core based on the grain size distribution data.
3. The average percentage for individual grain size classifications was calculated for the cores within each of the three grain size categories. Only data from cores that exhibited an appropriate median particle diameter (i.e., within the range of median particle diameters associated with the sediment type category) was used in this calculation. Cores that had median particle diameters outside of this range were not selected for testing (Table 1).

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4. Cores with less than 2 kg of dry sediment were excluded from consideration due to insufficient volume to conduct the testing.
5. Three cores were then selected within each sediment category in a manner designed to be representative of the range of median particle diameters and grain size percentage observed for each sediment type. One core was selected that had a percentage of the targeted sediment type that was near the average for the sediment type category. A second core was selected with a grain size percentage above this average, and a third core was selected with a grain size below average.

Of the cores recommended for the study, the fine sand cores average 65% fine sand with two general colors represented; the silt cores average 52% silt with 3 general colors represented; and the medium sand cores average 29% medium sand, with 2 general colors represented. All of the recommended cores have the targeted sediment type as the primary grain size fraction with the exception of 2 of the medium sand cores, where medium sand is the secondary sediment type. However, these cores have median particle diameters that are consistent with medium sand, have a significantly different grain size distribution than the silt or fine sand cores, and appear to be representative of the coarser grained sediment areas that will be dredged.

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Table 1: Cores Targeted for TSS Surrogate Study - Data Summary.

CORE ID	FIELD SAMPLE ID	TARGETED RESULTS	FINAL RESULTS												
		PRIMARY USCS SEDIMENT TYPE *(Median Diameter)*	GEOTECHNICAL ANALYSIS (%)						APROXIMATE MEDIAN DIAMETER (µm)	CALCULATED DRY SEDIMENT WEIGHT (kg)	DRY BULK DENSITY (g/cm3)	MOISTURE CONTENT (%)	TOC %	WET SEDIMENT WEIGHT (kg)	GENERAL SAMPLE DESCRIPTION
			GRAVEL	COARSE SAND	MEDIUM SAND	FINE SAND	SILT	CLAY							
RS1-9392-TS022*	RS1-9392-TS022-000060	**MS** (425-2000 µm)	27.8	16.5	35.05	16.2	3.3	1.15	1500	10.8	1.45	9.8	0.33	11.9	BLACK, GRAVEL, SOME CS, TRACE MS
RS1-9392-TS024*	RS1-9392-TS024-000024		18.9	13.2	30.7	33.8	1.3	2.2	850	4.6	1.57	15	0.28	5.4	DARK BROWN, CS, SOME GR, TRACE CL.
RS1-9392-TS020*	RS1-9392-TS020-000013		45.7	8.9	29.6	14.8	1	0	**3000**	2.0	1.23	19	0.28	2.5	SATURATED, DARK BROWN, GR, SOME CS, LITTLE WOOD, TRACE SHALE
RS1-9493-TS005	RS1-9493-TS005-000036		25.8	10.4	27.9	28.8	3.7	3.4	850	5.9	1.32	9.3	0.56	6.5	DARK BROWN, MS, SOME SI, TRACE COBBLES
RS1-9594-TS002	RS1-9594-TS002-000024		18	12	23.8	36.2	9.3	0.6	450	3.4	1.12	22	0.53	4.3	DARK BROWN, MS, LITTLE GR, TRACE WOOD, SULPHUR ODOR
RS1-9493-TS002	RS1-9493-TS002-000024		28	10.5	20.2	25.8	11.2	4.2	850	2.7	0.85	26	0.32	3.6	6 INCH VOID AT 12 IN. BLACK, SATURATED, MS, SOME SI, LITTLE WOOD TRACE GR. SULPHUR ODOR.
RS1-9594-TS020*	RS1-9594-TS020-000024		37.2	13.9	18.1	13.2	10.8	6.8	2000	3.2	1.09	30	0.38	4.6	BROWN, GR, SOME CL
RS1-9493-TS028*	RS1-9493-TS028-000039		9.1	6.3	10.1	10.7	17.8	45.9	**8**	5.3	1.09	25	0.34	7.1	GRAY, CL, SOME GR, LITTLE CS
Average Sediment Type (%)			26	13	26	26	7	3							
RS1-9190-TS001	RS1-9190-TS001-000024	**FS** (74-425 µm)	1.1	1.9	8.2	79.1	8	1.7	200	3.6	1.16	8.3	0.42	3.9	LIGHT BROWN, MS, TRACE SI,
RS1-9594-TS003	RS1-9594-TS003-000030		2.1	3	9.7	76.7	7.2	1.3	200	3.2	0.81	23	1.10	4.2	DARK BROWN, FS, SOME WOOD.
RS1-9392-TS003	RS1-9392-TS003-000024		3.5	1.6	11.6	68.5	10.6	4.2	180	2.4	0.79	35	2.50	3.7	DARK BROWN, SILT, SOME FS, TRACE WOOD
RS1-9493-TS001	RS1-9493-TS001-000030		16.4	8.9	19.2	48	5.1	2.4	425	3.8	1.02	29	12.00	5.4	DARK BROWN, MS, LITTLE SI, TRACE CS, AND WOOD
RS1-9190-TS003	RS1-9190-TS003-000024		6	4	7.8	46.8	32.4	3	160	2.1	0.69	42	3.90	3.7	DARK BROWN, SILT AND FINE SAND
RS1-9190-TS002	RS1-9190-TS002-000024		0.1	0.2	3	31.5	45.9	19.4	**50**	4.0	1.33	9	0.16	4.4	BROWN FS TRACE GR AND CLAY
RS1-9392-TS002	RS1-9392-TS002-000024		23.3	11.5	34.1	27.4	2.5	1.3	**850**	3.6	1.20	18	0.25	4.4	LIGHT BROWN TO BLACK ANGULAR GRAVEL, MS, TRACE WOOD
RS1-9493-TS008	RS1-9493-TS008-000042		8.3	6.6	17.5	24	18.8	24.9	130	5.7	1.08	24	1.90	7.5	MOIST, DARK BROWN SILT, SOME WOOD, LITTLE MS, TRACE CL
Average Sediment Type (%)			6	4	12	57	14	6							
RS1-9493-TS010	RS1-9493-TS010-000066	**SI** (5-74 µm)	0	0	2.7	13.6	70	13.8	40	2.8	0.31	64	7.20	7.9	DARK GRAY, CL, SOME SI, TRACE ORGANICS
RS1-9392-TS001	RS1-9392-TS001-000018		0	0	2.2	31.5	55	11.3	60	**0.9**	0.36	61	4.70	2.3	MOIST, DARK BROWN SILT, TRACE WOOD
RS1-9493-TS009	RS1-9493-TS009-000048		0	0.5	3.8	35.2	46.7	13.75	75	2.9	0.53	55	5.35	6.5	BLACK, MOIST, SILT, SOME CL, TRACE WOOD
RS1-9392-TS005	RS1-9392-TS005-000024		2.1	0.5	3.9	48.6	39.6	5.3	75	2.7	0.88	38	2.20	4.3	DARK BROWN SI, TRACE WOOD
RS1-9392-TS006	RS1-9392-TS006-000030		3.3	2.4	14	35.9	34.2	10.2	75	**1.9**	0.48	55	9.40	4.2	DARK BROWN, MOIST CLAY, TRACE MS, TRACE WOOD.
RS1-9594-TS001	RS1-9594-TS001-000036		0	0	11.9	45.9	32	10.2	**150**	3.6	0.79	36	5.00	5.7	LIGHT GRAY, FS, LITTLE ORGANIC, TRACE CL
RS1-9493-TS011	RS1-9493-TS011-000036		0	1.2	8.1	55	30.5	5.1	**100**	3.1	0.67	43	4.70	5.5	DARK BROWN, SILT, SOME CL, TRACE WOOD
RS1-9190-TS020*	RS1-9190-TS020-000030		13.3	9.8	19.3	50.6	5.5	1.5	**400**	**1.2**	0.30	67	7.90	3.7	DARK GRAY, MOIST, SI,
Average Sediment Type (%)			1	1	5	33	49	11							

Notes:

1) *Median diameters of cores considered for the TSS surrogate study are in black (outliers - cores with median diameter outsider the targeted sediment type, are in red)*
2) *Records highlighted in blue are cores recommended for the study.*
3) *Numbers highlighted in gray are average sediment compositions calculated from cores with median diameter consistent with targeted primary sediment type.*
4) *Cores with dry sediment weight <2 kg not selected due to insufficient sample volume (in red)*
5) *Core IDs with asterisk identify cores that were targeted in a second round of assignments*

Appendix 1

Photographs and Visual Description of Cores Targeted for TSS Surrogate Study

305 West Grand Avenue
Montvale, New Jersey 07645
201-930-9890 • 201-930-9805 Fax

www.qeallc.com

290 Elwood Davis Road
Liverpool, New York 13088
315-453-9009 • 315-453-9010 Fax

MEDIUM SAND

RS1-9392-TS022*

Targeted Sediment Type : MS

Processing Lab Description:

- Section processed 0 – 60”
- Weight 11.925
- Texture GR/CS/--/MS
- BLACK, GRAVEL, SOME CS, TRACE MS

Geotechnical Analysis Results:

- MS = 35.05 %

Selected for TSS study

RS1-9392-TS024*

Targeted Sediment Type : MS

Processing Lab Description:

- Section processed 0 – 24”
- Weight 5.360
- Texture CS/GR/--/CL
- DARK BROWN, CS, SOME GR, TRACE CL.

Geotechnical Analysis Results:

- MS = 30.7 %

NOT Selected for TSS study

RS1-9392-TS020*

Targeted Sediment Type : MS

Processing Lab Description:

- Section processed 0 – 13”
- Weight 2.460
- Texture GR/CS/--/--
- SATURATED, DARK BROWN, GR, SOME CS, LITTLE WOOD, TRACE SHALE

Geotechnical Analysis Results:

- MS = 29.6 %

NOT Selected for TSS study

RS1-9493-TS005

Targeted Sediment Type : MS

Processing Lab Description:

- Section processed 0 – 36”
- Weight 6.540
- Texture MS/SI/--/--
- DARK BROWN, MS, SOME SI, TRACE COBBLES

Geotechnical Analysis Results:

- MS = 27.9 %

Selected for TSS study

RS1-9594-TS002

Targeted Sediment Type : MS

Processing Lab Description:

- Section processed 0 – 24”
- Weight 4.310
- Texture MS/--/GR/--
- DARK BROWN, MS, LITTLE GR, TRACE WOOD, SULPHUR ODOR

Geotechnical Analysis Results:

- MS = 23.8 %

Selected for TSS study

RS1-9493-TS002

Targeted Sediment Type : MS

Processing Lab Description:

- Section processed 0 – 24”
- Weight 3.595
- Texture MS/SI/--/GR
- 6 INCH VOID AT 12 IN. BLACK, SATURATED, MS, SOME SI, LITTLE WOOD, TRACE GR. SULPHUR ODOR

Geotechnical Analysis Results:

- MS = 20.2 %

NOT selected for TSS study

RS1-9594-TS020*

Targeted Sediment Type : MS

Processing Lab Description:

- Section processed 0 – 24”
- Weight 4.625
- Texture GR/CL/--/--
- BROWN, GR, SOME CL

Geotechnical Analysis Results:

- MS = 18.1 %

NOT selected for TSS study

RS1-9493-TS028*

Targeted Sediment Type : MS

Processing Lab Description:

- Section processed 0 – 39”
- Weight 7.075
- Texture CL/GR/CS/--
- GRAY, CL, SOME GR, LITTLE CS

Geotechnical Analysis Results:

- MS = 10.1 %

NOT selected for TSS study

FINE SAND

RS1-9190-TS001

Targeted Sediment Type : FS

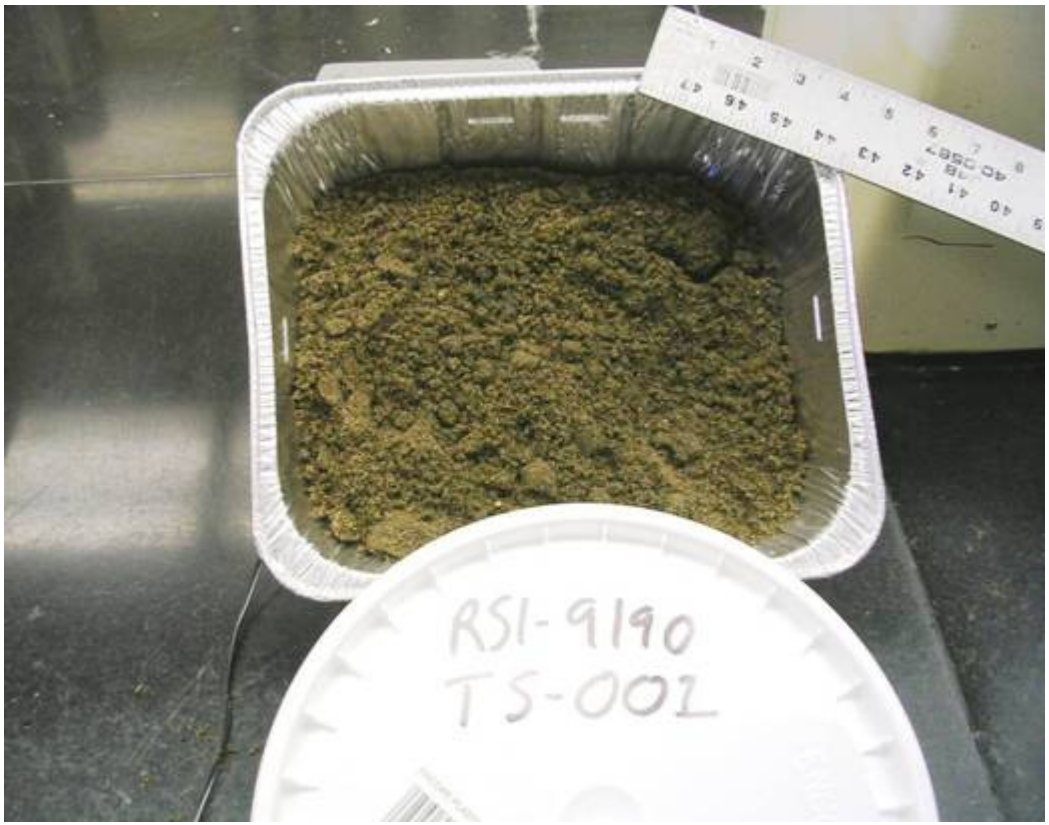
Processing Lab Description:

- Section processed 0 – 24”
- Weight 3.880
- Texture MS/--/--/SI
- LIGHT BROWN, MS, TRACE SI

Geotechnical Analysis Results:

- FS = 79.1%

Selected for TSS Study



RS1-9594-TS003

Targeted Sediment Type : FS

Processing Lab Description:

- Section processed 0 – 30”
- Weight 4.180
- Texture FS/--/--/--
- DARK BROWN, FS, SOME WOOD.

Geotechnical Analysis Results:

- FS = 76.7 %

NOT selected for TSS study

RS1-9392-TS003

Targeted Sediment Type : FS

Processing Lab Description:

- Section processed 0 – 24”
- Weight 3.745
- Texture SI/FS/--/--
- DARK BROWN, SILT, SOME FS, TRACE WOOD

Geotechnical Analysis Results:

- FS = 68.5 %

Selected for TSS study

RS1-9493-TS001

Targeted Sediment Type : FS

Processing Lab Description:

- Section processed 0 – 30”
- Weight 5.370
- Texture MS/--/SI/CS
- DARK BROWN, MS, LITTLE SI, TRACE CS, AND WOOD

Geotechnical Analysis Results:

- FS = 48 %

Not selected for TSS study

RS1-9190-TS003

Targeted Sediment Type : FS

Processing Lab Description:

- Section processed 0 – 24”
- Weight 3.690
- Texture SI/FS/--/--
- DARK BROWN, SILT AND FINE SAND

Geotechnical Analysis Results:

- FS = 46.8 %

Selected for TSS Study

RS1-9190-TS002

Targeted Sediment Type : FS

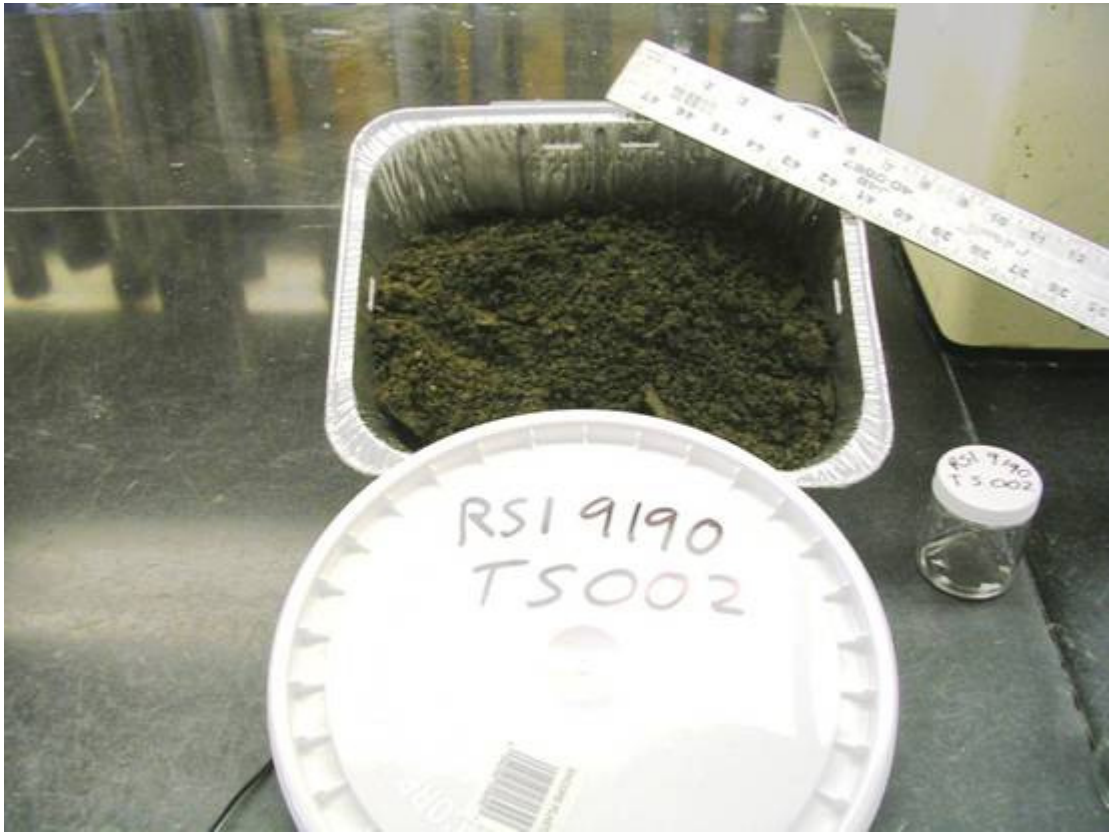
Processing Lab Description:

- Section processed 0 – 24”
- Weight 4.390
- Texture FS/--/--/GR
- BROWN FS TRACE GR AND CLAY

Geotechnical Analysis Results:

- FS = 31.5%

NOT Selected for TSS study



RS1-9392-TS002

Targeted Sediment Type : FS

Processing Lab Description:

- Section processed 0 – 24”
- Weight 4.385
- Texture GR/MS/--/--
- LIGHT BROWN TO BLACK ANGULAR GRAVEL, MS, TRACE WOOD

Geotechnical Analysis Results:

- FS = 27.4 %

NOT selected for TSS study

RS1-9493-TS008

Targeted Sediment Type : FS

Processing Lab Description:

- Section processed 0 – 42”
- Weight 7.450
- Texture SI/--/MS/CL
- MOIST, DARK BROWN SILT, SOME WOOD, LITTLE MS, TRACE CL

Geotechnical Analysis Results:

- FS = 24 %

NOT selected for TSS study

SILT

RS1-9493-TS010

Targeted Sediment Type : SI

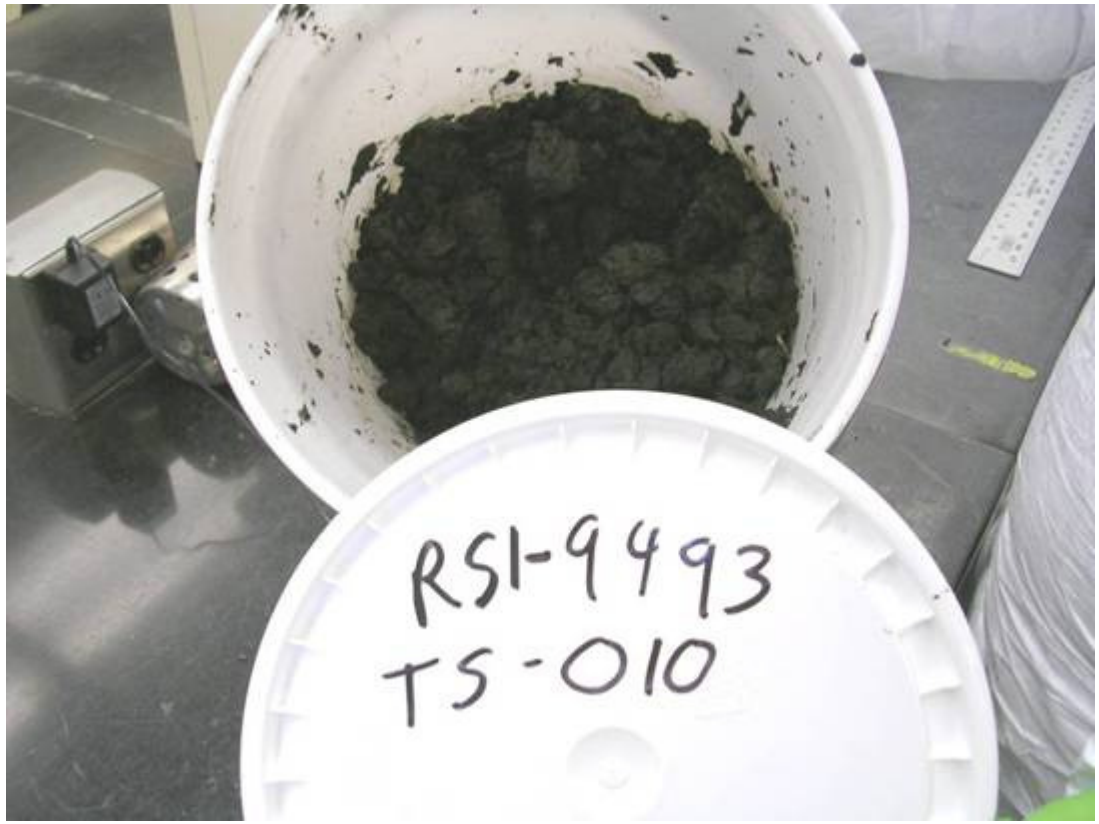
Processing Lab Description:

- Section processed 0 – 66”
- Weight 7.865
- Texture CL/SI/--/OR
- DARK GRAY, CL, SOME SI, TRACE ORGANICS

Geotechnical Analysis Results:

- SI = 70 %

Selected for TSS study



RS1-9392-TS001

Targeted Sediment Type : SI

Processing Lab Description:

- Section processed 0 – 18”
- Weight 2.280
- Texture SI/--/--/--
- MOIST, DARK BROWN SILT, TRACE WOOD

Geotechnical Analysis Results:

- SI = 55 %

NOT Selected for TSS study

RS1-9493-TS009

Targeted Sediment Type : SI

Processing Lab Description:

- Section processed 0 – 48”
- Weight 6.520
- Texture SI/CL/--/--
- BLACK, MOIST, SILT, SOME CL, TRACE WOOD

Geotechnical Analysis Results:

- SI = 46.7 %

Selected for TSS study

RS1-9392-TS005

Targeted Sediment Type : SI

Processing Lab Description:

- Section processed 0 – 24”
- Weight 4.285
- Texture SI/--/--/--
- DARK BROWN SI, TRACE WOOD

Geotechnical Analysis Results:

- SI = 39.6 %

Selected for TSS study

RS1-9392-TS006

Targeted Sediment Type : SI

Processing Lab Description:

- Section processed 0 – 30”
- Weight 4.220
- Texture CL/--/--/MS
- DARK BROWN, MOIST CLAY, TRACE MS, TRACE WOOD.

Geotechnical Analysis Results:

- SI = 34.2 %

NOT selected for TSS study

RS1-9594-TS001

Targeted Sediment Type : SI

Processing Lab Description:

- Section processed 0 – 36”
- Weight 5.660
- Texture FS/--/OR/CL
- LIGHT GRAY, FS, LITTLE ORGANIC, TRACE CL

Geotechnical Analysis Results:

- SI = 32 %

NOT selected for TSS study

RS1-9493-TS011

Targeted Sediment Type : SI

Processing Lab Description:

- Section processed 0 – 36”
- Weight 5.450
- Texture SI/CL/--/--
- DARK BROWN, SILT, SOME CL, TRACE WOOD

Geotechnical Analysis Results:

- SI = 30.5 %

NOT selected for TSS study

RS1-9190-TS020*

Targeted Sediment Type : SI

Processing Lab Description:

- Section processed 0 – 30”
- Weight 3.745
- Texture SI/--/--/--
- DARK GRAY, MOIST, SI,

Geotechnical Analysis Results:

- SI = 5.5 %

NOT selected for TSS study

APPENDIX 21
SOP FOR THE COLLECTION OF SAMPLES FOR DISSOLVED METALS ANALYSIS

APPENDIX 21
STANDARD OPERATING PROCEDURE FOR FIELD FILTRATION FOR DISSOLVED METAL SAMPLES

1.1 Scope & Application

This Standard Operating Procedure (SOP) is applicable to the field processing of water column samples for dissolved Target Analyte List (TAL) metals, mercury, and hexavalent chromium for the Hudson River Remedial Action Monitoring Program, and is based on USEPA's Method 1669 for sampling ambient water for trace metals (USEPA 1996).

1.2 Summary of Method

Samples will be collected in the same manner described in Appendix 1 (near-field transect samples), Appendix 2 (near-field buoy samples), or Appendix 3 (far-field samples). Before samples are collected, the sample collection vessels and sample containers will be cleaned using detergent, mineral acids, and reagent water. Reagent water is defined as water prepared by the laboratory in which the analytes of interest and potentially interfering substances are not detected at the Method Detection Limit (MDL) of the analytical method(s). After cleaning, sample containers will be filled with weak acid solution, and individually double-bagged using resealable plastic bags. Sample collection vessels will be placed in plastic bags to minimize contact with metal or atmospheric deposition of particles containing metal.

Samples to be analyzed for dissolved metals will be filtered prior to analysis. At the Thompson Island station, filtrations will be performed at the Test America Burlington facility upon arrival at the laboratory. For remaining locations, samples will be filtered through a 0.45 µm filter as soon after collection as practical at a field laboratory facility. The resulting filtrate will be placed in an appropriate container, double bagged, and placed in a cooler with ice prior to delivery to the laboratory. Preservation of samples with dilute nitric acid will be performed immediately upon arrival at the laboratory. Appropriate field documentation will be maintained using a computerized sample tracking system.

1.3 Health and Safety Warnings

Health and safety issues are addressed in the project Health and Safety Plan (HASP; Parsons 2008).

1.4 Contamination and Interferences

Potential sources of trace metals contamination during sampling include metallic or metal-containing sampling equipment, containers, personal protective equipment (PPE; e.g., gloves that contain zinc due to the presence of talc), reagent water, and improperly cleaned and stored equipment. Additionally, atmospheric inputs such as dirt and dust from automobile exhaust, tobacco smoke, nearby roads, bridges, wires, and poles can result in sample contamination. Sampling procedures specified in Appendices 1 and 2 have been designed to minimize these sources of contamination.

1.5 Personnel Qualifications

All field personnel are required to take a 40-hour OSHA Hazardous Waste Operations training course and annual refresher courses, and participate in a medical monitoring program prior to engaging in any field collection activities as required in 29 CFR 1910.120. Additionally, field personnel will be under the direct supervision of qualified professionals who are experienced in performing the tasks required for sample collection.

1.6 Equipment and Supplies

Equipment needed for collection of water samples for metals analysis includes:

- Glove bag/box
- Peristaltic pump
- Pre-cleaned tubing for peristaltic pump
- Pre-cleaned polyethylene fittings for connecting pump to filter
- Filter – 0.45 µm, 15 mm diameter or larger, tortuous-path capsule filters (Gelman Supor 12175 or equivalent)
- Power source for peristaltic pump
- Disposable gloves (talc free)
- Reagent water (free of metals; supplied by laboratory)
- 5-gallon plastic carboy (for storage of dilute acid wastes from pre-cleaned sample containers)

- Plastic (polyethylene) resealable food storage bags
- Plastic (polyethylene) food wrap
- Plastic (polyethylene) trash bags
- Dedicated, clean cooler with ice
- Laptop computer and printer
- Field database

1.7 Water Sample Filtration

Upon completing collection of the sample at each sampling location, samples will be filtered as soon as practical at a field laboratory facility to permit subsequent analysis for dissolved metals.

1. Set up the filtration system inside the glove bag, using the shortest runs of tubing possible.
2. "Dirty hands" places the peristaltic pump immediately outside of the glove bag and passes the cleaned tubing through a small hole in the glove bag. "Clean hands" attaches the tubing to the capsule filter inside the glove bag. Also, attach a short length of tubing to the outlet of the capsule filter for filling containers after filtration.
3. "Dirty hands" opens the cooler and the outside bag, allowing "clean hands" to remove the water sample from the inner storage bag and place the sample inside the glove bag. "Clean hands" also places the capsule filter, two clean empty sample bottles, a bottle containing reagent water, and a bottle for waste in the glove bag.
4. "Clean hands" opens the reagent water bottle and places the end of the pump tubing in the bottle.
5. "Dirty hands" starts the pump and pumps approximately 200 mL of reagent water through the tubing and filter into the waste bottle. "Clean hands" then moves the outlet tubing to a clean bottle and collects the remaining reagent water as a blank.
6. "Dirty hands" stops the pump. "Clean hands" removes the lid of the sample bottle and places the intake end of the tubing in the bottle.
7. "Dirty hands" starts the pump and passes approximately 50 mL through the tubing and filter into the remaining clean sample bottle and then stops the pump.
8. "Clean hands" uses the filtrate to rinse the bottle, discards the waste sample, and returns the outlet tube to the sample bottle.

9. "Dirty hands" starts the pump and the remaining sample is processed through the filter and collected in the sample bottle.
10. "Clean hands" replaces the lid on the bottle, and places the bottle in a new bag, and seals the bag. "Clean hands" then places the first bag into a second new bag held by "dirty hands".
11. "Dirty hands" seals the outer bag, and places the double-bagged sample bottle into the cooler for subsequent delivery to the laboratory.

1.8 Sample Handling and Preservation

Sample containers will be labeled prior to sample collection in accordance with labeling requirements specified in Section 10.1. Samples will be filtered, and placed in containers in accordance with the procedures described above. Each container will be placed in two re-sealable food storage bags (double bagged, one inside the other), and placed in a clean cooler dedicated to metals analysis for the Hudson River. The samples will be chilled with ice to approximately 4°C. A temperature blank will be placed in each cooler for use by the laboratory to measure the temperature of samples upon submittal. Samples will be shipped or transported to the laboratory at the end of each day and dissolved samples will be preserved with nitric acid upon arrival. Chain of custody procedures will be followed, as specified in Section 10.1 of this QAPP.

1.9 Data and Records Management

All data from water sample collection will be recorded in the field database provided by GE using a laptop computer. Upon completion of sampling at one location, all data from the location will be entered into the database and the field log for that location printed and the hard copy stored in the field notebook. This will limit the risk of losing sample information due to computer failure. Blank field log sheets can also be used to record information manually in case difficulties with data entry using the computer are encountered. Manually recorded data will be transcribed into the field database at the end of each day.

1.10 Quality Control and Quality Assurance (QA/QC)

QA/QC procedures are defined in Section 10.2 of this QAPP, and include the collection of field QA/QC samples. Field QA/QC samples to be collected are blind duplicate samples,

equipment blank samples, and matrix spike samples. One set of field QA/QC samples will be collected for each sampling event. Blind duplicate samples and matrix spike samples will be prepared by filling additional appropriately marked containers at pre-selected sampling stations (both samples will not be collected at the same station). The station where these samples are collected will be rotated randomly for each sampling event. Equipment blank samples will be prepared as follows:

1. Prepare for "clean hands/dirty hands" procedures (put on new disposable gloves).
2. Place a pre-cleaned sample collection vessel in the sampler ("clean hands").
3. "Clean hands" will slowly pour laboratory supplied reagent water into a clean sample collection vessel while "dirty hands" hold the vessel stable.
4. When the desired volume is reached, "clean hands" remove the sample collection vessel and distribute to appropriately labeled sample containers using "clean hands/dirty hands" procedures specified in Section 7, above.
5. Repeat as necessary to provide adequate sample volume.
6. If applicable, filter the field blank sample using techniques identical to those used to filter environmental samples, as described in Section 7, above.
7. After collection, handle equipment blank samples in a manner that is consistent with all other environmental samples.

1.11 References

Parsons. 2008. Phase 1 Remedial Action Health and Safety Plan, Hudson River PCBs Superfund Site. Prepared for General Electric Company, Albany, NY. August 2008.

USEPA. 1996. *Method 1669, Sampling Ambient Water for Trace Metals at EPA Water Quality Criteria Levels*. U.S. Environmental Protection Agency. Office of Water Engineering and Analysis Division (4303). July 1996.

APPENDIX 22
SOP FOR PROBE MEASUREMENTS: TEMPERATURE, CONDUCTIVITY, DO, PH, AND TSS SURROGATE

APPENDIX 22

STANDARD OPERATING PROCEDURE FOR PROBE MEASUREMENTS: TEMPERATURE, CONDUCTIVITY, DO, PH, AND TURBIDITY

1.1 Scope & Application

This Standard Operating Procedure (SOP) is applicable to the measurement of water quality (WQ) parameters including temperature, conductivity, pH, dissolved oxygen, and turbidity using a multi-parameter probe.

1.2 Summary of Method

Continuous WQ measurements for temperature, specific-conductivity, pH, DO, and turbidity will be performed at both the near and far-field monitoring stations. These measurements will be made using a YSI 6920 (or equivalent) multi-parameter probe. This instrument is designed for long term, in situ deployment with minimal maintenance required. The probe will be calibrated in accordance with the manufacturer's recommendations prior to deployment. Once installed at a monitoring station, the instrument calibration will be checked at routine intervals by deploying a second calibrated instrument at the same approximate location in the water column and performing an instantaneous comparison of the outputs. If the data vary by more than the criteria specified in Section 1.7 below, the continuously deployed probe will be re-calibrated or replaced with a calibrated instrument, as appropriate. If the output from a continuously deployed probe indicates an exceedence that will result in implementation of additional monitoring or other responses, the data will be field-verified with a second instrument prior to responding to the exceedence.

1.3 Health and Safety Warnings

Health and safety issues are addressed in the project Health and Safety Plan (HASP; Parsons 2008).

1.4 Interferences

- Improper calibration
- Accumulation of debris on probes
- Biological growth on probes

1.5 Personnel Qualifications

All field personnel are required to take a 40-hour OSHA Hazardous Waste Operations training course and annual refresher courses, and participate in a medical monitoring program prior to engaging in any field collection activities as required in 29 CFR 1910.120. Additionally, field personnel will be under the direct supervision of qualified professionals who are experienced in performing the tasks required for sample collection.

1.6 Equipment and Supplies

Equipment needed for the measurement of WQ parameter include:

- Disposable gloves
- YSI 6920 (or equivalent) multi-parameter probe with appropriate length of cable
- Calibrated YSI 6920 (or equivalent) multi-parameter probe (for performing calibration checks)
- Data logger
- Data transmission hardware
- Calibration standards
- Deionized water
- Laptop computer

1.7 WQ Parameter Measurement

Measurement Locations

Discrete WQ parameter measurements will be taken at the near-field and far-field monitoring stations. Water sample locations are defined in Section 2 of the main text of the QAPP.

Measurement Procedures

Deployment

1. Prior to deployment, calibrate the multi-parameter probe using a multi-parameter calibration fluid per the instrument manufacturer's instructions. Rinse the probe with deionized water and store per the manufacturer's recommendations.
2. Deploy the instruments. At the automated far-field monitoring stations, install the probe in the stilling well (approximately mid-depth of the tank). At the near-field monitoring stations, install the probe at the approximate mid-depth of the water column and secure the instrument to the buoy.
3. Upon installation, activate the instrument and verify that the time and date on the data logger is accurate and that sufficient memory and power are available.
4. Confirm that the instrument is collecting accurate data and transmitting the data to the data management system.

Calibration Checks

1. To allow uninterrupted collection of data and to minimize disturbance of the probe, calibration will be checked once per week. Calibration will also be checked as soon as practical if the output from a continuously deployed probe suggests that there may be a problem with an instrument (e.g., upstream stations report higher turbidity than downstream stations, or data reported is outside of typical baseline ranges). Additionally, calibration will be checked as soon as practical whenever an exceedence is reported at a monitoring station (i.e., the data will be field-verified with a second instrument prior to responding to the exceedence).
2. The calibration of each instrument will be checked by deploying a second calibrated instrument at the same approximate location in the water column and performing an instantaneous comparison of the outputs. A minimum of 3 paired sets of measurements will be obtained and compared to the criteria in the table below:

Parameter	Range	Range Between Paired WQ Data
Dissolved Oxygen	0-50 mg/L	± 5% of reading or 0.2 mg/L (whichever is greater)
Conductivity	0-100 mS/cm	± 5%
Temperature	-5 to 45 °C	±1 °C
pH	0-14	±0.2
Turbidity	0-1,000 NTU	± 10% of reading or 2 NTU (whichever is greater)

[1]*Based on a paper published by USEPA and Battelle, who performed verification testing of two identical multi-parameter YSI 6600 EDS water probes. Information can be found at:*

http://www.epa.gov/NHSRC/pubs/vrYSI031704.pdf
http://www.epa.gov/NHSRC/pubs/vrYSI2ndRnd071404.pdf

If a continuously deployed probe is found to be providing inaccurate data, the instrument will be re-calibrated or replaced with a calibrated instrument, as appropriate.

1.8 Sample Handling and Preservation

Probe measurements of WQ parameters are made directly in the river, no sample is taken.

1.9 Data and Records Management

Data from probes deployed at monitoring stations will be recorded by the instrument data logger and transmitted to the data management system. Additionally, data collected with the second instrument used during calibration checks will be downloaded to a laptop computer and maintained in a database to document calibration.

1.10 Quality Control and Quality Assurance

The primary QA/QC procedure for WQ parameter measurement with a multi-parameter probe is proper calibration of the instrument. Prior to deployment, the instrument will be calibrated following the manufacturer's instructions. During deployment, calibration checks will be performed routinely, as specified in Section 1.7 above.

1.11 References

Parsons. 2007. *Phase 1 Remedial Action Health and Safety Plan, Hudson River PCBs Superfudn Site.* Prepared for General Electric Company, Albany, NY. August 2008.

APPENDIX 23
SOP FOR HANDLING, PACKAGING, AND SHIPPING

STANDARD OPERATING PROCEDURE FOR HANDLING, PACKING, AND SHIPPING SAMPLES

1 SCOPE AND APPLICATION

This Standard Operating Procedure (SOP) describes the handling, packing, and shipping procedures for the delivery of samples that are protected from cross-contamination, tampering, misidentification, and breakage, and are maintained in a controlled environment from the time of collection until receipt by the analytical laboratory.

2 PERSONNEL QUALIFICATIONS

All field personnel are required to take a 40-hour OSHA Hazardous Waste Operations training course and annual refresher courses, and participate in a medical monitoring program prior to engaging in any field collection activities as required in 29 CFR 1910.120. Additionally, field personnel will be under the direct supervision of qualified professionals who are experienced in performing the tasks required for sample collection.

3 HEALTH AND SAFETY WARNINGS

Health and safety issues are addressed in the project Health and Safety Plan (HASP; Parsons 2008).

4 EQUIPMENT AND SUPPLIES

The following materials, as required, will be available during handling, packing, and shipping procedures:

- Indelible ink pens
- Polyethylene bags (resealable type)
- Clear packing tape, strapping tape, duct tape
- Custody seal evidence tape
- Appropriate sample containers, labels, and chain-of-custody forms
- Large (30- to 40-gallon) insulated coolers

- Ice or blue ice
- Cushioning and absorbent material (e.g., vermiculite, bubble wrap)
- Field notebook

5 PROCEDURES

5.1 Sample Handling

1. After completing the sample collection procedures, record the following information. If using a field database, enter the information using a computer. Otherwise, record the information in a field notebook.
   - Project number and site name
   - Sample identification code and other sample identification information, if appropriate.
   - Sampling method
   - Date
   - Name of sampler(s)
   - Time
   - Location (project reference)
   - Any comments
2. Print out a sample label using the field database; if a database is not used, fill in sample label with the following information in indelible ink:
   - Sample type (e.g., water)
   - Project number
   - Sample identification code and other sample identification information, if applicable
   - Analysis required
   - Date and time sampled
   - Initials of sampling personnel
   - Sample type (composite or grab)
   - Preservative added, if applicable
3. Cover the label with clear packing tape to secure the label onto the container.

4. Check the caps on the sample containers to seal them tightly.
5. Wrap the sample container cap with clear packing tape to prevent it from becoming loose.
6. Place a signed custody seal label over the cap such that the cap cannot be removed without breaking the custody seal. Alternatively, if shipping several containers in a cooler, custody seal evidence tape may be placed on the shipping container as described below.

5.2 Packing Procedures

1. Using duct tape, secure the outside and inside of the drain plug at the bottom of the cooler being used for sample transport.
2. Place each container or package in individual polyethylene bags (resealable type) and seal. If a cooler temperature blank is supplied by the laboratory, it should be packaged following the same procedures as the samples. If the laboratory did not include a temperature blank, do not add one since the sample temperature will be determined by the laboratory using a calibrated infrared thermometer.
3. Place 1 to 2 inches of cushioning material (e.g., vermiculite) at the bottom of the cooler.
4. Place the sealed sample containers upright in the cooler.
5. Package ice or blue ice in small resealable-type plastic bags and place loosely in the cooler. Do not pack ice so tightly that it may prevent the addition of sufficient cushioning material. Samples placed on ice will be cooled to maintain a temperature of approximately 4°C.
6. Fill the remaining space in the cooler with cushioning/absorbent material. The cooler must be securely packed and cushioned in an upright position and be surrounded by a sorbent material capable of absorbing spills from leaks or breaks of sample containers. (Note: to comply with 49 CFR 173.4, filled cooler must not exceed 64 pounds).
7. Place the completed chain-of-custody record(s) in a large resealable-type bag and tape the bag to the inside of the cooler lid.
8. Close the lid of the cooler and fasten with packing tape.
9. Wrap strapping tape around both ends of the cooler.

10. Mark the cooler on the outside with the following information: shipping address, return address, "Fragile, Handle with Care" labels on the top and on one side, and arrows indicating "This Side Up" on two adjacent sides.
11. Place custody seal evidence tape over front right and back left of the cooler lid and cover with clear plastic tape.

Note: Procedure numbers 2, 3, 5, and 6 may be modified in cases where laboratories provide customized shipping coolers. These coolers are designed so the sample bottles and ice packs fit snugly within preformed styrofoam cushioning and insulating packing material.

5.3 Shipping Procedures

1. All samples will be delivered by an express carrier within 48 hours of sample collection. Alternatively, a laboratory courier may be used for sample pickup, or samples may be dropped off at laboratories in close proximity by field sampling personnel.
2. The following chain-of-custody procedures will apply to sample shipping:
   - Relinquish the sample containers to the laboratory via express carrier or laboratory courier. The signed and dated forms should be included in the cooler. The express carrier will not be required to sign the chain-of-custody forms.
   - When the samples are received by the laboratory, laboratory personnel will complete the chain-of-custody by recording the date and time of receipt of samples, measuring and recording the internal temperature of the shipping container, and checking the sample identification numbers on the containers to provide that they correspond with the chain-of-custody forms.

6 DATA AND RECORDS MANAGEMENT

Copies of chain-of-custody forms will be maintained in the project file.

7 QUALITY CONTROL AND QUALITY ASSURANCE (QA/QC)

A copy of the completed chain-of-custody form forwarded with the samples to the laboratory will be sent to the Project Manager for review. Subsequent chain-of-custody form submissions to the Project Manager will be at the Project Manager's discretion.

8 REFERENCES

Parsons. 2008. *Phase 1 Remedial Action Health and Safety Plan, Hudson River PCBs Superfund Site.* Prepared for General Electric Company, Albany, NY. August 2008.

APPENDIX 24
SOP FOR THE EXTRACTION AND CLEANUP OF AQUEOUS SAMPLES FOR PCBS USING SW-846 METHOD 3535 (NE178_03)

STANDARD OPERATING PROCEDURE

NORTHEAST ANALYTICAL INC.

NE178_03.DOC

REVISION NUMBER: 3

STANDARD OPERATING PROCEDURE FOR THE EXTRACTION AND CLEANUP OF 1L AQUEOUS SAMPLES FOR POLYCHLORINATED BIPHENYLS (PCBs) USING US-EPA SW-846 METHOD 3535, SOLID PHASE EXTRACTION

April 04, 2009

COPY#_____

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STANDARD OPERATING PROCEDURE

LABORATORY PROCEDURE NE178_03.DOC

REVISION 3 (04/04/2009)

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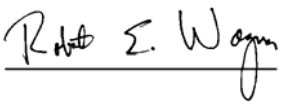

Robert E. Wagner
Laboratory Director

Approved by:

Christina L. Braidwood
Quality Assurance Officer

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1.0 IDENTIFICATION OF TEST METHOD

1.1 This is the Standard Operating Procedure (SOP) for the Extraction and Cleanup of 1 Liter (1L) aqueous samples by Solid Phase Extraction (SPE) for analysis of Polychlorinated Biphenyls (PCBs) Using EPA SW-846 Method 3535 - Solid Phase Extraction.

2.0 APPLICABLE MATRIX AND MATRICES

2.1 This method is applicable to surface water, groundwater, wastewater and other aqueous samples.

3.0 DETECTION LIMIT

3.1 Please consult determinative method for analysis of sample extracts derived by this extraction method and determination of detection limits.

4.0 SCOPE AND APPLICATION

4.1 The following procedure is utilized by Northeast Analytical, Inc. for the extraction and subsequent cleanup of PCBs from 1L aqueous samples using the solid phase extraction method. This method was developed to utilize an automated extraction system, which is the SPE-DEX® 4790 extractor from Horizon Technologies. The extraction disk used is a 50mm Bakerbond Speedisk™ styrene divinyl benzene filter.

5.1 SUMMARY OF TEST METHOD

5.1 Prepare Sample: Warm the sample to room temperature, check pH, acidify, spike and surrogate, foil and cap bottle.

5.2 Extractor Preparation: Turn on equipment, check gauges, check solvent and recovery bottles, purge.

5.3 Extract the Sample.

5.4 Concentrate, Florisil cleanup with backwashes, re-concentrate, set to volume, and clean-up with acid, and mercury.

5.5 Provide sample to GC department for analysis.

6.0 DEFINITIONS

6.1 **Surrogate Standard Solution:** The chemical composition and chromatography of surrogates are similar to the analytes of interest. Usually not found in environmental samples. These compounds are spiked into all samples, blanks, and matrix spike samples prior to analysis. Percent recoveries are calculated for each surrogate.

6.2 **Laboratory Method Blank:** A laboratory derived sample consisting of reagent water or other blank matrix that consists of all reagents, internal standards, and surrogate standards that is carried through the entire analytical procedure. The laboratory method blank is used to define the level of laboratory analyte background or other interferences that exist in the laboratory environment, the reagents, or apparatus.

6.3 **Laboratory Control Spike (LCS):** Also known as the Quality Control (QC) Check Standard or Quality Control (QC) Check Sample. The LCS consists of an aliquot of reagent water or other blank matrix to which known quantities of the method analytes are added. The LCS is extracted and analyzed exactly like a field sample, and its purpose is to determine whether the analysis is in control and whether the laboratory is capable of making accurate and precise measurements.

6.4 **Matrix Spike (MS):** An aliquot of a field sample that is fortified with known quantities of the method analytes and subject to the entire analytical procedure. Its purpose is to assess the appropriateness of the method for the matrix by measuring the recovery.

6.5 **Sample Matrix Spike Duplicate (MSD):** An exact copy of the Matrix Spike. This is an aliquot of a field sample which is fortified with known quantities of the method analytes and is subject to the entire analytical procedure. Its purpose is to assess the appropriateness of the method for the matrix by measuring the recovery.

6.6 **DI Water (De-ionized Water):** Water free from analytes that may interfere with the analytical test compounds.

7.0 INTERFERENCES

7.1 Method interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing equipment (such as the SPE-DEX 4790 extractor) that lead to discrete artifacts and/or elevated baselines in gas chromatograms. All of these materials and equipment must be routinely verified to be free from interferences by running laboratory method blanks.

7.2 All equipment must be kept scrupulously clean. Clean all equipment as soon as possible after use, and store in jars away from environmental contaminants.

7.3 The use of high purity solvent and reagents will minimize interference problems. Purification of reagents by washing with solvent will also help to reduce interference problems.

7.4 Laboratory contamination can occur by introduction of plasticizers (phthalate esters) into the samples through the use of flexible tubing, gloves, pipette bulbs, etc. Samples and extracts should not be exposed to plastic materials. Phthalate esters exhibit a response on electron capture detectors, usually as late eluting peaks and can interfere in PCB quantification.

7.5 The sample matrix itself is also a potential source for method analyte interference. The clean-up procedures provided in this SOP can be used to overcome many of these interferences.

8.0 SAFETY

8.1 The extraction chemist should have received in-house safety training and should know the location of first aid equipment and the emergency spill/cleanup equipment before handling any apparatus or equipment. Safety glasses and gloves must be worn when handling glassware and samples. Polychlorinated biphenyls have been classified as a known or suspected carcinogen. The extraction chemist must review the Material Safety Data Sheets (MSDS) for PCBs and all reagents used in the procedure before beginning the extractions. All equipment and solvents should be handled within a laboratory fume hood.

9.0 EQUIPMENT AND SUPPLIES

9.1 Automated Solid Phase Extractor; Horizon# 4790-08 Consisting of:

a) Envision Platform
b) SPE-DEX® 4790 Extractor
c) 10" Solvent Vapor Exhaust Hose (2" Diameter)
d) Water and Solvent Waste Vacuum Lines
e) Vacuum Supply Line Assembly
f) 8' Telco Communication Cable
g) Solvent Delivery Line Kit
h) Pressure Regulator Bracket Assembly
i) Solvent Delivery Bottle Plug Kit
j) Solvent Recovery Manifold Assembly
k) Water Recovery Manifold Assembly
l) Waste Solvent Recovery Bottle
m) Waste Water Recovery Bottle
n) Solvent Delivery Teflon Manifold Kit
o) 2.5 Liter Safety Coated Solvent Bottles
p) Vacuum Source – capable of 20 to 25" Hg
q) Dry Trap for the Vacuum Source
r) Dry Nitrogen Gas Supply – capable of minimum 60 PSI to maximum 80 PSI

9.2 Glass Sample Containers

1 liter amber glass bottle

The 1-liter sample bottles are available pre-cleaned and certified. The lab has an in-house verification procedure to test bottles at a rate of 1 per 50.

9.3 Bakerbond Speedisk™ DVB – Styrene Divinyl Benzene 50mm disk for sample extraction P/N 8059-06 or equivalent

9.4 Disk Adapter

9.5 Vials

40mL vials, with polyseal cap, for collection vessel
60mL vials, with polyseal cap, for sample extract
4 dram vials, with polyseal cap, for sample extract

9.6 Collection Vessel Adapter – 19/22 Taper

9.7 Bottle Adapters

33 × 400 adapter for 1L clear glass bottle or 38 x 400 adapter
33 × 430 adapter for 1L amber glass bottle
38 × 400 Teflon adapter for 4L amber glass bottle

9.8 Aluminum Foil Squares – purchased pre-cleaned

9.9 pH indicator Strips – EM Science P/N 9590 or equivalent

9.10 Pipettes

1 mL x 1/100, Kimble#72120-1100
5 mL x 1/10, Kimble# 72120-5110
10 mL x 1/10, Kimble# 72120-10110
Pasteur Glass Pasteur Pipettes: 9'', Krackeler-Brand# 67-450-900

9.11 Syringes

500µL Syringe, gas-tight, Hamilton #81217
1000µL Syringe, gas-tight, Hamilton #81317
250µL Syringe, gas-tight, Hamilton #81100

9.12 Vial Rack – plastic rack used to hold vials during processing of extracts. Scienceware

9.13 Beakers - assorted Pyrex 250mL, 600mL and 1000mL, used for liquid containment and pipette storage.

9.14 2 Liter Graduated Cylinder – Scienceware
4 Liter Graduated Cylinder - Nalgene

9.15 TurboVap LV Evaporator – Caliper

9.16 Centrifuge; International Equipment Co., Model CL (or equivalent)

9.17 Wrist Shaker; Burrell wrist action shaker, Model 75 and 88 (or equivalent)

9.18 Flask; Chemglass, 125mL Erlenmeyer filter flask for purge recovery

9.19 Keck Clip

10.0 REAGENTS AND STANDARDS

10.1 **1:1 Sulfuric Acid** - (H_2SO_4), Mallinckrodt #2468, UN1830
Preparation: To a beaker containing 500mL cold DI-water, add 500mL concentrated H_2SO_4 slowly and under constant stirring. Allow the mixture to cool after preparation. Then, transfer to a pre-cleaned 1L bottle for storage.

10.2 **DI Water** – (Reagent Water) 18 Megaohm water obtained form the laboratory's water purification system. Used for solid phase disk preparation, laboratory method blanks, laboratory control spikes, MDL studies, and Precision and Accuracy studies.

10.3 **Methanol** – Pesticide residue quality. EM Science OmniSolv. P/N MX0488P-1 or equivalent

10.4 **Acetone**- High purity solvent; (Burdick\Jackson) UN1090

10.5 **Hexane**- High purity solvent; (Burdick\Jackson) #UN1208

10.6 **Florisil -** J.T. Baker #M368-08, 10% deactivated, solvent washed and deactivated as per NE094.doc.

10.7 **Concentrated Sulfuric Acid-** Mallinckrodt #2468, #UN1830, Solvent washed as per NE174.doc

10.8 **Mercury**- Triple distilled, Mercury Waste Solutions Inc., Solvent washed as per NE175.doc (or equivalent)

10.9 **Sodium Hydroxide**- JT Baker, #5671-03

10.10 **Standard Solutions** – The following standards are used during extraction and preparation of sample extracts:

10.10.1 **Surrogate Standard (2,2',3,3',4,4',5,6,6'-Nonachlorobiphenyl) at 0.200ug/mL in Acetone** - To every water sample and QC sample, 0.5mL of Surrogate Standard is added before extraction is initiated. The Surrogate Standard must be replaced after six months.

10.10.2 **Aroclor 1242 Spiking Standard at 1.0ppm in Acetone -** To every laboratory control spike, matrix spike, and matrix spike duplicate, add 0.2mL of Aroclor 1242 spiking standard before extraction is initiated. The A1242 Spiking Standard must be replaced after six months.

11.0 SAMPLE COLLECTION, PRESERVATION, SHIPMENT, AND STORAGE

11.1 The samples should be collected in unpreserved 1 liter glass bottles with a Teflon lined cap.

11.2 All samples must be placed on ice or refrigerated at 4°C ± 2°C from the time they are collected until delivery to the lab.

11.3 The samples must be protected from light and refrigerated at 4°C (±2°C) from time of receipt until they are removed from storage for extraction. Typically the entire water sample grab will be consumed at time of extraction and no sample is left for log-term storage.

11.4 The sample extraction hold time for this method is seven days from the date the samples were collected.

11.5 Sample extracts must be protected from light and stored refrigerated at 4°C (±2°C). After analysis is complete, sample extracts will be discarded after 60 days or can be archived in a freezer at less than -20°C for longer periods of time depending on the program requirements.

12.0 QUALITY CONTROL

12.1 The extraction chemist should have completed an acceptable demonstration of precision and accuracy before performing the method without supervision. The addition of spiking material to a sample or blank must be witnessed by another extraction chemist and noted in Laboratory Information System (LIMS). All surrogates and matrix spikes must meet acceptable quality control limits.

12.2 A method blank sample must be prepared per each extraction batch or per 20 site samples, whichever is more frequent. If the laboratory blank is positive for PCB above the reporting limit (based on Total PCB concentration), the contamination must be traced down and eliminated before samples can be processed and analyzed. If non-PCB contamination occurs that interferes with PCB quantification, it too must be traced down and eliminated before proceeding with sample analysis.

12.3 A lab control spike (LCS) must be prepared per extraction batch or per 20 site samples, whichever is more frequent. This control spike must achieve a percent recovery of 60% to 140% based on Total PCB concentration. If the LCS recovery is not within limits, the cause must be identified and corrected. The samples associated with the Laboratory Control Spike that failed must be re-extracted and re-analyzed. If no sample is available, the data must be flagged to indicate a low or high LCS recovery.

12.4 A matrix spike (MS) / matrix spike duplicate (MSD), should be prepared for every 20 site samples or as per client specified quality assurance project plan (QAPP). There must be sufficient sample for analysis of MS/MSD samples. Matrix spike recovery information is used to assess the long-term precision and accuracy of the method for each encountered matrix. Matrix spike /matrix spike duplicate results are not used alone to qualify an extraction batch. Generally, percent recovery for MS/MSD samples should be greater than or equal to 60% and less than or equal to 140% based on the total PCB concentration. If the percent recovery is outside the acceptance limits, all calculations should be checked and the data should be narrated to describe possible matrix interference. Spike default for LCS, MS, MSD is 0.2mL A1242 @ 1.0ppm in Acetone for a 1L sample. Client and/or project specifications may dictate alternate amount or Aroclor.

The relative percent difference between the matrix spike and matrix spike duplicate sample should be less than or equal to 30 %.

12.5 Duplicate analysis of the same sample is performed to assess method precision. A duplicate can also be performed as a blind duplicate, so that identification with original sample is withheld. The analysis of a duplicate sample precludes that PCBs are to be found at appreciable levels in samples. If this is not known, the analysis of the matrix spike/matrix spike duplicate will provide more consistent quality control information. The relative percent difference of the two measurements on the sample is calculated on a total PCB concentration. The relative percent difference must be less than or equal to 30%.

12.6 PCB Surrogates are added to each sample prior to extraction to measure extraction/cleanup efficiency. Percent recovery should be 60% - 140%. Default surrogate is: 0.5mL NCBP (2,2',3,3',4,4',5,6,6'-Nonachlorobiphenyl) @ 0.2ppm in Acetone for a 1L sample. Client and/or project specifications may dictate alternate amount.

13.0 CALIBRATION AND STANDARDIZATION

13.1 Please see determinative method for Calibration and Standardization. Refer to method NE207 for operating conditions to analyze PCBs by congener-specific methodology.

14.0 PROCEDURE

Note: When rinsing or pre-rinsing is referred to in this SOP, it is performed using a pipette and beaker.

14.1 Sample Preparation

14.1.1 Throughout the entire process it should be noted that if the extraction chemist encounters any problems or difficulties with any samples or steps involved, all work should **STOP!!!** Any problems should be brought to the attention of the supervisor and documented in LIMS.

14.1.2 Remove the samples to be extracted from cold storage and allow them to warm up to room temperature. This can be done first while the extraction equipment is prepared to extract samples.

14.1.3 Before any steps are taken, the extraction chemist should first review the sample job folder, LIMS, and check the sample labels versus the original chain of custody. Any discrepancies should be brought to the attention of the supervisor and the sample login custodian.

14.1.4 Using amber bottles as appropriate to the samples, prepare a method blank and laboratory control spike sample using reagent water equal to the sample volume.

14.1.5 Mark the level of the sample on the outside of the sample container with a paint pen. Determine the pH by removing a small amount of sample with a Pasteur pipette (approximately 0.1mL) and wet a pH indicator strip. Record the pH in LIMS.

14.1.6 Add 1.0 mL of 1:1 sulfuric acid per liter of water to every sample and QC sample using a disposable pipette. Cap and invert the sample container several times to mix. Check the pH (Refer to Section 14.1.5) to determine the sample was adjusted to a pH of 2 or less. If the pH was not adjusted sufficiently, add 0.5 mL of 1:1 sulfuric acid and test again. Continue to add 1:1 sulfuric acid in 0.5 mL aliquots until the pH is 2 or less.

14.1.7 Using a gas tight syringe, add the surrogate standard solution to every sample and QC sample.

14.1.8 To the laboratory control sample, matrix spike, and matrix spike duplicate samples, add the matrix spike standard solution using a gas tight syringe.

14.1.9 Cap and invert each sample and QC sample several times to mix.

14.2 Extractor Preparation

14.2.1 Check solvent reservoir bottles, solvent recovery bottle and waste water recovery bottle. Fill solvent reservoirs if necessary. When filling the solvent reservoirs, care should be taken not to spill or drip solvent on the outside of the bottles as they are rubber coated, and some solvents may dissolve the rubber. Solvent reservoirs should never be filled past their rubber coating. The DI water reservoir should be emptied, rinsed with RO water, and re-filled weekly.

14.2.2 Empty the solvent recovery bottle into an approved waste container for proper disposal according to the Chemical Hygiene Plan.

14.2.3 If necessary, neutralize and empty the wastewater recovery container. Add sodium hydroxide until the pH reads between 5 and 9. Once neutral, the waste water may be disposed of down the drain.

14.2.4 Turn the vacuum pump on and adjust the main vacuum between 20” to 26” Hg. Determine that the water recovery manifold assemblies on the waste water containers are forming a good seal.

14.2.5 Turn on the pressurized gas source and adjust gas pressure between 60 and 80 PSI.

14.2.6 Turn on the Envision Platform controller and Computer.

14.2.7 Adjust the non-venting vacuum regulator attached to the solvent recovery manifold assembly on the solvent recovery bottle to a vacuum of 15” Hg or less. **NOTE:** DO NOT adjust the regulator higher than 15” Hg. Higher vacuum levels could cause an SPE disk to go dry during the methanol and reagent water pre-wet steps.

14.2.8 On the pressure bracket assembly, adjust the left regulator labeled SPE extractor pressure to between 45 and 50 PSI. Adjust the right regulator labeled solvent bottle pressure to between 15 and 20 PSI.

14.2.9 Attach the disk adapter to a Bakerbond Speedisk™ designated for purges. Then place this set up on the disk holder platform.

14.2.10 Attach a 125mL flask designated for purges to the tapered joint on the bottom of the platform. Secure with a keck clip.

14.2.11 Invert a purge bottle and place into bottle holder of the extractor unit. (Note: A purge bottle is prepared by attaching a cap adapter to an empty 1L glass bottle. Since purge bottles can be reused, a set should be prepared and stored for reuse.)

14.2.12 Open the browser on the computer. Enter the IP address corresponding to the Envision Platform controller. The Operations Screen should load. The Operations screen is used to control and monitor the status of each Extractor. The screen is divided into sections within the right and left pane. The right pane displays the status of all connected Extractors; the left pane is used to control and monitor one Extractor. The extractors now must be programmed for a purge.

14.2.13 On the left pane of the Operations Screen there will be "**Purge Methods**" with a drop-down menu beneath it. From the drop-down list select **NEA Purge**. Two options will begin to blink green: **Load** and **Load All**. The **Load All** option will load the method into all 8 extractors. The **Load** option will load the method into only the extractor displayed on the left pane. Since all 8 units will need to be purged prior to use, select the **Load All** option.

14.2.14 **Purge** and **Purge All** will begin to blink green. Choose **Purge All** to purge all 8 units at once, or choose **Purge** to purge only the unit displayed in the left pane. This will initiate the purge cycle sequence. The purge may also be started for each individual unit by pressing the **Purge** button on each unit. The purge cycle will clean the extractor unit by dispensing the pre-wet solvents and directing them to the solvent recovery bottle. Next the rinse solvents will be sprayed into the empty sample bottle and directed into the collection vessel. (**NOTE:** Always use an empty bottle when running a purge cycle.)

14.2.15 During the purge cycle, carefully observe the operation of the SPE-DEX® 4790 extractor unit. Make sure that it is functioning properly and that the check valve located in the disk holder assembly is operating correctly and solvents are being delivered to the correct locations.

14.2.16 Once the purge cycle is completed, the SPE-DEX® 4790 extractor unit is ready to process samples. (**NOTE:** A purge cycle needs to be run before starting each day, between sample extractions and before shutting down at the end of the day.)

14.2.17 Detach the flask, and empty it into a properly labeled waste container.

14.2.18 Remove the purge bottle from the bottle holder.

14.2.19 Remove the Bakerbond Speedisk™ from the disk holder platform. Save the disk as it can be reused for future purge cycles.

14.3 Sample Extraction

14.3.1 Install a new Bakerbond Speedisk™ DVB onto the disk holder platform with the disk adapter.

14.3.2 Attach a vial adapter to the tapered joint on the bottom of the disk holder platform and place the keck clip on the adapter to secure it to the tapered joint. Attach a hexane pre-rinsed and properly labeled 40mL vial to the vial adapter.

14.3.3 Remove the bottle cap from the first sample. For a sample in a 1L amber bottle: place a 2" × 2" piece of pre-cleaned aluminum foil over the mouth of the bottle. Gently screw the amber bottle adapter (33 × 430) over the aluminum foil onto the screw threads of the bottle. When done properly the aluminum foil will be taut and no rips will be evident. If a tear is detected, the adapter must be removed and a new piece of aluminum foil must be installed.

14.3.4 Invert the sample bottle and inspect for any leaks or rising bubbles from the seal of the bottle and the adapter. If no bubbles or leaks are detected then a good seal has been made and the sample bottle can be installed onto the bottle holder assembly. If a leak or bubbles are observed, the adapter may need to be tightened or a new piece of aluminum foil may need to be installed. Test again until a good seal is made.

14.3.5 With the bottle inverted, place the bottle into the bottle holder assembly making sure that the solvent rinse stem (needle) is inside the bottle adapter. Gently lower and then firmly push the sample bottle into the bottle holder assembly. A bubble should escape into the bottle. Turn the bottle clockwise until a large bubble floats up into the bottle. (**NOTE:** Do not turn more than three quarters of the way around). This breaks an opening in the aluminum foil and allows the sample to flow freely.

14.3.6 Once the sample bottle has been installed, the Envision Platform controller will need to be programmed with a sample method. To the left of the "**Purge Methods**" on the left pane of the Operations Screen there will be "**Current Method**" with another drop-down menu. Select **First Bottle** from the list. The **Load**, **Load All** options will blink green. Just like the purge cycles, the **Load All** option will load the method into all 8 extractors and the **Load** option will load the method into only the extractor displayed on the left pane. Choose the **Load All** option.

14.3.7 Again the options **Start** and **Start All** blink green on the Operations Screen. Choose to either start all units at once by clicking **Start All** or each unit individually by choosing an extractor so that it is displayed in the left pane and then clicking **Start**. Each unit can also be individually started by pressing the **Start** button on the unit. The "Purge Method" and the "Current Method" will remain programmed in unless they are changed.

14.3.8 The SPE-DEX® 4790 extractor will automatically pre-wet the solid phase disk, extract the sample, air dry the disk post extraction and extract the disk to recover the analytes of interest. See Attachment 23.2. Each extractor will flash a green light while running: one blink for pre-wet, two for sample extraction (sample drop), three for wash (we don't use wash), four for air dry, five for rinse or disk extraction. The Envision Platform will also display the current status of each extractor unit.

14.3.9 Once the extraction process is completed the 40mL vial is removed from the vial adapter, capped with a pre-rinsed 40mL polyseal cap, and then the vial is placed in a rack. The

sample is then ready to be stored in cold storage or taken through the required cleanup steps. The vial adapter is removed and placed in the hood to be cleaned.

14.3.10 Remove the sample bottle from the bottle holder assembly. Remove the cap adapter and place in the hood to be cleaned.

14.3.11 Remove the Bakerbond Speedisk™ and disk adapter from the disk holder platform. Throw the used Bakerbond Speedisk™ in the garbage, and place the disk adapter in the hood to be cleaned.

14.3.12 Fill the sample bottle(s) with tap water to the mark made before the extraction. Measure the volume of the water using a 2L graduated cylinder to the nearest 10mLs. Record the volume in LIMS.

14.3.13 Re-purge the units that were used as in section 14.2. Shut down the system in the reverse order as startup; starting with the computer browser, controller, nitrogen source, and pump. Break the seal on the water recovery jug.

14.3.14 Clean all used equipment in the hood according to SOP NE235.

14.4 Sample Extract Concentration and Cleanup Procedures

14.4.1 Extract Solvent Reduction

14.4.1.1 The sample extract will have two layers, the top layer will be composed of the Hexane/Acetone used to elute components from the solid phase disk and the bottom layer will be composed of residual water and Acetone from the extraction process. Carefully transfer the top layer of solvent to a hexane pre-rinsed and properly labeled 60mL vial using a hexane pre-rinsed disposable 10mL pipette.

14.4.1.2 Backwash the residual water/Acetone in the 40mL with three Pasteur pipette volumes of Hexane. Shake by hand in a chemical fume hood for 5 to 10 seconds. Allow to settle, forming two layers like the original sample. Transfer top Hexane layer carefully into the vessel holding the rest of the extract. Repeat this two more times, for a total of three rinses.

14.4.1.3 After all the rinses have been transferred, rinse the outside of the 10mL pipette with hexane into the sample vial. Rinse the sides of the vial, and bring the volume of all the extracts up to just below the base of the vial neck.

14.4.1.4 Dump any remaining residual water from the water/Acetone layer into a waste jar for evaporation in hood. This jar will be saved for reuse.

14.4.1.5 The LV Turbo Vap Evaporator systems are used to reduce the sample volume. They use a heated water bath and positive pressure Nitrogen flow with vortex action. The units maintain a slight equilibrium imbalance between the liquid and the gaseous phases of the solvent extract, which allows for fractional reduction of the solvent without loss of higher boiling point analytes.

14.4.1.6 Turn on the LV Turbo Vap Evaporator and allow it to heat up to 40°C ± 2°C. Check the water level in the LV Turbo Vap and fill, if necessary, to the second stage from the top. On the top of the unit press the **START/PAUSE** key, a green light will light up to the right of it. Then press the Tube station keys corresponding to the rows needed to concentrate the samples.

14.4.1.7 As a precaution the TurboVap Evaporator system regulators should be checked to assure that there is no residual gas pressure within the system and that the gas pressure regulator is off before placing samples in the apparatus. Residual gas pressure may cause splashing and therefore cause cross contamination of samples. Make sure that the lid and regulator are closed, and that the cells or rows are turned on. Bleed any residual gas until the regulator gauge reads "0" psi.

14.4.1.8 Wipe down the inside of the LV Turbo Vap Evaporator with a Hexane wetted paper towel including the top lid and pins. Close the lid and turn on the regulator to dry the Turbo Vap LV. Turn off the gas regulator before loading samples. Place the 60mL vials containing the sample extract into the LV TurboVap and close the lid.

14.4.1.9 Slowly open the pressure regulator, by turning it towards yourself. Keep the gas pressure very low, until the solvent level is decreased, to avoid splashing. Increase the gas pressure as the sample reduces maintaining uniform flow throughout the volume reduction.

14.4.1.10 The process of solvent (Hexane) reduction takes approximately 20 – 30 minutes. DO NOT leave the unit unattended as extracts may be blown to dryness and loss of PCB as well as surrogate and matrix spike may occur. Immediately notify the extraction supervisor if an extract is blown to dryness and note the incident in the sample extraction logbook.

14.4.1.11 Concentrate the extract to approximately 5mLs. Remove the 60mL vial from the Evaporator unit, being careful not to drip.

14.4.2 Florisil Absorption (Slurry)

14.4.2.1 The Florisil slurry removes co-extracted polar compounds, residual water and residual acid.

14.4.2.2 Add one spatula of Florisil to a pre-rinsed and properly labeled 4 dram vial.

Note: See supervisor for the appropriate Florisil deactivation concentration to be used.

14.4.2.3 Transfer the 5mLs of sample from the 60mL vial to the 4 dram vial containing Florisil.

14.4.2.4 Rinse the 60mL vial with one Pasteur pipette volume of Hexane (approximately 2.0mL) and add this rinse to the same 4 dram vial. Set aside the 60mL vial with the Pasteur pipette used to transfer. They will be used to transfer the extract back.

14.4.2.5 Cap and shake the 4 dram vial by hand for 30 seconds in a chemical fume hood. Allow the Florisil to settle. Swirl the extract if necessary to get the Florisil off the sides of the 4 dram vial.

14.4.2.6 Transfer the extract back into the 60mL VOA vial, using the Pasteur pipette previously used.

14.4.2.7 Backwash the Florisil. Add three pipette volumes (approximately 10mL) of Hexane to the Florisil in the 4 dram vial. Cap and shake the vial in a chemical fume hood for 5 to 10 seconds. Swirl the extract if necessary to get the Florisil off the sides of the 4 dram vial.

14.4.2.8 Transfer this rinse in to the 60mL VOA vial with the rest of the extract. Repeat this backwash procedure twice more for a total of three rinses.

14.4.2.9 After the final transfer, rinse the outside of the Pasteur pipette into the 60mL vial.

14.4.2.10 Following the TurboVap LV Evaporator procedure described above, concentrate the extract to approximately 2.5mL. Remove the 60mL vial from the evaporator unit being careful not to drip.

14.4.3 Set Volume

14.4.3.1 Carefully transfer the extract into a pre-rinsed 5.0mL volumetric.

14.4.3.2 Rinse the 60mL vial with approximately 1.0mL of Hexane and add this to the 5.0mL volumetric. Repeat this process two more times, adding the rinses to the 5.0 volumetric, making sure to bring the volume to 5.0mL only.

14.4.3.3 Stopper with a pre-rinsed stopper and invert the volumetric several times to mix thoroughly.

14.4.3.4 Transfer the extract into a pre-rinsed and properly labeled 4 dram vial.

14.4.4 Sulfuric Acid Cleanup

NOTE: The concentrated Sulfuric acid treatment removes hydrocarbons and other organic compounds, which are co-extracted with the PCB residues.

14.4.4.1 Add one disposable Pasteur pipette volume full of solvent washed concentrated Sulfuric acid (NE174.doc) to each extract vial and shake by hand in a chemical fume hood for 30 seconds.

14.4.4.2 Centrifuge sample vials for at least one minute on setting #4. Transfer the Hexane layer (upper layer) to a correctly labeled and pre-rinsed 4 dram vial.

14.4.4.3 Repeat, beginning at section 14.4.4.1 if the sample extract appears to be heavily loaded (opaque) with colored material. Two or three acid washes may be required. **NOTE:** It is entirely possible that all colored material will not be removed from the extract.

14.4.5 Mercury Cleanup

NOTE: Mercury is a highly toxic metal. All operations involving Mercury should be performed within a chemical fume hood. Prior to using Mercury, the extraction chemist should become acquainted with proper handling and emergency spill/cleanup procedures associated with this metal and must have reviewed the Material Safety Data Sheets (MSDS). Sulfur in the sample will be converted to Mercuric Sulfide and precipitate out of the sample extract. A black precipitate may be seen in the sample extracts containing elemental sulfur.

14.4.5.1 Using a disposable Pasteur pipette add 2-3 drops of solvent washed Mercury (NE175.doc) to the sample extracts and cap.

14.4.5.2 Handshake for 30 seconds. If the Mercury changes color or breaks up into tiny balls and will not reform the original ball, change the Mercury. To change the Mercury transfer the extract into a new correctly labeled and Hexane pre-rinsed 4 dram vial and add new Mercury to it. Repeat previous step.

14.4.5.3 Place on wrist shaker for 30 minutes.

14.4.5.4 Remove the sample extracts from the wrist shaker.

14.5 Final Extract Preparation

14.5.1 Transfer the extract to a Hexane pre-rinsed and correctly labeled final 4-dram vial.

14.5.2 Complete all information in LIMS. Print the Extraction Log sheet, and the GC sheet. Submit samples and project folder to GC Analyst.

15.0 CALCULATIONS

15.1 All calculations pertaining to data analysis and reporting can be found in the determinative method SOP NE207.

16.0 METHOD PERFORMANCE

16.1 Please consult determinative methods (NE207.doc) for Method Performance details.

17.0 POLLUTION PREVENTION

17.1 Please see NEA168.SOP for pollution prevention measures.

18.0 DATA ASSESSMENT AND ACCEPTANCE CRITERIA FOR QC MEASURES

18.1 Please consult determinative methods (NE207.doc) for Data Assessment and Acceptance Criteria for Quality Control Measures.

19.0 CORRECTIVE ACTION FOR OUT-OF-CONTROL DATA

19.1 Please consult determinative methods (NE207.doc) for Corrective Action for Out-Of-Control Data.

20.0 CONTIGENCIES FOR HANDLING OUT-OF-CONTROL DATA

20.1 Please consult determinative methods (NE207.doc) for Contingencies for Handling Out-Of-Control or Unacceptable Data.

21.0 WASTE MANAGEMENT

21.1 Please see NEA054.SOP, NEA083.SOP and NEA089.SOP

22.0 REFERENCES

22.1 US EPA 40 CFR Part 136, "Guidelines Establishing Test Procedures for the Analysis of Pollutants," July, 1988.

22.2 US EPA SW-846, "Test Methods for Evaluating Solid Waste Physical/Chemical Methods,"
Office of Solid Waste and Emergency Response, 3rd Edition, 1986 and its updates.

22.3 Horizon Technology, "SPE-DEX® 4790 Series Extractor: Automated Solid Phase Extractor System User's Guide," July 2001.

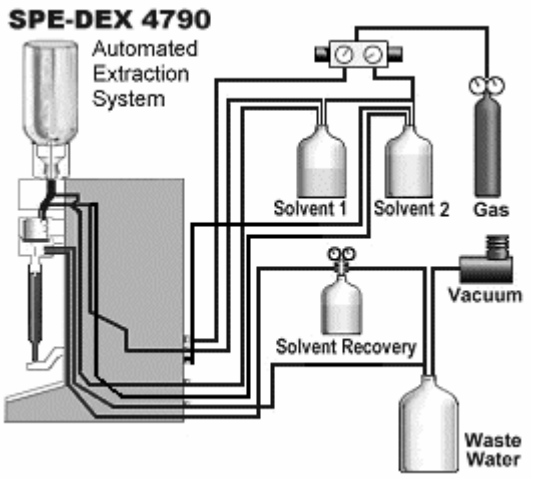
23.0 ATTACHMENTS

23.1 SPE Extractor Diagram

23.2 Extraction Method

23.3 Method Flow Chart

23.1 SPE EXTRACTOR DIAGRAM*

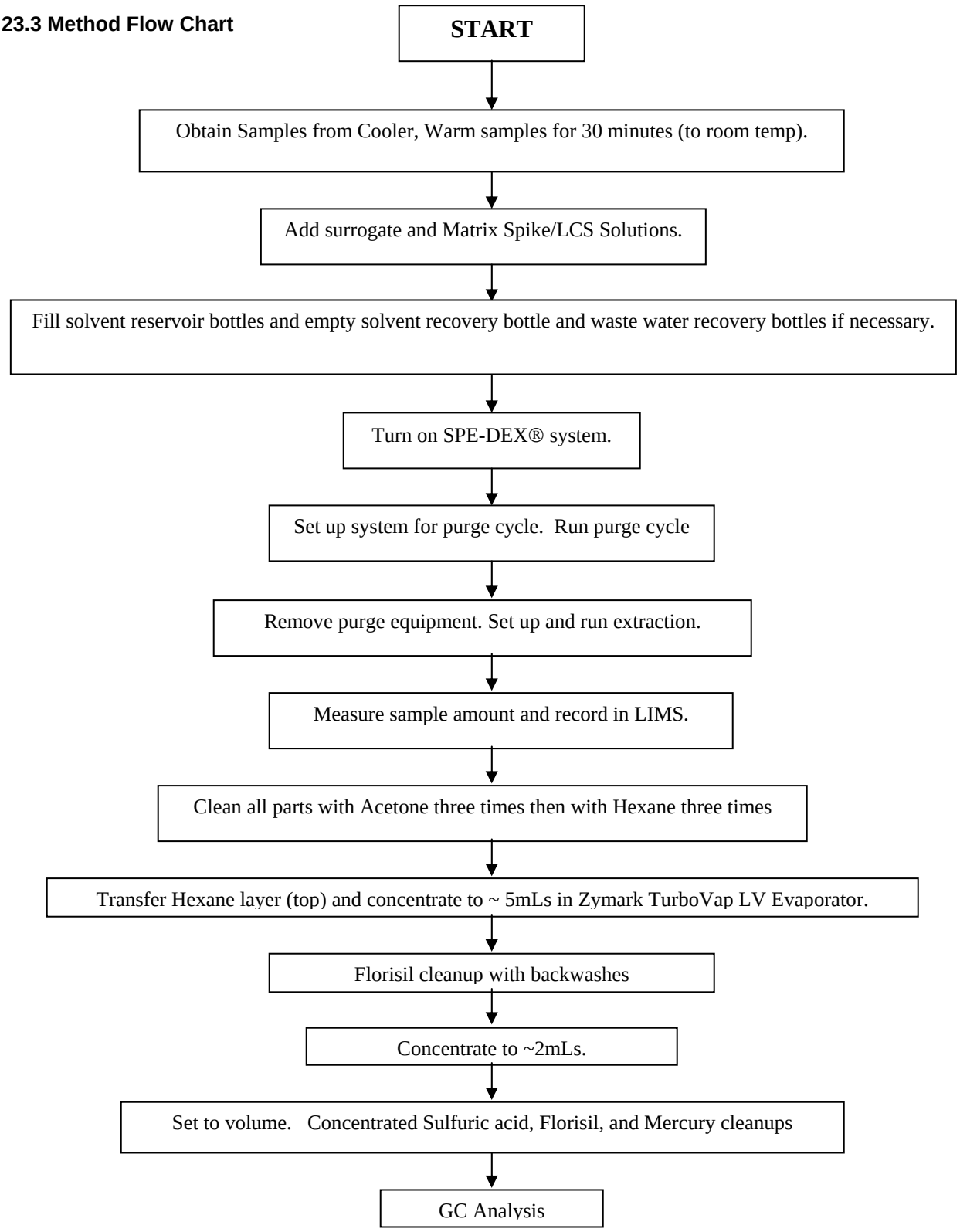


***NOTE: Limited diagram of the SPE-DEX® extractor set up. There are actually eight solvent bottles, five pre-wet solvents and three rinse solvents.**

23.2 Extraction Method

Step Number	Procedure
Step 1: Pre-wet Solvent: Dichloromethane	Soak Time: 1:00 minute Air Dry Time: 30 seconds
Step 2: Pre-wet Solvent: Hexane	Soak Time: 1:00 minute Air Dry Time: 30 seconds
Step 3: Pre-wet Solvent: Acetone	Soak Time: 1:00 minutes Air Dry Time: 30 seconds
Step 4: Pre-wet Solvent: Methanol	Soak Time: 1:30 minute Air Dry Time: 0:00 minutes
Step 5: Pre-wet Solvent: Reagent Water	Soak Time: 1:00 minute Air Dry Time: 0:00 minutes
Step 6: Pre-wet Solvent: Reagent Water	Soak Time: 1:00 minute Air Dry Time: 0:00 minutes
Step 7: Sample Extraction / Water Drop	Time depends on particulates and sample flow through the solid phase disk.
Step 8: Air Dry Disk	Air Dry Time: 5:00 minutes
Step 9: Rinse Solvent: Acetone	Soak Time: 1:30 minutes Air Dry Time: 1:00 minute
Step 10: Rinse Solvent Hexane	Soak Time: 1:30 minutes Air Dry Time: 1:00 minute
Step 11: Rinse Solvent Hexane	Soak Time: 1:30 minutes Air Dry Time: 1:00 minute
Step 12: Rinse Solvent Hexane	Soak Time: 1:30 minutes Air Dry Time: 1:00 minute

23.3 Method Flow Chart



APPENDIX 25
SOP FOR THE EXTRACTION AND CLEANUP OF AQUEOUS SAMPLES BY SOLID PHASE EXTRACTION (SPE) FOR PCBS USING MODIFIED EPA METHOD 508.1 (NE273_01)

STANDARD OPERATING PROCEDURE

NORTHEAST ANALYTICAL, INC.

NE273_01.DOC

REVISION NUMBER: 01

EXTRACTION AND CLEANUP OF AQUEOUS SAMPLES BY SOLID PHASE EXTRACTION (SPE) FOR POLYCHLORINATED BIPHENYLS (PCBs) USING MODIFIED EPA METHOD 508.1

COPY #_____

NORTHEAST ANALYTICAL, INC
2190 TECHNOLOGY DRIVE
SCHENECTADY, NY 12308

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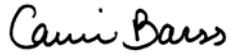
STANDARD OPERATING PROCEDURE

LABORATORY PROCEDURE NE273_01.DOC

REVISION 1 (03/24/2009)

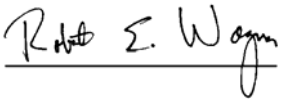
Author: Carrie Barss

Reviewed by:



Carrie Barss
Extractions Manager

Reviewed by:



Robert E. Wagner
Laboratory Director

Approved by:

Christina L. Braidwood
Quality Assurance Officer

Table of Contents

1.0 IDENTIFICATION OF TEST METHOD

1.1 This is the Standard Operating Procedure (SOP) for the Extraction and Cleanup of Aqueous Samples by Solid Phase Extraction (SPE) for analysis of Polychlorinated Biphenyls (PCBs) Using Modified EPA Method 508.1.

2.0 APPLICABLE MATRIX AND MATRICES

2.1 This method is applicable to surface water, groundwater, wastewater and other aqueous samples.

3.0 DETECTION LIMITS

3.1 Please consult determinative method EPA Method 508 (NE231.doc) for detection limits.

4.0 SCOPE AND APPLICATION

4.1 The following procedure is utilized by Northeast Analytical, Inc. for the extraction and subsequent cleanup of PCBs from aqueous samples using the solid phase extraction method. This method was developed to utilize an automated extraction system, which is the SPE-DEX® 4790 extractor from Horizon Technologies. The extraction disk used is a 50 mm Bakerbond Speedisk™ styrene divinyl benzene filter.

5.0 SUMMARY OF TEST METHOD

5.1 Prepare Sample: Warm the sample to room temperature, check pH, acidify, spike and surrogate, foil and cap bottle.

5.2 Extractor Preparation: Turn on equipment, check gauges, check solvent and recovery bottles, purge.

5.3 Extract the Sample.

5.4 Solvent exchange to Hexane, concentrate, set to volume, and clean-up with acid, Florisil, and mercury.

5.5 Present sample to GC/GCMS for PCB Aroclor analysis.

6.0 DEFINITIONS

6.1 **Surrogate Standard Solution:** The chemical composition and chromatography of surrogates are similar to the analytes of interest. Usually not found in environmental samples. These compounds are spiked into all samples, blanks, and matrix spike samples prior to analysis. Percent recoveries are calculated for each surrogate.

6.2 **Laboratory Method Blank:** A laboratory derived sample consisting of reagent water or other blank matrix that consists of all reagents, internal standards, and surrogate standards that is carried through the entire analytical procedure. The laboratory method blank is used to define the level of laboratory analyte background or other interferences that exist in the laboratory environment, the reagents, or apparatus.

6.3 Laboratory Control Spike (LCS): Also known as the Quality Control (QC) Check Standard or Quality Control (QC) Check Sample. The LCS consists of an aliquot of reagent water or other blank matrix to which known quantities of the method analytes are added. The LCS is extracted and analyzed exactly like a field sample, and its purpose is to determine whether the analysis is in control and whether the laboratory is capable of making accurate and precise measurements.

6.4 Matrix Spike (MS): An aliquot of a field sample that is fortified with known quantities of the method analytes and subject to the entire analytical procedure. Its purpose is to assess the appropriateness of the method for the matrix by measuring the recovery.

6.5 Sample Matrix Spike Duplicate (MSD): An exact copy of the Matrix Spike. This is an aliquot of a field sample which is fortified with known quantities of the method analytes and is subject to the entire analytical procedure. Its purpose is to assess the appropriateness of the method for the matrix by measuring the recovery.

6.6 DI Water (De-ionized Water): Water free from analytes that may interfere with the analytical test compounds.

7.0 INTERFERENCES

7.1 Method interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing equipment (such as the SPE-DEX 4790 extractor) that lead to discrete artifacts and/or elevated baselines in gas chromatograms. All of these materials and equipment must be routinely verified to be free from interferences by running laboratory method blanks.

7.2 All equipment must be kept scrupulously clean. Clean all equipment as soon as possible after use, and store in jars away from environmental contaminants.

7.3 The use of high purity solvent and reagents will minimize interference problems. Purification of reagents by washing with solvent will also help to reduce interference problems.

7.4 Laboratory contamination can occur by introduction of plasticizers (phthalate esters) into the samples through the use of flexible tubing, gloves, pipette bulbs, etc. Samples and extracts should not be exposed to plastic materials. Phthalate esters exhibit a response on electron capture detectors, usually as late eluting peaks and can interfere in PCB quantification.

7.5 The sample matrix itself is also a potential source for method analyte interference. The clean-up procedures provided in this SOP can be used to overcome many of these interferences.

8.0 SAFETY

8.1 The extraction chemist should have received in-house safety training and should know the location of first aid equipment and the emergency spill/cleanup equipment before handling any apparatus or equipment. Safety glasses and gloves must be worn when handling glassware and samples. Polychlorinated biphenyls have been classified as a known or suspected carcinogen. The extraction chemist must review the Material Safety Data Sheets

(MSDS) for PCBs and all reagents used in the procedure before beginning the extractions. All equipment and solvents should be handled within a laboratory fume hood.

9.0 EQUIPMENT AND SUPPLIES

9.1 Automated Solid Phase Extractor; Horizon# 4790-08 Consisting of:

a) Envision Platform
b) SPE-DEX® 4790 Extractor
c) 10" Solvent Vapor Exhaust Hose (2" Diameter)
d) Water and Solvent Waste Vacuum Lines
e) Vacuum Supply Line Assembly
f) 8' Telco Communication Cable
g) Solvent Delivery Line Kit
h) Pressure Regulator Bracket Assembly
i) Solvent Delivery Bottle Plug Kit
j) Solvent Recovery Manifold Assembly
k) Water Recovery Manifold Assembly
l) Waste Solvent Recovery Bottle
m) Waste Water Recovery Bottle
n) Solvent Delivery Teflon Manifold Kit
o) 2.5 Liter Safety Coated Solvent Bottles
p) Vacuum Source – capable of 20 to 25" Hg
q) Dry Trap for the Vacuum Source
r) Dry Nitrogen Gas Supply – capable of minimum 60 PSI to maximum 80 PSI

9.2 Glass Sample Containers

1 liter amber glass bottle
4 liter amber glass bottle

9.3 Bakerbond Speedisk™ DVB – Styrene Divinyl Benzene 50mm disk for sample extraction P/N 8059-06 or equivalent

9.4 Disk Adapter

9.5 Vials

40mL vials, with polyseal cap, for collection vessel
60mL vials, with polyseal cap, for sample extract
4 dram vials, with polyseal cap, for sample extract

9.6 Collection Vessel Adapter – 19/22 Taper

9.7 Bottle Adapters

33 × 400 adapter for 1L clear glass bottle or 38 x 400 adapter
33 × 430 adapter for 1L amber glass bottle
38 × 400 Teflon adapter for 4L amber glass bottle

9.8 Aluminum Foil Squares – purchased pre-cleaned

9.9 pH indicator Strips – EM Science P/N 9590 or equivalent

9.10 Pipettes

1mL x 1/100, Kimble#72120-1100
5mL x 1/10, Kimble# 72120-5110
10mL x 1/10, Kimble# 72120-10110
Pasteur Glass Pasteur Pipettes: 9'', Krackler-Brand# 67-450-900

9.11 Syringes

500µL Syringe, gas-tight, Hamilton #81217
1000µL Syringe, gas-tight, Hamilton #81317
250µL Syringe, gas-tight, Hamilton #81100

9.12 Vial Rack – plastic rack used to hold vials during processing of extracts. Scienceware

9.13 Beakers - assorted Pyrex 250mL, 600mL and 1000mL, used for liquid containment and pipette storage.

9.14 2 Liter Graduated Cylinder – Scienceware
4 Liter Graduated Cylinder - Nalgene

9.15 TurboVap LV Evaporator – Caliper

9.16 Centrifuge; International Equipment Co., Model CL (or equivalent)

9.17 Wrist Shaker; Burrel wrist action shaker, Model 75 and 88 (or equivalent)

9.18 Flask; Chemglass, 125mL Erlenmeyer filter flask for purge recovery

9.19 Keck Clip

10.0 REAGENTS AND STANDARDS

10.1 **1:1 Sulfuric Acid** - (H_2SO_4), Mallinckrodt #2468, UN1830
Preparation: To a beaker containing 500mL cold DI-water, add 500mL concentrated H_2SO_4 slowly and under constant stirring. Allow the mixture to cool after preparation. Then, transfer to a pre-cleaned 1L bottle for storage.

10.2 **DI Water** – (Reagent Water) 18 Megaohm water obtained form the laboratory's water purification system. Used for solid phase disk preparation, laboratory method blanks, laboratory control spikes, MDL studies, and Precision and Accuracy studies.

10.3 **Methanol** – Pesticide residue quality. EM Science OmniSolv. P/N MX0488P-1 or equivalent

10.4 **Acetone**- High purity solvent; (Burdick\Jackson) UN1090

10.5 **Hexane**- High purity solvent; (Burdick\Jackson) #UN1208

10.6 **Florisil -** J.T. Baker #M368-08, 10% deactivated, solvent washed and deactivated as per NE094.doc.

10.7 **Concentrated Sulfuric Acid-** Mallinckrodt #2468, #UN1830, Solvent washed as per NE174.doc

10.8 **Mercury**- Triple distilled, Mercury Waste Solutions Inc., Solvent washed as per NE175.doc (or equivalent)

10.9 **Sodium Hydroxide**- JT Baker, #5671-03

10.10 **Standard Solutions** – The following standards are used during extraction and preparation of sample extracts:

10.10.1 Surrogate Standard (0.05ppm TCMX / 0.5ppm DCBP) in Acetone - To every water sample and QC sample, 0.5mL of Surrogate Standard is added before extraction is initiated. The Surrogate Standard must be replaced after six months.

10.10.2 Aroclor 1242 Spiking Standard at 0.5ppm in Acetone - To every laboratory control spike, matrix spike, and matrix spike duplicate, add 0.5mL of Aroclor 1242 spiking standard before extraction is initiated. The A1242 Spiking Standard must be replaced after six months.

11.0 SAMPLE COLLECTION, PRESERVATION, SHIPMENT, AND STORAGE

11.1 The samples should be collected in unpreserved 1 liter glass bottles with a Teflon lined cap. All samples must be placed on ice or refrigerated at 4°C ± 2°C from the time they are collected, until delivery to the lab. The sample extraction hold time for this method is seven days from the date the samples were collected.

12.0 QUALITY CONTROL

12.1 The extraction chemist should have completed an acceptable demonstration of precision and accuracy before performing the method without supervision. The addition of spiking material to a sample or blank must be witnessed by another extraction chemist and noted in Laboratory Information System (LIMS). All surrogates and matrix spikes must meet acceptable quality control limits.

12.2 A method blank sample must be prepared per each extraction batch or per 20 site samples, whichever is more frequent. If the laboratory blank is positive for PCB above the reporting limit (based on Total PCB concentration), the contamination must be traced down and eliminated before samples can be processed and analyzed. If non-PCB contamination occurs that interferes with PCB quantification, it too must be traced down and eliminated before proceeding with sample analysis.

12.3 A lab control spike (LCS) must be prepared per extraction batch or per 20 site samples, whichever is more frequent. This control spike must achieve a percent recovery of 70% to 130% based on Total PCB concentration. If the LCS recovery is not within limits, the cause must be identified and corrected. The samples associated with the Laboratory Control

Spike that failed must be re-extracted and re-analyzed. If no sample is available, the data must be flagged to indicate a low or high LCS recovery.

12.4 A matrix spike (MS) / matrix spike duplicate (MSD), should be prepared for every 20 site samples or as per client specified quality assurance project plan (QAPP). There must be sufficient sample for analysis of MS/MSD samples. Matrix spike recovery information is used to assess the long-term precision and accuracy of the method for each encountered matrix. Matrix spike /matrix spike duplicate results are not used alone to qualify an extraction batch. Generally, percent recovery for MS/MSD samples should be greater than or equal to 70% and less than or equal to 130% based on the total PCB concentration. If the percent recovery is outside the acceptance limits, all calculations should be checked and the data should be narrated to describe possible matrix interference. Spike default for LCS, MS, MSD is 0.5mL A1242 @ 0.5ppm in Acetone for a 1L sample. Client and/or project specifications may dictate alternate amount or Aroclor.

12.5 Duplicate analysis of the same sample is performed to assess method precision. A duplicate can also be performed as a blind duplicate, so that identification with original sample is withheld. The analysis of a duplicate sample precludes that PCBs are to be found at appreciable levels in samples. If this is not known, the analysis of the matrix spike/matrix spike duplicate will provide more consistent quality control information. The relative percent difference of the two measurements on the sample is calculated on a total PCB concentration. The relative percent difference must be less than or equal to $\leq$ 20%.

12.6 PCB Surrogates are added to each sample prior to extraction to measure extraction/cleanup efficiency. Percent recovery should be 70% - 130%. Default surrogate is: 0.5mL 0.05ppm TCMX / 0.5ppm DCBP in Acetone for a 1L sample. Client and/or project specifications may dictate alternate amount.

13.0 CALIBRATION AND STANDARDIZATION

13.1 Please see determinative method (EPA Method 508, NE231.doc) for Calibration and Standardization.

14.0 PROCEDURE

Note: When rinsing or pre-rinsing is referred to in this SOP, it is performed using a pipette and beaker.

14.1 Sample Preparation

14.1.1 Throughout the entire process it should be noted that if the extraction chemist encounters any problems or difficulties with any samples or steps involved, all work should **STOP!!!** Any problems should be brought to the attention of the supervisor and documented in LIMS.

14.1.2 Remove the samples to be extracted from cold storage and allow them to warm up to room temperature (at least 30 minutes for a 1L sample). This can be done first while the extraction equipment is prepared to extract samples.

14.1.3 Before any steps are taken, the extraction chemist should first review the sample job folder, LIMS, and check the sample labels versus the original chain of custody. Any

discrepancies should be brought to the attention of the supervisor and the sample login custodian.

14.1.4 Using amber bottles as appropriate to the samples, prepare a method blank and laboratory control spike sample using reagent water equal to the sample volume.

14.1.5 Mark the level of the sample on the outside of the sample container with a paint pen. Determine the pH by removing a small amount of sample with a Pasteur pipette (approximately 0.1mL) and wet a pH indicator strip. Record the pH in LIMS.

14.1.6 Add 1.0mL of 1:1 sulfuric acid per liter of water to every sample and QC sample using a disposable pipette. Cap and invert the sample container several times to mix. Check the pH (Refer to Section 14.1.5) to determine the sample was adjusted to a pH of 2 or less. If the pH was not adjusted sufficiently, add 0.5mL of 1:1 sulfuric acid and test again. Continue to add 1:1 sulfuric acid in 0.5mL aliquots until the pH is 2 or less.

14.1.7 Using a gas tight syringe, add the surrogate standard solution to every sample and QC sample.

14.1.8 To the laboratory control sample, matrix spike, and matrix spike duplicate samples, add the matrix spike standard solution using a gas tight syringe.

14.1.9 Cap and invert each sample and QC sample several times to mix.

14.2 Extractor Preparation

14.2.1 Check solvent reservoir bottles, solvent recovery bottle and waste water recovery bottle. Fill solvent reservoirs if necessary. When filling the solvent reservoirs, care should be taken not to spill or drip solvent on the outside of the bottles as they are rubber coated, and some solvents may dissolve the rubber. Solvent reservoirs should never be filled past their rubber coating. The DI water reservoir should be emptied, rinsed with RO water, and re-filled weekly.

14.2.2 Empty the solvent recovery bottle into an approved waste container for proper disposal according to the Chemical Hygiene Plan.

14.2.3 If necessary, neutralize and empty the wastewater recovery container. Add sodium hydroxide until the pH reads between 5 and 9. Once neutral, the waste water may be disposed of down the drain.

14.2.2 Turn the vacuum pump on and adjust the main vacuum between 20 in. Hg to 26” Hg. Determine that the water recovery manifold assemblies on the waste water containers are forming a good seal.

14.2.3 Turn on the pressurized gas source and adjust gas pressure between 60 and 80 PSI.

14.2.4 Turn on the Envision Platform controller and Computer.

14.2.5 Adjust the non-venting vacuum regulator attached to the solvent recovery manifold assembly on the solvent recovery bottle to a vacuum of 15” Hg or less. **NOTE:** DO NOT adjust the regulator higher than 15” Hg. Higher vacuum levels could cause an SPE disk to go dry during the methanol and reagent water pre-wet steps.

14.2.6 On the pressure bracket assembly, adjust the left regulator labeled SPE extractor pressure to between 45 and 50 PSI. Adjust the right regulator labeled solvent bottle pressure to between 15 and 20 PSI.

14.2.7 Attach the disk adapter to a Bakerbond Speedisk™ designated for purges. Then place this set up on the disk holder platform.

14.2.8 Attach a 125 mL flask designated for purges to the tapered joint on the bottom of the platform. Secure with a keck clip.

14.2.9 Invert a purge bottle and place into bottle holder of the extractor unit. (Note: A purge bottle is prepared by attaching a cap adapter to an empty 1L glass bottle. Since purge bottles can be reused, a set should be prepared and stored for reuse.)

14.2.10 Open the browser on the computer. Enter the IP address corresponding to the Envision Platform controller. The Operations Screen should load. The Operations screen is used to control and monitor the status of each Extractor. The screen is divided into sections within the right and left pane. The right pane displays the status of all connected Extractors; the left pane is used to control and monitor one Extractor. The extractors now must be programmed for a purge.

14.2.11 On the left pane of the Operations Screen there will be "**Purge Methods**" with a drop-down menu beneath it. From the drop-down list select **NEA Purge**. Two options will begin to blink green: **Load** and **Load All**. The **Load All** option will load the method into all 8 extractors. The **Load** option will load the method into only the extractor displayed on the left pane. Since all 8 units will need to be purged prior to use, select the **Load All** option.

14.2.12 **Purge** and **Purge All** will begin to blink green. Choose **Purge All** to purge all 8 units at once, or choose **Purge** to purge only the unit displayed in the left pane. This will initiate the purge cycle sequence. The purge may also be started for each individual unit by pressing the **Purge** button on each unit. The purge cycle will clean the extractor unit by dispensing the pre-wet solvents and directing them to the solvent recovery bottle. Next the rinse solvents will be sprayed into the empty sample bottle and directed into the collection vessel. (**NOTE:** Always use an empty bottle when running a purge cycle.)

14.2.13 During the purge cycle, carefully observe the operation of the SPE-DEX® 4790 extractor unit. Make sure that it is functioning properly and that the check valve located in the disk holder assembly is operating correctly and solvents are being delivered to the correct locations.

14.2.14 Once the purge cycle is completed, the SPE-DEX® 4790 extractor unit is ready to process samples. (**NOTE:** A purge cycle needs to be run before starting each day, between sample extractions and before shutting down at the end of the day.)

14.2.15 Detach the flask, and empty it into a properly labeled waste container.

14.2.16 Remove the purge bottle from the bottle holder.

14.2.17 Remove the Bakerbond Speedisk™ from the disk holder platform. Save the disk as it can be reused for future purge cycles.

14.3 Sample Extraction

14.3.1 Install a new Bakerbond Speedisk™ DVB onto the disk holder platform with the disk adapter.

14.3.2 Attach a vial adapter to the tapered joint on the bottom of the disk holder platform and place the keck clip on the adapter to secure it to the tapered joint. Attach a hexane pre-rinsed and properly labeled 40mL vial to the vial adapter.

14.3.3 Remove the bottle cap from the first sample. For a sample in a 1L amber bottle: place a 2" × 2" piece of pre-cleaned aluminum foil over the mouth of the bottle. Gently screw the amber bottle adapter (33 × 430) over the aluminum foil onto the screw threads of the bottle. When done properly the aluminum foil will be taut and no rips will be evident. If a tear is detected, the adapter must be removed and a new piece of aluminum foil must be installed.

14.3.4 Invert the sample bottle and inspect for any leaks or rising bubbles from the seal of the bottle and the adapter. If no bubbles or leaks are detected then a good seal has been made and the sample bottle can be installed onto the bottle holder assembly. If a leak or bubbles are observed, the adapter may need to be tightened or a new piece of aluminum foil may need to be installed. Test again until a good seal is made.

14.3.5 With the bottle inverted, place the bottle into the bottle holder assembly making sure that the solvent rinse stem (needle) is inside the bottle adapter. Gently lower and then firmly push the sample bottle into the bottle holder assembly. A bubble should escape into the bottle. Turn the bottle clockwise until a large bubble floats up into the bottle. (**NOTE:** Do not turn more than three quarters of the way around). This breaks an opening in the aluminum foil and allows the sample to flow freely.

14.3.6 Once the sample bottle has been installed, the Envision Platform controller will need to be programmed with a sample method. To the left of the "**Purge Methods**" on the left pane of the Operations Screen there will be "**Current Method**" with another drop-down menu. Select **First Bottle** from the list. The **Load**, **Load All** options will blink green. Just like the purge cycles, the **Load All** option will load the method into all 8 extractors and the **Load** option will load the method into only the extractor displayed on the left pane. Choose the **Load All** option.

14.3.7 Again the options **Start** and **Start All** blink green on the Operations Screen. Choose to either start all units at once by clicking **Start All** or each unit individually by choosing an extractor so that it is displayed in the left pane and then clicking **Start**. Each unit can also be individually started by pressing the **Start** button on the unit. The "Purge Method" and the "Current Method" will remain programmed in unless they are changed.

14.3.8 The SPE-DEX® 4790 extractor will automatically pre-wet the solid phase disk, extract the sample, air dry the disk post extraction and extract the disk to recover the analytes of interest. See Attachment 23.2. Each extractor will flash a green light while running: one blink for pre-wet, two for sample extraction (sample drop), three for wash (we don't use

wash), four for air dry, five for rinse or disk extraction. The Envision Platform will also display the current status of each extractor unit.

14.3.9 Once the extraction process is completed the 40mL vial is removed from the vial adapter, capped with a pre-rinsed 40mL polyseal cap, and then the vial is placed in a rack. The sample is then ready to be stored in cold storage or taken through the required cleanup steps. The vial adapter is removed and placed in the hood to be cleaned.

14.3.10 Remove the sample bottle from the bottle holder assembly. Remove the cap adapter and place in the hood to be cleaned.

14.3.11 Remove the Bakerbond Speedisk™ and disk adapter from the disk holder platform. Throw the used Bakerbond Speedisk™ in the garbage, and place the disk adapter in the hood to be cleaned.

14.3.12 Fill the sample bottle(s) with tap water to the mark made before the extraction. Measure the volume of the water using a 2L or 4L graduated cylinder to the nearest 10mLs. Record the volume in LIMS.

14.3.13 Re-purge the units that were used as in section 14.2. Shut down the system in the reverse order as startup; starting with the computer browser, controller, nitrogen source, and pump. Break the seal on the water recovery jug.

14.3.14 Clean all used equipment in the hood according to SOP NE235.

14.4 Sample Extract Concentration and Cleanup Procedures

14.4.1 Extract Solvent Reduction

14.4.1.1 The sample extract will have two layers, the top layer will be composed of the Hexane/Acetone used to elute components from the solid phase disk and the bottom layer will be composed of residual water and Acetone from the extraction process. Carefully transfer the top layer of solvent to a hexane pre-rinsed and properly labeled 60mL vial using a hexane pre-rinsed disposable 10mL pipette.

14.4.1.2 Backwash the residual water/Acetone in the 40mL with three Pasteur pipette volumes of Hexane. Shake by hand in a chemical fume hood for 5 to 10 seconds. Allow to settle, forming two layers like the original sample. Transfer top Hexane layer carefully into the vessel holding the rest of the extract. Repeat this two more times, for a total of three rinses.

14.4.1.3 After all the rinses have been transferred, rinse the outside of the 10mL pipette with hexane into the sample vial. Rinse the sides of the vial, and bring the volume of all the extracts up to just below the base of the vial neck.

14.4.1.4 Dump any remaining residual water from the water/Acetone layer into a waste jar for evaporation in hood. This jar will be saved for reuse.

14.4.1.5 The LV Turbo Vap Evaporator systems are used to reduce the sample volume. They use a heated water bath and positive pressure Nitrogen flow with vortex action. The units maintain a slight equilibrium imbalance between the liquid and the

gaseous phases of the solvent extract, which allows for fractional reduction of the solvent without loss of higher boiling point analytes.

14.4.1.6 Turn on the LV Turbo Vap Evaporator and allow it to heat up to 40°C ± 2°C. Check the water level in the LV Turbo Vap and fill, if necessary, to the second stage from the top. On the top of the unit press the **START/PAUSE** key, a green light will light up to the right of it. Then press the Tube station keys corresponding to the rows needed to concentrate the samples.

14.4.1.7 As a precaution the TurboVap Evaporator system regulators should be checked to assure that there is no residual gas pressure within the system and that the gas pressure regulator is off before placing samples in the apparatus. Residual gas pressure may cause splashing and therefore cause cross contamination of samples. Make sure that the lid and regulator are closed, and that the cells or rows are turned on. Bleed any residual gas until the regulator gauge reads "0" psi.

14.4.1.8 Wipe down the inside of the LV Turbo Vap Evaporator with a Hexane wetted paper towel including the top lid and pins. Close the lid and turn on the regulator to dry the Turbo Vap LV. Turn off the gas regulator before loading samples. Place the 60mL vials containing the sample extract into the LV TurboVap and close the lid.

14.4.1.9 Slowly open the pressure regulator, by turning it towards yourself. Keep the gas pressure very low, until the solvent level is decreased, to avoid splashing. Increase the gas pressure as the sample reduces maintaining uniform flow throughout the volume reduction.

14.4.1.10 The process of solvent (Hexane) reduction takes approximately 20 – 30 minutes. DO NOT leave the unit unattended as extracts may be blown to dryness and loss of PCB as well as surrogate and matrix spike may occur. Immediately notify the extraction supervisor if an extract is blown to dryness and note the incident in the sample extraction logbook.

14.4.1.11 Concentrate the extract to approximately 10mLs. Remove the 60mL vial from the Evaporator unit, being careful not to drip.

14.4.1.12 Fill the sample vial back up to just below the base of the neck of the vial with Hexane.

14.4.1.18 Following the TurboVap LV Evaporator procedure described above, concentrate the extract to approximately 2.0mL. Remove the 60mL vial from the evaporator unit being careful not to drip.

14.4.1.19 Carefully transfer the extract into a pre-rinsed 5.0mL volumetric.

14.4.1.20 Rinse the 60mL vial with approximately 1.0mL of Hexane and add this to the 5.0mL volumetric. Repeat this process two more times, adding the rinses to the 5.0 volumetric, making sure to bring the volume to 5.0mL only.

14.4.1.21 Stopper with a pre-rinsed stopper and invert the volumetric several times to mix thoroughly.

14.4.1.22 Transfer the extract into a pre-rinsed and properly labeled 4 dram vial.

14.4.2 Sulfuric Acid Cleanup

NOTE: The concentrated Sulfuric acid treatment removes hydrocarbons and other organic compounds, which are co-extracted with the PCB residues.

14.4.2.1 Add one disposable Pasteur pipette volume full of solvent washed concentrated Sulfuric acid (NE174.doc) to each extract vial and shake by hand in a chemical fume hood for 30 seconds. Then centrifuge for at least one minute on setting #4. Transfer the Hexane layer (upper layer) to a correctly labeled and pre-rinsed 4 dram vial.

14.4.2.2 Repeat 14.4.2.2 if the sample extract appears to be heavily loaded (opaque) with colored material. Two or three acid washes may be required. **NOTE:** It is entirely possible that all colored material will not be removed from the extract.

14.4.3 Florisil Absorption (Slurry)

14.4.3.1 The florisil slurry removes co-extracted polar compounds, residual water and residual acid.

14.4.3.2 Add one spatula of florisil to each extract vial

Note: See supervisor for the appropriate florisil deactivation concentration to be used.

14.4.3.3 In a fume hood vigorously shake the vial for approximately 30 seconds by hand. Swirl to get any florisil off the walls of the vial, then allow to settle.

14.4.3.4 Transfer the hexane (upper) layer to a correctly labeled, pre-rinsed, 4 dram vial.

14.4.4 Mercury Cleanup

NOTE: Mercury is a highly toxic metal, all operations involving Mercury should be performed within a chemical fume hood. Prior to using Mercury, the extraction chemist should become acquainted with proper handling and emergency spill/cleanup procedures associated with this metal and must have reviewed the Material Safety Data Sheets (MSDS). Sulfur in the sample will be converted to Mercuric Sulfide and precipitate out of the sample extract. A black precipitate may be seen in the sample extracts containing elemental sulfur.

14.4.4.1 Using a disposable Pasteur pipette add 2-3 drops of solvent washed Mercury (NE175.doc) to the sample extracts and cap. Handshake for 30 seconds. If the Mercury changes color or breaks up into tiny balls and will not reform the original ball, change the Mercury. To change the Mercury transfer the extract into a new correctly labeled and Hexane pre-rinsed 4 dram vial and add new Mercury to it. Repeat previous step.

14.4.4.2 Place on wrist shaker for 30 minutes.

14.4.4.3 Remove the sample extracts from the wrist shaker.

14.5 Final Extract Preparation

14.5.1 Transfer the extract to a Hexane pre-rinsed and correctly labeled final 4-dram vial.

14.5.2 Complete all information in LIMS. Print the Extraction Log sheet, and the GC sheet. Submit samples and project folder to GC Analyst.

15.0 CALCULATIONS

15.1 Consult determinative methods (EPA Method 508, NE231.doc) for calculations.

16.0 METHOD PERFORMANCE

16.1 Consult determinative methods (EPA Method 508, NE231.doc) for Method Performance details.

17.0 POLLUTION PREVENTION

17.1 See NEA168.SOP for pollution prevention measures

18.0 DATA ASSESSMENT AND ACCEPTANCE CRITERIA FOR QC MEASURES

18.1 Consult determinative methods (EPA Method 508, NE231.doc) for Data Assessment and Acceptance Criteria for Quality Control Measures.

19.0 CORRECTIVE ACTION FOR OUT-OF-CONTROL DATA

19.1 Consult determinative methods (EPA Method 508, NE231.doc) for Corrective Action for Out-Of-Control Data

20.0 CONTIGENCIES FOR HANDLING OUT-OF-CONTROL DATA

20.1 Consult determinative methods (EPA Method 508, NE231.doc) for Contingencies for Handling Out-Of-Control or Unacceptable Data

21.0 WASTE MANAGEMENT

21.1 See NEA054.SOP, NEA083.SOP and NEA089.SOP

22.0 REFERENCES

22.1 U.S. EPA SW-846 “Test Methods for Evaluation Solid Waste; Volume 1B Laboratory Manual Physical/Chemical Methods,” Office of Solid Waste and Emergency Response, Third Edition, Final Update III, December 1996.

22.2 “Guide to Environmental Analytical Methods,” Fourth Edition, Genium Publishing Corporation, 1998.

22.3 U.S. EPA 40 CFR Part 136, “Guidelines Establishing Test Procedures for the Analysis of Pollutants,” July 1988.

22.4 Horizon Technology, "SPE-DEX® 4790 Series Extractor: Automated Solid Phase Extractor System User's Guide," July 2001.

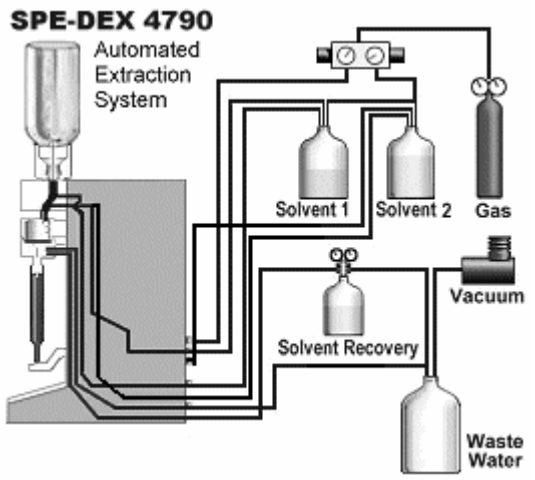
23.0 ATTACHMENTS

23.1 SPE Extractor Diagram

23.2 Extraction Method "First Bottle"

23.3 Method Flow Chart

23.1 SPE EXTRACTOR DIAGRAM*



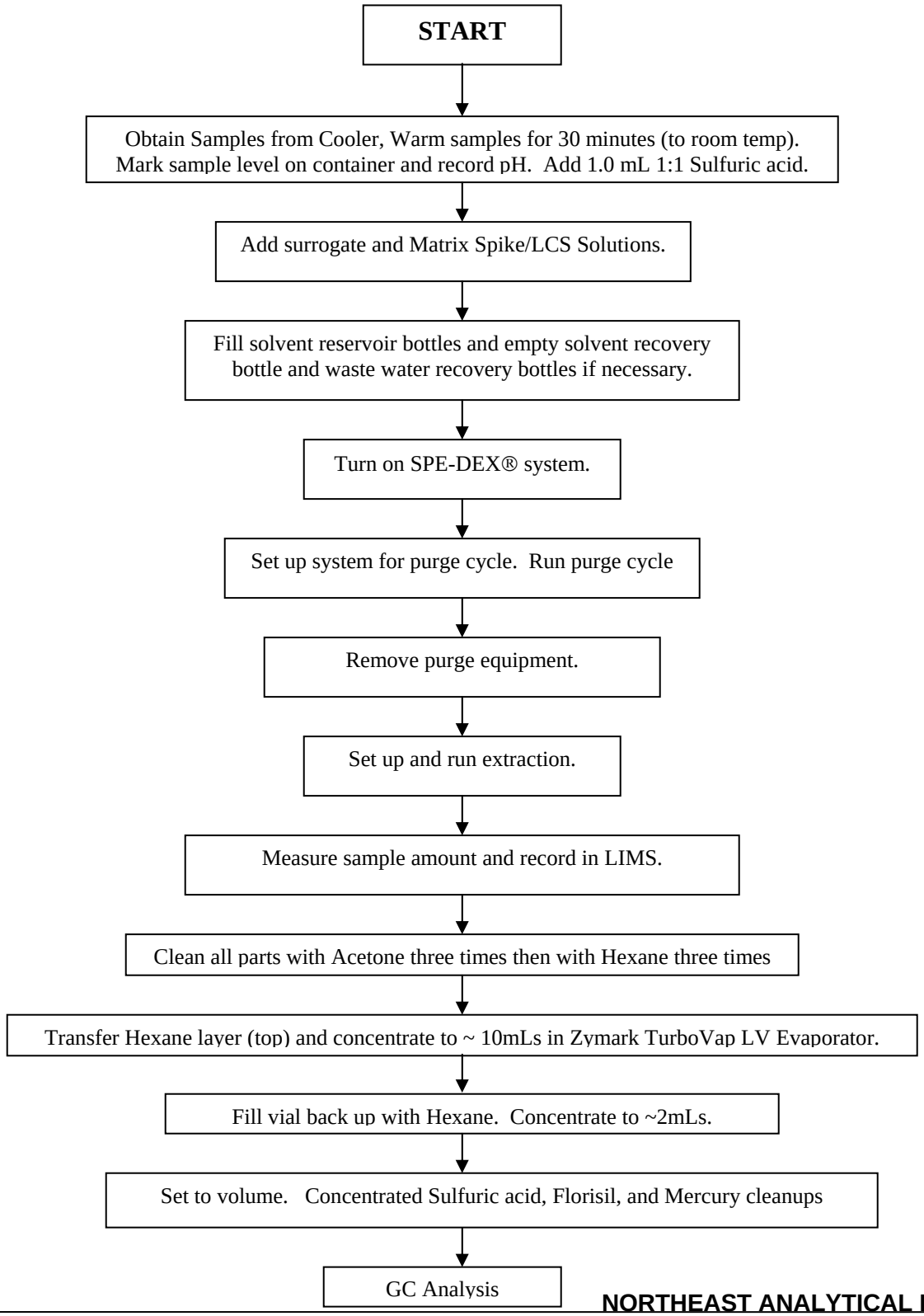
***NOTE: Limited diagram of the SPE-DEX® extractor set up. There are actually eight solvent bottles, five pre-wet solvents and three rinse solvents.**

23.2 Extraction Method for "First Bottle"

Extraction Method "First Bottle"

Step Number	Procedure
Step 1: Pre-wet Solvent: Dichloromethane	Soak Time: 1:00 minute Air Dry Time: 30 seconds
Step 2: Pre-wet Solvent: Hexane	Soak Time: 1:00 minute Air Dry Time: 30 seconds
Step 3: Pre-wet Solvent: Acetone	Soak Time: 1:00 minutes Air Dry Time: 30 seconds
Step 4: Pre-wet Solvent: Methanol	Soak Time: 1:30 minute Air Dry Time: 0:00 minutes
Step 5: Pre-wet Solvent: Reagent Water	Soak Time: 1:00 minute Air Dry Time: 0:00 minutes
Step 6: Pre-wet Solvent: Reagent Water	Soak Time: 1:00 minute Air Dry Time: 0:00 minutes
Step 7: Sample Extraction / Water Drop	Time depends on particulates and sample flow through the solid phase disk.
Step 8: Air Dry Disk	Air Dry Time: 5:00 minutes
Step 9: Rinse Solvent: Acetone	Soak Time: 1:30 minutes Air Dry Time: 1:00 minute
Step 10: Rinse Solvent Hexane	Soak Time: 1:30 minutes Air Dry Time: 1:00 minute
Step 11: Rinse Solvent Hexane	Soak Time: 1:30 minutes Air Dry Time: 1:00 minute
Step 12: Rinse Solvent Hexane	Soak Time: 1:30 minutes Air Dry Time: 1:00 minute

23.3 Method Flow Chart



APPENDIX 26
SOP FOR THE EXTRACTION AND CLEANUP OF LARGE VOLUME AQUEOUS SAMPLES FOR PCBS USING SW-846 METHOD 3535; SFE (NE208_03)

STANDARD OPERATING PROCEDURE

NORTHEAST ANALYTICAL, INC.

NE208_03.DOC

REVISION NUMBER: 03

STANDARD OPERATING PROCEDURE FOR THE EXTRACTION AND CLEANUP OF LARGE VOLUME AQUEOUS SAMPLES FOR POLYCHLORINATED BIPHENYLS (PCBs) USING US-EPA SW-846 METHOD 3535, SOLID PHASE EXTRACTION

April 22, 2009

COPY #_____

NORTHEAST ANALYTICAL, INC
2190 TECHNOLOGY DRIVE
SCHENECTADY, NY 12308

(518) 346-4592

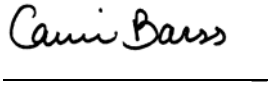
STANDARD OPERATIONG PROCEDURE

LABORATORY PROCEDURE NE208_03.DOC

REVISION 3 (04/22/2009)

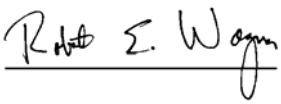
Revision Author: Carrie Barss

Reviewed by:



Carrie Barss
Extraction Supervisor

Reviewed by:



Robert E. Wagner
Laboratory Director

Approved by:

Christina L. Braidwood
Quality Assurance Officer

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1.0 IDENTIFICATION OF TEST METHOD

1.1 This is the Standard Operating Procedure (SOP) for the Extraction and Cleanup of large volume (8-Liter) aqueous samples by Solid Phase Extraction (SPE) for analysis of Polychlorinated Biphenyls (PCBs) Using EPA SW-846 Method 3535 - Solid Phase Extraction.

2.0 APPLICABLE MATRIX AND MATRICES

2.1 This method is applicable to surface water, groundwater, wastewater and other aqueous samples.

3.0 DETECTION LIMIT

3.1 Please consult determinative method for analysis of sample extracts derived by this extraction method and determination of detection limits.

4.0 SCOPE AND APPLICATION

4.1 The following procedure is utilized by Northeast Analytical, Inc. for the extraction and subsequent cleanup of PCBs from large volume aqueous samples using the solid phase extraction method. This method was developed to utilize an automated extraction system, which is the SPE-DEX® 4790 extractor from Horizon Technologies. The extraction disk used is a 50mm Bakerbond Speedisk™ styrene divinyl benzene filter.

5.0 SUMMARY OF TEST METHOD

5.1 Prepare Sample: Warm the sample to room temperature, check pH, acidify, spike and surrogate, foil and cap bottle.

5.2 Extractor Preparation: Turn on equipment, check gauges, check solvent and recovery bottles, purge.

5.3 Extract the Sample.

5.4 Concentrate, Florisil cleanup with backwashes, re-concentrate, set to volume, and clean-up with acid, and mercury.

5.5 Provide sample to GC department for analysis.

6.0 DEFINITIONS

6.1 **Surrogate Standard Solution:** The chemical composition and chromatography of surrogates are similar to the analytes of interest. Usually not found in environmental samples. These compounds are spiked into all samples, blanks, and matrix spike samples prior to analysis. Percent recoveries are calculated for each surrogate.

6.2 **Laboratory Method Blank:** A laboratory derived sample consisting of reagent water or other blank matrix that consists of all reagents, internal standards, and surrogate

standards that is carried through the entire analytical procedure. The laboratory method blank is used to define the level of laboratory analyte background or other interferences that exist in the laboratory environment, the reagents, or apparatus.

6.3 **Laboratory Control Spike (LCS):** Also known as the Quality Control (QC) Check Standard or Quality Control (QC) Check Sample. The LCS consists of an aliquot of reagent water or other blank matrix to which known quantities of the method analytes are added. The LCS is extracted and analyzed exactly like a field sample, and its purpose is to determine whether the analysis is in control and whether the laboratory is capable of making accurate and precise measurements.

6.4 **Matrix Spike (MS):** An aliquot of a field sample that is fortified with known quantities of the method analytes and subject to the entire analytical procedure. Its purpose is to assess the appropriateness of the method for the matrix by measuring the recovery.

6.5 **Sample Matrix Spike Duplicate (MSD):** An exact copy of the Matrix Spike. This is an aliquot of a field sample which is fortified with known quantities of the method analytes and is subject to the entire analytical procedure. Its purpose is to assess the appropriateness of the method for the matrix by measuring the recovery.

6.6 **DI Water** (De-ionized Water): Water free from analytes that may interfere with the analytical test compounds.

7.0 INTERFERENCES

7.1 Method interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing equipment (such as the SPE-DEX 4790 extractor) that lead to discrete artifacts and/or elevated baselines in gas chromatograms. All of these materials and equipment must be routinely verified to be free from interferences by running laboratory method blanks.

7.2 All equipment must be kept scrupulously clean. Clean all equipment as soon as possible after use, and store in jars away from environmental contaminants.

7.3 The use of high purity solvent and reagents will minimize interference problems. Purification of reagents by washing with solvent will also help to reduce interference problems.

7.4 Laboratory contamination can occur by introduction of plasticizers (phthalate esters) into the samples through the use of flexible tubing, gloves, pipette bulbs, etc. Samples and extracts should not be exposed to plastic materials. Phthalate esters exhibit a response on electron capture detectors, usually as late eluting peaks and can interfere in PCB quantification.

7.5 The sample matrix itself is also a potential source for method analyte interference. The clean-up procedures provided in this SOP can be used to overcome many of these interferences.

8.0 SAFETY

8.1 The extraction chemist should have received in-house safety training and should know the location of first aid equipment and the emergency spill/cleanup equipment before handling any apparatus or equipment. Safety glasses and gloves must be worn when handling glassware and samples. Polychlorinated biphenyls have been classified as a known or suspected carcinogen. The extraction chemist must review the Material Safety Data Sheets (MSDS) for PCBs and all reagents used in the procedure before beginning the extractions. All equipment and solvents should be handled within a laboratory fume hood.

9.0 EQUIPMENT AND SUPPLIES

9.1 Automated Solid Phase Extractor; Horizon# 4790-08 Consisting of:

a) Envision Platform
b) SPE-DEX® 4790 Extractor
c) 10" Solvent Vapor Exhaust Hose (2" Diameter)
d) Water and Solvent Waste Vacuum Lines
e) Vacuum Supply Line Assembly
f) 8' Telco Communication Cable
g) Solvent Delivery Line Kit
h) Pressure Regulator Bracket Assembly
i) Solvent Delivery Bottle Plug Kit
j) Solvent Recovery Manifold Assembly
k) Water Recovery Manifold Assembly
l) Waste Solvent Recovery Bottle
m) Waste Water Recovery Bottle
n) Solvent Delivery Teflon Manifold Kit
o) 2.5 Liter Safety Coated Solvent Bottles
p) Vacuum Source – capable of 20 to 25" Hg
q) Dry Trap for the Vacuum Source
r) Dry Nitrogen Gas Supply – capable of minimum 60 PSI to maximum 80 PSI

9.2 Glass Sample Containers

4 liter amber glass bottle

The 4-liter bottles are not available pre-cleaned and certified. The following procedure is used to clean bottles before use:

a) Rinse bottle (cap and shake) with 50mLs of hexane. Repeat a total of 3 times.
b) Rinse bottle (cap and shake) with 50mLs of acetone. Repeat a total of 3 times.
c) Allow caps to dry in chemical fume hood.
d) Rinse bottle with tap water. Repeat a total of 3 times.
e) Rinse bottle with RO water. Repeat a total of 3 times.
f) Place bottle in drying oven at 120°C until dry.

9.3 Bakerbond Speedisk™ DVB – Styrene Divinyl Benzene 50mm disk for sample extraction P/N 8059-06 or equivalent

9.4 Disk Adapter

9.5 Vials

40mL vials, with polyseal cap, for collection vessel
60mL vials, with polyseal cap, for sample extract
4 dram vials, with polyseal cap, for sample extract

9.6 Collection Vessel Adapter – 19/22 Taper

9.7 Bottle Adapters

33 × 400 adapter for 1L clear glass bottle or 38 x 400 adapter
38 × 400 Teflon adapter for 4L amber glass bottle

9.8 Aluminum Foil Squares – purchased pre-cleaned

9.9 pH indicator Strips – EM Science P/N 9590 or equivalent

9.10 Pipettes

1 mL x 1/100, Kimble#72120-1100
5 mL x 1/10, Kimble# 72120-5110
10 mL x 1/10, Kimble# 72120-10110
Pasteur Glass Pasteur Pipettes: 9'', Krackeler-Brand# 67-450-900

9.11 Syringes

500µL Syringe, gas-tight, Hamilton #81217
1000µL Syringe, gas-tight, Hamilton #81317
250µL Syringe, gas-tight, Hamilton #81100

9.12 Vial Rack – plastic rack used to hold vials during processing of extracts. Scienceware

9.13 Beakers - assorted Pyrex 250mL, 600mL and 1000mL, used for liquid containment and pipette storage.

9.14 2 Liter Graduated Cylinder – Scienceware
4 Liter Graduated Cylinder - Nalgene

9.15 TurboVap LV Evaporator – Caliper

9.16 Centrifuge; International Equipment Co., Model CL (or equivalent)

9.17 Wrist Shaker; Burrell wrist action shaker, Model 75 and 88 (or equivalent)

9.18 Flask; Chemglass, 125mL Erlenmeyer filter flask for purge recovery

9.19 Keck Clip

9.20 Speedisk ™ Reservoir – 185 mL

10.0 REAGENTS AND STANDARDS

10.1 **1:1 Sulfuric Acid** - (H_2SO_4), Mallinckrodt #2468, UN1830
Preparation: To a beaker containing 500mL cold DI-water, add 500mL concentrated H_2SO_4 slowly and under constant stirring. Allow the mixture to cool after preparation. Then, transfer to a pre-cleaned 1L bottle for storage.

10.2 **DI Water** – (Reagent Water) 18 Megaohm water obtained form the laboratory's water purification system. Used for solid phase disk preparation, laboratory method blanks, laboratory control spikes, MDL studies, and Precision and Accuracy studies.

10.3 **Methanol** – Pesticide residue quality. EM Science OmniSolv. P/N MX0488P-1 or equivalent

10.4 **Acetone**- High purity solvent; (Burdick\Jackson) UN1090

10.5 **Hexane**- High purity solvent; (Burdick\Jackson) #UN1208

10.6 **Florisil -** J.T. Baker #M368-08, 10% deactivated, solvent washed and deactivated as per NE094.doc.

10.7 **Concentrated Sulfuric Acid-** Mallinckrodt #2468, #UN1830, Solvent washed as per NE174.doc

10.8 **Mercury**- Triple distilled, Mercury Waste Solutions Inc., Solvent washed as per NE175.doc (or equivalent)

10.9 **Sodium Hydroxide**- JT Baker, #5671-03

10.10 **Standard Solutions** – The following standards are used during extraction and preparation of sample extracts:

10.10.1 **Surrogate Standard (2,2',3,3',4,4',5,6,6'-Nonachlorobiphenyl) at 0.02ug/mL in Acetone** - To every water sample and QC sample, 0.5mL of Surrogate Standard is added before extraction is initiated. The Surrogate Standard must be replaced after six months.

10.10.2 **Aroclor 1242 Spiking Standard at 0.05ppm in Acetone -** To every laboratory control spike, matrix spike, and matrix spike duplicate, add 1.0mL of Aroclor 1242 spiking standard before extraction is initiated. The A1242 Spiking Standard must be replaced after six months.

11.0 SAMPLE COLLECTION, PRESERVATION, SHIPMENT, AND STORAGE

11.1 The samples should be collected in 4 liter amber glass bottles with a Teflon lined cap. The bottles should be pre-cleaned to EPA specification protocol A - recommended for extractable organic, semivolatile and pesticide analysis.

11.2 All samples must be placed on ice or refrigerated at 4°C ± 2°C from the time they are collected until delivery to the lab.

11.3 The samples must be protected from light and refrigerated at 4°C (±2°C) from time of receipt until they are removed from storage for extraction. Typically the entire water sample grab will be consumed at time of extraction and no sample is left for log-term storage.

11.4 The sample extraction hold time for this method is seven days from the date the samples were collected.

11.5 Sample extracts must be protected from light and stored refrigerated at 4°C (±2°C). After analysis is complete, sample extracts will be discarded after 60 days or can be archived in a freezer at less than -20°C for longer periods of time depending on the program requirements.

12.0 QUALITY CONTROL

12.1 The extraction chemist should have completed an acceptable demonstration of precision and accuracy before performing the method without supervision. The addition of spiking material to a sample or blank must be witnessed by another extraction chemist and noted in Laboratory Information System (LIMS). All surrogates and matrix spikes must meet acceptable quality control limits.

12.2 A method blank sample must be prepared per each extraction batch or per 20 site samples, whichever is more frequent. If the laboratory blank is positive for PCB above the reporting limit (based on Total PCB concentration), the contamination must be traced down and eliminated before samples can be processed and analyzed. If non-PCB contamination occurs that interferes with PCB quantification, it too must be traced down and eliminated before proceeding with sample analysis.

12.3 A lab control spike (LCS) must be prepared per extraction batch or per 20 site samples, whichever is more frequent. This control spike must achieve a percent recovery of 60% to 140% based on Total PCB concentration. If the LCS recovery is not within limits, the cause must be identified and corrected. The samples associated with the Laboratory Control Spike that failed must be re-extracted and re-analyzed. If no sample is available, the data must be flagged to indicate a low or high LCS recovery.

12.4 A matrix spike (MS) / matrix spike duplicate (MSD), should be prepared for every 20 site samples or as per client specified quality assurance project plan (QAPP). There must be sufficient sample for analysis of MS/MSD samples. Matrix spike recovery information is used to assess the long-term precision and accuracy of the method for each encountered matrix. Matrix spike /matrix spike duplicate results are not used alone to qualify an extraction batch. Generally, percent recovery for MS/MSD samples should be greater than or equal to 60% and less than or equal to 140% based on the total PCB concentration. If the percent recovery is outside the acceptance limits, all calculations should be checked and the data should be narrated to describe possible matrix interference. Spike default for LCS, MS, and MSD is 1.0mL A1242 @ 0.05ppm in Acetone for an 8L sample. Client and/or project specifications may dictate alternate amount or Aroclor. The relative percent difference between the matrix spike and matrix spike duplicate sample should be less than or equal to 30 %.

12.5 Duplicate analysis of the same sample is performed to assess method precision. A duplicate can also be performed as a blind duplicate, so that identification with original sample is withheld. The analysis of a duplicate sample precludes that PCBs are to be found at appreciable levels in samples. If this is not known, the analysis of the matrix spike/matrix spike duplicate will provide more consistent quality control information. The relative percent difference of the two measurements on the sample is calculated on a total PCB concentration. The relative percent difference must be less than or equal to 30%.

12.6 PCB Surrogates are added to each sample prior to extraction to measure extraction/cleanup efficiency. Percent recovery should be 60% - 140%. Default surrogate is: 0.5mL NCBP (2,2',3,3',4,4',5,6,6'-Nonachlorobiphenyl) @ 0.02ppm in Acetone for an 8L sample. Client and/or project specifications may dictate alternate amount.

13.0 CALIBRATION AND STANDARDIZATION

13.1 Please see determinative method for Calibration and Standardization. Refer to method NE207 for operating conditions to analyze PCBs by congener-specific methodology.

14.0 PROCEDURE

Note: When rinsing or pre-rinsing is referred to in this SOP, it is performed using a pipette and beaker.

14.1 Sample Preparation

14.1.1 Throughout the entire process it should be noted that if the extraction chemist encounters any problems or difficulties with any samples or steps involved, all work should **STOP!!!** Any problems should be brought to the attention of the supervisor and documented in LIMS.

14.1.2 Remove the samples to be extracted from cold storage and allow them to warm up to room temperature. This can be done first while the extraction equipment is prepared to extract samples.

14.1.3 Before any steps are taken, the extraction chemist should first review the sample job folder, LIMS, and check the sample labels versus the original chain of custody. Any discrepancies should be brought to the attention of the supervisor and the sample login custodian.

14.1.4 Using 4L amber bottles as appropriate to the samples, prepare a method blank and laboratory control spike sample using reagent water equal to the sample volume.

14.1.5 Mark the level of the sample on the outside of the sample container with a paint pen. Determine the pH by removing a small amount of sample with a Pasteur pipette (approximately 0.1mL) and wet a pH indicator strip. Record the pH in LIMS.

14.1.6 Add 1.0mL of 1:1 sulfuric acid per liter of water to every sample and QC sample using a disposable pipette (4mL of 1:1 sulfuric acid per 4L bottle). Cap and invert the sample

container several times to mix. Check the pH (Refer to Section 14.1.5) to determine the sample was adjusted to a pH of 2 or less. If the pH was not adjusted sufficiently, add 0.5mL of 1:1 sulfuric acid and test again. Continue to add 1:1 sulfuric acid in 0.5mL aliquots until the pH is 2 or less.

14.1.7 Using a gas tight syringe, add the surrogate standard solution to every sample and QC sample.

14.1.8 To the laboratory control sample, matrix spike, and matrix spike duplicate samples, add the matrix spike standard solution using a gas tight syringe.

14.1.9 Cap and invert each sample and QC sample several times to mix.

14.2 Extractor Preparation

14.2.1 Check solvent reservoir bottles, solvent recovery bottle and waste water recovery bottle. Fill solvent reservoirs if necessary. When filling the solvent reservoirs, care should be taken not to spill or drip solvent on the outside of the bottles as they are rubber coated, and some solvents may dissolve the rubber. Solvent reservoirs should never be filled past their rubber coating. The DI water reservoir should be emptied, rinsed with RO water, and re-filled weekly.

14.2.2 Empty the solvent recovery bottle into an approved waste container for proper disposal according to the Chemical Hygiene Plan.

14.2.3 If necessary, neutralize and empty the wastewater recovery container. Add sodium hydroxide until the pH reads between 5 and 9. Once neutral, the waste water may be disposed of down the drain.

14.2.4 Turn the vacuum pump on and adjust the main vacuum between 20” Hg to 26” Hg. Determine that the water recovery manifold assemblies on the waste water containers are forming a good seal.

14.2.5 Turn on the pressurized gas source and adjust gas pressure between 60 and 80 PSI.

14.2.6 Turn on the Envision Platform controller and Computer.

14.2.7 Adjust the non-venting vacuum regulator attached to the solvent recovery manifold assembly on the solvent recovery bottle to a vacuum of 15” Hg or less. **NOTE:** DO NOT adjust the regulator higher than 15” Hg. Higher vacuum levels could cause an SPE disk to go dry during the methanol and reagent water pre-wet steps.

14.2.8 On the pressure bracket assembly, adjust the left regulator labeled SPE extractor pressure to between 45 and 50 PSI. Adjust the right regulator labeled solvent bottle pressure to between 15 and 20 PSI.

14.2.9 Attach the disk adapter to a Bakerbond Speedisk™ designated for purges. Then place this set up on the disk holder platform.

14.2.10 Attach a 125mL flask designated for purges to the tapered joint on the bottom of the platform. Secure with a keck clip.

14.2.11 Invert a purge bottle and place into bottle holder of the extractor unit. (Note: A purge bottle is prepared by attaching a cap adapter to an empty 1L glass bottle. Since purge bottles can be reused, a set should be prepared and stored for reuse.)

14.2.12 Open the browser on the computer. Enter the IP address corresponding to the Envision Platform controller. The Operations Screen should load. The Operations screen is used to control and monitor the status of each Extractor. The screen is divided into sections within the right and left pane. The right pane displays the status of all connected Extractors; the left pane is used to control and monitor one Extractor. The extractors now must be programmed for a purge.

14.2.13 On the left pane of the Operations Screen there will be "**Purge Methods**" with a drop-down menu beneath it. From the drop-down list select **NEA Purge**. Two options will begin to blink green: **Load** and **Load All**. The **Load All** option will load the method into all 8 extractors. The **Load** option will load the method into only the extractor displayed on the left pane. Since all 8 units will need to be purged prior to use, select the **Load All** option.

14.2.14 **Purge** and **Purge All** will begin to blink green. Choose **Purge All** to purge all 8 units at once, or choose **Purge** to purge only the unit displayed in the left pane. This will initiate the purge cycle sequence. The purge may also be started for each individual unit by pressing the **Purge** button on each unit. The purge cycle will clean the extractor unit by dispensing the pre-wet solvents and directing them to the solvent recovery bottle. Next the rinse solvents will be sprayed into the empty sample bottle and directed into the collection vessel. (**NOTE:** Always use an empty bottle when running a purge cycle.)

14.2.15 During the purge cycle, carefully observe the operation of the SPE-DEX® 4790 extractor unit. Make sure that it is functioning properly and that the check valve located in the disk holder assembly is operating correctly and solvents are being delivered to the correct locations.

14.2.16 Once the purge cycle is completed, the SPE-DEX® 4790 extractor unit is ready to process samples. (**NOTE:** A purge cycle needs to be run before starting each day, between sample extractions and before shutting down at the end of the day.)

14.2.17 Detach the flask, and empty it into a properly labeled waste container.

14.2.18 Remove the purge bottle from the bottle holder.

14.2.19 Remove the Bakerbond Speedisk™ from the disk holder platform. Save the disk as it can be reused for future purge cycles.

14.3 Sample Extraction

14.3.1 Install a new Bakerbond Speedisk™ DVB onto the disk holder platform with the disk adapter. Securely place a Speedisk™ 185mL reservoir to the top of the disk.

14.3.2 Attach a vial adapter to the tapered joint on the bottom of the disk holder platform and place the keck clip on the adapter to secure it to the tapered joint. Attach a hexane pre-rinsed and properly labeled 40mL vial to the vial adapter.

14.3.3 Remove the bottle cap from the first sample. For a sample in a 4L amber bottle two adapters will be needed. Place a 38 × 400 Teflon adapter (4L bottle adapter) onto the threads of the bottle and tighten securely. Place a 2" × 2" piece of pre-cleaned aluminum foil over the adapter. Gently screw a 33 × 400 adapter (clear bottle adapter) over the aluminum foil onto the screw threads of the first adapter. When done properly the aluminum foil will be taut and no rips will be evident. If a tear is detected, the adapter must be removed and a new piece of aluminum foil must be installed.

14.3.4 Invert the sample bottle and inspect for any leaks or rising bubbles from the seal of the bottle and the adapters. If no bubbles or leaks are detected then a good seal has been made and the sample bottle can be installed onto the bottle holder assembly. If a leak or bubbles are observed, one or both of the adapters may need to be tightened or a new piece of aluminum foil may need to be installed. Test again until a good seal is made.

14.3.5 With the bottle inverted, place the bottle into the bottle holder assembly making sure that the solvent rinse stem (needle) is inside the bottle adapter. Gently lower and then firmly push the sample bottle into the bottle holder assembly. A bubble should escape into the bottle. Turn the bottle clockwise until a large bubble floats up into the bottle. (**NOTE:** Do not turn more than three quarters of the way around). This breaks an opening in the aluminum foil and allows the sample to flow freely.

14.3.6 Once the sample bottle has been installed, the Envision Platform controller will need to be programmed with a sample method. To the left of the "**Purge Methods**" on the left pane of the Operations Screen there will be "**Current Method**" with another drop-down menu. Select **First Bottle** from the list. The **Load**, **Load All** options will blink green. Just like the purge cycles, the **Load All** option will load the method into all 8 extractors and the **Load** option will load the method into only the extractor displayed on the left pane. Choose the **Load All** option.

14.3.7 Again the options **Start** and **Start All** blink green on the Operations Screen. Choose to either start all units at once by clicking **Start All** or each unit individually by choosing an extractor so that it is displayed in the left pane and then clicking **Start**. Each unit can also be individually started by pressing the **Start** button on the unit. The "Purge Method" and the "Current Method" will remain programmed in unless they are changed.

14.3.8 The SPE-DEX® 4790 extractor will automatically pre-wet the solid phase disk, extract the sample, air dry the disk post extraction and extract the disk to recover the analytes of interest. See Attachment 23.2. Each extractor will flash a green light while running: one blink for pre-wet, two for sample extraction (sample drop), three for wash (we don't use wash), four for air dry, five for rinse or disk extraction. The Envision Platform will also display the current status of each extractor unit.

14.3.9 A large volume sample will come in two bottles. If this is the case, the extraction of the first bottle must be stopped before the air dry step begins. Press **Fault/Abort** on the unit to pause the extraction of the fist bottle **before the disk goes dry**.

14.3.10 Remove the first bottle from the extractor bottle holder assembly. Using the same bottle adapters from the first bottle, prepare and load the second bottle as in sections 14.3.3 – 14.3.5. Cap and set aside the first bottle for use later.

14.3.11 The extractor will need to be re-programmed for the second bottle so that the disk prep steps are skipped. Select **Second Bottle** from the "**Current Method**" list. The **Load**, **Load All** options will blink green. Again, the **Load All** option will load the method into all 8 extractors and the **Load** option will load the method into only the extractor displayed on the left pane.

14.3.12 Once the method has been loaded the extractor can be started by pressing the **Start** or **Start All** options that will be blinking green on the Envision Platform, or by pressing **Start** on the unit.

14.3.13 The "second bottle" method will start at the second step: sample drop (two blinks) and continue through the extraction. The sensors must be dry for the unit to start. If the sensors are in contact with the water remaining in the disk, hold the platform down while starting the unit, then immediately release the platform as the sample drops.

14.3.14 Once the extraction process is completed the 40mL vial is removed from the vial adapter, capped with a pre-rinsed 40mL polyseal cap, and placed in a rack.

14.3.15 During the rinse/disk extraction step (step five), the sample bottle is rinsed with solvent. Since the first bottle was stopped before this step, it must be rinsed manually. Rinse the sample bottle using six Pasteur pipette volumes of Hexane, and pour the hexane rinse into its corresponding 40mL vial.

14.3.16 The sample is then ready to be stored in cold storage or taken through the required cleanup steps. The vial adapter is removed and placed in the hood to be cleaned.

14.3.17 Remove the sample bottle from the bottle holder assembly. Remove the cap adapter and place in the hood to be cleaned.

14.3.18 Remove the Bakerbond Speedisk™ and disk adapter from the disk holder platform. Throw the used Bakerbond Speedisk™ in the garbage, and place the reservoir and disk adapter in the hood to be cleaned.

14.3.19 Fill the sample bottles with tap water to the mark made before the extraction. Measure the volume of the water using a 2L or 4L graduated cylinder to the nearest 10mLs. Record the volume in LIMS.

14.3.20 Re-purge the units that were used as in section 14.2. Shut down the system in the reverse order as startup; starting with the computer browser, controller, nitrogen source, and pump. Break the seal on the water recovery jug.

14.3.21 Clean all used equipment in the hood according to SOP NE235.

14.4 Sample Extract Concentration and Cleanup Procedures

14.4.1 Extract Solvent Reduction

14.4.1.1 The sample extract will have two layers, the top layer will be composed of the Hexane/Acetone used to elute components from the solid phase disk and the bottom layer will be composed of residual water and Acetone from the extraction process. Carefully transfer the top layer of solvent to a hexane pre-rinsed and properly labeled 60mL vial using a hexane pre-rinsed disposable 10mL pipette.

14.4.1.2 Backwash the residual water/Acetone in the 40mL with three Pasteur pipette volumes of Hexane. Shake by hand in a chemical fume hood for 5 to 10 seconds. Allow to settle, forming two layers like the original sample. Transfer top Hexane layer carefully into the vessel holding the rest of the extract. Repeat this two more times, for a total of three rinses.

14.4.1.3 After all the rinses have been transferred, rinse the outside of the 10mL pipette with hexane into the sample vial. Rinse the sides of the vial, and bring the volume of all the extracts up to just below the base of the vial neck.

14.4.1.4 Dump any remaining residual water from the water/Acetone layer into a waste jar for evaporation in hood. This jar will be saved for reuse.

14.4.1.5 The LV Turbo Vap Evaporator systems are used to reduce the sample volume. They use a heated water bath and positive pressure Nitrogen flow with vortex action. The units maintain a slight equilibrium imbalance between the liquid and the gaseous phases of the solvent extract, which allows for fractional reduction of the solvent without loss of higher boiling point analytes.

14.4.1.6 Turn on the LV Turbo Vap Evaporator and allow it to heat up to 40°C ± 2°C. Check the water level in the LV Turbo Vap and fill, if necessary, to the second stage from the top. On the top of the unit press the **START/PAUSE** key, a green light will light up to the right of it. Then press the Tube station keys corresponding to the rows needed to concentrate the samples.

14.4.1.7 As a precaution the TurboVap Evaporator system regulators should be checked to assure that there is no residual gas pressure within the system and that the gas pressure regulator is off before placing samples in the apparatus. Residual gas pressure may cause splashing and therefore cause cross contamination of samples. Make sure that the lid and regulator are closed, and that the cells or rows are turned on. Bleed any residual gas until the regulator gauge reads "0" psi.

14.4.1.8 Wipe down the inside of the LV Turbo Vap Evaporator with a Hexane wetted paper towel including the top lid and pins. Close the lid and turn on the regulator to dry the Turbo Vap LV. Turn off the gas regulator before loading samples. Place the 60mL vials containing the sample extract into the LV TurboVap and close the lid.

14.4.1.9 Slowly open the pressure regulator, by turning it towards yourself. Keep the gas pressure very low, until the solvent level is decreased, to avoid splashing. Increase the gas pressure as the sample reduces maintaining uniform flow throughout the volume reduction.

14.4.1.10 The process of solvent (Hexane) reduction takes approximately 20 – 30 minutes. DO NOT leave the unit unattended as extracts may be blown to dryness and loss of

PCB as well as surrogate and matrix spike may occur. Immediately notify the extraction supervisor if an extract is blown to dryness and note the incident in the sample extraction logbook.

14.4.1.11 Concentrate the extract to approximately 5mLs. Remove the 60mL vial from the Evaporator unit, being careful not to drip.

14.4.2 Florisil Absorption (Slurry)

14.4.2.1 The Florisil slurry removes co-extracted polar compounds, residual water and residual acid.

14.4.2.2 Add one spatula of Florisil to a pre-rinsed and properly labeled 4 dram vial.

Note: See supervisor for the appropriate Florisil deactivation concentration to be used.

14.4.2.3 Transfer the 5mLs of sample from the 60mL vial to the 4 dram vial containing Florisil.

14.4.2.4 Rinse the 60mL vial with one Pasteur pipette volume of Hexane (approximately 2.0mL) and add this rinse to the same 4 dram vial. Set aside the 60mL vial with the Pasteur pipette used to transfer. They will be used to transfer the extract back.

14.4.2.5 Cap and shake the 4 dram vial by hand for 30 seconds in a chemical fume hood. Allow the Florisil to settle. Swirl the extract if necessary to get the Florisil off the sides of the 4 dram vial.

14.4.2.6 Transfer the extract back into the 60mL VOA vial, using the Pasteur pipette previously used.

14.4.2.7 Backwash the Florisil. Add three pipette volumes (approximately 10mL) of Hexane to the Florisil in the 4 dram vial. Cap and shake the vial in a chemical fume hood for 5 to 10 seconds. Swirl the extract if necessary to get the Florisil off the sides of the 4 dram vial.

14.4.2.8 Transfer this rinse in to the 60mL VOA vial with the rest of the extract. Repeat this backwash procedure twice more for a total of three rinses.

14.4.2.9 After the final transfer, rinse the outside of the Pasteur pipette into the 60mL vial.

14.4.2.10 Following the TurboVap LV Evaporator procedure described above, concentrate the extract to approximately 2.5mL. Remove the 60mL vial from the evaporator unit being careful not to drip.

14.4.3 Set Volume

14.4.3.1 Carefully transfer the extract into a pre-rinsed 5.0mL volumetric.

14.4.3.2 Rinse the 60mL vial with approximately 1.0mL of Hexane and add this to the 5.0mL volumetric. Repeat this process two more times, adding the rinses to the 5.0 volumetric, making sure to bring the volume to 5.0mL only.

14.4.3.3 Stopper with a pre-rinsed stopper and invert the volumetric several times to mix thoroughly.

14.4.3.4 Transfer the extract into a pre-rinsed and properly labeled 4 dram vial.

14.4.4 Sulfuric Acid Cleanup

NOTE: The concentrated Sulfuric acid treatment removes hydrocarbons and other organic compounds, which are co-extracted with the PCB residues.

14.4.4.1 Add one disposable Pasteur pipette volume full of solvent washed concentrated Sulfuric acid (NE174.doc) to each extract vial and shake by hand in a chemical fume hood for 30 seconds.

14.4.4.2 Centrifuge sample vials for at least one minute on setting #4. Transfer the Hexane layer (upper layer) to a correctly labeled and pre-rinsed 4 dram vial.

14.4.4.3 Repeat, beginning at section 14.4.2.1 if the sample extract appears to be heavily loaded (opaque) with colored material. Two or three acid washes may be required. **NOTE:** It is entirely possible that all colored material will not be removed from the extract.

14.4.5 Mercury Cleanup

NOTE: Mercury is a highly toxic metal. All operations involving Mercury should be performed within a chemical fume hood. Prior to using Mercury, the extraction chemist should become acquainted with proper handling and emergency spill/cleanup procedures associated with this metal and must have reviewed the Material Safety Data Sheets (MSDS). Sulfur in the sample will be converted to Mercuric Sulfide and precipitate out of the sample extract. A black precipitate may be seen in the sample extracts containing elemental sulfur.

14.4.5.1 Using a disposable Pasteur pipette add 2-3 drops of solvent washed Mercury (NE175.doc) to the sample extracts and cap.

14.4.5.2 Handshake for 30 seconds. If the Mercury changes color or breaks up into tiny balls and will not reform the original ball, change the Mercury. To change the Mercury transfer the extract into a new correctly labeled and Hexane pre-rinsed 4 dram vial and add new Mercury to it. Repeat previous step.

14.4.5.3 Place on wrist shaker for 30 minutes.

14.4.5.4 Remove the sample extracts from the wrist shaker.

14.5 Final Extract Preparation

14.5.1 Transfer the extract to a Hexane pre-rinsed and correctly labeled final 4-dram vial.

14.5.2 Complete all information in LIMS. Print the Extraction Log sheet, and the GC sheet. Submit samples and project folder to GC Analyst.

15.0 CALCULATIONS

15.1 All calculations pertaining to data analysis and reporting can be found in the determinative method SOP NE207.

16.0 METHOD PERFORMANCE

16.1 Please consult determinative methods (NE207.doc) for Method Performance details.

17.0 POLLUTION PREVENTION

17.1 Please see NEA168.SOP for pollution prevention measures.

18.0 DATA ASSESSMENT AND ACCEPTANCE CRITERIA FOR QC MEASURES

18.1 Please consult determinative methods (NE207.doc) for Data Assessment and Acceptance Criteria for Quality Control Measures.

19.0 CORRECTIVE ACTION FOR OUT-OF-CONTROL DATA

19.1 Please consult determinative methods (NE207.doc) for Corrective Action for Out-Of-Control Data.

20.0 CONTIGENCIES FOR HANDLING OUT-OF-CONTROL DATA

20.1 Please consult determinative methods (NE207.doc) for Contingencies for Handling Out-Of-Control or Unacceptable Data.

21.0 WASTE MANAGEMENT

21.1 Please see NEA054.SOP, NEA083.SOP and NEA089.SOP

22.0 REFERENCES

22.1 US EPA 40 CFR Part 136, “Guidelines Establishing Test Procedures for the Analysis of Pollutants,” July, 1988.

22.2 US EPA SW-846, “Test Methods for Evaluating Solid Waste Physical/Chemical Methods,”
Office of Solid Waste and Emergency Response, 3rd Edition, 1986 and its updates.

22.3 Horizon Technology, “SPE-DEX® 4790 Series Extractor: Automated Solid Phase Extractor System User’s Guide,” July 2001.

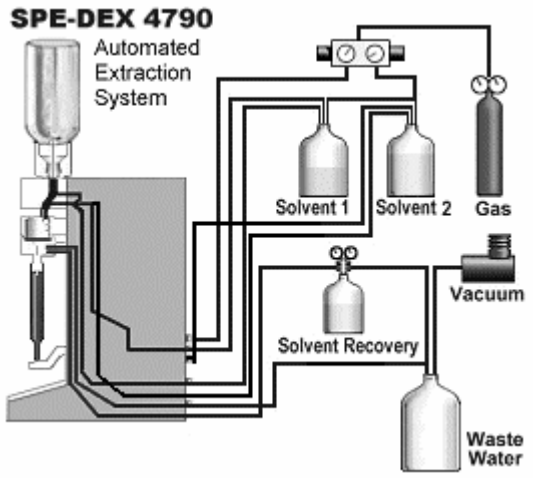
23.0 ATTACHMENTS

23.1 SPE Extractor Diagram

23.2 Extraction Methods

23.3 Method Flow Chart

23.1 SPE EXTRACTOR DIAGRAM*



***NOTE: Limited diagram of the SPE-DEX® extractor set up. There are actually eight solvent bottles, five pre-wet solvents and three rinse solvents.**

23.2 Extraction Methods

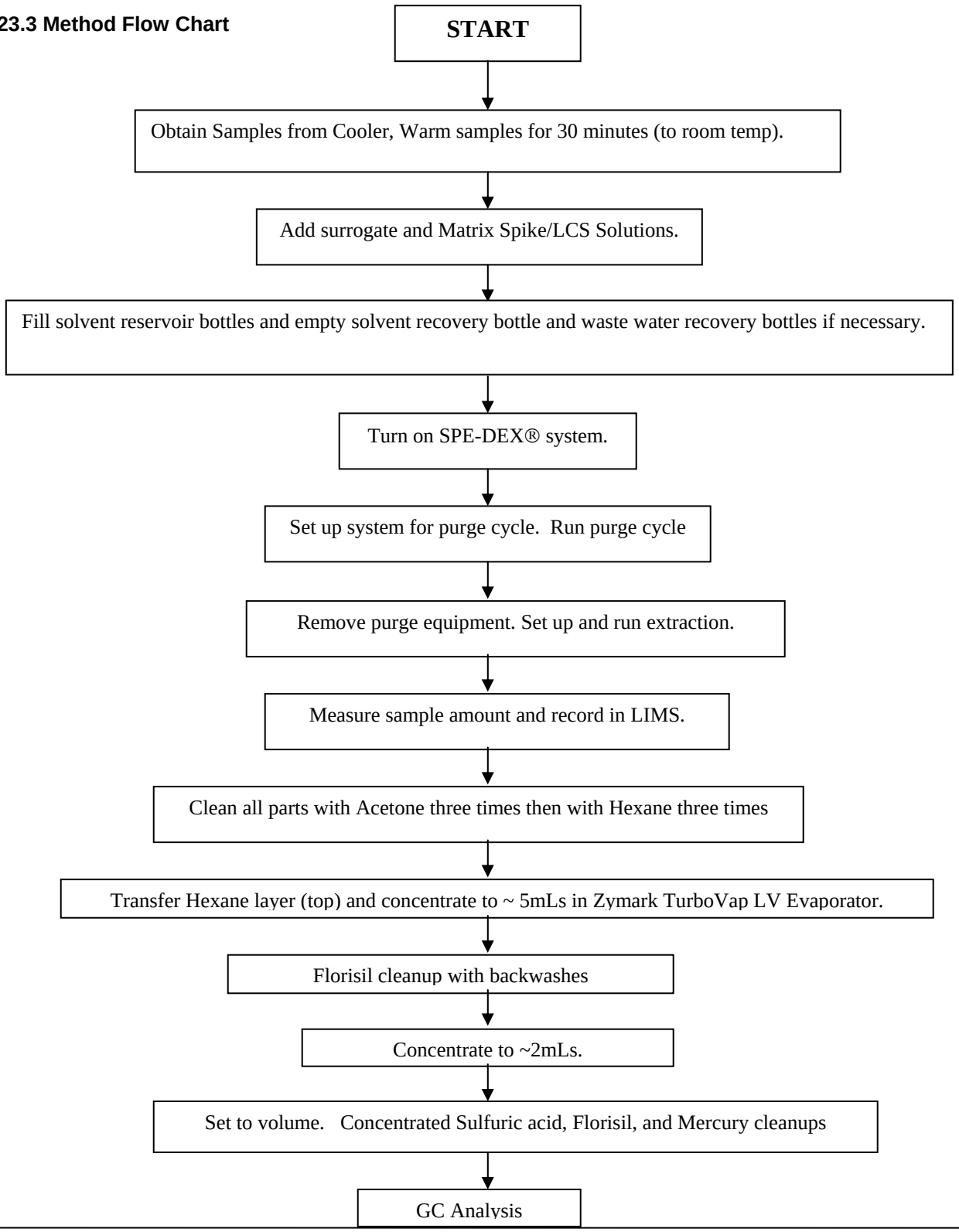
Extraction Method "First Bottle"

Step Number	Procedure
Step 1: Pre-wet Solvent: Dichloromethane	Soak Time: 1:00 minute Air Dry Time: 30 seconds
Step 2: Pre-wet Solvent: Hexane	Soak Time: 1:00 minute Air Dry Time: 30 seconds
Step 3: Pre-wet Solvent: Acetone	Soak Time: 1:00 minutes Air Dry Time: 30 seconds
Step 4: Pre-wet Solvent: Methanol	Soak Time: 1:30 minute Air Dry Time: 0:00 minutes
Step 5: Pre-wet Solvent: Reagent Water	Soak Time: 1:00 minute Air Dry Time: 0:00 minutes
Step 6: Pre-wet Solvent: Reagent Water	Soak Time: 1:00 minute Air Dry Time: 0:00 minutes
Step 7: Sample Extraction / Water Drop	Time depends on particulates and sample flow through the solid phase disk.
Step 8: Air Dry Disk	Air Dry Time: 5:00 minutes
Step 9: Rinse Solvent: Acetone	Soak Time: 1:30 minutes Air Dry Time: 1:00 minute
Step 10: Rinse Solvent Hexane	Soak Time: 1:30 minutes Air Dry Time: 1:00 minute
Step 11: Rinse Solvent Hexane	Soak Time: 1:30 minutes Air Dry Time: 1:00 minute
Step 12: Rinse Solvent Hexane	Soak Time: 1:30 minutes Air Dry Time: 1:00 minute

Extraction Method "Second Bottle"

Steps 1 - 6	Skipped
Step 7: Sample Extraction / Water Drop	Time depends on particulates and sample flow through the solid phase disk.
Step 8: Air Dry Disk	Air Dry Time: 5:00 minutes
Step 9: Rinse Solvent: Acetone	Soak Time: 1:30 minutes Air Dry Time: 1:00 minute
Step 10: Rinse Solvent Hexane	Soak Time: 1:30 minutes Air Dry Time: 1:00 minute
Step 11: Rinse Solvent Hexane	Soak Time: 1:30 minutes Air Dry Time: 1:00 minute
Step 12: Rinse Solvent Hexane	Soak Time: 1:30 minutes Air Dry Time: 1:00 minute

23.3 Method Flow Chart



APPENDIX 27
SOP FOR THE DETERMINATION OF PCBS IN WATER BY MODIFIED EPA METHOD 508 (NE231_02)

STANDARD OPERATING PROCEDURE

NORTHEAST ANALYTICAL, INC.

NE231_02.SOP

REVISION NUMBER: 02

ANALYSIS OF POLYCHLORINATED BIPHENYLS BY EPA METHOD 508

COPY #____

NORTHEASET ANALYTICAL, INC.
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STANDARD OPERATING PROCEDURE

LABORATORY PROCEDURE NE231_02.DOC

REVISION 2 (09/17/08)

Author:

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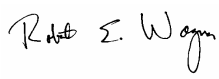


Robert E. Wagner
Laboratory Director

Approved by:

Christina Braidwood
Quality Assurance Officer

1.0 IDENTIFICATION OF TEST METHOD

1.1 This is a Standard Operating procedure (SOP) for the analysis of Polychlorinated Biphenyls (PCBs) by Gas Chromatography (GC) with Electron Capture Detection (ECD) for Total PCB Aroclor Quantification and PCB Aroclor Identification. This method analyzes PCB Aroclor by Capillary Column on the GC.

2.0 APPLICABLE MATRIX AND MATRICES

2.1 This SOP is applicable in the determination and quantification of PCBs as outlined in EPA Method 508. It is applicable to the following matrices: finished drinking water and raw source water for potable water systems.

3.0 DETECTION LIMITS

3.1 Method Detection Limits (MDL) studies are statistically determined per 40CFR Part 136 Appendix B. MDLs are initially established and are re-established if major equipment changes are undertaken. MDLs for this method generally range from 7.00 to 11.0 ng/L for each Aroclor. See Attachment F for data on MDL studies. MDLs are verified annually via a single point low level MDL verification standard which is extracted and processed in the same fashion as an unknown site sample. The Practical Quantitation Limit (PQL) as defined by the lowest calibration standard of the low level initial calibration sequence is 0.0500 ug/L.

4.0 SCOPE AND APPLICATION

4.1 The purpose of this SOP is to provide a detailed written document for measurement of Polychlorinated Biphenyls (PCBs) according to EPA Method 508 specifications based upon guidance provided in EPA Method 508 for Aroclor identification and Aroclor Quantitation.

4.2 This SOP is designed to provide appropriate guidance for compliance with EPA Method 508 as required by the New York State Department of Health Environmental Laboratory Approval Program NYS-DOH ELAP. (ELAP Method Code # 9084) which requires the laboratory to identify the Aroclor(s) present in a sample and provide an optional “screening” quantitation. This method does not quantify total “PCBs as Decachlorobiphenyl” as is performed by EPA Method 508A. This method is also designed to meet the general requirements of the National Environmental Laboratory Approval Council (NELAC) certification program.

4.3 The following compounds can be determined by this method:

Compound	CAS Number
Aroclor 1016	12674-11-2
Aroclor-1221	11104-28-2
Aroclor 1232	11141-16-5
Aroclor 1242	53469-21-9
Aroclor 1248	12672-29-6
Aroclor 1254	11097-69-1
Aroclor 1260	11096-82-5

5.0 SUMMARY OF TEST METHOD

5.1 Samples are extracted with a pesticide grade solvent (Methylene Chloride) by Separatory Funnel (Ref. NEA Lab SOP # NE141). The extracts are further processed by concentration and solvent exchange to Hexane* followed by a series of extract clean-up techniques performed to remove potential co-extracted interference

compounds. The sample extract is then analyzed by injecting onto a gas chromatographic system and detected by an electron capture detector.

*(Note: Methyl Tert Butyl Ether (MTBE) is not used as an exchange/GC analysis solvent in this method modification. This modification follows procedures found in EPA Method 508 for solvent usage.)

5.2 This SOP provides detailed instructions for gas chromatographic conditions, calibration, and analysis of PCBs by gas chromatography. Sample extraction and cleanup procedures are described separately in additional laboratory Standard Operating Procedures.

5.3 Extensive knowledge of this SOP and EPA Method 508 is required. The analysis portion of this method should be performed by a skilled chemist or by an analyst trained in the quantification of trace organics by gas chromatography.

6.0 DEFINITIONS

6.1 **Accuracy**: Accuracy means the nearness of a result or the mean (±) of a set of results to the true value. Accuracy is assessed by the extraction and analysis of reference samples and percent recoveries.

6.2 **Analytical Batch**: The basic unit for analytical quality control is the analytical batch. The analytical batch is defined as samples which are analyzed together whereas the sample method sequence, the reagent lots, and manipulations are common to each sample within the same time period or in continuous sequential time periods. Samples in each batch should be of similar composition (e.g. ground water, sludge, ash, etc.).

6.3 **Aroclor:** Polychlorinated biphenyls (PCBs) were commercially produced for a variety of uses including, transformers, capacitors, inks, paints, de-dusting agents, and pesticides to list several. Monsanto Corporation was a major producer and sold PCBs under the trade name Aroclor.

6.4 **Blank:** A blank is an artificial sample designed to monitor the introduction of artifacts into the process. For aqueous samples, reagent water is used as a blank matrix, however, a universal blank matrix does not exist for solid samples so sodium sulfate is used as a blank matrix. The blank is taken through the appropriate steps of the process. A reagent blank is an aliquot of analyte-free water or solvent analyzed with the analytical batch. Field blanks are aliquots of analyte-free water or solvents brought to the field in sealed containers and transported back to the laboratory with the sample containers. Trip blanks and equipment blanks are two specific types of field blanks. Trip blanks are not opened in the field. They are a check on sample contamination originating from sample transport, shipping and from site conditions. Equipment blanks are opened in the field and the contents are poured appropriately over or through the sample collection device, collected in a sample container, returned to the laboratory as a sample. Equipment blanks are a check on sampling device cleanliness.

6.5 **Calibration Check Standard:** Standard used to determine the state of calibration of an instrument between periodic recalibration. A calibration check is done by analyzing for analyte standards in an appropriate solvent. Calibration check solutions are made from a stock solution which is different from the stock used to prepare standards.

6.6 **CAS Number:** An assigned number used to identify a chemical. CAS stands for Chemical Abstracts Service, an organization that indexes information published in Chemical Abstracts by the American Chemical Society and that provides index guides by which information about particular substances may be located in the abstracts. Sequentially assigned CAS numbers identify specific chemicals, except when followed by an asterisk (*) which signifies a compound (often naturally occurring) of variable composition. The numbers have no chemical significance. The CAS number is a concise, unique means of material identification. (Chemical Abstracts Service, Division of American Chemical Society, Box 3012,

Columbus, OH 43210:[614] 447-3600.)

6.7 Laboratory Control Spike: A blank which has been spiked with the analyte(s) from an independent source in order to monitor the execution of the analytical method is called a check sample. The level of the spike shall be at the regulatory action level when applicable. Otherwise, the spike shall be at 5 times the estimate of the quantification limit. The matrix used shall be phase matched with the samples and well characterized: for example, reagent grade water is appropriate for an aqueous sample.

6.8 Duplicate: A second aliquot of a sample that is treated the same as the original sample in order to determine the precision of the method.

6.9 Environmental Sample: An environmental sample or field sample is a representative sample of any material (aqueous, non-aqueous, or multimedia) collected from any source for which determination of composition or contamination as requested or required. Environmental samples are normally classified as follows:

6.9.1 Drinking Water--delivered (treated or untreated) water designated as potable water; Water/Wastewater--raw source waters for public drinking water supplies, ground waters, municipal influents/effluents, and industrial influents/effluent.

6.9.2 Sludge--municipal sludges and industrial sludges.

6.9.3 Waste--aqueous and non-aqueous liquid wastes, chemical solids, contaminated soils, and industrial liquid and solid wastes.

6.10 Initial Calibration: Analysis of analytical standards for a series of different specified concentrations; used to define the linearity and dynamic range of the response of the analytical detector or method.

6.11 Instrument Calibration: Analysis of analytical standards for a series of different specified concentrations; used to define the quantitative response, linearity, and dynamic range of the instrument to target analytes.

6.12 Matrix: The predominant material of which the sample to be analyzed is composed. Matrix is not synonymous with phase (liquid or solid).

6.13 Matrix Spike: Aliquot of a sample (water or soil) fortified (spiked) with known quantities of specific compounds and subjected to the entire analytical procedure in order to indicate the appropriateness of the method for the matrix by measuring recovery.

6.14 Matrix Spike Duplicate: A second aliquot of the same matrix as the matrix spike (above) that is spiked in order to determine the precision of the method.

6.15 Method Blank: An analytical control consisting of all reagents, internal standards and surrogate standards, which is carried through the entire analytical procedure. The method blank is used to define the level of laboratory background and reagent contamination.

6.16 MSDS: Material safety data sheet. OSHA has established guidelines for the descriptive data that should be concisely provided on a data sheet to serve as the basis for written hazard communication programs. The thrust of the law is to have those who make, distribute, and use hazardous materials responsible for effective communication. See the Hazard Communication Rule, 29 CFR, Part 1910, 1200, as amended, Sec. g. See Schedule I, Sec. 12, of the Canadian Hazardous Products Act.

6.17 PCB: Polychlorinated biphenyls (PCBs) are a class of 209 individual chemical compounds (congeners), in

which one to ten chlorine atoms are attached to biphenyl. Use of PCBs has made them a frequent environmental pollutant.

6.18 **Precision:** Precision is the agreement between a set of replicate measurements without assumption of knowledge of the true value. Precision is assessed by means of duplicate/replicate sample analysis.

6.19 **Quality Control:** Set of measures within a sample analysis methodology to assure that the process is in control.

6.20 **Standard Curve:** A standard curve is a curve which plots concentrations of known analyte standards versus the instrument response to the analyte. Calibration standards are prepared by diluting the stock analyte solution in graduated amounts which cover the expected range of the samples being analyzed. Standards should be prepared at the frequency specified in the appropriate section. The calibration standards must be prepared using the same type of acid or solvent and at the same concentration as will result in the samples following sample preparation. This is applicable to organic and inorganic chemical analyses.

6.21 **Stock Solution:** Standard solution which can be diluted to derive other standards.

6.22 **Surrogate:** Surrogates are organic compounds which are similar to analytes of interest in chemical composition, extraction, and chromatography, but which are not normally found in environmental samples. These compounds are spiked into all blanks, calibration and check standards, samples (including duplicates and QC reference samples) and spiked samples prior to analysis. Percent recoveries are calculated for each surrogate.

6.23 **Surrogate Standard:** A pure compound added to a sample in the laboratory prior to extraction so that the overall efficiency of a method can be assessed.

7.0 INTERFERENCES

7.1 One of the major sources of interference in the analysis of PCBs is from Organochlorine Pesticides that are co-extracted from the samples. Several of the commonly found pesticides and associated degradation products (DDT, DDE, DDD) overlap the PCB profile envelope and co-elute with several PCB GC peaks and therefore cannot be accurately measured. The analyst must be careful in chromatographic pattern review and flag peaks that are suspected of being contaminated so that they are not included in the total PCB values generated.

7.2 Laboratory contamination can occur by introduction of plasticizers (phthalate esters) into the samples through the use of flexible tubing, gloves, etc. Samples and extracts should not be exposed to plastic materials. Phthalate esters respond on electron capture detectors, usually as late eluting peaks, and can interfere in PCB quantification.

7.3 Elemental Sulfur may be present in samples and will respond on the electron capture detector as a large broad eluting peak in the PCB elution window and interfere with identification and quantitation. Elemental Sulfur may be removed by extract cleanup procedures described in NEA Lab SOP # NE141.doc.

8.0 SAFETY

8.1 Safety glasses and disposable gloves must be worn when handling samples and extracts.

8.2 All manipulations of sample extracts should be conducted inside a chemical fume hood. The analyst should minimize manipulation of sample extracts outside of a fume hood.

8.3 Safe laboratory practices should be followed by the analyst at all times when conducting work in the lab. The analyst should refer to the reference file of material safety data sheets to familiarize themselves with the precautions of handling applicable solvents and chemicals used to process samples. The analyst should refer to the laboratory chemical hygiene plan for further safety information.

8.4 Samples remaining after analysis should be either returned to the customer for disposal or disposed of through the laboratory's disposal plan. Refer to the sample custodian for assistance in this matter and also standard operating procedure NE054, disposal of laboratory waste.

9.0 EQUIPMENT AND SUPPLIES

9.1 Instrumentation

9.1.1 Gas chromatograph: Varian Model 3800 (or equivalent), equipped with a temperature programmable oven, electron capture detector, and Model 8400 autosampler (or equivalent).

9.1.2 Chromatograph Data System: A data system for measuring peak height and peak area. An Empower computer network based workstation (Waters Associates) will be employed to capture detector response and digitally store the chromatographic information. This system will allow for chromatographic review of data from the gas chromatograph, electronic peak integration for precise calculations, database structuring of the analytical information, and archival capabilities.

9.1.3 Column : ZB-5, Phenomenex Cat. No. ZB-5-G002-11; 30m x 0.25mm x 0.25 um or DB-5, J&W Part No. 122-5032; 30m x 0.25 mm x0.25 um (or equivalent).

9.1.4 Column : ZB-1, Phenomenex Cat. No. 7HG-G001-11; 30 m x 0.25mm x 0.25 um ; or DB-1, J&W Part No. 122-1032; 30 m x 0.25 mm x 0.25 um ;(or equivalent).

9.2 Glassware and Accessories

9.2.1 25 mL volumetric flasks, Class A, pre-solvent cleaned, (Pyrex) or equivalent.

9.2.2 5 mL volumetric flasks, Class A, pre-solvent cleaned, (Pyrex) or equivalent.

9.2.3 10 mL volumetric flasks, Class A, pre-solvent cleaned, (Pyrex) or equivalent.

9.2.4 50 mL volumetric flasks, Class A, pre-solvent cleaned, (Pyrex) or equivalent.

9.2.5 100 mL volumetric flasks, Class A, pre-solvent cleaned, (Pyrex) or equivalent.

9.2.6 4 dram vials for sample extract storage, pre-solvent cleaned, (Kimble) or equivalent

9.2.7 8 dram vials for sample extract storage, pre-solvent cleaned, (Kimble) or equivalent.

9.2.8 Pasteur pipettes (Kimble) or equivalent.

9.2.9 250 mL beakers, glass (Baxter) or equivalent.

9.2.10 100 mL beakers, glass (Baxter) or equivalent.

9.2.11 Disposable 10 mL pipettes (Baxter) or equivalent.

9.2.12 Disposable 5 mL pipettes (Baxter) or equivalent.

9.2.13 Disposable 1.0 mL pipette (Baxter) or equivalent.

9.2.14 250 uL Syringe, Hamilton 81100 .

10.0 Reagents and Standards

10.1 Chemicals

10.1.1 Hexane, pesticide grade quality, Burdick and Jackson, (Cat.No. 212-4) or equivalent.

10.1.2 Acetone, pesticide grade quality, Burdick and Jackson, (Cat.No.010-4) or equivalent.

10.1.3 Toluene, pesticide grade, Baker, (Cat.No. 9336-03) or equivalent.

10.1.4 Methylene Chloride, pesticide grade, Burdick and Jackson, (Cat. No. 300-4) or equivalent.

10.1.5 Sodium Thiosulfate Preservative Sigma Aldrich Cat # 217263-250G

10.2 Analytical Standard Solutions

10.2.1 Aroclor Stock Standard Solutions

10.2.1.1 Polychlorinated Biphenyls - Neat commercial material for standard preparation. These materials are multi-component mixtures of PCB congeners and are the actual materials that were used in products such as electric power transformers and capacitors.

PCB Stock Standard Preparation Table

PCB Formulation	Supplier	Catalog #	Standard weight(mg)	Conc. (PPM)
A1016	Monsanto Neat Archive	NA	100.0	1000.0
A1221	Monsanto Neat Archive	NA	100.0	1000.0
A1232	Monsanto Neat Archive	NA	100.0	1000.0
A1242	Monsanto Neat Archive	NA	100.0	1000.0
A1248	AccuStandard	C-248N-50mg	100.0	1000.0
A1254	Monsanto Neat Archive	NA	100.0	1000.0
A1260	Monsanto Neat Archive	NA	100.0	1000.0
TCMX/DCBP	Ultra Scientific	CUS-4911*	0.5/5.0	500/5000

Note: Unless otherwise noted hexane is the solution used to make all dilutions. *Custom Order

10.2.1.2 Stock standards are prepared from individual Aroclor formulations by weighing an exact amount of the neat material to the nearest 0.1 mg, and dissolving and diluting to volume in a 100 mL volumetric flask with hexane. See above Table for exact weights of each compound.

10.2.1.3 The stock standards are transferred into Boston bottles and stored in a freezer (≤0°C) protected from light.

10.2.1.4 Stock PCB standards must be replaced after one year or sooner if comparison with certified check standards indicates a problem.

10.2.2 PCB Continuing Calibration Stock Standards:

PCB	Supplier	Catalog #	Conc. (ug/mL)
A1016	Chem Service	F107AS	1000
A1221	Chem Service	F108AS	1000
A1232	Chem Service	F113AS	1000
A1242	Chem Service	F109AS	1000
A1248	Chem Service	F110AS	1000
A1254	Chem Service	F111AS	1000
A1260	Chem Service	F112BS	1000

10.2.3 For quality control and general labeling requirements refer to standard operating procedure NE050, Preparation of Standards.

11.0 Sample Collection, Preservation and Storage

11.1.1 Sample Collection and Storage

Grab samples are collected in clean 1-Liter glass bottles with Teflon lined caps. Samples are shipped to the lab chilled (4 +/- 2 degrees Celsius) and are stored under refrigeration at (4 +/- 2 degrees Celsius). Samples that are collected within driving distance of the laboratory and delivered the same day may not have reached temperature acceptance limits. These samples are deemed acceptable if evidence of cooling is present (i.e. they are received with ice in the cooler). The extraction hold time for aqueous samples is 7 days from the date collected.

11.1.2 Sample Preservation

Finished drinking water samples may have residual chlorine present originating from the chlorination disinfection process. If residual chlorine is present, add 80 mg of sodium thiosulfate per liter of sample to the sample bottle prior to collecting the sample. After adding the sample to the bottle containing Sodium Thiosulfate, seal the sample bottle and shake until dissolved.

12.0 Quality Control

12.1 This section outlines the necessary quality control samples that need to be initiated at the time of sample extraction. The data from these quality control samples is maintained to document the overall precision and accuracy of the data generated.

12.2 Each analyst and extraction/preparation technician must demonstrate competency in accuracy and precision on quality control samples before beginning unsupervised analysis of unknown samples (Initial Demonstration of Performance). This demonstration must be on-going and be repeated if there is any modification to the method. Additionally, on going demonstration of performance is required by the National Environmental Laboratory Approval Council (NELAC)

Initial Demonstration of Performance (IDOP) Procedure:

12.2.1 Prepare 4 replicates of a fortified laboratory blank sample (using laboratory reagent water) by spiking each 1 liter sample with 1.0 mL of 0.500 ug/mL Aroclor solution (typically Aroclor 1242). Prepare one method blank sample with the batch. Extract and analyze each aliquot according to procedures beginning in Section 14.0 below.

12.2.2 For each replicate the recovery value of the sample must fall in the range of 70±30 % and the percent RSD must be < 20 % for the method performance to be considered acceptable. See Section 23 Attachment G for example IDOP study.

12.2.3 This procedure must be repeated using four fresh samples until satisfactory performance has been demonstrated. The initial demonstration of capability is used primarily to preclude the laboratory from analyzing unknown samples via a new, unfamiliar method prior to obtaining some experience with it. It is expected that as laboratory personnel gain experience with this method the quality of data will improve beyond those required here.

Continuing Demonstration of Performance Procedure:

12.2.4 Annual continuing demonstration of performance may be satisfied by a repeat Initial Demonstration of Performance, the acceptable analysis of an unknown samples (for example PT test sample), or the acceptable analysis of 4 consecutive Laboratory Control Spike samples. Records of continuing demonstration of performance are maintained by the laboratory Quality Assurance Department.

12.3 With each batch of samples to be extracted a method blank is processed. The method blank is carried through all stages of sample preparation and measurement steps. For water samples an organic-free reagent water blank is processed.

12.3.1 The method blank should exhibit PCB levels less than the practical quantification limit (PQL). If the method blank exhibits PCB contamination above the reportable PQL, the samples associated with the contaminated blank should be re-extracted and analysis repeated when appropriate. If there is no original sample available for re-extraction or if the associated sample concentrations greatly exceed the blank concentration, then all positive concentration results for the associated samples should be flagged with a "B" indicating blank contamination and a case narrative describing the situation prepared.

12.4 A matrix spike is to be analyzed at a rate of 1 matrix spike per every 10 samples. A duplicate sample may be prepared in lieu of a matrix spike when detectable PCB concentrations are

known to be present.

12.4.1 Analyze one unspiked and one spiked sample. Calculate the percent recovery based on Aroclor concentration of both samples. (See 15.0) The default spike amount for the matrix spike is 1.0mL of A1242 @ 0.5ppm yielding a final sample added concentration of 0.500 ug/L. *Note: Project specific requirements may indicate an alternate spike amount or Aroclor.

12.4.2 Compare the percent recovery calculated with project specified limits, the lab established limits, or the default lab limits of 70-130% where appropriate. If the concentrations of the matrix spikes are *greater* than five times the calculated sample amount then the quality control limits may be applied. If the concentrations of the matrix spikes are *less* than five times the sample than there are no established limits applicable. If the percent recovery falls outside the acceptance range for the given Aroclor used as the spiking analyte, then the matrix spike recovery failed the acceptance criteria. Inform quality control manager and document matrix spike recoveries.

12.4.3 A relative percent difference (RPD) is calculated for Duplicates. (See 15.0)

12.4.4 If the concentrations of the sample/duplicate set are *greater* than five times the calculated PQL then an RPD of twenty percent or less is acceptable. If the concentrations of the matrix spike set are less than five times the PQL there are no established limits applicable to the RPD.

12.5 A QC reference check standard (laboratory control spike sample) is also prepared and analyzed. Spike one liter of laboratory organic free water, extract, and analyze. Calculate the percent recovery for the Aroclor spike and compare to the lab-established limits or the default limits of 70-130%. If the percent recovery for the QC reference check standard (laboratory control spike sample) is out of criteria, the analysis is out of control for that analyte and the problem should be immediately corrected. The entire batch of samples will need to be re-extracted and re-run. If no samples are available for re-extraction the data is delivered to the client with a case narrative. The default matrix spike amount for the LCS is 1.0mL of A1242 @ 0.5ppm for a final sample concentration of 0.500 ug/L. *Note: Project specific requirements may indicate an alternate spike amount or Aroclor.

12.6 Method accuracy, based on matrix spike and laboratory control spike data is maintained by the laboratory as part of the QC program. For each sample matrix, upper and lower warning and control limits for method performance are established. Upper and lower warning limits (p ± 2SD) and upper and lower control limits (p ± 3SD) are established. Laboratory established limits are compared to default limits and are updated with new data periodically.

12.7 Surrogate compounds are added to each sample, matrix spike, matrix spike duplicate, duplicate, method blank, and QC reference check standard (laboratory control spike sample) at time of extraction. Surrogate compounds chosen for this method are Tetra-Chloro-meta-Xylene (TCMX) and Decachlorobiphenyl (DCBP). The following are typical surrogate amounts added to normal encountered matrices. These amounts may be adjusted by the analyst, if PCB background levels are high and surrogates are being diluted out of analysis range. The surrogate spike amount added for water samples is normally: 1.0 mL of 0.05ppm TCMX/0.5ppm DCBP

12.7.1 Surrogate percent recovery data for each matrix is tabulated as part of the on-going

laboratory QC program. The standard deviation is calculated once enough surrogate data is available for each matrix, typically based on 25 to 30 samples. Upper and lower warning limits (p ± 2SD) and upper and lower control limits (p ± 3SD) are established. Laboratory limits are compared to default limits and are updated with new data periodically.

12.7.2 Only one surrogate analyte needs to meet established control limits for the analysis to be valid. The recovery data is compared to the project specified limits, lab-established limits or the default limits of 70-130% as appropriate. If percent surrogate recovery is not within limits for either surrogate, the following steps are required.

12.7.2.1 Review calculations that were used to generate surrogate percent recovery values to make certain there are no errors.

12.7.2.2 Check by GC analysis surrogate solutions used during sample extraction steps to ensure that no problems exist with spiking solutions.

12.7.2.3 When appropriate, re-analyze the extracts that did not meet control limits, either at the previously analyzed dilution or at a more dilute level to assess if the sample matrix interfered with surrogate measurement.

12.7.2.4 If the above steps do not give satisfactory results, re-extract and re-analyze the sample when appropriate. Report this data if surrogate recovery is within limits. If surrogate percent recovery is out of limits for the re-extracted samples, low or high surrogate recovery may be due to matrix affects and the data can be reported as estimated and the data user is notified in the form of a case narrative.

13.0 Calibration and Standardization

13.1 Calibration standards are prepared at five concentration levels using a prepared working standard. A calibration set is prepared for each Aroclor. See Attachment A, Tables for the preparation and exact concentrations of the working standards.

13.1.1 The following nominal* concentrations make up the five point initial calibration curve standard set:

	Calibration Level
Std 1.	5.0 ng/mL (0.005 PPM)
Std 2.	10 ng/mL (0.010 PPM)
Std 3.	20 ng/mL (0.020 PPM)
Std 4.	50 ng/mL (0.050 PPM)
Std 5.	100 ng/mL (0.100 PPM)

Note:** **Calibration standards are prepared from neat Aroclors which are weighed to the nearest 0.1 mg. The actual concentration of each calibration standard is provided in the attached standard preparation tables (Attachment A).

13.1.2 The two surrogate compounds TCMX and DCBP are included in the A1254 calibration standards. The stock standard for TCMX/DCBP is prepared by diluting 1 mL of Surrogate solution (ULTRA, cat. #CUS-4911, at 500/5000 ug/mL or equivalent) into a 1000 mL volumetric flask resulting in a solution of TCMX /DCBP at 0.5/5.0 PPM. . Label and Store in Boston Bottles in a refrigerator (4 ± 2°C) or freezer (≤0°C).

13.1.2.1 Refer to Attachment A, Tables 3 and 3A for instructions on preparation of the high and low level calibration standards containing A1254 and the surrogates. Refer to Attachment A, Tables 2 and 2A for instructions on preparing the remaining calibration standards.

13.1.2.2 Transfer all calibration standards to 8 dram vials and store in a refrigerator at (4 ± 2°C), protected from light. Calibration standards must be replaced after six months, or sooner, if comparison with check standards indicates a problem.

13.2 **Continuing Calibration Check Standards (CCV):** Continuing calibration check standards for high and low level calibration curves are prepared independently from calibration standards, by using an alternate source purchased from reference standard vendors. Refer to Attachment B, Tables 1-3 for instructions on preparation of these standards.

14.0 Procedure

14.1 Gas Chromatographic Operating Conditions

14.1.1 Establish the gas chromatograph (GC) operating parameters as follows:

14.1.1.1 Single Column Autosampler parameters: Press Select/Edit , Edit Single Method Automation, at Injector Position: Enter Pos.1 or Pos.2 ; First Injector : Enter Pos. 1 or Pos.2

14.1.1.2 Dual Column Autosampler parameters: Press Select/Edit, Edit Single Method Automation, at Injector Position:Enter both ; First Injector : Enter Pos. 1

14.1.1.3 Refer to Attachment C for all other GC operating procedures, alternate parameters may be established for other GC instrumentation to meet method requirements.

***Note:* GC helium gas flow is optimized after instrument maintenance by adjusting the helium flow to elute a PCB calibration standard to a known retention time.**

14.2 Data Acquisition

14.2.1 Chromatographic information will be collected and processed utilizing a computer based data acquisition workstation (Waters Associates, Empower computer network based workstation) The GC workstation acquires the millivolt detector signal, performs an analog to digital conversion and stores the digital chromatogram on the computer network's disk. The chromatography software performs all data reduction including, long term data storage on magnetic media, chromatographic peak integration, all calculations, report generation, chromatogram plots, and calibration functions.

14.3 Initial GC Calibration

14.3.1 GC calibration will be performed by the external calibration procedure. Prior to running samples the system must be calibrated and system performance must be verified.

14.3.2 Establish the gas chromatographic operating parameters outlined in Section 14.1 (Attachment

C) and prepare the calibration standards at the five concentrations outlined in Section 13.0(Attachment A).

14.3.3 Inject each calibration standard using the GC autosampler and the parameters outlined in section 14.1, which are those used for actual samples.

14.3.4 For each Aroclor, 5 peaks are selected to prepare calibration curves. The peaks selected from the multi-component Aroclor formulations were based on maximizing the separation for each Aroclor (i.e., minimizing peak overlap in retention time). Consideration was also given to selecting peaks that normally did not have problems with co-elution with interfering peaks or possible co-elution with organochlorine pesticides. The determined area of the five peaks selected for calibration is processed by the data workstation as a group, combining the area for calculations of the calibration factors. The following table lists the Aroclors that are included in the initial calibration and the peak numbers used

Aroclor	Peak Numbers
A1221	1 , 2 , 3 , 4 , 5
A1232	5 , 7 , 8 , 9 , 10
A1016	6 , 7 , 8 , 9 , 10
A1242	6 , 7 , 8 , 9 , 10
A1248	11 , 12 , 13 , 14 , 15
A1254	16 , 17 , 18 , 19 , 20
A1260	20 , 21 , 22 , 23 , 24

14.3.5 Attachment D is an example of chromatograms of reference standards of each Aroclor for a DB1 column with peaks selected for calibration labeled.

14.3.6 For the initial calibration curve to be considered valid, the percent relative standard deviation must be $\leq$ 20% over the working range if using the Average Response Factor. If the calibration curve is used for quantification in every case and is not replaced with the Average Response Factor the Linear Regression Correlation Coefficient must be greater than 0.995. See 15.0 for an example of response factors and the calculation of the percent relative standard deviation.

14.4 Retention Time Windows

14.4.1 The GC system should be checked by the analyst to make sure it is functioning properly before establishing retention time windows. Make three injections of each Aroclor at a midlevel concentration throughout a minimum 72-hour time period.

14.4.2 For the 5 peaks selected for calibration of each Aroclor, calculate the standard deviation resulting from the variation in the three retention times for that peak.

14.4.3 The retention time window is defined as plus or minus three times the standard deviation of the three retention time determinations.

14.4.4 If the standard deviation of the selected peak is zero, the standard deviation of the peak eluting after it is used. If it is the last eluting peak that has zero for the standard deviation, then substitute the standard deviation of the peak eluting before the last peak.

14.4.5 Retention time windows established in section 14.4.3 to 14.4.4 may not be practical when samples containing matrix interferences are injected onto the GC column. The default R.T. Window of +/- 0.07 minutes is employed when the established windows are too narrow. Besides using retention time windows to assign peaks for quantification, the analysts should rely on their

experience in pattern recognition of multi-response chromatographic response exhibited by PCB Aroclors.

14.4.6 Attachment F provides examples of calculated retention time windows generated by the above outlined procedures.

14.5 Gas Chromatographic Analysis

14.5.1 Prior to conducting any analyses on samples, calibrate the system as specified in Section 14.3

14.5.2 To start an analytical sequence, the 500 ppb (or 50 ppb) calibration standard is injected and analyzed for the seven Aroclors that the system is calibrated for, if more than 24-hours has elapsed since the last valid continuing calibration check standard. If less than 24-hours has elapsed since the last valid continuing calibration check standard, select one 500 ppb (or 50 ppb) continuing calibration check standard. Selection of the continuing calibration check standard should be based on anticipated Aroclor contamination that the samples may exhibit. Selection of the continuing calibration check standard should also be alternated among the seven Aroclors.

14.5.3 The calculated value for the continuing calibration check standard must be ±15.0% for it to be valid and analysis to proceed. If this criterion is exceeded, the analyst should inspect the system to determine the cause and perform maintenance as necessary. The system can then be recalibrated and sample analysis can proceed. Note that all samples which are not bracketed by valid check standards must be re-analyzed when the system is in-control.

14.5.4 The daily retention time windows must be established. Use the retention time for the selected 5 peaks of the continuing calibration check standard as the midpoint of the window for that day. If all seven Aroclors were analyzed as the initial continuing calibration check standard, then establish retention time windows using the retention time plus or minus the windows established in Section 14.4. If only one Aroclor was analyzed as the continuing calibration check standard (i.e., less than 24-hours had elapsed), use the retention time from this standard as the midpoint plus or minus the windows established in Section 14.4. to establish the daily retention time windows. For the remaining six Aroclors, go back to the previous time all seven Aroclors were analyzed as the initial calibration check standards and use those retention times plus or minus the windows established in Section 14.4 to develop daily retention time windows.

14.5.6 All succeeding continuing calibration check standards analyzed during an analysis sequence must also have a percent difference of ±15% or less when compared to the initial calibration generated from the 5 point calibration curve.

14.5.7 All succeeding standards in an analysis sequence should exhibit retention times that fall within the daily retention time window established by the first continuing calibration check standard(s) of that analytical sequence. If the retention times are outside the established windows instrument maintenance must be performed and recalibration may be required.

14.5.8 The following is the order that initial calibration standards, continuing calibration check standards, method blanks, QC samples, and samples are placed in an analytical sequence. A continuing calibration check standard is run every tenth injection in the analytical sequence. All analytical sequences must end with a continuing calibration check standard regardless of the number of samples analyzed.

ANALYTICAL SEQUENCE

INJECTION	MATERIAL INJECTED
1-3	Hexane Blank
4-38	Initial Calibration Standards
39-45	Continuing Calibration Check Standard
46-53	Samples analyses, including method blanks, matrix spikes, matrix duplicates, matrix spike duplicates, and QC reference check standard. A maximum of 9 samples between continuing calibration check standards.
54	Continuing calibration check standard
55	and higher repeat inject. 46-53 sequence

14.6 Analyte Identification

14.6.1 PCB Aroclors are identified based upon pattern recognition and comparison of retention times of characteristic peaks to the retention time of references standards. The identified peaks should fall within the retention time windows established in section 14.4. At least 3 major PCB quantification peaks must be present to positively identify a PCB Aroclor.

14.6.2 Identification requires expert judgment when sample components are not resolved chromatographically. When GC peaks obviously represent more than one sample component (i.e., broadened peak with shoulder(s) or valley between two or more maxima), or any time doubt exists over the identification of a peak on a chromatogram, appropriate alternate techniques, to help confirm peak identification, need to be employed. For example, more positive identification may be made by the use of an alternative detector which operates on a chemical/physical principle different from that originally used; e.g., mass spectrometry, or the use of a second chromatography column (see section 9.1.3).

14.7 Data Reporting

14.7.1 Aroclor Identification and sample concentration results are electronically captured and reported through the NEA LIMs (Laboratory Information Management) System. Final concentration results are reviewed by QA department or other approved manager before release to the client.

14.7.2 Data Qualifiers:

Sample Concentration Reports (Certificates of Analysis, Data Package Form 1's and Electronic Data Deliverables (EDDs) are generated using the appropriate data qualifiers as follows:

U – Denotes analyte not detected at concentration greater than or equal to the Practical Quantitation Limit (PQL). Note: PQLs are adjusted for sample weight/volume and dilution factors.

J - Denotes an estimated concentration. The concentration result is greater than or equal to the Method Detection Limit (MDL) but less than the Practical Quantitation Limit (PQL).

P - Indicates relative percent difference between primary and secondary GC column analysis exceeds 40 %.

C- Denotes analyte confirmed by secondary GC column analysis.

B - Denotes analyte observed in associated method blank. Analyte concentration should be considered as estimated.

E - Denotes analyte concentration exceeded calibration range of instrument. Sample could not be re-analyzed at secondary dilution due to insufficient sample amount, quick turn-around request, sample matrix interference or hold time excursion. Concentration result should be considered as estimated.

Z - Laboratory Reserved Qualifier (explained in associated Case Narrative)

14.7.3 EPA Method 508 Specific Reporting Requirements:

This SOP is designed to provide appropriate guidance for compliance with EPA Method 508 as required by the New York State Department of Health Environmental Lab Approval Program NYS-DOH ELAP. (ELAP Method Code # 9084) which requires the laboratory to identify the Aroclor(s) present and provide an optional "screening" quantitation. This method does not quantify total "PCBs as Decachlorobiphenyl" as is performed by EPA Method 508A. Concentration results reported by the method are qualified as "screening result" on the final data report.

15.0 CALCULATIONS

Example Calculations

15.1 Initial Calibration Curve by first Order Linear Regression with intercept (Inverse Concentration Weighted (1/x):

Note: The Chromatography Software performs the regression calculation

$Y=A+Bx$

Y = Response µV-sec (area sum of 5 quant peaks)
A = Constant (Intercept) µV-sec
B = First Order Coefficient (slope)
x = Solution Concentration (ng/ml)

x (Solution Conc.)= (Y-A)/B For A1242 A = 76.5
B = 156.0

x = (Y-76.5)/(156.0)

15.2 Unknown Sample Solution Concentration:

For NEA ID: AJ15564 Y(meas) = 8984 uV-sec for A1242

$x = \frac{(Y_{(meas)}-A)}{B}$

x (soln. conc.) = 57.099

Unknown Sample Final Concentration:

$$\text{Conc. (ug/L)} = \frac{(x)(v_t)(\text{D.F.})\ (1/1000)}{V(t)}$$

x= Solution Concentration (ng/ml) = 57.099
v_t = Concentrated Extract Volume (ml) = 10
D.F. = Analytical Dilution Factor = 1
Vt = Sample Total Volume (L) = 1.06

$$\text{Sample AJ15564} \quad \frac{57.099\ \text{ng/ml})(10\ \text{ml})\ (\ 1\ )(1/1000\ \text{ug/ng})}{1.06\ \text{L}} = 0.539\ \text{ug/L}$$

15.3 Percent Recovery of Spiked Samples :

A = concentration of spiked sample
B = concentration of unspiked sample (background)
T = known true value of the spike
Percent Recovery (p) = 100 (A-B) %/T

15.4 Relative Percent Difference for Duplicates :

A = Concentration of original sample
B = Concentration of duplicate sample

RPD = [(A-B)/{(A+B)/2}] x 100
where (A-B) *is taken as an absolute value*

16.0 METHOD PERFORMANCE

16.1 Method performance statistics for matrix spikes and surrogate spikes and reference samples and are maintained by the QA/QC Department. Other method performance information is generated by the initial demonstration of performance studies and method detection limit studies.

16.2 Initial Demonstration of Performance (IDOP) Procedure:

16.2.1 Prepare 4 replicates of a fortified laboratory blank sample (using laboratory reagent water) by spiking each 1 liter sample with 1.0 mL of 0.500 ug/mL Aroclor solution (typically Aroclor 1242). Prepare one method blank sample with the batch. Extract and analyze each aliquot according to procedures contained in this SOP.

16.2.2 For each replicate the recovery value of the sample must fall in the range of 70±30 % and the percent RSD must be < 20 % for the method performance to be considered acceptable. See Section 23 Attachment G for example IDOP study.

16.2.3 This procedure must be repeated using four fresh samples until satisfactory performance has been demonstrated. The initial demonstration of capability is used primarily to preclude the laboratory from analyzing unknown samples via a new, unfamiliar method prior to obtaining some experience with it. It is expected that as laboratory personnel gain experience with this method the quality of data will improve beyond those required here.

16.3 Method Detection Limit

16.3.1 A method detection limit will be determined for this method whenever major modification to the extraction or analysis procedures. A minimum of seven laboratory organic free water samples are spiked with the seven Aroclors reported by this method at a low level and taken through all extraction and analytical procedures. Method detection limit data will be determined for each Arolcor based on the following equation:

$MDL = S * t_{(n-1,\ 1\text{-}alpha=0.99)}$
Where:

S = Standard deviation of the replicate analyses
n = Number of replicates
$t_{(n-1,\ 1\text{-}alpha=0.99)}$ = Student's t value for the 99% confidence level with n-1

For example: t for 8 replicates = $t_{(7,0.99)} = 2.998$

16.3.2 The determined MDL must be less than the concentration spiked but greater than one tenth (1/10) the spiked concentration. If not, repeat the MDL determination at an appropriate spike concentration for affected analytes.

17.0 POLLUTION PREVENTION

17.1 For Pollution Prevention Procedures please see SOP NE168 for details

18.0 DATA ASSESSMENT ANAD ACCEPTANCE CRITERIA FOR QC MEASURES

18.1 The GC analyst is responsible for generating the data and also is the initial individual to review the data. This would include inspection of the chromatographic data, processing the raw data, producing all required data forms, inspection of calibration curves for compliance, surrogate recovery, laboratory control spike recovery, matrix spike/matrix spike duplicate recovery, and continuing calibration compliance.

18.2 Once the initial review of the data is performed by the analyst, decisions are made at that time to accept the data if all criteria are met or to reject sample data if any of the quality control parameters or limits are out of control. Depending on the situation, samples requiring re-extraction will be notified to the appropriate extraction personnel, sample extracts requiring re-injection will be queued for analysis, new calibrations may have to be performed, or samples re-analyzed due to failing continuing check standards.

18.3 The analyst may also consult with the quality control officer as to the best form of action to take or if the situation warrants corrective action beyond routine practices. If no recourse is available and the data is to be reported out of criteria, a Case Narrative Report is generated and the deviation is documented and reported to the client. The Case Narrative Report is filed with the data and is also useful for production of case narratives that are issued with the final data reports. If a problem exists that requires follow-up to rectify, a Corrective Action Report (CAR) is issued to document the problem found, steps taken to resolve the problem, and what samples were affected. This CAR form is filed by the quality control officer and reviewed by management to verify that appropriate actions have been taken to correct the problem.

19.0 Corrective Action for Out-Of-Control Data

19.1 The table below outlines the data assessment, acceptance criteria, and corrective action procedures for out-of-control data.

Quality Control Item	Frequency	Acceptance Criteria	Corrective Action
Initial Calibration	The five point calibration is analyzed initially and when Continuing Calibration Check standard fails criteria.	- %RSD ≤20% for the relative response factors for the five peaks in the five point calibration. - Relative response factors are to be calculated using total area for the five quantitation peaks of each Aroclor within the five standard concentrations. Linear Regression Correlation Coefficient must be greater than 0.995.	- Re-analyze the initial calibration standard and/or evaluate/correct instrument malfunction to obtain initial calibration and continuing calibration check standards that meet criteria.
Continuing Calibration Check Standard (CCV)	- Initially analyze a CCV immediately following a calibration standard analysis. - After the initial CCV of the sequence, a CCV must be analyzed after 9 samples. - Analytical sequence must end with analysis of a CCV.	- Calibration factor for the continuing calibration check must be less than ± 15% difference for each Aroclor. - Retention time of all quantitated peaks must be within RT window (reset with each initial CCV of a sequence). - The percent recovery for the surrogates (TCMX/ DCBP) in the Continuing Calibration Check Standard must be within ± 15 % Difference. - All samples must be bracketed by CCV's that meet all criteria stated above.	- If the reason for the failure of the CCV appears to be a poor injection (or a degraded standard solution), the CCV will be re-injected (or re-prepared and re-injected) immediately following the failed CCV. This can only occur if the instrument is being attended by an analyst. If upon re-injection, the CCV meets all the acceptance criteria and there is no apparent impact on the sample data (i.e., acceptable surrogate recoveries are observed), the analytical sequence will continue and samples will not be reanalyzed. The associated sample data will be reported. - If CCV failure was not due to a poor injection (or degraded standard solution) or the instrument was unattended at the time of the CCV failure, correct system, and if necessary, recalibrate. Initial calibration and CCV criteria
			must be met before sample analysis may begin. Samples that are not bracketed by compliant CCV's must be

			reanalyzed. -If acceptable CCV's are observed later in the sequence, samples bracketed by acceptable CCV's will be reported. Samples between the failed CCV and prior/ subsequent compliant CCV will be re-analyzed.
-Retention Time (RT)	- Use the retention time for peak in the CCV's to determine midpoint of the relative retention time window for the analysis sequence. -Each sample analysis: Rely on RT windows to identify PCB quant. peaks to report. Also use pattern recognition and professional judgment for peaks that shift from RT windows, because congener composition may shift RT for GC peaks.	- Each quantitated peak and surrogate peak should be within established windows.	-Inspect chromatographic system for malfunction, correct problem. Perform re-analysis if necessary.
Method Blank	-One per extraction batch of ≤20 samples of the same matrix per day. -Must be analyzed on each instrument used to analyze associated samples. -Must undergo all sample preparative procedures.	- Concentration does not exceed the total PCB method reporting limit. - Must meet surrogate criteria of 70-130% recovery.	- Re-analyze method blank to determine if instrument contamination was the cause. If method blank re-analysis passes, then report samples. -If method blank is found to contain PCB contamination above total PCB reporting limit, then re-extract and re-analyze all associated samples. If no sample exists for re-extraction, report data flagged to indicate method blank contamination or have client re-sample if possible.

Laboratory Control Spike (LCS)	- One per extraction batch of ≤20 samples per matrix per day. The LCS is typically Aroclor 1242.	-Percent recovery of Aroclor 1242 on a total PCB basis must be within method limits of 70-130% -Must meet surrogate criteria of 70-130% recovery.	-Re-analyze LCS to determine if instrument was the cause. If LCS passes, then report samples. -If LCS recovery is still out of limits, the re-extract and re-analyze all associated samples. If no sample exist for re-extraction, report data flagged to indicate LCS failed recovery or have client re-sample if possible.
Matrix Spike/Matrix Spike Duplicate (MS/MSD)	-Normal method procedure is to extract and analyze a matrix spike sample. One MS per extraction batch of ≤20 samples per matrix per day. The MS is typically Aroclor 1242 -If requested, an MSD can be extracted and analyzed. The MSD would follow the above criteria as for the MS.	- Percent recovery for MS on a total PCB basis should be 70-130%. - If MS/MSD is analyzed, relative percent difference (RPD) should be within 20%. -Must meet surrogate criteria of 70-130% (unless original unspiked sample is also outside of criteria)	-Re-analyze MS and/or MSD to determine if instrument was the cause. If MS and/or MSD pass, then report samples. -Check for errors such as calculations and spike preparation. -Check original unspiked sample results and surrogate recovery for indications of matrix effects. -If no errors are found, and the associated LCS is within 70-130%, then sample matrix effects are likely the cause. Note exceedence in Case Narrative.
Surrogates	-Surrogates are added to all samples and QC samples when the sample is prepared for analysis. 2,4,5,6-Tetrachloro-m-xylene (TCMX) and Decachlorobiphenyl surrogate compounds are added from a solution prepared from a Custom ordered stock solution in	- Percent recovery for the surrogate(s) should be 70-130%.	-Re-analyze the affected sample or QC sample to determine if instrument was the cause. If surrogate passes, then report samples. -Check for errors in surrogate calculation and surrogate solutions. -If no problem is found, then re-extract and re-analyze the sample. -If re-analysis is within limits and sample extract holding time, then

	Hexane.		report only the re-analysis. -If the re-analysis is within limits, but out of extraction holding time, then report both sets of data. -If the re-extraction produces surrogate recovery still out of limits, then report both sets of data, if sample exists for re-extraction, report data flagged to indicate surrogate failed recovery or have a client re-sample.

20.0 ONTIGENCIES FOR HANDLING OUT-OF-CONTROL DATA OR UNACCEPTABEL DATA

20.1 Data that is found to be out-of-control for any reason, when compared to method acceptance criteria, will addressed in the following manner:

20.1.1 If the problem exists with the gas chromatographic instrumentation, appropriate action will be taken to repair and perform maintenance to bring the instrument back to operation condition. Once the instrumentation is determined to be correctly operating analysis can begin again.

20.1.2 If the problem exists with calibration standard solutions, the analyst will prepare new standards and discard the standard solutions that are suspect. Instrument calibration can be performed and analysis can begin once system is control.

20.1.3 If the problem exists with sample extraction and extract preparation, the extraction step that is producing the out-of-control situation will be diagnosed and rectified. Once the troubleshooting procedures correct the problem extraction can once again occur and analysis can continue.

20.2 In situations where data is reported under out-of-control conditions, the data will be annotated with data qualifiers and/or appropriate descriptive comments defining the nature of the excursion in the Sample Delivery Group Case Narrative. If warranted, a corrective action report (CAR) will be issued to define the problem, steps to correct the problem, and final resolution.

21.0 WASTE MANAGEMENT

21.0 Waste Management: see SOPS NE054.SOP, NE083.SOP and NE089.SOP for details.

22.0 REFERENCES

22.1 EPA Method 508 Revision 3.1, J. W. Munch 1995.

22.2 EPA Method 608 -U.S. EPA 40 CFR Part 136, "Guidelines Establishing Test Procedures for the Analysis
of Pollutants", July 1988.

22.3 Standard Methods for the Examination of Water and Waste Water, 18th Edition 1992, American Public Health Association, American Water Works Association, Water Pollution Control Federation.

22.4 New York State Department of Health, "Environmental Laboratory Approval Program Certification

Manual", Wadsworth Center for laboratories and Research, 1988, updated 2005.

22.5 "Guide to Environmental Analytical Methods", fourth edition, Genium Publishing Corporation, 1998.

23.0 Attachments

23.1 Attachment A: PCB Standards Preparation Tables.

23.2 Attachment B: PCB Continuing Calibration Tables.

23.3 Attachment C: GC Operating Conditions.

23.4 Attachment D: Chromatograms of PCB standards.

23.5 Attachment E: Retention Time Windows.

23.6 Attachment F: MDL Studies.

23.7 Attachment G: Initial Demonstration of Precision (Precision and Accuracy) Study

ATTACHMENT A

Table 1
PCB Working Standard Preparation Table

PCB Stock Standards	Init. Volume (mL)	Final Volume (mL)	Conc. (ug/mL)
A1016 @ 1000 ppm	1.0	100	10.0
A1221 @ 1000 ppm	1.0	100	10.0
A1232 @ 1000 ppm	1.0	100	10.0
A1242 @ 1000 ppm	1.0	100	10.0
A1248 @ 1000 ppm	1.0	100	10.0
A1254 @ 1000 ppm	1.0	100	10.0
A1260 @ 1000 ppm	1.0	100	10.0

Actual concentrations for each Aroclor.

ATTACHMENT A cont'd

Table 2
PCB Calibration Standard Preparation Table (High Level Calibration Curve)

Initial Volume (mL)	Initial Conc. (ug/mL)	Final Volume (mL)	Final Concentration (ug/mL)					
			A1016	A1221	A1232	A1242	A1248	A1260
5.0	(10.0)	50.0	1.000	1.000	1.000	1.000	1.000	1.000
2.5	(10.0)	50.0	0.500	0.500	0.500	0.500	0.500	0.500
1.25	(10.0)	50.0	0.250	0.250	0.250	0.250	0.250	0.250
1.00	(10.0)	50.0	0.200	0.200	0.200	0.200	0.200	0.200
0.500	(10.0)	50.0	0.100	0.100	0.100	0.100	0.100	0.100
5.0	(0.200)	50.0	0.020	0.020	0.020	0.020	0.020	0.020

Actual Concentration, see Table 1 for actual working standard concentrations for each Aroclor

Table 2A
PCB Calibration Standard Preparation Table (Low Level Calibration Curve)

Init. Volume (mL)	Initial Conc. (ug/mL	Final Volume (mL)	Final Concentration (ug/mL)					
			A1016	A1221	A1232	A1242	A1248	A1260
0.5	(10.0)	50.0	0.100	0.100	0.100	0.100	0.100	0.100
2.5	(1.0)	50.0	0.050	0.050	0.050	0.050	0.050	0.050
1.0	(1.0)	50.0	0.020	0.020	0.020	0.020	0.020	0.020
1.0	(0.500)	50.0	0.010	0.010	0.010	0.010	0.010	0.010
0.50	(0.500)	50.0	0.005	0.005	0.005	0.005	0.005	0.005

Actual Concentration, see Tables 1 and 2 for actual working standard concentrations for each Aroclor.

Table 3
PCB A1254 Calibration Standard Preparation Table (for High Level Curve)

Initial Volume (mL) A1254	Initial Conc. (ug/mL) A1254	Initial Volume (mL) 0.5/5.0 –ug/mL Surrogate	Final Volume (mL)	Final Concentration (ug/mL)		
				A1254	TCMX	DCBP
5.0	10.0	0	50	1.000	0	0
2.5	10.0	0	50	0.500	0	0
10.0	10.00	4.0	100	1.000	0.020	0.200
25.0*	1.000		50	0.500	0.010	0.100
1.25	10.0	0.800	50	0.250	0.008	0.080
0.500	10.0	0.500	50	0.100	0.005	0.050
1.000**	1.000	0.200	50	0.020	0.002	0.020

*This initial volume is of the A1254 1.000 ug/mL calibration standard WITH surrogates.
**This initial volume is of the A1254 1.000 ug/mL secondary stock solution WITHOUT surrogates.

Table 3A
PCB A1254, TCMX and DCBP Calibration Standard Preparation Table (for Low Level Curve)

Initial Volume A1254 (mL)	Initial Conc. A1254 (ug/mL)	Initial Volume (mL) 0.5/5.0 Surrogate	Final Volume (mL)	Final Concentration (ug/mL)		
				A1254	TCMX	DCBP
5.00	1.000	0.80	50	0.100	0.00800	0.0800
2.50	1.000	0.50	50	0.050	0.00500	0.0500
1.0	1.000	0.40	50	0.020	0.00400	0.0400
1.0	0.500	0.250	50	0.010	0.00250	0.0250
0.50	0.500	0.100	50	0.005	0.00100	0.0100

ATTACHMENT B

Table 1
PCB Continuing Calibration Working Standards
prepared from 1000 ug/mL Stock Standards

PCB	Initial Volume (mL)	Final Volume (mL)	Concentration (ug/mL)
A1016	1.0	100	10.0
A1221	1.0	100	10.0
A1232	1.0	100	10.0
A1242	1.0	100	10.0
A1248	1.0	100	10.0
A1254	1.0	100	10.0
A1260	1.0	100	10.0

Table 2
PCB Continuing Calibration Standards (High Level)
prepared from 10 ug/mL CCV Working Standards

PCB	Initial Volume (mL)	Final Volume (mL)	Concentration (ug/mL)
A1016	2.5	50	0.500
A1221	2.5	50	0.500
A1232	2.5	50	0.500
A1242	2.5	50	0.500
A1248	2.5	50	0.500
A1254 and Surrogate*	2.5 and 1.0	50	0.500 and (0.010/0.100)*
A1260	2.5	50	0.500

*Surrogate stock solution 0.500 ug/mL TCMX and 5.0 ug/mL DCBP

Table 3A
PCB Continuing Calibration Standards (low Level)
prepared from 0.500 PPM CCV Standards

PCB	Initial Volume (mL)	Final Volume (mL)	Concentration (ug/mL)
A1016	1.0	10	0.050
A1221	1.0	10	0.050
A1232	1.0	10	0.050
A1242	1.0	10	0.050
A1248	1.0	10	0.050
A1254 and Surrogate*	1.0 and 0.100*	10	0.0500 and (0.005/0.050)*
A1260	1.0	10	0.500

*Surrogate stock solution 0.500 ug/mL TCMX and 5.0 PPM ug/mL

Attachment C: Gas Chromatograph Operating Parameters:

GC-19 Low Level PCB Method

GC #:	**19**
Method:	**508 Low Level PCB**
GC Method #:	**5**
Date:	**10/27/2006**
Analyst:	**AJM**
File Name:	**S:\FORMS\LOG\GC\[GC19_Parameters.xls]8082 LL M5**
Column:	**19F ZB-1**
	19B ZB-5

Sample Delivery:

Single Method **Method 5**

CP-8400

Injection Mode:	**User**		
Sample Penetration Depth (%)	95	Viscosity Delay (sec)	1.0
Solvent Penetration Depth (%)	95	Plunger Speed During Fill (ul/sec)	1.0
		Plunger Speed During Injection (ul/sec)	5.0
Air Plug after Sample (ul)	1.0	Pre Injection Delay (sec)	3.0
Sample Air Gap	No	Post Injection Delay (sec)	3.0
Number of Fill Strokes	0		
Fill Volume for Fill Strokes	5.0		

Default Clean

Default Clean Vial	I
Default Clean Volume (ul)	5
Number of Clean Strokes	1
Default Clean Drawup Spped (ul/sec)	5

Clean Mode

Number of Pre-Injection Solvent Clean Flushes	1
Number of Post-Injection Solvent Clean Flushes	1
Number of Pre-Injection Sample Clean Flushes	0
Clean Solvent Source Vial	I+II

Solvent Plug

Vial for Solvent Plug	III
Solvent Plug Size (ul)	0.2
Solvent Drawup Speed (ul/sec)	5.0
Solvent Pause Time	1.0
Solvent Air Gap	NO

Select Edit

Select Automation Mode:	Single Method		
Edit Single Method Automation Method:	5		
Initial Sample:	0	Injection Possition	Both
Final Sample:	99	First Injector used	Pos. 1
Injections / Sample:	1	Use Injection Delay	No
First Injection Volume (ul):	1.1*	Delay between Injections	0.5
Second Injection Volume (ul):	1.3*	Advance Carrousel between Injections	No
	*can vary	Clean between Injections	Yes

Column Oven:

Step	Temp (°C)	Rate (°C/min)	Hold (min)	Total (min)
Initial	140	-------	2.00	2.00
2	200	10	0.00	8.00
3	245	5	13.23	30.23

Stabilization Time (min): 0.20

Injector: **Front CP-1177**

1177 Oven Power:	ON
1177 Temperature (°C)	300

Time	Split State	Split Ratio
Initial	ON	20

Flow/PSI(Front EFC, Type 1):

Step	Pres (psi)	Rate (psi/min)	Hold (min)	Total (min)
Initial	*23.1**	-------	30.30	30.30

*last adjustment

Constant Flow Mode Enable:	NO
Column Flow Rate (ml/min):	1.5

Injector: **Middle CP-1177**

1177 Oven Power:	ON
1177 Temperature (°C)	300

Time	Split State	Split Ratio
Initial	ON	20

Flow/PSI(Front EFC, Type 1):

Step	Pres (psi)	Rate (psi/min)	Hold (min)	Total (min)
Initial	*29.5**	-------	30.30	30.30

Constant Flow Mode Enable:	NO
Column Flow Rate (ml/min):	1.5

Detector: **Front ECD**

ECD Oven Power:	ON
Temperature (°C)	300
Electronics:	ON
Range:	1

Time	Range	Autozero
Initial	1	YES

Front ECD Adjustment	
Time Constant:	Fast
Cell Current:	CAP
Contact Potential (mV):	-110
Date of last adjustment	5/2/2006
Make-Up Flow (ml/min):	manually set and measured.

Middle ECD

ECD Oven Power:	**OFF**
Temperature (°C)	50
Electronics:	ON
Range:	1

Time	Range	Autozero
Initial	1	YES

Time Constant:	Fast
Cell Current:	CAP
Contact Potential (mV):	-20
Date of last adjustment	5/2/2006

Analog Output

Detectors: Front: ECD
Middle: ECD
Rear: None

Time	Signal Source	Attenuation
Initial	Front Detector	1
Time	Signal Source	Attenuation
Initial	Middle Detector	1
Time	Signal Source	Attenuation
Initial	Rear Detector	1

Valve Table:

Time	1 None	2 None	3 None	4 None	5 None	6 None	7 None
Initial	-----	-----	-----	-----	-----	-----	-----

Initial valve state=Off

GC-19 8082 High Level PCB Method

GC #:	**19**
Method:	**8082 High Level PCB**
GC Method #:	**7**
Date:	**2/15/2006**
Analyst:	**KLL**
File Name:	**S:\FORMS\LOG\GC\[GC19_Parameters.xls]8082 HL M7**
Column:	**19F ZB-1**
	19B ZB-5

Sample Delivery:

Single Method **Method 7**

CP-8400

Injection Mode:	**User**		
Sample Penetration Depth (%)	95	Viscosity Delay (sec)	1.0
Solvent Penetration Depth (%)	95	Plunger Speed During Fill (ul/sec)	1.0
		Plunger Speed During Injection (ul/sec)	5.0
Air Plug after Sample (ul)	1.0	Pre Injection Delay (sec)	3.0
Sample Air Gap	No	Post Injection Delay (sec)	3.0
Number of Fill Strokes	0		
Fill Volume for Fill Strokes	5.0		

Default Clean

Default Clean Vial	I
Default Clean Volume (ul)	5
Number of Clean Strokes	1
Default Clean Drawup Spped (ul/sec)	5

Clean Mode

Number of Pre-Injection Solvent Clean Flushes	1
Number of Post-Injection Solvent Clean Flushes	1
Number of Pre-Injection Sample Clean Flushes	0
Clean Solvent Source Vial	I+II

Solvent Plug

Vial for Solvent Plug	III
Solvent Plug Size (ul)	0.2
Solvent Drawup Speed (ul/sec)	5.0
Solvent Pause Time	1.0
Solvent Air Gap	NO

Select Edit

Select Automation Mode:	Single Method		
Edit Single Method Automation Method:	7		
Initial Sample:	0	Injection Possition	Both
Final Sample:	99	First Injector used	Pos. 1
Injections / Sample:	1	Use Injection Delay	No
First Injection Volume (ul):	1	Delay between Injections	0.5
Second Injection Volume (ul):	1	Advance Carrousel between Injections	No
		Clean between Injections	Yes

Column Oven:

Step	Temp (°C)	Rate (°C/min)	Hold (min)	Total (min)
Initial	140	-------	2.00	2.00
2	200	10	0.00	8.00
3	245	5	13.23	30.23

Stabilization Time (min): 0.20

Injector: Front CP-1177

1177 Oven Power:	ON
1177 Temperature (°C)	300

Time	Split State	Split Ratio
Initial	ON	35

Flow/PSI(Front EFC, Type 1):

Injector: Middle CP-1177

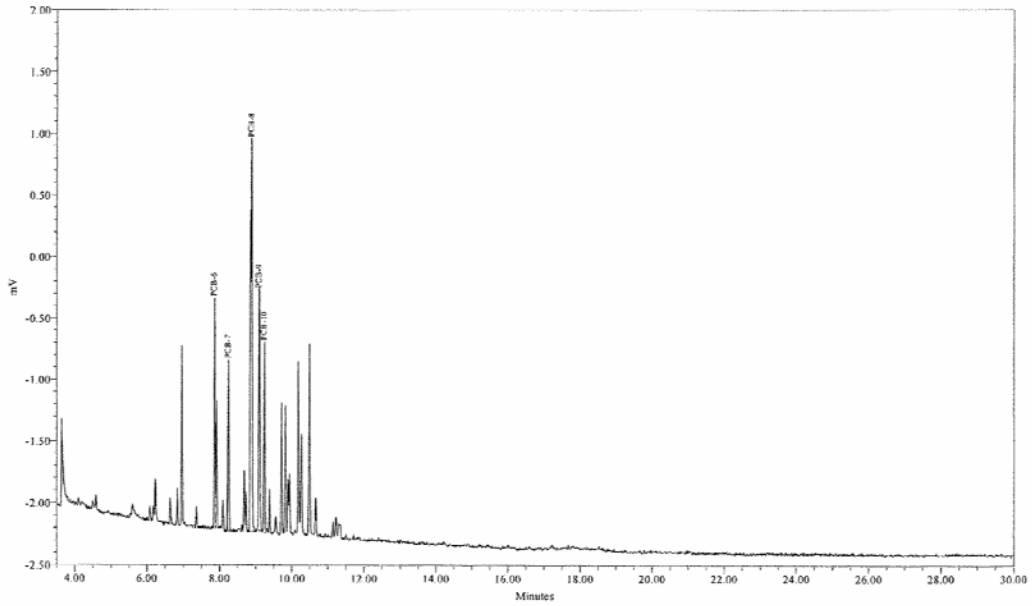
1177 Oven Power:	ON
1177 Temperature (°C)	300

Time	Split State	Split Ratio
Initial	ON	35

Flow/PSI(Front EFC, Type 1):

ATTACHMENT D

Northeast Analytical, Inc., 2190 Technology Drive, Schenectady, NY 12308
Phone: (518) 346-4592 Fax: (518) 381-6055
www.nealab.com

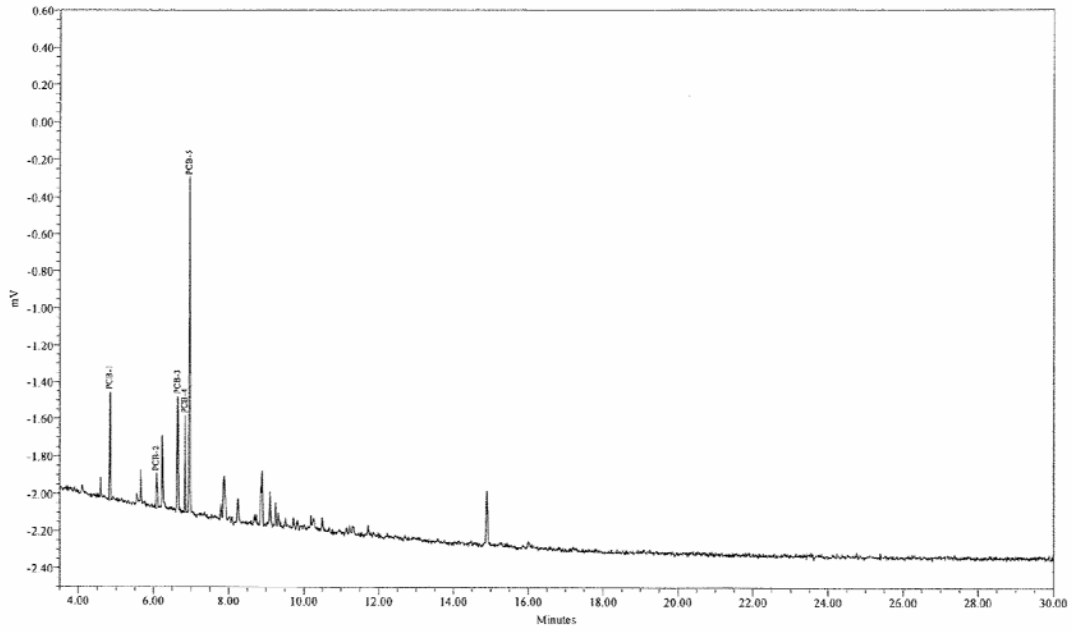


Sample Name:	042116E	Sample Amount:	1
Sample ID:	A1016 100 PPB	Dilution:	1
Date Acquired:	04/21/2008 13:28:12 EDT	Processing Method:	GC11_CC_042308
		LIMS File ID:	GC11-680-34

Sample Name: 042116E

1 of 1

Northeast Analytical, Inc., 2190 Technology Drive, Schenectady, NY 12308
Phone: (518) 346-4592 Fax: (518) 381-6055
www.nealab.com



Sample Name:	042121E	Sample Amount:	1
Sample ID:	A1221 100 PPB	Dilution:	1
Date Acquired:	04/21/2008 16:09:05 EDT	Processing Method:	GC11_CC_042308
		LIMS File ID:	GC11-680-39

Sample Name: 042121E

1 of 1

Northeast Analytical, Inc., 2190 Technology Drive, Schenectady, NY 12308
Phone: (518) 346-4592 Fax: (518) 381-6055
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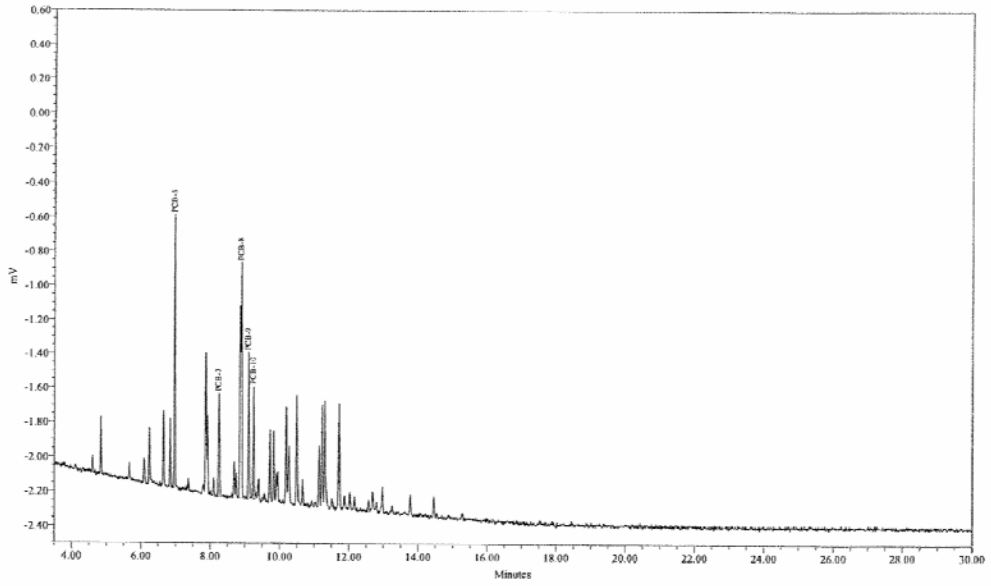
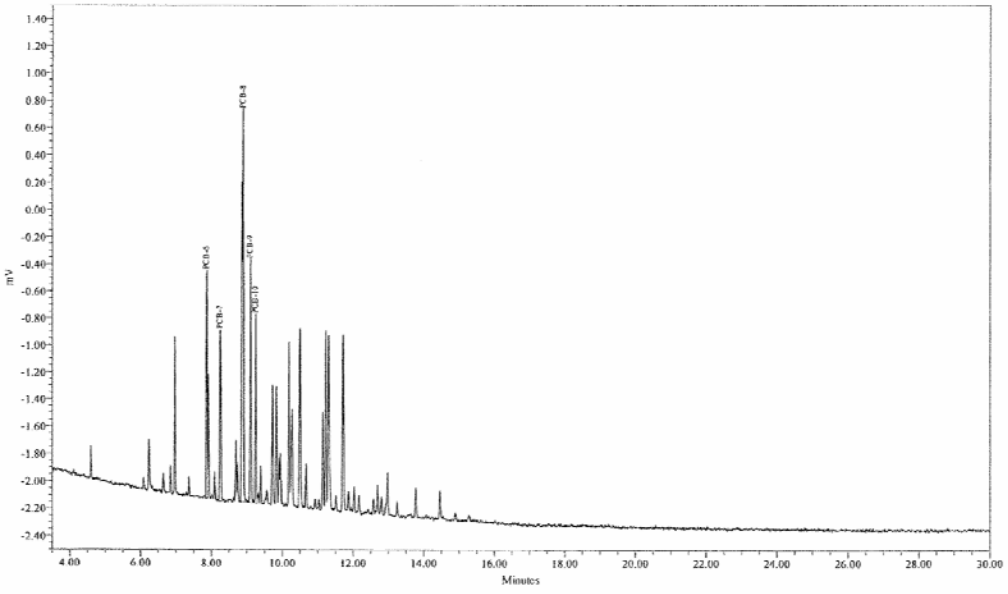


Sample Name:	042132E	Sample Amount:	1
Sample ID:	A1232 100 PPB	Dilution:	1
Date Acquired:	04/21/2008 18:49:56 EDT	Processing Method:	GC11_CC_042308
		LIMS File ID:	GC11-680-44

Sample Name: 042132E

1 of 1

Northeast Analytical, Inc., 2190 Technology Drive, Schenectady, NY 12308
Phone: (518) 346-4592 Fax: (518) 381-6055
www.nealab.com



Sample Name:	042242E	Sample Amount:	1
Sample ID:	A1242 100 PPB	Dilution:	1
Date Acquired:	04/22/2008 19:32:46 EDT	Processing Method:	GC11_CC_042308
		LIMS File ID:	GC11-680-39

Sample Name: 042242E

1 of 1

Northeast Analytical, Inc., 2190 Technology Drive, Schenectady, NY 12308
Phone: (518) 346-4592 Fax: (518) 381-6055
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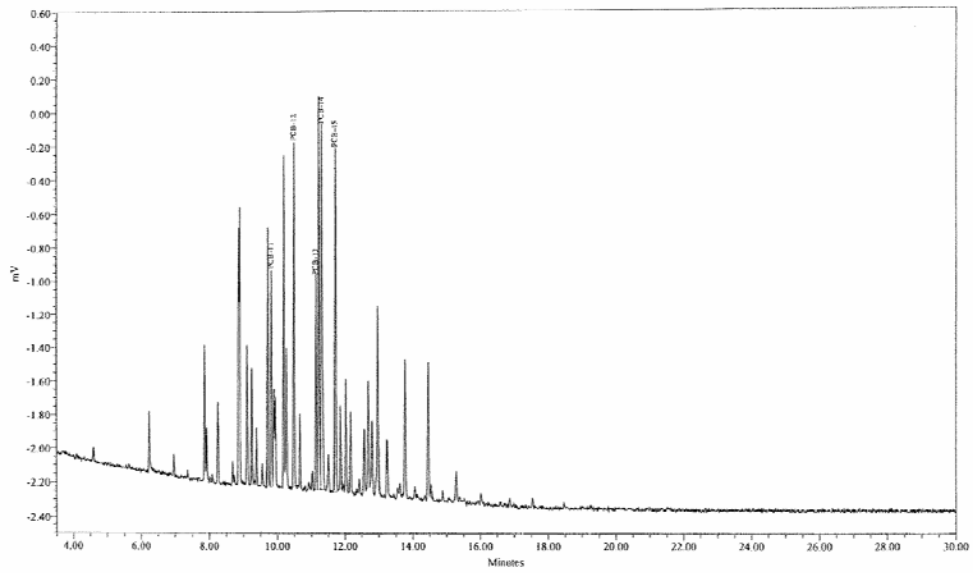

Sample Name:	042148E	Sample Amount:	1
Sample ID:	A1248 100 PPB	Dilution:	1
Date Acquired:	04/22/2008 00:11:42 EDT	Processing Method:	GC11_CC_042308
		LIMS File ID:	GC11-680-49

Sample Name: 042148E

1 of 1

Northeast Analytical, Inc., 2190 Technology Drive, Schenectady, NY 12308
Phone: (518) 346-4592 Fax: (518) 381-6055
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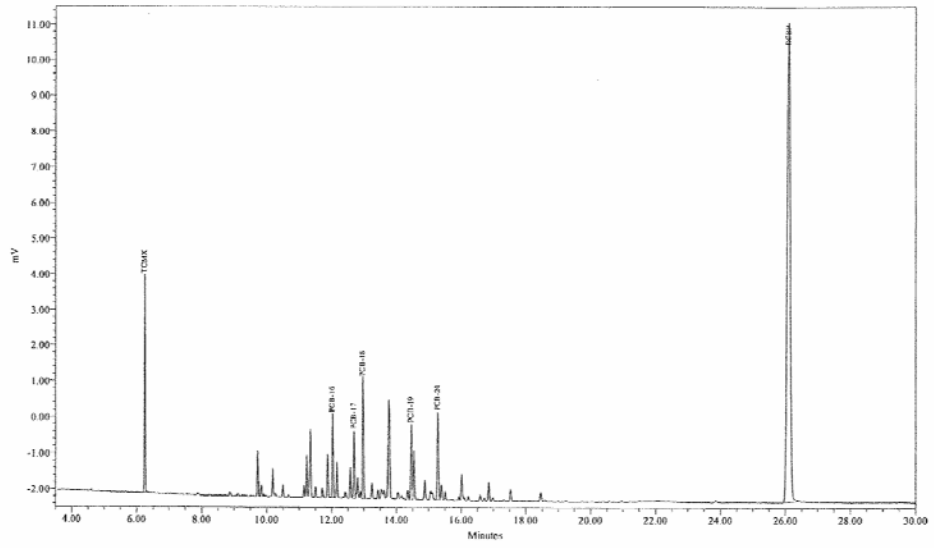
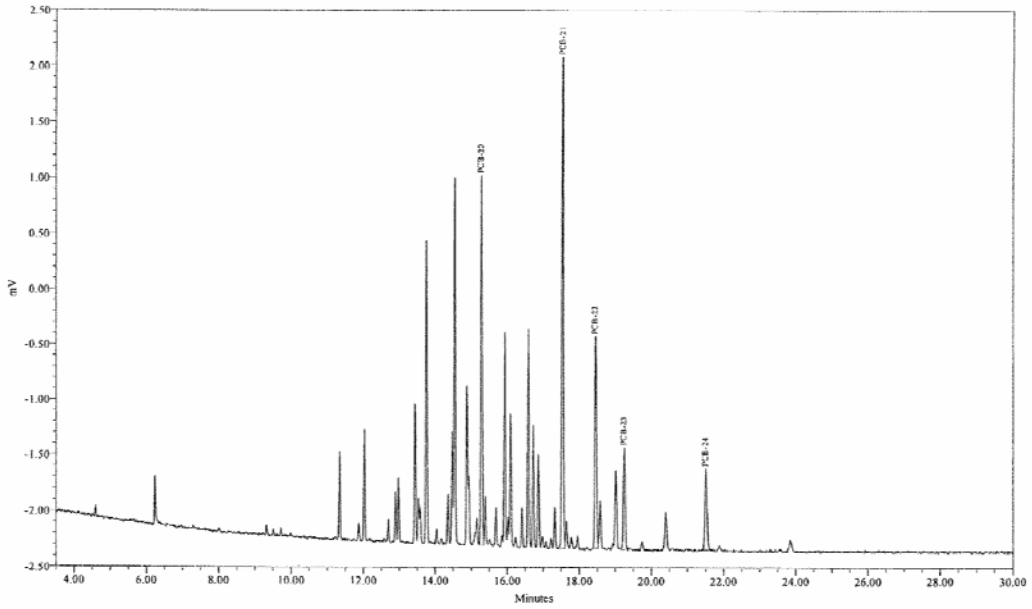


Sample Name:	042354E	Sample Amount:	1
Sample ID:	A1254 100 PPB	Dilution:	1
Date Acquired:	04/23/2008 16:26:25 EDT	Processing Method:	GC11_CC_042308
		LIMS File ID:	GC11-680-8

Sample Name: 042354E

1 of 1

Northeast Analytical, Inc., 2190 Technology Drive, Schenectady, NY 12308
Phone: (518) 346-4592 Fax: (518) 381-6055
www.nealab.com



Sample Name:	042160E	Sample Amount:	1
Sample ID:	A1260 100 PPB	Dilution:	1
Date Acquired:	04/22/2008 06:05:42 EDT	Processing Method:	GC11_CC_042308
		LIMS File ID:	GC11-680-54

Sample Name: 042160E

1 of 1

ATTACHMENT E

Northeast Analytical Inc 03/30/06

Retention Time Window Study Instrument: GC 11

for Aroclors (PCB) by GC/ECD Column: DB-1

EPA Method 508

Analyte	PEAK	Standard 1 50 PPB R.T. Min	Standard 2 50 PPB R.T. Min	Standard 3 50 PPB R.T. Min	STD. DEV Min	%RSD	Window +/- Min.
		CS_0327A	CS_0328A	CS_0329A			
Aroclor 1016	6	8.304	8.300	8.298	0.0031	0.0368	0.009
	7	8.680	8.675	8.673	0.0036	0.0416	0.011
	8	9.295	9.290	9.288	0.0036	0.0388	0.011
	9	9.501	9.497	9.494	0.0035	0.0370	0.011
	10	9.640	9.635	9.633	0.0036	0.0374	0.011
Aroclor 1221	1	5.455	5.452	5.450	0.0025	0.0462	0.008
	2	6.636	6.634	6.640	0.0031	0.0460	0.009
	3	7.164	7.159	7.159	0.0029	0.0403	0.009
	4	7.348	7.343	7.342	0.0032	0.0438	0.010
	5	7.461	7.456	7.455	0.0032	0.0431	0.010
Aroclor 1232	5	7.460	7.454	7.457	0.0030	0.0402	0.009
	7	8.681	8.671	8.676	0.0050	0.0576	0.015
	8	9.295	9.288	9.291	0.0035	0.0378	0.011
	9	9.501	9.494	9.498	0.0035	0.0370	0.011
	10	9.640	9.631	9.636	0.0045	0.0468	0.014
Aroclor 1242	6	8.301	8.301	8.297	0.0023	0.0278	0.007
	7	8.675	8.676	8.673	0.0015	0.0176	0.005
	8	9.291	9.292	9.288	0.0021	0.0224	0.006
	9	9.497	9.498	9.493	0.0026	0.0279	0.008
	10	9.636	9.636	9.632	0.0023	0.0240	0.007
Aroclor 1248	11	10.191	10.192	10.188	0.0021	0.0204	0.006
	12	10.834	10.836	10.831	0.0025	0.0232	0.008
	13	11.457	11.458	11.455	0.0015	0.0133	0.005
	14	11.614	11.616	11.611	0.0025	0.0217	0.008
	15	12.008	12.008	12.004	0.0023	0.0192	0.007
Arolcor 1254	16	12.303	12.302	12.304	0.0010	0.0081	0.003
	17	12.941	12.941	12.941	0.0000	0.0000	0.000
	18	13.212	13.210	13.211	0.0010	0.0076	0.003
	19	14.631	14.631	14.632	0.0006	0.0039	0.002

	20	15.410	15.411	15.411	0.0006	0.0037	0.002
Arolcor 1260	20	15.411	15.414	15.406	0.0040	0.0262	0.012
	21	17.551	17.554	17.544	0.0051	0.0292	0.015
	22	18.428	18.433	18.422	0.0055	0.0299	0.017
	23	19.185	19.195	19.180	0.0076	0.0398	0.023
	24	21.362	21.366	21.352	0.0072	0.0338	0.022
TCMX (SURROGATE)	Surr.	6.803	6.801	6.801	0.0012	0.0170	0.003
DCB (SURROGATE)	Surr.	25.790	25.791	25.791	0.0006	0.0022	0.002

Northeast Analytical, Inc.

Method Detection Limits

Date: 10-Apr-06

Method Detection Limit (MDL) calculations as based on procedures outlined in 40 CFR, part 136, App B; 1-July-85.

Compound:	A1016	Analysis:	EPA METHOD 508
Matrix:	WATER	Instrument:	GC-11
Extraction:	CLLE	Column:	DB-1
Spike conc:	50.0 ng/L		

NEA Sample ID	Extraction Date	File Name	Analysis Date	Measured Concentration ng/L	Percent Recovery (%)
A1016/A1260 # 1 CLLE	03/23/06	AJ02939	03/24/06	50.8	102%
A1016/A1260 # 2 CLLE	03/23/06	AJ02940	03/24/06	44.2	88.3%
A1016/A1260 # 3 CLLE	03/23/06	AJ02941	03/24/06	43.1	86.2%
A1016/A1260 # 4 CLLE	03/23/06	AJ02942	03/24/06	45.5	91.0%
A1016/A1260 # 5 CLLE	03/23/06	AJ02943	03/24/06	46.8	93.6%
A1016/A1260 # 6 CLLE	03/23/06	AJ02944	03/24/06	47.5	95.0%
A1016/A1260 # 7 CLLE	03/23/06	AJ02945	03/24/06	45.9	91.7%
A1016/A1260 # 8 CLLE	03/23/06	AJ02946	03/24/06	43.6	87.2%

One sided Student's t values (t) at the 99% confidence level.

Number (n)	(t) value
7	3.143
8	2.998

Number (n):	8	
AVG:	45.9	ng/L
STD (s):	2.49	ng/L
%RSD:	5.42%	
MDL:	7.46	ng/L
PQL:	37.3	ng/L
VALID:	Yes	

MDL calculations:

MDL = t * s

Where:
t = one sided Student's t value for the number of replicates at the 99% level
s = standard deviation of the population

PQL calculations:

PQL = MDL * 5

Northeast Analytical, Inc.

Method Detection Limits

Date: 10-Apr-06

Method Detection Limit (MDL) calculations as based on procedures outlined in 40 CFR, part 136, App B; 1-July-85.

Compound:	A1221	Analysis:	EPA METHOD 508
Matrix:	WATER	Instrument:	GC-11
Extraction:	CLLE	Column:	DB-1
Spike conc:	50.0 ng/L		

NEA Sample ID	Extraction Date	File Name	Analysis Date	Measured Concentration ng/L	Percent Recovery (%)
A1221/A1254 # 1 CLLE	04/07/06	AJ02947	04/07/06	50.8	102%
A1221/A1254 # 1 CLLE	04/07/06	AJ02948	04/07/06	45.5	91.1%
A1221/A1254 # 1 CLLE	04/07/06	AJ02949	04/07/06	47.7	95.5%
A1221/A1254 # 1 CLLE	04/07/06	AJ02950	04/07/06	42.5	85.0%
A1221/A1254 # 1 CLLE	04/07/06	AJ02951	04/07/06	53.2	106%
A1221/A1254 # 1 CLLE	04/07/06	AJ02952	04/07/06	46.2	92.3%
A1221/A1254 # 1 CLLE	04/07/06	AJ02953	04/07/06	52.7	105%
A1221/A1254 # 1 CLLE	04/07/06	AJ02954	04/07/06	50.3	101%

One sided Student's t values (t) at the 99% confidence level.

Number (n)	(t) value
7	3.143
8	2.998

Number (n):	8	
AVG:	48.6	ng/L
STD (s):	3.76	ng/L
%RSD:	7.74%	
MDL:	11.28	ng/L
PQL:	56.4	ng/L
VALID:	Yes	

MDL calculations:

MDL = t * s

Where:
t = one sided Student's t value for the number of replicates at the 99% level
s = standard deviation of the population

Northeast Analytical, Inc.

Method Detection Limits

Date: 25-Apr-06

Method Detection Limit (MDL) calculations as based on procedures outlined in 40 CFR, part 136, App B; 1-July-85.

Compound:	A1232	Analysis:	EPA METHOD 508
Matrix:	WATER	Instrument:	GC-11
Extraction:	CLLE	Column:	DB-1
Spike conc:	50.0 ng/L		

NEA Sample ID	Extraction Date	File Name	Analysis Date	Measured Concentration ng/L	Percent Recovery (%)
A1232 CLLE #1	04/14/06	AJ02955	04/14/06	43.5	86.9%
A1232 CLLE #2	04/14/06	AJ02956	04/14/06	50.9	102%
A1232 CLLE #3	04/14/06	AJ02957	04/14/06	47.5	95.1%
A1232 CLLE #4	04/14/06	AJ02958	04/14/06	48.4	96.8%
A1232 CLLE #5	04/14/06	AJ02959	04/14/06	47.8	95.5%
A1232 CLLE #6	04/14/06	AJ02960	04/14/06	49.5	99.0%
A1232 CLLE #7	04/14/06	AJ02961	04/14/06	50.4	101%
A1232 CLLE #8	04/14/06	AJ02962	04/14/06	44.4	88.8%

One sided Student's t values (t) at the 99% confidence level.

Number (n)	(t) value
7	3.143
8	2.998

Number (n):	8	
AVG:	47.8	ng/L
STD (s):	2.68	ng/L
%RSD:	5.60%	
MDL:	8.03	ng/L
PQL:	40.1	ng/L
VALID:	Yes	

MDL calculations:

MDL = t * s

Where:
t = one sided Student's t value for the number of replicates at the 99% level
s = standard deviation of the population

PQL calculations:

PQL = MDL * 5

Northeast Analytical, Inc.

Method Detection Limits

Date: 10-Apr-06

Method Detection Limit (MDL) calculations as based on procedures outlined in 40 CFR, part 136, App B; 1-July-85.

Compound:	A1242	Analysis:	EPA METHOD 508
Matrix:	WATER	Instrument:	GC-11
Extraction:	CLLE	Column:	DB-1
Spike conc:	50.0 ng/L		

NEA Sample ID	Extraction Date	File Name	Analysis Date	Measured Concentration ng/L	Percent Recovery (%)
A1242 #1 CLLE	03/28/06	AJ02963	03/31/06	46.0	92.0%
A1242 #1 CLLE	03/28/06	AJ02964	03/31/06	48.6	97.1%
A1242 #1 CLLE	03/28/06	AJ02965	03/31/06	48.1	96.1%
A1242 #1 CLLE	03/28/06	AJ02966	03/31/06	48.3	96.7%
A1242 #1 CLLE	03/28/06	AJ02967	03/31/06	44.0	88.0%
A1242 #1 CLLE	03/28/06	AJ02968	04/01/06	51.4	103%
A1242 #1 CLLE	03/28/06	AJ02969	04/01/06	48.8	97.6%
A1242 #1 CLLE	03/28/06	AJ02970	04/01/06	50.9	102%

One sided Student's t values (t) at the 99% confidence level.

Number (n)	(t) value
7	3.143
8	2.998

Number (n):	8	
AVG:	48.3	ng/L
STD (s):	2.41	ng/L
%RSD:	4.99%	
MDL:	7.23	ng/L
PQL:	36.1	ng/L
VALID:	Yes	

MDL calculations:

MDL = t * s

Where:
t = one sided Student's t value for the number of replicates at the 99% level
s = standard deviation of the population

PQL calculations:

PQL = MDL * 5

Northeast Analytical, Inc.

Method Detection Limits

Date: 25-Apr-06

Method Detection Limit (MDL) calculations as based on procedures outlined in 40 CFR, part 136, App B; 1-July-85.

Compound:	A1248	Analysis:	EPA METHOD 508
Matrix:	WATER	Instrument:	GC-11
Extraction:	CLLE	Column:	DB-1
Spike conc:	50.0 ng/L		

NEA Sample ID	Extraction Date	File Name	Analysis Date	Measured Concentration ng/L	Percent Recovery (%)
A1248 CLLE #1	04/11/06	AJ02971	04/11/06	50.4	101%
A1248 CLLE #2	04/11/06	AJ02972	04/11/06	51.1	102%
A1248 CLLE #3	04/11/06	AJ02973	04/11/06	47.9	95.7%
A1248 CLLE #4	04/11/06	AJ02974	04/11/06	51.3	103%
A1248 CLLE #5	04/11/06	AJ02975	04/11/06	51.4	103%
A1248 CLLE #6	04/11/06	AJ02976	04/11/06	54.4	109%
A1248 CLLE #7	04/11/06	AJ02977	04/11/06	56.4	113%
A1248 CLLE #8	04/11/06	AJ02978	04/11/06	52.2	104%

One sided Student's t values (t) at the 99% confidence level.

Number (n)	(t) value
7	3.143
8	2.998

Number (n):	8	
AVG:	51.9	ng/L
STD (s):	2.57	ng/L
%RSD:	4.96%	
MDL:	7.71	ng/L
PQL:	38.5	ng/L
VALID:	Yes	

MDL calculations:

MDL = t * s

Where:
t = one sided Student's t value for the number of replicates at the 99% level
s = standard deviation of the population

PQL calculations:

PQL = MDL * 5

Northeast Analytical, Inc.

Method Detection Limits

Date: 10-Apr-06

Method Detection Limit (MDL) calculations as based on procedures outlined in 40 CFR, part 136, App B; 1-July-85.

Compound:	A1254	Analysis:	EPA METHOD 508
Matrix:	WATER	Instrument:	GC-11
Extraction:	CLLE	Column:	DB-1
Spike conc:	50.0 ng/L		

NEA Sample ID	Extraction Date	File Name	Analysis Date	Measured Concentration ng/L	Percent Recovery (%)
A1221/A1254 # 1 CLLE	04/07/06	AJ02947	04/07/06	54.3	109%
A1221/A1254 # 1 CLLE	04/07/06	AJ02948	04/07/06	58.0	116%
A1221/A1254 # 1 CLLE	04/07/06	AJ02949	04/07/06	54.2	108%
A1221/A1254 # 1 CLLE	04/07/06	AJ02950	04/07/06	52.0	104%
A1221/A1254 # 1 CLLE	04/07/06	AJ02951	04/07/06	49.5	99.0%
A1221/A1254 # 1 CLLE	04/07/06	AJ02952	04/07/06	55.0	110%
A1221/A1254 # 1 CLLE	04/07/06	AJ02953	04/07/06	48.7	97.3%
A1221/A1254 # 1 CLLE	04/07/06	AJ02954	04/07/06	57.4	115%

One sided Student's t values (t) at the 99% confidence level.

Number (n)	(t) value
7	3.143
8	2.998

Number (n):	8	
AVG:	53.6	ng/L
STD (s):	3.37	ng/L
%RSD:	6.29%	
MDL:	10.11	ng/L
PQL:	50.5	ng/L
VALID:	Yes	

MDL calculations:

MDL = t * s

Where:
t = one sided Student's t value for the number of replicates at the 99% level
s = standard deviation of the population

PQL calculations: PQL = MDL * 5

Northeast Analytical, Inc.

Method Detection Limits

Date: 10-Apr-06

Method Detection Limit (MDL) calculations as based on procedures outlined in 40 CFR, part 136, App B; 1-July-85.

Compound:	A1260	Analysis:	EPA METHOD 508
Matrix:	WATER	Instrument:	GC-11
Extraction:	CLLE	Column:	DB-1
Spike conc:	50.0 ng/L		

NEA Sample ID	Extraction Date	File Name	Analysis Date	Measured Concentration ng/L	Percent Recovery (%)
A1016/A1260 # 1 CLLE	03/23/06	AJ02939	03/24/06	55.2	110%
A1016/A1260 # 2 CLLE	03/23/06	AJ02940	03/24/06	54.9	110%
A1016/A1260 # 3 CLLE	03/23/06	AJ02941	03/24/06	50.6	101%
A1016/A1260 # 4 CLLE	03/23/06	AJ02942	03/24/06	51.6	103%
A1016/A1260 # 5 CLLE	03/23/06	AJ02943	03/24/06	56.5	113%
A1016/A1260 # 6 CLLE	03/23/06	AJ02944	03/24/06	51.0	102%
A1016/A1260 # 7 CLLE	03/23/06	AJ02945	03/24/06	54.7	109%
A1016/A1260 # 8 CLLE	03/23/06	AJ02946	03/24/06	55.5	111%

Number (n):	8	
AVG:	53.8	ng/L
STD (s):	2.30	ng/L
%RSD:	4.28%	
MDL:	6.90	ng/L
PQL:	34.5	ng/L
VALID:	Yes	

One sided Student's t values (t) at the 99% confidence level.

Number (n)	(t) value
7	3.143
8	2.998

MDL calculations:

MDL = t * s

Where:
t = one sided Student's t value for the number of replicates at the 99% level
s = standard deviation of the population

PQL calculations: PQL = MDL * 5

Northeast Analytical Inc.

Quality Assurance/Quality Control

Date: 03/18/08

MDL VERIFICATION STUDY

Method(s):	SW-846 508	Analysis:	External Standard
Compound:	7 Aroclors	Instrument:	GC-11
Matrix:	Liquid	Column:	DB-1
Extraction:	CLLE	Detector:	ECD
Spike Concentration:	0.030 ug/L		
Date Extracted:	02/07/07		
Date Analyzed:	02/09/07		

NEA Sample I.D.	LRF #	PCB Aroclor	Spiked Concentration ug/L	Measured Concentration ug/L	Percent Recovery	Recovery Limits* %
AK00544	07010080	Aroclor 1016	0.030	0.034	114	>0
AK00545	07010081	Aroclor 1221	0.030	0.031	104	>0
AK00546	07010082	Aroclor 1232	0.030	0.024	81.0	>0
AK00547	07010083	Aroclor 1242	0.030	0.037	122	>0
AK00548	07010084	Aroclor 1248	0.030	0.030	100	>0
AK00549	07010085	Aroclor 1254	0.030	0.028	94.8	>0
AK00550	07010086	Aroclor 1260	0.030	0.029	96.4	>0

*No Recovery Limits Ranges exist for qualitative MDL verification analysis as per NELAC Quality Systems 2003. Each analyte must be observed however with recovery greater than zero.

Northeast Analytical Inc.

Date: 03/18/08

Quality Assurance/Quality Control

MDL VERIFICATION STUDY

Method(s):	508	Analysis:	External Standard
Compound:	7 Aroclors	Instrument:	GC-11
Matrix:	Liquid	Column:	DB-1
Extraction:	CLLE	Detector:	ECD
Spike Concentration:	0.030 ug/L		
Date Extracted:	02/07/07		
Date Analyzed:	02/09/07		

NEA Sample I.D.	LRF #	PCB Aroclor	Spiked Concentration ug/L	Measured Concentration ug/L	Percent Recovery	Recovery Limits* %
AK00544	07010080	Aroclor 1016	0.030	0.034	114	>0
AK00545	07010081	Aroclor 1221	0.030	0.031	104	>0
AK00546	07010082	Aroclor 1232	0.030	0.024	81.0	>0
AK00547	07010083	Aroclor 1242	0.030	0.037	122	>0
AK00548	07010084	Aroclor 1248	0.030	0.030	100	>0
AK00549	07010085	Aroclor 1254	0.030	0.028	94.8	>0
AK00550	07010086	Aroclor 1260	0.030	0.029	96.4	>0

*No Recovery Limits Ranges exist for qualitative MDL verification analysis as per NELAC Quality Systems 2003. Each analyte must be observed however with recovery greater than zero.

Northeast Analytical, Inc.

Method Detection Limits

Date: 28-Jun-06

Method Detection Limit (MDL) calculations as based on procedures outlined in 40 CFR, part 136, App B; 1-July-85.

Compound:	A1016	Analysis:	EPA METHOD 508
Matrix:	WATER	Instrument:	GC-19B
Extraction:	Sep. Funnel	Column:	ZB-5
Spike conc:	50.0 ng/L		

NEA Sample ID	Extraction Date	File Name	Analysis Date	Measured Concentration ng/L	Percent Recovery (%)
A1016/A1260 #1 SEPFUN	04/28/06	AJ04170	06/23/06	41.6	83.2%
A1016/A1260 #2 SEPFUN	04/28/06	AJ04171	06/23/06	44.3	88.7%
A1016/A1260 #3 SEPFUN	04/28/06	AJ04172	06/23/06	48.9	97.8%
A1016/A1260 #4 SEPFUN	04/28/06	AJ04173	06/23/06	47.7	95.3%
A1016/A1260 #5 SEPFUN	04/28/06	AJ04174	06/23/06	49.6	99.2%
A1016/A1260 #6 SEPFUN	04/28/06	AJ04175	06/23/06	46.5	93.0%
A1016/A1260 #7 SEPFUN	04/28/06	AJ04176	06/23/06	48.8	97.6%
A1016/A1260 #8 SEPFUN	04/28/06	AJ04177	06/23/06	48.1	96.2%

Number (n):	8	
AVG:	46.9	ng/L
STD (s):	2.73	ng/L
%RSD:	5.81%	
MDL:	8.18	ng/L
PQL:	40.9	ng/L
VALID:	Yes	

One sided Student's t values (t) at the 99% confidence level.

Number (n)	(t) value
7	3.143
8	2.998

MDL calculations:

MDL = t * s

Where:
t = one sided Student's t value for the number of replicates at the 99% level
s = standard deviation of the population

Northeast Analytical, Inc.

Method Detection Limits

Date: 28-Jun-06

Method Detection Limit (MDL) calculations as based on procedures outlined in 40 CFR, part 136, App B; 1-July-85.

Compound:	A1221	Analysis:	EPA METHOD 508
Matrix:	WATER	Instrument:	GC-19B
Extraction:	Sep. Funnel	Column:	ZB-5
Spike conc:	50.0 ng/L		

NEA Sample ID	Extraction Date	File Name	Analysis Date	Measured Concentration ng/L	Percent Recovery (%)
A1221/A1254 # 1 CLLE	05/08/06	AJ04178	06/24/06	51.3	103%
A1221/A1254 # 1 CLLE	05/08/06	AJ04179	06/24/06	49.7	99.4%
A1221/A1254 # 1 CLLE	05/08/06	AJ04180	06/24/06	44.2	88.4%
A1221/A1254 # 1 CLLE	05/08/06	AJ04181	06/24/06	47.9	95.8%
A1221/A1254 # 1 CLLE	05/08/06	AJ04182	06/24/06	44.2	88.5%
A1221/A1254 # 1 CLLE	05/08/06	AJ04183	06/24/06	45.4	90.8%
A1221/A1254 # 1 CLLE	05/08/06	AJ04184	06/24/06	50.3	101%
A1221/A1254 # 1 CLLE	05/08/06	AJ04185	06/24/06	52.8	106%

One sided Student's t values (t) at the 99% confidence level.

Number (n)	(t) value
7	3.143
8	2.998

Number (n):	8	
AVG:	48.2	ng/L
STD (s):	3.31	ng/L
%RSD:	6.87%	
MDL:	9.93	ng/L
PQL:	49.7	ng/L
VALID:	Yes	

MDL calculations:

MDL = t * s

Where:
t = one sided Student's t value for the number of replicates at the 99% level
s = standard deviation of the population

PQL calculations: PQL = MDL * 5

Northeast Analytical, Inc.

Method Detection Limits

Date: 28-Jun-06

Method Detection Limit (MDL) calculations as based on procedures outlined in 40 CFR, part 136, App B; 1-July-85.

Compound:	A1232	Analysis:	EPA METHOD 508
Matrix:	WATER	Instrument:	GC-19B
Extraction:	Sep. Funnel	Column:	ZB-5
Spike conc:	50.0 ng/L		

NEA Sample ID	Extraction Date	File Name	Analysis Date	Measured Concentration ng/L	Percent Recovery (%)
A1232 #1 SEPFUN	05/23/06	AJ04186	06/24/06	55.3	111%
A1232 #2 SEPFUN	05/23/06	AJ04187	06/24/06	57.5	115%
A1232 #3 SEPFUN	05/23/06	AJ04188	06/24/06	51.2	102%
A1232 #4 SEPFUN	05/23/06	AJ04189	06/24/06	49.3	98.7%
A1232 #5 SEPFUN	05/23/06	AJ04190	06/24/06	53.1	106%
A1232 #6 SEPFUN	05/23/06	AJ04191	06/24/06	47.1	94.3%
A1232 #7 SEPFUN	05/23/06	AJ04192	06/24/06	53.1	106%
A1232 #8 SEPFUN	05/23/06	AJ04193	06/24/06	54.8	110%

One sided Student's t values (t) at the 99% confidence level.

Number (n)	(t) value
7	3.143
8	2.998

Number (n):	8	
AVG:	52.7	ng/L
STD (s):	3.36	ng/L
%RSD:	6.39%	
MDL:	10.08	ng/L
PQL:	50.4	ng/L
VALID:	Yes	

MDL calculations:

MDL = t * s

Where:
t = one sided Student's t value for the number of replicates at the 99% level
s = standard deviation of the population

PQL calculations:

PQL = MDL * 5

Northeast Analytical, Inc.

Method Detection Limits

Date: 28-Jun-06

Method Detection Limit (MDL) calculations as based on procedures outlined in 40 CFR, part 136, App B; 1-July-85.

Compound:	A1242	Analysis:	EPA METHOD 508
Matrix:	WATER	Instrument:	GC-19B
Extraction:	Sep. Funnel	Column:	ZB-5
Spike conc:	50.0 ng/L		

NEA Sample ID	Extraction Date	File Name	Analysis Date	Measured Concentration ng/L	Percent Recovery (%)
A1242 #1 SEPFUN	06/20/06	AJ04194	06/24/06	46.2	92.5%
A1242 #2 SEPFUN	06/20/06	AJ04195	06/24/06	50.9	102%
A1242 #3 SEPFUN	06/20/06	AJ04196	06/24/06	52.4	105%
A1242 #4 SEPFUN	06/20/06	AJ04197	06/24/06	48.2	96.5%
A1242 #5 SEPFUN	06/20/06	AJ04198	06/24/06	52.2	104%
A1242 #6 SEPFUN	06/20/06	AJ04199	06/24/06	50.3	101%
A1242 #7 SEPFUN	06/20/06	AJ04200	06/24/06	52.5	105%
A1242 #8 SEPFUN	06/20/06	AJ04201	06/24/06	46.1	92.2%

Number (n):	8	
AVG:	49.8	ng/L
STD (s):	2.67	ng/L
%RSD:	5.35%	
MDL:	7.99	ng/L
PQL:	40.0	ng/L
VALID:	Yes	

One sided Student's t values (t) at the 99% confidence level.

Number (n)	(t) value
7	3.143
8	2.998

MDL calculations:

MDL = t * s

Where:
t = one sided Student's t value for the number of replicates at the 99% level
s = standard deviation of the population

PQL calculations:

PQL = MDL * 5

Northeast Analytical, Inc.

Method Detection Limits

Date: 28-Jun-06

Method Detection Limit (MDL) calculations as based on procedures outlined in 40 CFR, part 136, App B; 1-July-85.

Compound:	A1248	Analysis:	EPA METHOD 508
Matrix:	WATER	Instrument:	GC-19B
Extraction:	Sep. Funnel	Column:	ZB-5
Spike conc:	50.0 ng/L		

NEA Sample ID	Extraction Date	File Name	Analysis Date	Measured Concentration ng/L	Percent Recovery (%)
A1248 #1 SEPFUN	04/25/06	AJ04202	06/24/06	43.7	87.4%
A1248 #2 SEPFUN	04/25/06	AJ04203	06/24/06	44.2	88.5%
A1248 #3 SEPFUN	04/25/06	AJ04204	06/24/06	41.5	82.9%
A1248 #4 SEPFUN	04/25/06	AJ04205	06/24/06	43.9	87.9%
A1248 #5 SEPFUN	04/25/06	AJ04206	06/24/06	46.1	92.2%
A1248 #6 SEPFUN	04/25/06	AJ04207	06/24/06	42.0	84.1%
A1248 #7 SEPFUN	04/25/06	AJ04208	06/24/06	50.3	101%
A1248 #8 SEPFUN	04/25/06	AJ04209	06/24/06	49.7	99.4%

Number (n):	8	
AVG:	45.2	ng/L
STD (s):	3.30	ng/L
%RSD:	7.30%	
MDL:	9.89	ng/L
PQL:	49.4	ng/L
VALID:	Yes	

One sided Student's t values (t) at the 99% confidence level.

Number (n)	(t) value
7	3.143
8	2.998

MDL calculations:

MDL = t * s

Where:
t = one sided Student's t value for the number of replicates at the 99% level
s = standard deviation of the population

PQL calculations: PQL = MDL * 5

Northeast Analytical, Inc.

Method Detection Limits

Date: 28-Jun-06

Method Detection Limit (MDL) calculations as based on procedures outlined in 40 CFR, part 136, App B; 1-July-85.

Compound:	A1254	Analysis:	EPA METHOD 508
Matrix:	WATER	Instrument:	GC-19B
Extraction:	Sep. Funnel	Column:	ZB-5
Spike conc:	50.0 ng/L		

NEA Sample ID	Extraction Date	File Name	Analysis Date	Measured Concentration ng/L	Percent Recovery (%)
A1221/A1254 # 1 CLLE	05/08/06	AJ04178	06/24/06	41.4	82.7%
A1221/A1254 # 1 CLLE	05/08/06	AJ04179	06/24/06	40.7	81.4%
A1221/A1254 # 1 CLLE	05/08/06	AJ04180	06/24/06	42.5	85.0%
A1221/A1254 # 1 CLLE	05/08/06	AJ04181	06/24/06	41.8	83.7%
A1221/A1254 # 1 CLLE	05/08/06	AJ04182	06/24/06	42.5	85.1%
A1221/A1254 # 1 CLLE	05/08/06	AJ04183	06/24/06	48.3	96.6%
A1221/A1254 # 1 CLLE	05/08/06	AJ04184	06/24/06	42.6	85.2%
A1221/A1254 # 1 CLLE	05/08/06	AJ04185	06/24/06	47.5	95.0%

One sided Student's t values (t) at the 99% confidence level.

Number (n)	(t) value
7	3.143
8	2.998

Number (n):	8	
AVG:	43.4	ng/L
STD (s):	2.86	ng/L
%RSD:	6.59%	
MDL:	8.57	ng/L
PQL:	42.9	ng/L
VALID:	Yes	

MDL calculations:

MDL = t * s

Where:
t = one sided Student's t value for the number of replicates at the 99% level
s = standard deviation of the population

PQL calculations:

PQL = MDL * 5

Northeast Analytical, Inc.

Method Detection Limits

Date: 28-Jun-06

Method Detection Limit (MDL) calculations as based on procedures outlined in 40 CFR, part 136, App B; 1-July-85.

Compound:	A1260	Analysis:	EPA METHOD 508
Matrix:	WATER	Instrument:	GC-19B
Extraction:	Sep. Funnel	Column:	ZB-5
Spike conc:	50.0 ng/L		

NEA Sample ID	Extraction Date	File Name	Analysis Date	Measured Concentration ng/L	Percent Recovery (%)
A1016/A1260 #1 SEPFUN	04/28/06	AJ04170	06/23/06	45.1	90.3%
A1016/A1260 #2 SEPFUN	04/28/06	AJ04171	06/23/06	41.5	82.9%
A1016/A1260 #3 SEPFUN	04/28/06	AJ04172	06/23/06	42.2	84.3%
A1016/A1260 #4 SEPFUN	04/28/06	AJ04173	06/23/06	43.7	87.4%
A1016/A1260 #5 SEPFUN	04/28/06	AJ04174	06/23/06	42.6	85.3%
A1016/A1260 #6 SEPFUN	04/28/06	AJ04175	06/23/06	44.1	88.3%
A1016/A1260 #7 SEPFUN	04/28/06	AJ04176	06/23/06	47.6	95.3%
A1016/A1260 #8 SEPFUN	04/28/06	AJ04177	06/23/06	40.9	81.7%

One sided Student's t values (t) at the 99% confidence level.

Number (n)	(t) value
7	3.143
8	2.998

Number (n):	8	
AVG:	43.5	ng/L
STD (s):	2.20	ng/L
%RSD:	5.06%	
MDL:	6.60	ng/L
PQL:	33.0	ng/L
VALID:	Yes	

MDL calculations:

MDL = t * s

Where:
t = one sided Student's t value for the number of replicates at the 99% level
s = standard deviation of the population

PQL calculations: PQL = MDL * 5

Northeast Analytical, Inc.

Method Detection Limits

Date: 28-Jun-06

Method Detection Limit (MDL) calculations as based on procedures outlined in 40 CFR, part 136, App B; 1-July-85.

Compound:	A1016	Analysis:	EPA METHOD 508
Matrix:	WATER	Instrument:	GC-19F
Extraction:	Sep. Funnel	Column:	ZB-1
Spike conc:	50.0 ng/L		

NEA Sample ID	Extraction Date	File Name	Analysis Date	Measured Concentration ng/L	Percent Recovery (%)
A1016/A1260 #1 SEPFUN	04/28/06	AJ04170	06/23/06	45.8	91.6%
A1016/A1260 #2 SEPFUN	04/28/06	AJ04171	06/23/06	43.6	87.3%
A1016/A1260 #3 SEPFUN	04/28/06	AJ04172	06/23/06	46.2	92.4%
A1016/A1260 #4 SEPFUN	04/28/06	AJ04173	06/23/06	48.4	96.9%
A1016/A1260 #5 SEPFUN	04/28/06	AJ04174	06/23/06	41.9	83.9%
A1016/A1260 #6 SEPFUN	04/28/06	AJ04175	06/23/06	43.7	87.3%
A1016/A1260 #7 SEPFUN	04/28/06	AJ04176	06/23/06	42.6	85.2%
A1016/A1260 #8 SEPFUN	04/28/06	AJ04177	06/23/06	47.8	95.6%

One sided Student's t values (t) at the 99% confidence level.

Number (n)	(t) value
7	3.143
8	2.998

Number (n):	8	
AVG:	45.0	ng/L
STD (s):	2.40	ng/L
%RSD:	5.34%	
MDL:	7.21	ng/L
PQL:	36.0	ng/L
VALID:	Yes	

MDL calculations:

MDL = t * s

Where:
t = one sided Student's t value for the number of replicates at the 99% level
s = standard deviation of the population

PQL calculations: PQL = MDL * 5

Northeast Analytical, Inc.

Method Detection Limits

Date: 28-Jun-06

Method Detection Limit (MDL) calculations as based on procedures outlined in 40 CFR, part 136, App B; 1-July-85.

Compound:	A1221	Analysis:	EPA METHOD 508
Matrix:	WATER	Instrument:	GC-19F
Extraction:	Sep. Funnel	Column:	ZB-1
Spike conc:	50.0 ng/L		

NEA Sample ID	Extraction Date	File Name	Analysis Date	Measured Concentration ng/L	Percent Recovery (%)
A1221/A1254 # 1 CLLE	05/08/06	AJ04178	06/24/06	60.9	122%
A1221/A1254 # 1 CLLE	05/08/06	AJ04179	06/24/06	54.3	109%
A1221/A1254 # 1 CLLE	05/08/06	AJ04180	06/24/06	57.5	115%
A1221/A1254 # 1 CLLE	05/08/06	AJ04181	06/24/06	55.6	111%
A1221/A1254 # 1 CLLE	05/08/06	AJ04182	06/24/06	53.6	107%
A1221/A1254 # 1 CLLE	05/08/06	AJ04183	06/24/06	50.3	101%
A1221/A1254 # 1 CLLE	05/08/06	AJ04184	06/24/06	57.2	114%
A1221/A1254 # 1 CLLE	05/08/06	AJ04185	06/24/06	59.2	118%

One sided Student's t values (t) at the 99% confidence level.

Number (n)	(t) value
7	3.143
8	2.998

Number (n):	8	
AVG:	56.1	ng/L
STD (s):	3.36	ng/L
%RSD:	5.99%	
MDL:	10.07	ng/L
PQL:	50.4	ng/L
VALID:	Yes	

MDL calculations:

MDL = t * s

Where:
t = one sided Student's t value for the number of replicates at the 99% level
s = standard deviation of the population

PQL calculations:

PQL = MDL * 5

Northeast Analytical, Inc.

Method Detection Limits

Date: 28-Jun-06

Method Detection Limit (MDL) calculations as based on procedures outlined in 40 CFR, part 136, App B; 1-July-85.

Compound:	A1232	Analysis:	EPA METHOD 508
Matrix:	WATER	Instrument:	GC-19F
Extraction:	Sep. Funnel	Column:	ZB-1
Spike conc:	50.0 ng/L		

NEA Sample ID	Extraction Date	File Name	Analysis Date	Measured Concentration ng/L	Percent Recovery (%)
A1232 #1 SEPFUN	05/23/06	AJ04186	06/24/06	52.7	105%
A1232 #2 SEPFUN	05/23/06	AJ04187	06/24/06	50.4	101%
A1232 #3 SEPFUN	05/23/06	AJ04188	06/24/06	49.0	98.1%
A1232 #4 SEPFUN	05/23/06	AJ04189	06/24/06	50.0	100%
A1232 #5 SEPFUN	05/23/06	AJ04190	06/24/06	46.2	92.4%
A1232 #6 SEPFUN	05/23/06	AJ04191	06/24/06	49.4	98.7%
A1232 #7 SEPFUN	05/23/06	AJ04192	06/24/06	53.3	107%
A1232 #8 SEPFUN	05/23/06	AJ04193	06/24/06	52.5	105%

One sided Student's t values (t) at the 99% confidence level.

Number (n)	(t) value
7	3.143
8	2.998

Number (n):	8	
AVG:	50.4	ng/L
STD (s):	2.36	ng/L
%RSD:	4.69%	
MDL:	7.09	ng/L
PQL:	35.4	ng/L
VALID:	Yes	

MDL calculations:

MDL = t * s

Where:
t = one sided Student's t value for the number of replicates at the 99% level
s = standard deviation of the population

PQL calculations:

PQL = MDL * 5

Northeast Analytical, Inc.

Method Detection Limits

Date: 28-Jun-06

Method Detection Limit (MDL) calculations as based on procedures outlined in 40 CFR, part 136, App B; 1-July-85.

Compound:	A1242	Analysis:	EPA METHOD 508
Matrix:	WATER	Instrument:	GC-19F
Extraction:	Sep. Funnel	Column:	ZB-1
Spike conc:	50.0 ng/L		

NEA Sample ID	Extraction Date	File Name	Analysis Date	Measured Concentration ng/L	Percent Recovery (%)
A1242 #1 SEPFUN	06/20/06	AJ04194	06/24/06	43.7	87.4%
A1242 #2 SEPFUN	06/20/06	AJ04195	06/24/06	45.5	90.9%
A1242 #3 SEPFUN	06/20/06	AJ04196	06/24/06	47.7	95.3%
A1242 #4 SEPFUN	06/20/06	AJ04197	06/24/06	49.8	99.5%
A1242 #5 SEPFUN	06/20/06	AJ04198	06/24/06	43.4	86.9%
A1242 #6 SEPFUN	06/20/06	AJ04199	06/24/06	47.5	95.0%
A1242 #7 SEPFUN	06/20/06	AJ04200	06/24/06	45.0	90.1%
A1242 #8 SEPFUN	06/20/06	AJ04201	06/24/06	43.1	86.3%

One sided Student's t values (t) at the 99% confidence level.

Number (n)	(t) value
7	3.143
8	2.998

Number (n):	8	
AVG:	45.7	ng/L
STD (s):	2.38	ng/L
%RSD:	5.21%	
MDL:	7.14	ng/L
PQL:	35.7	ng/L
VALID:	Yes	

MDL calculations:

MDL = t * s

Where:
t = one sided Student's t value for the number of replicates at the 99% level
s = standard deviation of the population

PQL calculations:

PQL = MDL * 5

Northeast Analytical, Inc.

Method Detection Limits

Date: 28-Jun-06

Method Detection Limit (MDL) calculations as based on procedures outlined in 40 CFR, part 136, App B; 1-July-85.

Compound:	A1248	Analysis:	EPA METHOD 508
Matrix:	WATER	Instrument:	GC-19F
Extraction:	Sep. Funnel	Column:	ZB-1
Spike conc:	50.0 ng/L		

NEA Sample ID	Extraction Date	File Name	Analysis Date	Measured Concentration ng/L	Percent Recovery (%)
A1248 #1 SEPFUN	04/25/06	AJ04202	06/24/06	49.9	99.9%
A1248 #2 SEPFUN	04/25/06	AJ04203	06/24/06	51.2	102%
A1248 #3 SEPFUN	04/25/06	AJ04204	06/24/06	50.4	101%
A1248 #4 SEPFUN	04/25/06	AJ04205	06/24/06	55.0	110%
A1248 #5 SEPFUN	04/25/06	AJ04206	06/24/06	52.3	105%
A1248 #6 SEPFUN	04/25/06	AJ04207	06/24/06	54.8	110%
A1248 #7 SEPFUN	04/25/06	AJ04208	06/24/06	59.9	120%
A1248 #8 SEPFUN	04/25/06	AJ04209	06/24/06	54.5	109%

Number (n):	8	
AVG:	53.5	ng/L
STD (s):	3.25	ng/L
%RSD:	6.08%	
MDL:	9.76	ng/L
PQL:	48.8	ng/L
VALID:	Yes	

One sided Student's t values (t) at the 99% confidence level.

Number (n)	(t) value
7	3.143
8	2.998

MDL calculations:

MDL = t * s

Where:
t = one sided Student's t value for the number of replicates at the 99% level
s = standard deviation of the population

PQL calculations:

PQL = MDL * 5

Northeast Analytical, Inc.

Method Detection Limits

Date: 28-Jun-06

Method Detection Limit (MDL) calculations as based on procedures outlined in 40 CFR, part 136, App B; 1-July-85.

Compound:	A1254	Analysis:	EPA METHOD 508
Matrix:	WATER	Instrument:	GC-19F
Extraction:	Sep. Funnel	Column:	ZB-1
Spike conc:	50.0 ng/L		

NEA Sample ID	Extraction Date	File Name	Analysis Date	Measured Concentration ng/L	Percent Recovery (%)
A1221/A1254 # 1 CLLE	05/08/06	AJ04178	06/24/06	45.6	91.2%
A1221/A1254 # 1 CLLE	05/08/06	AJ04179	06/24/06	46.5	93.0%
A1221/A1254 # 1 CLLE	05/08/06	AJ04180	06/24/06	49.3	98.6%
A1221/A1254 # 1 CLLE	05/08/06	AJ04181	06/24/06	44.1	88.1%
A1221/A1254 # 1 CLLE	05/08/06	AJ04182	06/24/06	47.7	95.4%
A1221/A1254 # 1 CLLE	05/08/06	AJ04183	06/24/06	49.3	98.7%
A1221/A1254 # 1 CLLE	05/08/06	AJ04184	06/24/06	44.0	88.0%
A1221/A1254 # 1 CLLE	05/08/06	AJ04185	06/24/06	46.2	92.4%

One sided Student's t values (t) at the 99% confidence level.

Number (n)	(t) value
7	3.143
8	2.998

Number (n):	8	
AVG:	46.6	ng/L
STD (s):	2.09	ng/L
%RSD:	4.48%	
MDL:	6.25	ng/L
PQL:	31.3	ng/L
VALID:	Yes	

MDL calculations:

MDL = t * s

Where:
t = one sided Student's t value for the number of replicates at the 99% level
s = standard deviation of the population

PQL calculations:

PQL = MDL * 5

Northeast Analytical, Inc.

Method Detection Limits

Date: 28-Jun-06

Method Detection Limit (MDL) calculations as based on procedures outlined in 40 CFR, part 136, App B; 1-July-85.

Compound:	A1260	Analysis:	EPA METHOD 508
Matrix:	WATER	Instrument:	GC-19F
Extraction:	Sep. Funnel	Column:	ZB-1
Spike conc:	50.0 ng/L		

NEA Sample ID	Extraction Date	File Name	Analysis Date	Measured Concentration ng/L	Percent Recovery (%)
A1016/A1260 #1 SEPFUN	04/28/06	AJ04170	06/23/06	43.4	86.9%
A1016/A1260 #2 SEPFUN	04/28/06	AJ04171	06/23/06	45.0	90.1%
A1016/A1260 #3 SEPFUN	04/28/06	AJ04172	06/23/06	43.7	87.4%
A1016/A1260 #4 SEPFUN	04/28/06	AJ04173	06/23/06	46.0	92.0%
A1016/A1260 #5 SEPFUN	04/28/06	AJ04174	06/23/06	45.1	90.3%
A1016/A1260 #6 SEPFUN	04/28/06	AJ04175	06/23/06	49.6	99.1%
A1016/A1260 #7 SEPFUN	04/28/06	AJ04176	06/23/06	48.0	95.9%
A1016/A1260 #8 SEPFUN	04/28/06	AJ04177	06/23/06	44.7	89.5%

One sided Student's t values (t) at the 99% confidence level.

Number (n)	(t) value
7	3.143
8	2.998

Number (n):	8	
AVG:	45.7	ng/L
STD (s):	2.09	ng/L
%RSD:	4.58%	
MDL:	6.28	ng/L
PQL:	31.4	ng/L
VALID:	Yes	

MDL calculations:

MDL = t * s

Where:
t = one sided Student's t value for the number of replicates at the 99% level
s = standard deviation of the population

PQL calculations:

PQL = MDL * 5

Example G: IDOP Study

Northeast Analytical Inc. 01/16/06

Quality Assurance/Quality Control

Precision & Accuracy Study

Method(s):	EPA 508	Analysis:	External Standard by Area
Compound:	Aroclor 1242	Instrument:	GC-20
Matrix:	H2O	Column:	DB-1
Extraction:	SEP. FUNNEL	Detector:	ECD
Spike Concentration:	0.500 ug/L		
Date Extracted:	01/12/06		
Date Analyzed:	01/12/06		

NEA Sample I.D.	Spiked Concentration ug/L	Measured Concentration ug/L	Percent Recovery	Recovery Limits* %
060112CB1	0.500	0.430	86.0	70-130
060112CB2	0.500	0.423	84.6	70-130
060112CB3	0.500	0.413	82.6	70-130
060112CB4	0.500	0.436	87.1	70-130
		% RSD	2.27	< 20

*Recovery Limits based upon lab established values

Preparation Chemist:	Carrie Barss	Date:	01/16/06
Analyst:	Anthony Maiello	Date:	01/16/06
QA/QC Officer:		Date:	01/16/06
Lab Director:	Robert E. Wagner	Date:	01/16/06

NOTES:

APPENDIX 28
SOP FOR CONGENER-SPECIFIC PCB ANALYSIS (LOW LEVEL CALIBRATION METHOD) (NEA207_03_R01)

STANDARD OPERATING PROCEDURE

NORTHEAST ANALYTICAL, INC.

NE207_03.DOC

REVISION NUMBER: 03

STANDARD OPERATING PROCEDURE FOR CONGENER-SPECIFIC POLYCHLORINATED BIPHENYL (PCB) ANALYSIS

(Low-level Calibration Method)

METHOD FOR CONGENER-SPECIFIC POLYCHLORINATED BIPHENYL (PCB) QUANTIFICATION AND IDENTIFICATION BY CAPILLARY COLUMN/GAS CHROMATOGRAPHY WITH ELECTRON CAPTURE DETECTION

August 5, 2008

COPY #_____

NORTHEAST ANALYTICAL, INC.
2190 TECHNOLOGY DRIVE
SCHENECTADY, NEW YORK 12308
(518) 346-4592

STANDARD OPERATING PROCEDURE

LABORATORY METHOD NE207_03.DOC

REVISION 3 (8/05/2008)

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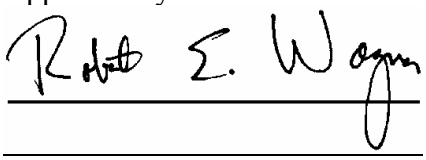


Robert E. Wagner/Laboratory Director

Northeast Analytical, Inc.
Issuing Section: Organics Laboratory
SOP Name: NE207_03.DOC

Date: 08/05/08
Revision: 03

Lab Method NE207_03.SOP

Congener-Specific Polychlorinated Biphenyl (PCB) Analysis

(Low-level Calibration Method)

Method for Congener-Specific Polychlorinated Biphenyl (PCB) Quantification and Identification by Capillary Column/Gas Chromatography with Electron Capture Detection

1.0 Scope:

1.1 This method is applicable in the determination and quantification of Polychlorinated Biphenyls (PCB) in water. This method is a congener-specific determination, employing a high resolution fused-silica capillary chromatographic column. The method has been, in part, developed from the following documents:

1.) "Quality Assurance Plan, Green Bay Mass Balance Study, 1. PCBs and Dieldrin, US EPA Great Lakes National Program Office", prepared by Deborah L. Swackhamer, Quality Assurance Coordinator, Field and Analytical Methods Committees, University of Minnesota, December 11, 1987. This document outlines quality assurance and quality control procedures to be followed by laboratories participating in the Green Bay Mass Balance Study. Where applicable, Northeast Analytical, Inc., will incorporate and utilize this information in quality control of data generated. Instrumental analysis and conditions (Mullin, M.D., 1985, PCB Workshop, US EPA Large Lakes Research Station, Gross Ile, MI, June.) cited in the Green Bay Mass Balance Study document will be refined to be applicable to an in-house data management software package.

2.) "Comprehensive, Quantitative, Congener-Specific Analyses of Eight Aroclors and Complete PCB Congener Assignments on DB-1 Capillary GC Columns", George M. Frame, Robert E. Wagner, James C. Carnahan, John F. Brown, Jr., Ralph J. May, Lynn A. Smullen, and Donna L. Bedard, Chemosphere, Vol. 33, No. 4, pp. 603-623, 1996. This journal publication provides complete assignment of all 209 PCB congeners to the GC peaks separable on a DB-1 capillary column. It also provides weight percent information for PCB congeners in Aroclor formulations used in labeling protocols for reporting purposes.

3.) "Standard Operating Procedure for the Gas Chromatographic Analysis of Hydrophobic Organic Contaminant Extracts from Great Lakes Water Samples", USEPA Great Lakes National Program Office, 77 West Jackson Boulevard, Chicago, IL 60604-2590, GLNPO Organics SOP – 10, 6/1/94:Revision 2. This USEPA SOP summarizes M. Mullin's congener composition of the mixed Aroclor standard used for calibration.

4.) "Biphenyls and Halogenated Pesticides by High Resolution Gas Chromatography", M.D. Mullin, Large Lakes Research Station, LLRS-SOP-ORG-013, revision 2, August 3, 1990, p 1-10. This LLRS SOP written by M. Mullin summarizes the calibration composition of the mixed Aroclor standard reported in "Mullin, M.D., PCB Workshop, U.S. EPA Large Lakes Research Station, Grosse Ile, MI, June 1985.

1.2 This gas chromatographic capillary column method, utilizing an electron capture detector, will effectively separate 112 or more peaks representing 209 PCB congeners.

2.0 Summary of Method:

2.1 This method provides detailed instructions for gas chromatographic conditions for analysis of PCBs by capillary gas chromatography.

2.2 This method utilizes a mixed Aroclor standard (Aroclor 1232/1248/1262 in the ratio of 25:18:18) for calibration. A three- or four-point internal standard calibration will be performed for quantification. Method detection limit and practical quantitation limit will be established experimentally using the procedure in USEPA 40 CFR, Part 136, App. B.

2.3 In general, samples are first extracted with a pesticide-grade solvent. The extracts are further processed through a series of clean-up techniques. The sample is then analyzed by direct liquid injection onto the gas chromatographic column and detected by an electron capture detector. This method should be performed by a skilled chemist or by an analyst trained in the quantification of trace organics by gas chromatography.

2.4 A key component of this method is the importance placed on the chromatographic separation that must be achieved for this congener specific technique. A total of 112 chromatographic peaks are detected, containing 209 PCB congeners in various ratios. This allows an almost complete profile of environmentally occurring PCBs.

3.0 Definitions:

3.1 Surrogate Analyte: Surrogates are organic compounds which are similar to analytes of interest in chemical composition, extraction, and chromatography, but which are not normally found in environmental samples. These compounds are added to all laboratory method blanks, laboratory QC reference samples (Laboratory Control Spikes), laboratory duplicates, calibration and continuing check standards, field samples, field duplicate samples, field matrix spike samples, field matrix spike duplicate samples prior to extraction and/or analysis. Percent recovery is calculated for each surrogate to assess extraction efficiency.

3.2 Stock Standard Solution: A concentrated standard solution containing the method analytes. This stock standard can be used to prepare other more dilute standards.

3.3 Primary Standard Solution: A solution of several analytes prepared from stock solutions that can be diluted as needed to prepare calibration solutions and to prepare other standard solutions.

3.4 Calibration Standard: A series of known standard solutions used by the analyst for instrument calibration. Calibration standards are prepared are prepared from primary standard and/or stock standard solutions.

3.5 Continuing Calibration Check Standard: An analytical standard that is prepared from an alternate source than the one used to prepare the calibration standards. The continuing calibration check standard contains all the target analytes found in the calibration standards and is used to verify that the initial calibration is prepared correctly and that the instrument system is correctly calibrated as defined by the method calibration criteria.

3.6 Laboratory Method Blank: A laboratory derived sample consisting of reagent water or other blank matrix that consists of all reagents, internal standards and surrogate standards, that is carried through the entire analytical procedure. The laboratory method blank is used to define the level of laboratory analyte background or other interferences that exist in the laboratory environment, the reagents, or the apparatus.

3.7 Laboratory Control Sample (LCS): Also known as the Quality Control (QC) Check Standard or Quality Control (QC) Check Sample. The LCS consists of an aliquot of reagent water or other blank matrix to which known quantities of the method analytes are added. The LCS is extracted and analyzed exactly like a field sample, and its purpose is to determine whether the analysis is in control and whether the laboratory is capable of making accurate and precise measurements.

3.8 Sample Matrix Spike/Sample Matrix Spike Duplicate (MS/MSD): An aliquot of a field sample that is fortified with known quantities of the method analytes and subjected to the entire analytical procedure. Its purpose is to assess the appropriateness of the method for the matrix by measuring recovery.

4.0 Interference:

4.1 One of the major sources of interference in the analysis of PCBs is from organochlorine pesticides that are co-extracted from the samples. Several of these ECD responding pesticides can be separated cleanly from the PCB profile by the resolving characteristics of the capillary column. Several of the commonly found pesticides and degradation products (DDT, DDE, DDD) overlap the PCB profile envelope and co-elute with several of the PCB congeners found in environmental samples. The analyst must be careful in chromatographic pattern review and flag peaks that are suspected of being contaminated so that they are not included in total PCB values generated.

4.2 The sample matrix itself is also a potential source for method analyte interference. Sample preparation, extraction procedures, and extract clean-up protocols are covered in separate SOPs that deal exclusively with sample extraction and clean-up procedures.

4.3 Laboratory contamination can occur by introduction of plasticizers (phthalate esters) into the samples through the use of flexible tubing. Samples and extracts should not be exposed to plastic materials. Phthalate esters exhibit response on

electron capture detectors, usually as late eluting peaks and can interfere in PCB quantification.

5.0 Safety:

5.1 Safe laboratory practices should be followed by the analyst at all times when conducting work in the lab. The analyst should refer to the reference file of material safety data sheets (MSDS) to familiarize themselves with the hazards of handling the compounds used for standards and samples.

5.2 Each chemical should be regarded as a potential health hazard and exposure to these compounds should be as low as reasonably achievable. Specifically, all solvents and standards should be manipulated in a chemical fume hood. All sample extracts should be manipulated in a chemical fume hood.

6.0 Equipment and Apparatus:

6.1 Gas Chromatograph: Complete system for high resolution, capillary column capability and all required accessories. Northeast Analytical, Inc. will use an Agilent Model 6890 gas chromatograph (or equivalent), equipped with a capillary split/splitless injector (or equivalent), temperature programmable oven, Model 7683 automatic sampler (or equivalent), and Micro-ECD electron capture detector (or equivalent). A data system (Waters Associates, Millennium_32 Workstation or equivalent) for chromatographic operations and integration of detector signal is interfaced to the gas chromatograph.

6.1.1 GC Column: The gas chromatograph column to be used for analysis will be a DB-1 (J&W Company), bonded polydimethylsilicone, 30 meter fused silica capillary column with an internal diameter of 0.25mm and phase coating thickness of 0.25 microns. This column is capable of resolving 112 chromatographic peaks from the full spectrum of all PCB congeners that could be expected in an environmental sample. Refer to Appendix A and Appendix B for a complete description of PCB congeners identified in each GC chromatographic peak and achievable chromatographic separations.

6.2 Chromatograph Data System: A data system for measuring peak height and peak area. A Millennium_32 computer network based workstation (Waters Associates), will be employed to capture detector response and digitally store the chromatographic information. This system will allow for chromatographic review of data from the gas chromatograph, electronic peak integration for precise calculations, database structuring of the analytical information, and archival capabilities.

6.3 Volumetric Flasks: 10, 50 and 100mL, ground-glass stopper. For standard preparation.

6.4 Microsyringe: 10, 100, 500 and 1000uL for standard preparation.

6.5 Pipettes: Class A volumetric, 1mL, 5mL, and 10mL.

6.6 Vials: Glass, 10 and 20mL capacity for sample extracts.

6.7 Bottles: Glass, 120mL capacity for standard storage.

7.0 Reagents and Standards:

7.1 Solvents: Pesticide grade quality. Hexane, acetone, toluene, methylene chloride.

7.2 Octachloronaphthalene: Obtained from Ultra Scientific (Hope, RI) with a purity greater than 95%.

7.3 Polychlorinated Biphenyls: Neat commercial material or solutions for standard preparation. These materials are multi-component mixtures of PCB congeners and are the actual materials that were used in products such as transformers and capacitors. Monsanto was the largest producer of PCB formulations and sold them under the tradename Aroclor.

7.4 PCB Congeners: A complete set of all 209 PCB congeners to individually verify the exact elution on the chosen chromatographic system. A subset of congeners is also used as a secondary supplemental calibration standard for those congeners that do not exist at a high enough level in the Aroclor based calibration standard. Obtained from AccuStandard or Ultra Scientific.

7.5 Stock Standard Solutions:

7.5.1 Stock standards are prepared from individual neat Aroclor formulations by weighing approximately 0.1000g to the nearest 0.2 mg and dissolving and diluting to volume in a 100mL volumetric flask with hexane. This will give a stock concentration of 1,000ug/mL.

7.5.2 The stock standard is transferred into screw-cap 120mL boston bottles and stored in a refrigerator, protected from light. Stock standards should be checked at frequent intervals for signs of evaporation, especially just prior to preparing calibration standards.

7.5.3 Stock PCB standards must be replaced after one year, or sooner if comparison with continuing calibration check standards indicate a problem.

7.5.4 Stock standards for the following are prepared by the above procedure:

Aroclor 1232
Aroclor 1248

Aroclor 1262

7.6 Mixed Aroclor Stock Standard at 62.7ug/mL: A primary standard is prepared at 62.7ug/mL that is used for preparing secondary stock standards and calibration standards. This stock standard is prepared by combining Aroclor 1232, Aroclor 1248, and Aroclor 1262 in a 25:18:18 ratio with a final mixture concentration of 25.7ug/mL, 18.6ug/mL, and 18.4ug/mL respectively (total=62.7ug/mL). These ratios are strictly maintained so that the percent composition data remains applicable, since it was developed for use under these fixed mixture parameters. The final concentration of the mixed standard may vary to accommodate instrument sensitivity or more closely represent sample concentrations, but the same ratio values must be maintained. Using a 5.0mL Class A pipette, accurately add 2.49mL of stock Aroclor 1232 standard (1,033ug/mL) to a 100mL volumetric flask. Using a 2.0mL Class A pipette, accurately add 1.82mL of stock Aroclor 1248 standard (1,019ug/mL) and 1.80mL of stock Aroclor 1262 standard (1,024ug/mL) to the same 100mL volumetric flask. Make volume to the 100mL mark with hexane.

7.6.1 Store the Mixed Aroclor Stock Standard at 62.7ug/mL in a refrigerator in a tightly capped bottle. This standard must be replaced after one year, or sooner, if comparison with continuing check standards indicate a problem.

7.7 Mixed Aroclor Secondary Stock Standard at 6.27ug/mL: The secondary stock standard is prepared from the 62.7ug/mL mixed Aroclor stock standard. Using a 10.0mL Class A pipette, accurately add 10.0mL of the 62.7 stock standard into a 100mL volumetric flask. Make to volume with hexane. Transfer the standard solution to a 120-ml boston bottle and store in a refrigerator.

7.7.1 The 6.27ug/mL Secondary Stock Standard must be replaced after one year, or sooner, if comparison with continuing check standards indicate a problem.

7.8 Mixed Aroclor Calibration Standard 1 at 313.5ng/mL with Internal Standard (OCN) at 18.18ng/mL: The Calibration Standard 1 at 313.5ng/mL with Internal Standard (OCN) at 18.18ng/mL is prepared from the Mixed Aroclor Secondary Stock Standard at 6.27ug/mL and the Internal Standard Calibration Standard at 20.2ug/mL. Using a 5.0mL Class A pipette, accurately transfer 2.5mL of the Mixed Aroclor Secondary Stock Standard at 6.27ug/mL into a 50mL volumetric flask. Into the same 50mL volumetric flask transfer, using a 100-microliter syringe, 45 microliters of the 20.2ug/mL Internal Standard Calibration Standard. Make to volume with hexane and transfer the standard solution to a 125mL boston bottle, tightly cap, and store in a refrigerator. This will give a concentration of Mixed Aroclor Calibration Standard 1 of 313.5ng/mL and Internal Standard (OCN) of 18.18ng/mL. The Mixed Aroclor Calibration Standard 1 at 313.5ng/mL with Internal Standard at 18.18ng/mL must be replaced after six months.

7.9 Mixed Aroclor Calibration Standard 2 at 125ng/mL with Internal Standard (OCN) at 18.18ng/mL: The Calibration Standard 2 at 125ng/mL with Internal Standard (OCN) at 18.18ng/mL is prepared from the Mixed Aroclor Secondary Stock Standard at 6.27ug/mL and the Internal Standard Calibration Standard at 20.2ug/mL. Using a 1.0mL Class A pipette, accurately transfer 1.0mL of the Mixed Aroclor Secondary Stock Standard at 6.27ug/mL into a 50mL volumetric flask. Into the same 50mL volumetric flask transfer, using a 100-microliter syringe, 45 microliters of the 20.2ug/mL Internal Standard Calibration Standard. Make to volume with hexane and transfer the standard solution to a 125mL boston bottle, tightly cap, and store in a refrigerator. This will give a concentration of Mixed Aroclor Calibration Standard 2 of 125ng/mL and Internal Standard (OCN) of 18.18ng/mL. The Mixed Aroclor Calibration Standard 2 at 125ng/mL with Internal Standard at 18.18ng/mL must be replaced after six months.

7.10 Mixed Aroclor Calibration Standard 3 at 12.5ng/mL with Internal Standard (OCN) at 18.18ng/mL: The Calibration Standard 3 at 12.5ng/mL with Internal Standard (OCN) at 18.18ng/mL is prepared from the Mixed Aroclor Secondary Stock Standard at 6.27ug/mL and the Internal Standard Calibration Standard at 20.2ug/mL. Using a 100-microliter syringe, accurately transfer 100 microliters of the Mixed Aroclor Secondary Stock Standard at 6.27ug/mL into a 50mL volumetric flask. Into the same 50mL volumetric flask transfer, using a 100-microliter syringe, 45 microliters of the 20.2ug/mL Internal Standard Calibration Standard. Make to volume with hexane and transfer the standard solution to a 125mL boston bottle, tightly cap, and store in a refrigerator. This will give a concentration of Mixed Aroclor Calibration Standard 3 of 12.5ng/mL and Internal Standard (OCN) of 18.18ng/mL. The Mixed Aroclor Calibration Standard 3 at 12.5ng/mL with Internal Standard at 18.18ng/mL must be replaced after six months.

7.11 Mixed Aroclor Secondary Stock Standard at 125ng/mL: The Mixed Aroclor Secondary Stock Standard at 125ng/mL is prepared from the Mixed Aroclor Secondary Stock Standard at 6.27ug/mL. Using a 1.0mL Class A pipette, accurately transfer 1.0mL of the Mixed Aroclor Secondary Stock Standard at 6.27ug/mL into a 50mL volumetric flask. Make to volume with hexane and transfer the standard solution to a 125mL boston bottle, tightly cap, and store in a refrigerator. This will give a concentration of Mixed Aroclor Secondary Stock Standard of 125ng/mL. The Mixed Aroclor Secondary Stock Standard at 125ng/mL must be replaced after six months.

7.12 Mixed Aroclor Calibration Standard 4 at 6.25ng/mL with Internal Standard (OCN) at 18.18ng/mL: The Calibration Standard 4 at 6.25ng/mL with Internal Standard (OCN) at 18.18ng/mL is prepared from the Mixed Aroclor Secondary Stock Standard at 125ng/mL and the Internal Standard Calibration Standard at 20.2ug/mL. Using a 5.0mL Class A pipette, accurately transfer 2.50mL of the Mixed Aroclor Secondary Stock Standard at 125ng/mL into a 50mL volumetric flask. Into the same 50mL volumetric flask transfer, using a 100-microliter

syringe, 45 microliters of the 20.2ug/mL Internal Standard Calibration Standard. Make to volume with hexane and transfer the standard solution to a 125mL boston bottle, tightly cap, and store in a refrigerator. This will give a concentration of Mixed Aroclor Calibration Standard 4 of 6.25ng/mL and Internal Standard (OCN) of 18.18ng/mL. The Mixed Aroclor Calibration Standard 4 at 6.25ng/mL with Internal Standard at 18.18ng/mL must be replaced after six months. This calibration standard will be analyzed to produce a four-point calibration curve for the majority of the DB-1 peaks/congeners. There are, however, 22 DB-1 peaks that cannot be measured in Calibration Standard 4 and only a three-point calibration curve will be generated for the following peaks: DB-1 peaks 10, 13, 20, 44, 52, 55, 56, 67, 72, 79, 84, 87, 89, 91, 98, 101, 104, 108, 111, 113, 114, and 118.

7.13 Supplemental Congener Standard: A Supplemental Congener Standard is analyzed along with the four calibration standards. This standard contains congeners that exist at low levels in the mixed Aroclor standard and comprises congeners that are not typically found in Aroclor formulations, but could become important in by-product PCB analysis or the study of model experiments that use unusual PCB congeners. This standard is analyzed to supply accurate retention time information and response factors for quantification.

7.13.1 Supplemental Congener Stock Standard at 2.00ug/mL: All stock standards are purchased as solutions at 100ug/mL from Ultra Scientific. All supplemental congeners are diluted together (except 3-Chlorobiphenyl) to 2.00ug/mL. Using a 1000uL syringe, pipette 2.0mL of the 100ug/mL stock standard into the same 100mL volumetric flask and make to volume with hexane. The 3-Chlorobiphenyl, due to its low ECD response, will be added to the secondary stock standard. Transfer the standard solution to a 120mL boston bottle and store in a refrigerator. This stock standard must be replaced after one year.

7.13.2 Supplemental Congener Secondary Stock Standard at 0.0500ug/mL: Into a 50mL volumetric flask pipette, using a 1000uL syringe, 1.25mL of the Supplemental Congener Stock Standard. To the same 50mL volumetric flask pipette, using a 1000uL syringe, 1.0mL of the 3-Chlorobiphenyl purchased stock standard at 100ug/mL. To the same 50mL volumetric flask pipette, using a 100uL syringe, 45uL of the Octachloronaphthalene Stock Standard at 202ug/mL. Make to volume with hexane and transfer the standard solution to a 120mL boston bottle and store in a refrigerator. The octachloronaphthalene is used as an internal standard for instrument calibration and is at a concentration of 0.1818ug/mL in the standard. The standard concentration is 2.00ug/mL for 3-Chlorobiphneyl and 0.050ug/mL for all other congeners in the standard.

7.13.3 Supplemental Congener Calibration Standard at 0.00500ug/mL: The Supplemental Congener Calibration Standard is prepared by a 10-fold dilution of the Supplemental Congener Secondary Stock Standard at

0.0500ug/mL. Into a 50mL volumetric flask, using a 5mL Class A pipette, transfer 5.0mL of the Supplemental Congener Secondary Stock Standard at 0.0500ug/mL. Make to volume with hexane and transfer the standard solution to a 120mL boston bottle and store in a refrigerator. The standard concentration is 0.200ug/mL for 3-Chlorobiphneyl and 0.00500ug/mL for all other congeners in the standard. The octachloronaphthalene is used as an internal standard for instrument calibration and is at a concentration of 0.01818ug/mL in the standard. The following table lists the congeners included in this standard and the DB-1 peaks where they elute and also lists the other non-Aroclor congeners that co-elute with these 14 congeners. The Supplemental Congener Calibration Standard must be replaced after one year.

Supplemental Congener Standard Calibration Standard

DB-1 Peak Number	IUPAC Congener Number	(IUPAC #) PCB Congener Analyzed		Conc ug/mL
3	2	(2)	3-Chlorobiphenyl	0.200
9	14	(14)	3,5-Dichlorobiphenyl	0.00500
11	30	(30)	2,4,6-Trichlorobiphenyl	0.00500
12	11	(11)	3,3'-Dichlorobiphenyl	0.00500
19	23,34,54	(34)	2',3,5-Trichlorobiphenyl	0.00500
28	36	(36)	3,3',5-Trichlorobiphenyl	0.00500
30	39	(39)	3,4',5-Trichlorobiphenyl	0.00500
35	62,65	(65)	2,3,5,6-Tetrachlorobiphenyl	0.00500
36	35	(35)	3,3',4-Trichlorobiphenyl	0.00500
41	68,96	(96)	2,2',3,6,6'-Pentachlorobiphenyl	0.00500
43	57,103	(103)	2,2',4,5',6-Pentachlorobiphenyl	0.00500
62	154	(154)	2,2'4,4',5,6'-Hexachlorobiphenyl	0.00500
68	123	(123)	2',3,4,4',5-Pentachlorobiphenyl	0.00500
70	140	(140)	2,2',3,4,4',6'-Hexachlorobiphenyl	0.00500
76	127,168,184	(127)	3,3',4,5,5'-Pentachlorobiphenyl	0.00500

7.14 Internal Standard Stock Standard at 202ug/mL: The internal standard used for capillary gas chromatography of PCBs will be octachloronaphthalene (OCN). Weigh 10.1mg of solid octachloronaphthalene (OCN) into a 5mL vial. Quantitatively transfer the OCN using six successive 2-mL washings of toluene to a 50mL volumetric flask. Be sure to rinse the 5mL vial walls carefully so that all OCN is completely transferred to the 50mL volumetric flask. Make the solution to volume using toluene and mix the internal standard solution by shaking the flask several times. This will give a concentration of OCN of 202ug/mL. Carefully transfer the internal standard solution to 25mL vials, tightly cap, and store in a refrigerator. OCN internal standard must be replaced after one year.

7.15 Internal Standard Calibration Standard at 20.2ug/mL: The Internal Standard Calibration Standard is prepared from the Internal Standard Stock Standard. Into a 10mL volumetric flask, using a 1mL Class A pipette, transfer 1.0mL of the Internal Standard Stock Standard at 202ug/mL. Make to volume with toluene and transfer the standard solution to a 5mL reacti-vial with a Teflon syringe-valve cap and store in a refrigerator. This will give a concentration of OCN of 20.2ug/mL. The react-vial minimizes evaporation since the cap does not have to be removed.

7.15.1 The OCN internal standard is added to all calibration standards, continuing check standards, blanks, samples, and QC samples at the same amount. In most cases this will be achieved by spiking 4.5uL of OCN internal standard solution at 20.2ug/mL to 5mL of standard or sample extract to give a concentration of 0.01818ug/mL.

7.15.2 The internal standard will be added to calibration standards, sample extracts, blanks, and QC samples prior to gas chromatographic analysis. Thus, the internal standard is used as a quantification spiking standard and will eliminate sample injection volume variations, but will not correct for analytical losses during sample preparation.

7.15.3 OCN internal standard must be replaced after one year.

7.16 Surrogate Stock Standard (2,2',3,3',4,4',5,6,6'-Nonachlorobiphenyl) at 100ug/mL: The surrogate stock standard is prepared from a solid standard. Weigh 5.0mg of the solid surrogate standard into a solvent rinsed 10mL vial. Quantitatively transfer the surrogate standard using six successive 2-mL washings of hexane to a 50mL volumetric flask. Be sure to rinse the 10mL vial walls carefully so that the entire surrogate standard is completely transferred to the 50mL volumetric flask. Make to volume with hexane and mix the surrogate standard solution by shaking the flask several times. This will give a concentration of surrogate standard of 100ug/mL. Carefully transfer the surrogate standard solution to a 125mL boston bottle, tightly cap, and store in a refrigerator. The surrogate standard must be replaced after one year.

7.17 Surrogate Secondary Stock Standard (2,2',3,3',4,4',5,6,6'-Nonachlorobiphenyl) at 20.0ng/mL with Internal Standard at 181.8ng/mL: The Surrogate Secondary Stock Standard is prepared from the 100ug/mL Surrogate Stock Standard and the 202ug/mL Internal Standard Stock Standard. Into a 100mL volumetric flask, using a 50-microliter syringe, transfer 20uL of the Surrogate Stock Standard at 100ug/mL. Into the same 100mL volumetric flask transfer, using a 100-microliter syringe, 90 microliters of the 202ug/mL Internal Standard Stock Standard. Make to volume with hexane and transfer the standard solution to a 125mL boston bottle, tightly cap, and store in a refrigerator. This will give a concentration of Surrogate Secondary Stock Standard of 20ng/mL and Internal Standard (OCN) of 181.8ng/mL. The Surrogate Secondary Stock Standard with Internal Standard must be replaced after six months.

7.18 Surrogate Standard (2,2',3,3',4,4',5,6,6'-Nonachlorobiphenyl) at 2.00ng/mL with Internal Standard at 18.18ng/mL: The Surrogate Standard is prepared from the 20.0ng/mL Surrogate Secondary Stock Standard with Internal Standard at 181.8ng/mL Into a 50mL volumetric flask, using a Class A 5mL pipette, transfer 5.0mL of the Surrogate Secondary Stock Standard at 20.0ng/mL with Internal Standard at 181.8ng/mL. Make to volume with hexane and transfer the standard solution to a 125mL boston bottle, tightly cap, and store in a refrigerator. This will give a concentration of Surrogate Standard of 2.00ng/mL and Internal Standard (OCN) of 18.18ng/mL. The Surrogate Stock Standard with Internal Standard must be replaced after six months. This standard is used to calibrate the gas chromatograph to measure surrogate recoveries in field samples and QC samples.

7.19 Continuing Calibration Check Standard: A continuing calibration check standard at 0.122ug/mL is prepared from Aroclor solutions obtained from a different source (ULTRA Scientific) than the calibration standard. The continuing calibration check standard is a mixed Aroclor 1232, 1248, and 1262 in the fixed ratio used to prepare the calibration standard and must be strictly adhered to.

7.19.1 50.0ug/mL Continuing Calibration Check Stock Standards: Aroclor 1232, Aroclor 1248, and Aroclor 1262 are obtained from ULTRA Scientific at 1000ug/mL in isooctane. Using a 500uL syringe transfer 0.5mL of 1000ug/mL Aroclor 1232 to a 10.0mL volumetric flask and make to volume with hexane. This procedure is repeated for Aroclor 1248 and Aroclor 1262. The 50ug/mL stock standards are transferred to a 10mL vial, tightly capped and stored in a refrigerator. These stock standards must be replaced after one year.

7.19.2 1.22ug/mL Continuing Calibration Check Standard without OCN: Using a 1000uL syringe transfer 1.0mL of 50.0ug/mL Aroclor 1232, 0.72mL of 50.0ug/mL Aroclor 1248, and 0.72mL of 50.0ug/mL Aroclor 1262 into a 100mL volumetric flask. Make to volume with hexane and mix well by shaking and inverting flask several times. The prepared continuing calibration check solution will contain a total of 1.22ug/mL PCB (0.500ug/mL Aroclor 1232, 0.360ug/mL Aroclor 1248, and 0.360ug/mL Aroclor 1262).

7.19.2.1 Transfer the 1.22ug/mL Continuing Calibration Check Standard without OCN to a 120mL boston bottle, cap tightly, and store in a refrigerator. A new continuing calibration check standard must be prepared every six months. This continuing calibration check standard without OCN is used to prepare the 0.122ug/mL Continuing Calibration Check Standard with OCN.

7.19.3 0.122ug/mL Continuing Calibration Check Standard with OCN: Using a 10.0mL Class A pipette transfer 10.0mL of 1.22ug/mL Continuing Calibration Check Standard without OCN to a 100mL volumetric flask. Using a 100uL syringe, add 90.0uL of 20.2ug/mL OCN internal standard (final concentration of 0.01818ug/mL). Make to volume with hexane and mix well by shaking and inverting flask several times. The prepared continuing calibration check solution will contain a total of 0.122ug/mL PCB (0.050ug/mL Aroclor 1232, 0.036ug/mL Aroclor 1248, and 0.036ug/mL Aroclor 1262).

7.19.3.1 Transfer the 0.122ug/mL Continuing Calibration Check Standard with OCN to a 120mL boston bottle, cap tightly, and store in a refrigerator. A new continuing calibration check standard must be prepared every six months.

8.0 Sample Collection, Preservation, Shipment and Storage:

8.1 Sample Collection and Preservation:

8.1.1 Routine 1-liter water samples should be collected in 1-liter clear glass narrow-mouth bottles, fitted with a Teflon-lined cap. The bottles should be pre-cleaned to EPA specification protocol A - recommended for extractable organic, semivolatile and pesticide analysis. Protect samples from light. Low-level water samples should be collected in 4-liter amber jugs, fitted with a Teflon-lined cap. Two 4-liter jugs should be collected for each sample, providing an 8-liter sample for processing. The specific requirements for sample collection at the site is outlined and detailed by the client.

8.1.2 All samples must be placed on ice or refrigerated at 4°C (±2°C) from the time they are collected until delivery to the lab.

8.2 Sample Shipment:

8.2.1 Sample shipment is accomplished through a carrier such as Federal Express or United Postal Service for overnight 1-day delivery to the lab. Shipment is normally handled by the field personnel collecting the samples and coordinated with sample receiving department at the lab. Samples can also be picked up by the lab courier service if samples are collected within driving distance to the lab.

8.3 Sample Storage:

8.3.1 The samples must be protected from light and refrigerated at 4°C (±2°C) from time of receipt until they are removed from storage for extraction. Typically the entire water sample grab will be consumed at time of extraction and no sample is left for log-term storage.

8.3.2 Low-level water samples are stored in a refrigerator dedicated for this type of sample to further minimize exposure to potential contaminants.

8.4 Sample Extract Storage:

8.4.1 Sample extracts must be protected from light and stored refrigerated at 4°C (±2°C) during the analysis. After analysis is complete, sample extracts will be discarded after 60 days or can be archived in a freezer at less than -20°C for longer periods of time depending on the program requirements.

8.4.2 Field samples, sample extracts, and calibration standards must be stored separately.

8.5 Required Holding Times:

8.5.1 Extraction of water samples by appropriate technique must be completed within seven days from sample collection.

8.5.2 Sample extracts must be analyzed within forty days of sample extraction.

9.0 Quality Control:

9.1 The following table lists the Quality Control samples required for capillary gas chromatography analysis of PCBs.

Quality Control Requirements

QC Sample	Frequency
Lab Blank	With each sample batch (up to 20 samples)
Lab Control Spike	With each sample batch (up to 20 samples)
Cont Cal Check Std	Analyzed prior to each sample batch and at a frequency of one per ten injections. Each analytical sequence must close with a Continuing Calibration Check Standard.
Duplicate Analysis	Field generated sample – analyzed at discretion of client
Matrix Spike	One matrix spike per 20 field samples or designated sample batch may be performed as specified in the client site plan.
Matrix Spike Duplicate	One matrix spike duplicate per 20 field samples or designated sample batch may be performed as specified in the client site plan.

9.1.1 Laboratory Blank: The laboratory blank will monitor and assess whether contamination or excessive interference is occurring from laboratory solvents, reagents, and glassware used in processing samples for analysis. The laboratory blank is taken through the sample extraction and clean-up procedures to include all manipulations exposed to actual samples (required volume of solvents, concentration steps, clean-up procedures, *etc*.) If the laboratory blank is positive for PCB above the reporting limit (based on Total PCB concentration), the contamination must be traced down and eliminated before samples can be processed and analyzed. If non-PCB contamination occurs that interferes with PCB quantification, it too must be traced down and eliminated before proceeding with sample analysis. The laboratory blank will consist of organic free water for water samples.

9.1.1.1 Samples associated with a positive laboratory blank should be flagged when the data is reported. If a laboratory blank is positive for PCBs, the source of contamination must be located and eliminated. If the contamination occurred during the extraction procedure and more sample is available the samples will require re-extraction and re-analysis. If the contamination occurred after this step, then re-extraction may not be required and the existing extracts will be reanalyzed. Any aliquots of the extracts (*i.e.,* injection vials), which could have become contaminated, will be discarded.

9.1.2 Laboratory Control Spike: A Laboratory Control Spike sample is analyzed with each extraction batch. An Aroclor is spiked into organic free water. This Control Spike must achieve a percent recovery of 60 to 140 percent based on Total PCB concentration. If the Control Spike recovery is not within limits, the cause must be tracked down and corrected. If there is sufficient sample, the samples associated with the Laboratory Control Spike that failed must be re-extracted and re-analyzed. If no more sample is available, the data must be flagged to indicate low or high Control Spike recovery.

9.1.3 Continuing Calibration Check Standard: As outlined in Section 9.1.8, a Continuing Calibration Check Standard will be analyzed on each working day prior to sample analysis and at an interval of one Continuing Calibration Check Standard per 10 samples. The Continuing Calibration Check Standard must meet the acceptance criteria established in Section 10.3.2.1. If the Continuing Calibration Check Standard fails to meet the acceptance criteria, the following guidance must be followed.

9.1.3.1 If samples are being run using an autoanalyzer (*i.e.,* the instrument is unattended) and a Continuing Calibration Check Standard that fails to meet the acceptance criteria is

present in the analytical sequence but acceptable Continuing Calibration Check Standards are observed later in the analytical sequence, samples bracketed by acceptable Continuing Calibration Check Standards will be reported.

9.1.3.2 If the reason for the failure of the Continuing Calibration Check Standard appears to be a poor injection (or a degraded standard solution), the Continuing Calibration Check Standard will be re-injected (or reprepared and re-injected) immediately following the failed Continuing Calibration Check Standard. This can only occur if the instrument is being attended by an analyst. If upon re-injection, the Continuing Calibration Check Standard meets all the acceptance criteria established in Section 10.3.2.1 and there is no apparent impact on the sample data (*i.e.*, acceptable internal standard areas and surrogate recoveries are observed), the analytical sequence will continue and samples will not be reanalyzed. The associated sample data will be reported.

9.1.3.3 If the Continuing Calibration Check Standard fails to meet the acceptance criteria, the initial calibration standards must be re-analyzed and new response factors generated. After re-calibration, the Continuing Calibration Check Standard must be analyzed again and compared to the acceptance criteria. If the Continuing Calibration Check Standard fails to meet the acceptance criteria after re-calibration, sample analysis must not proceed until the problem is corrected.

9.1.3.4 All samples that were analyzed directly before or after the Continuing Calibration Check Standard exceeded established criteria must be re-analyzed.

9.1.4 Duplicate Analysis: Duplicate analysis of the same sample is performed to assess method precision. A duplicate can also be performed as a blind duplicate, so that identification with original sample is withheld. The analysis of a duplicate sample precludes that PCBs are to be found at appreciable levels in samples. If this is not known the analysis of matrix spike / matrix spike duplicates provide more consistent quality control information. The relative percent difference of the two measurements on the sample is calculated on total PCB concentration by the following equation:

$$RPD = (DUP1 - DUP2)/AVG \times 100$$

Where: RPD = Relative Percent Difference.
DUP1 = The greater of the measured values.

DUP2 = The lesser of the measured values.
AVG = Average of the two analysis.

9.1.4.1 The relative percent difference must be less than or equal to 30%.

9.1.5 Matrix Spike and Matrix Spike Duplicate (MS/MSD): Spiked sample matrix data are analyzed to assess analytical accuracy and recovery of analytes of interest. Thus the sample is spiked and carried through sample analytical procedures including extraction, clean up, and GC analysis. Depending on the specific project plans and at the discretion of the client a matrix spike or matrix spike and matrix spike duplicate can be analyzed.

9.1.5.1 There must be sufficient sample for analysis of matrix spike/matrix spike duplicate samples and the sample must be homogeneous in PCB distribution for valid data to be produced. Spike MS and/or MSD samples with the Aroclor matrix spike standard at a concentration approximately two to five times the sample concentration. Extract and analyze the two spiked samples following procedures used for actual sample analysis. Calculate the percent recovery of the matrix spike/matrix spike duplicate by the following equation:

$$P = A-B/T \times 100$$

Where: P = Percent recovery, %.
A = concentration of analyte in the spike sample aliquot
T = Known true value of the spike concentration
B = Background concentration of PCB in the unspiked sample aliquot

9.1.5.2 Matrix spike recovery information is used to assess the long-term precision and accuracy of the method for each encountered matrix. Matrix spike/matrix spike duplicate results are not used alone to qualify an extraction batch. Generally, percent recovery for MS/MSD samples should be greater than or equal to 60% and less than or equal to 140% based on the total PCB concentration. If the percent recovery is outside the limits, all calculations should be checked and the data should be narrated to describe possible matrix interference.

9.1.6 Surrogates: Surrogate-spiking compounds monitor the exaction efficiency and sample processing procedures for each sample. Surrogate compounds are chosen which do not chromatographically interfere with the PCB target congeners and which behave similarly to the target PCB congeners during extraction and sample processing.

9.1.6.1 Surrogate spike additions are made to each field sample, method blank, and extracted QC check sample prior to extraction. Congener IUPAC 207 (2,2',3,3',4,4',5,6,6'-Nonachlorobiphenyl) is used as the surrogate spike compound.

9.1.6.2 Calculate the surrogate percent recovery as follows:

% Recovery = (Surr. Amount spiked / Theoretical Spike conc.) * 100

9.1.6.3 The percent recovery limits for the surrogate:

IUPAC 207 60% - 140%

9.1.7 Retention Time Windows:

9.1.7.1 Refer to the table entitled "Quality Control Acceptance Criteria and Corrective Action Plan" in Section 15.4 for retention time window and retention time shift acceptance criteria and corrective action.

9.1.7.2 The Initial Continuing Calibration Check Standard of each analytical sequence is used to establish the retention time window for each analyte. The retention time window equals the absolute retention time of the Initial Continuing Calibration Check Standard for a given batch of samples ±0.07 minutes.

9.1.7.3 Besides using the retention time window to assign peaks for quantification, the analyst should also rely on their experience in pattern recognition of multi-response sample analysis.

9.1.8 Analytical Sequence Queue:

A typical analytical sequence is as follows:

1)	Initial Continuing Calibration Check Standard
2)	Method Blank
3)	Lab Control Spike
4 to 10)	Samples (including Duplicates, MS/MSD)
11)	Continuing Calibration Check Standard
12 to 20)	Samples (including Duplicates, MS/MSD)
21)	Continuing Calibration Check Standard; repeat 12 to 20

10.0 Calibration and Standardization:

10.1 Calibration:

10.1.1 Gas chromatographic Operation Parameters:

Establish the gas chromatographic operation parameters as follows:

GC Column: DB-1 (J&W, bonded polydimethylsilicone), 30 meters, 0.25 mm internal diameter, 0.25 micron phase coating.

Oven Temperature Program: 50°C for 2.5 min hold time, 50°C to 150°C at 15.0°C/min hold at 150°C for 0.01 min., 150°C to 220°C at 4.3°C/min hold at 220°C for 35.1 min.

GC Column Velocity: Pressure approximately 23.6 PSI (adjusted to elute OCN Internal Standard between 42.0 and 48.0 minutes).

Detector: Electron Capture Detector (micro-ECD), attenuation 0, range 4 (adjusted for sensitivity).

Detector Temperature: 300°C.

Injector Temperature: Splitless injection, 250°C, purge time 0.75 min., purge flow 15.0 mL/min.

Detector Make-up Gas: Approximately 70.0mL/min Nitrogen. Adjusted for signal sensitivity.

Autosampler: 0.5uL sample volume (adjustable based on signal sensitivity). Sample pumps 4, viscosity delay 3, sample wash 2, solvent A 2 washes, solvent B 2 washes, slow plunger OFF, sampling offset OFF, solvent A pre-wash 1, solvent B pre-wash 1.

10.2 Initial GC Calibration:

Prior to running samples the system must be calibrated and the Initial Continuing Calibration Check Standard must be verified.

10.2.1 Establish the gas chromatographic operation parameters outlined in Section 11.1.1 and prepare the appropriate calibration standards composed of a mixture of Aroclors 1232, 1248, and 1262 as outlined in Sections 7.6 through 7.11.

10.2.2 Prior to sample analysis, a four-point or three-point calibration for each separable (single PCB congener or congener mixture) chromatographic peak is performed. There are 22 DB-1 peaks that cannot be measured in Calibration Standard 4 (low-calibration standard) and only a three-point calibration curve will be generated for the following peaks: DB-1 peaks 10, 13, 20, 44, 52, 55, 56, 67, 72, 79, 84, 87, 89, 91, 98, 101, 104, 108, 111, 113, 114, and 118.

10.2.3 The initial calibration sequence is analyzed as follows:

Injection	Calibration Standard ID
1	Hexane Instrument Blank
2	Hexane Instrument Blank
3	0.00625ug/mL Calibration Std 4
4	0.0125ug/mL Calibration Std 3
5	0.125ug/mL Calibration Std 2
6	0.3135ug/mL Calibration Std 1
7	Hexane Instrument Blank
8	Supplemental Congener Calibration Std
9	Surrogate Calibration Std
10	Hexane Instrument Blank
11	0.122ug/mL Initial Continuing Cal Check Std

10.2.4 Calibration Curve Criteria: The correlation coefficient of the three-or four-point calibration curve must be greater than or equal to 0.995 for each quantified peak using a linear equation with 1/X weighting. The three- or four-point calibration curve must also meet a percent relative standard deviation of less than or equal to 20% for each quantified peak.

10.2.5 Chromatographic Resolution Criteria: Chromatographic resolution is measured by peak height to valley height for two pairs of closely eluting peaks. The peak valley height formed between DB-1 peaks 14 and 15 must be equal to or less than the half height of peak 15. The peak valley height formed between DB-1 peaks 74 and 75 must be equal to or less than one-third the height of peak 74. This peak resolution must be established initially and maintained throughout sample analysis. This measurement is performed on the Initial Continuing Calibration Check Standard and all other subsequent Continuing Calibration Check Standards. This measurement is performed with a millimeter ruler on the chromatogram displayed on the computer terminal.

10.2.6 Retention Time Window: The ±0.07 minutes retention time window is the default window used in Contract Laboratory Program, Statement of Work for Organic Analysis for PCB/Pesticide analysis. The retention times for compounds in the Continuing Calibration Check Standards

must fall within the established retention time windows from the Initial Continuing Calibration Check Standard.

10.2.7 Our laboratory will use a computer based data acquisition workstation (Waters Associates, Millennium_32 workstation software or equivalent), interfaced to the gas chromatograph. The workstation processes the detector signal, performs an analog to digital conversion, and stores the digitized chromatograms on the computer hard disk. All data analysis will be done on the specialized software package including peak integration, calculating calibration curves/response factors, report generation, chromatogram hardcopies, and archival of data. Calculate the response factor for each separated and identified peak.

10.2.8 After the above criteria are met system calibration for sample analysis can be performed. Appendix A identifies which congener and or congeners compose each resolvable GC peak in the calibration standard, along with the amount that each congener or co-eluting group of congeners are represented in the calibration standard. Throughout this document the IUPAC PCB numbering system will be used for congener identification. Appendix B is an example of an acceptable chromatogram of the calibration standard, along with peak congener labels for cross-reference to data in Appendix A. Analyze the four initial calibration standards to initiate calibration of the GC system. Also analyze the Supplemental Congener Standard to calculate relative response factors for congeners that do not exist in the four initial calibration standards. Response factors are calculated relative to the internal standard by the following equation:

$$RRF = (A_x/A_{is})*(C_{is}/C_x)$$

Where:
- RRF = Relative response factor of congener(s)
- A_x = Area of peak for the congener(s).
- A_{is} = Area of peak for the internal standard.
- C_x = Concentration of the congener(s).
- C_{is} = Concentration of the internal standard.

The calibration curve is based on 1/X weighted linear regression, not forced through zero.

10.3 Continuing Calibration

10.3.1 Chromatographic Resolution: Chromatographic resolution is measured by peak height to valley height for two pairs of closely eluting peaks. The peak valley height formed between DB-1 peaks 14 and 15 must be equal to or less than the half height of peak 15. The peak valley height formed between DB-1 peaks 74 and 75 must be equal to or less than one-third the height of peak 74. This peak resolution must be established initially and maintained throughout sample analysis.

10.3.2 Response Factor Verification:

10.3.2.1 The relative response factors calculated from the initial calibration curve will be verified on each working day by analyzing a Continuing Calibration Check Standard, calculating the selected congener concentrations and comparing to their known concentration. A subset of six congeners and Total PCBs will be used to verify the relative response factors before samples are processed. The Percent Difference for Total PCBs must be ±15%. The six congeners include:

DB-1 Peak Number	IUPAC Congener Number	Relative Peak Level in Calibration Standard	Peak Concentration 0.122ug/mL Continuing Calibration Std (ng/mL)	Percent Difference Limits
7	6	Low level peak in standard	1.35	±30
116	205	Low level peak in standard	0.0788	±30
47	70	Medium level peak in standard	2.42	±15
93	174,181	Medium level peak in standard	2.28	±15
37	104,44	High level peak in standard	3.06	±15
102	180	High level peak in standard	4.35	±15

10.3.2.2 After the Continuing Calibration Check Standard is analyzed calculate the amount for these six congeners and Total PCBs and compare those values to the known concentrations by the following equation:

Percent Difference = [Amt(1)-Amt(2)]/Amt(2) x 100

Where: Amt(1) = Amount calculated for congener or Total PCBs.
Amt(2) = Known amount for congener or Total PCBs.

10.3.2.3 A percent difference greater than ±30% for the two low-level peaks (7 and 116) indicates an instrument problem or unacceptable relative response factors. A percent difference greater than ±15% for the medium level (47 and 93) and high-level (37 and 102) peaks also indicates an instrument problem or unacceptable relative response factors. If any of the evaluation congeners or Total PCBs fail to meet the percent difference acceptance criteria, the guidance provided in Section 9.1.3 must be followed.

10.3.2.4 The percent recovery for the internal standard octachloronaphthalene (OCN) in the Continuing Calibration Check Standard must be within 50-150% of the average OCN area among the associated initial calibration standards. If the OCN area fails to meet the acceptance

criteria, the guidance provided in Section 9.1.3 must be followed.

10.3.2.5 If re-calibration is performed, the Continuing Calibration Check Standard must be analyzed again and values calculated using the new relative response factors. If the Continuing Calibration Check Standard fails to meet the percent difference criteria after re-calibration, sample analysis must not proceed until the problem is found and corrected (*i.e.,* GC gas leak, autosampler syringe plugged, broken injector liner).

11.0 Procedure

11.1 Sample Extraction and Preparation:

11.1.1 This low-level analytical procedure is specifically performed for analysis of water samples. The following SOPs detail sample extraction procedures that may be utilized in preparing samples for analysis by this analytical method:

SOP NAME	TITLE
NE006	Separatory Funnel PCB Extraction
NE124	CLLE PCB Extraction
NE178	Solid Phase PCB Extraction

11.2 Gas Chromatograph Procedures:

11.2.1 Sample extracts are set to a volume of 5mLs at which time the internal standard is added. Approximately 1.0mL of the extract is transferred to an autosampler vial.

11.2.3 The sequence for the analytical queue is set up in the chromatography software in the sample set file and given a unique sample set name. This file contains the exact order in which standards, instrument blanks, and samples will run. Once the sample set is in place the GC autosampler tray can be loaded with the autosampler vials and verified to printed sample set for correct position.

11.2.4 The following labeling will be used on the autosampler vial and for the sample set file created for the analytical queue:

11.2.4.1 The Initial Calibration Standards will be labeled as CS0731A, CS0731B, and CS0731C. Substitute the actual date of analysis in the file name.

11.2.4.2 The Supplemental Congener Standard will be labeled SCS0731. Substitute the actual date of analysis in the file name.

11.2.4.3 The Surrogate Standard will be labeled SS0731. Substitute the actual date of analysis in the file name.

11.2.4.4 The Instrument blanks will be labeled 030731B1, B2, B3, *etc*. Substitute the actual date of analysis in the file name.

11.2.4.5 The Continuing Calibration Check Standards will be labeled CCCS0731A, CCCS0731B, *etc*. Substitute the actual date of analysis in the file name.

11.2.4.6 Samples are labeled with the laboratory identification number on the autosampler vial. In the sample set file the laboratory identification number along with the client identification are entered.

11.2.5 At this point the chromatography software can be initiated to start data collection. The gas chromatograph is placed into run mode and sample analysis is performed until the analytical queue is complete.

11.3 Peak Integration and Analyte Identification:

11.3.1 Due to the complex nature of the PCB patterns encountered and the range of peak intensities that can occur in the sample chromatograms, manual peak integration is performed to accurately integrate the samples. Manual peak integration is also performed on standards to best address the changing signal intensities. Manual integration provides for better peak start and peak end positioning, better control of peak baselines and more accurate data.

11.3.2 Analytes are identified by matching retention time to the calibrated peak in the initial calibration standard that are within the retention time window of ±0.07 minutes. The analyst must also use judgment in pattern recognition.

11.3.3 The PCB congener composition of DB-1 peaks is identified in Appendix A. DB-1 peaks may include one or more coeluting PCB congeners. In the case of some peaks, the congeners assigned to the peak consist of coeluting congeners and a congener that is resolved or is just slightly out of the normal retention time window of ± 0.07 minutes. With exception of congeners IUPAC 77 and 122, the resolved peaks are found at trace levels in Aroclors (and, therefore, not present in the calibration standards) and are addressed in this method in the event they are detected. If these

congeners are detected in a sample, the retention time window of the assigned DB-1 peak is set to ensure the congener is quantitated. A standard comment is included on the Congener Weight and Mole Report (see Appendix B) identifying this issue. If detection of one of the resolved congeners occurs, a comment will be included in the report narrative indicating that the assigned DB-1 peak includes the presence of the resolved congener. The DB-1 peaks consisting of coeluting congeners and a congener that is resolved are as follows:

DB-1 Peak[1]	Resolved Congener (IUPAC #)
37 (**44**, *104*)	*104*
48 (**66**, *76*, *98*, *80*, *93*, **95**, **102**, *88*)	*80*, *88*, *93*
56 (*78*, **83**, *112*, *108*)	*108*
61 (**77**, **110**, 148)	**77**
72 (**122**, 131, 133, 142)	**122**
89 (**128**, *162*)	*162*
105 (**200**, *169*)	*169*

1 - IUPAC congener numbers listed in boldface font were found to be present in at least one of the Aroclors at or above 0.05 weight percent. These congeners should be considered the primary congeners existing in a peak composed of co-eluting congeners. IUPAC congener numbers listed in italic font were absent or present below 0.05 weight percent.

12.0 Calculations:

12.1 Internal Standard Calibration:

12.1.1 The capillary column GC analysis will be done by the internal standard calibration technique. Calibration and sample quantification will be performed by a commercial GC software package. The capillary GC will be standardized by using an Aroclor mixture that encompasses all the possible PCB congeners present in environmental samples.

12.1.2 Response factors for each separated and identified peak in the standard will be calculated using the following formula:

$RRF = (A_x/A_{is}) \times (C_{is}/C_x)$

Where: RRF = Relative response factor of congener(s).
A_x = Area of peak for the congener(s).
A_{is} = Area of peak for the internal standard.
C_x = Concentration of the congener(s) (ng/mL).
C_{is} = Concentration of the internal standard (ng/mL).

12.2 Sample Calculations:

12.2.1 The sample PCB concentration of each standardized PCB peak is calculated as follows:

$$\text{Concentration (ng/L)} = \frac{[(A_x)(C_{is})(V)(D)]}{[(A_{is})(RRF)(L_s)]}$$

Where: A_x = Peak area for congener(s) being measured.
C_{is} = Amount of internal standard added to sample extract (ng/mL).
D = Dilution factor, if sample was diluted prior to analysis.
V = Extract volume (mL).
A_{is} = Peak area of added internal standard.
RRF = Relative response factor for congener(s) being measured from initial calibration curve.
L_s = Volume of sample extracted (L).

12.2.2.1 The calculated PCB concentration for each PCB peak will be compared to its respective sample-specific reporting limit (RL) and method detection limit (MDL). The results for peaks with concentrations at or above the MDL but below the RL will be reported as detects and flagged as estimated ("J"). The results for peaks with concentrations at or above the RL would be reported as unqualified numeric values.

12.2.2.2 The Total PCB concentration will be calculated and reported as follows:

12.2.3.1 All peak results above their respective MDL (both "J" flagged and unqualified results) will be summed and compared to the sample-specific Total PCB MDL and RL.

12.2.3.2 If no peaks are detected above their respective MDL, the Total PCB results will be reported as not detected at or above the sample-specific Total PCB MDL.

12.2.3.3 If the summed peaks from Section 12.2.3.1 are below the Total PCB MDL the result would be reported as less than ("<") the sample-specific Total PCB MDL.

12.2.3.4 If the summed peaks from Section 12.2.3.1 are at or above the Total PCB MDL but below the Total PCB RL, the summed result will be flagged as estimated ("J").

12.2.3.5 If the summed peaks from Section 12.2.3.1 are at or above the Total PCB RL, the Total PCB result will be reported as the unqualified numeric value.

12.3 Data Output and Reporting Format:

12.3.1 Reporting limit: The reporting limit for the method is established on a Total PCB basis. The reporting limit is generated from the 6.25ng/mL Calibration Standard 4 (low-level calibration standard) plus the 22 peaks from the 12.5ng/mL Calibration Standard 3 that cannot be measured in the low-level calibration standard. The concentration from the summing of the two calibration standards is 6.36ng/mL. There also exist several instances where the method detection limit (MDL) for several peaks exceeded the reporting limit (RL) for the one-liter and eight-liter water MDL studies. For these instances, where the MDL was higher than the RL, the RL has been raised to be equal to the MDL value. This will establish a reporting limit of 32.3ng/L for a one-liter water sample and 4.00ng/L for an eight-liter water sample. Data reported below the reporting limit but above the current compliant method detection limit will be flagged estimated as "J".

12.3.2 Several specialized software routines have been developed for high resolution PCB analysis to aid the data user in understanding and organizing the complex data generated from this extremely detailed analysis. Appendix C contains examples of the sample hard copy format that will be used in reporting sample information. This data is also available in electronic format as an Excel™ file or other electronic formats as required by the client.

12.4 Data adjustments for Hudson River water samples:

12.4.1 In 1997 a report was issued by General Electric to EPA (HydroQual, 1997. Development of Corrections for Analytical Biases in the 1991 – 1997 GE Hudson River PCB Database. Prepared for General Electric Company Corporate Environmental Programs, Albany, NY.) that outlined concentration corrections required for several DB-1 GC peaks containing more than one PCB congener. These PCB congeners were present in different proportions in Hudson River water samples compared to the method calibration standards. The technical details

and research that support the following data conversion can be found in the above referenced document.

12.4.2 The EPA 1993 Reassessment Remedial Investigation and Feasibility Study (RRI/FS) Phase II Hudson River water column data were used as a qualitative benchmark for data comparison to the GE weekly Hudson River water column study. This 1993 data set was chosen because EPA collected a significant number of samples to compare to the GE weekly sampling events.

12.4.3 Significant concentration differences were detected in Green Bay method GC peaks 5, 8, and 14 (which are comprised of congeners IUPAC 4 and 10; IUPAC 5 and 8; and IUPAC 15 and 18, respectively) when compared to the EPA database, which determined concentrations of these congeners as individual eluting GC peaks. These congeners differ in gas chromatographic response between each other when analyzed individually. It was determined that when these congeners were measured in Hudson River water samples as co-elutions their composition did not match the calibration standard congener composition in peaks 5, 8, and 14 and measurement was not as precise as when these congeners were determined by the EPA analytical method.

12.4.4 To address this measurement bias for the above peaks, a correction ratio was determined and applied to the concentration values obtained by the initial quantification. The correction ratio was derived by analysis of Hudson River water column extracts on a chromatographic system that was calibrated using individual congeners as standards and that could baseline resolve the co-elution congeners found in Green Bay method GC peaks 5, 8, and 14. These results were utilized to report a more accurate concentration value for the congeners comprising Green Bay method peaks 5, 8, and 14. The correction factors historically used were 0.65, 0.45, 1.44 for DB-1 peaks 5, 8, and 14, respectively. The correction ratios were confirmed and verified in March 2004 by conducting confirmatory analyses utilizing the gas chromatographic system that baseline resolved the six PCB congeners that required the correction ratio. GE confirmed and updated the correction factors for DB-1 peaks 5, 8 and 14 in a manner consistent with the approach described in the above report. The results of the evaluation of the correction factors for DB-1 peaks, 5, 8, and 14 were delivered to EPA via email on March 31, 2004 in a technical memorandum. Based on the findings summarized in the technical memorandum, upon initiation of the BMP, the correction factors developed based on the 2003 data set (0.61, 0.36 and 1.26) will be used to adjust DB-1 peaks 5, 8 and 14, respectively, for the bias identified in HydroQual 1997.

12.4.5 After the concentration values are corrected for Green Bay method peaks 5, 8, and 14 several other parameters require re-calculation prior to data reporting. These include the following: total PCB concentration, Homolog distribution, weight percent per peak, chlorination levels (ortho-Cl per biphenyl, meta+para-Cl per biphenyl, and total Cl per biphenyl), total micromoles, and average molecular weight.

13.0 Method Performance:

13.1 Precision and Accuracy Determination: Precision and accuracy data is obtained for the method by analyzing four laboratory control spikes at a reasonable concentration above the calibration standard 4 and below the calibration standard 1. The analyte will be added to a laboratory organic free water sample and taken through all extraction and analytical procedures. Aroclor 1242 is used as the analyte and recovery on a total basis is used to calculate percent recovery. To be valid, Aroclor 1242 will be recovered between the limits of 70 to 130 percent. Also, a percent relative standard deviation will be calculated for the replicates will be less than or equal to 20% to be valid.

13.2 Method Detection Limit: A method detection limit will be determined for this method whenever major modification to the extraction or analysis procedures are made or at a minimum frequency of every 2 years. A minimum of seven laboratory organic free water samples will be prepared with the mixed Aroclor calibration standard at a low level and taken through all extraction and analytical procedures. Method detection limit data will be determined for each chromatographic peak (comprising one or more PCB congeners) based on the following equation:

$$MDL = S * t_{(n-1,\ 1\text{-}alpha=0.99)}$$

Where:

S = Standard deviation of the replicate analyses
n = Number of replicates
$t_{(n-1,\ 1\text{-}alpha=0.99)}$ = Student's t value for the 99% confidence level with n-1

For example: t for 8 replicates = $t_{(7,0.99)} = 2.998$

13.2.1 The determined MDL must be less than the concentration spiked but greater than one tenth (1/10) the spiked concentration. If not, repeat the MDL determination at an appropriate spike concentration for affected analytes.

14.0 Pollution Prevention:

14.1 Pollution prevention is practiced in the laboratory by minimizing usage of solvents and chemicals, so that disposal of waste generated is held to the smallest amount possible. This is directly linked to the types of extraction procedures in place at the laboratory to reduce the volumes of solvents used for semi-volatile extraction procedures. Northeast Analytical employs extraction procedures such as continuous liquid/liquid and solid phase extraction methods to reduce solvent requirements for water extraction protocols.

14.2 Pollution prevention also relies on minimizing to the best extent the chemicals and solvents required to perform extraction and analysis procedures. The laboratory personnel strive to purchase chemicals and standards that will be consumed based on anticipated workload.

14.3 For additional information about laboratory pollution prevention, please refer to laboratory SOP NE168.

15.0 Data Assessment and Acceptance Criteria for Quality Control Measures and Corrective Actions for Out-of-Control Data:

15.1 The GC analyst is responsible for generating the data and also is the initial individual to review the data. This would include inspection of the chromatographic data, processing the raw data, producing all required data forms, inspection of calibration curves for compliance, surrogate recovery, laboratory control spike recovery, matrix spike/matrix spike duplicate recovery, and continuing calibration compliance.

15.2 Once the initial review of the data is performed by the analyst, decisions are made at that time to accept the data if all criteria are met or to reject sample data if any of the quality control parameters or limits are out of control. Depending on the situation, samples requiring re-extraction will be notified to the appropriate extraction personnel, sample extracts requiring re-injection will be queued for analysis, new calibrations may have to be performed, or samples re-analyzed due to failing continuing check standards.

15.3 The analyst may also consult with the quality control officer as to the best form of action to take or if the situation warrants corrective action beyond routine practices. A Corrective Action Report (CAR) is issued to document the problem found, steps taken to resolve the problem, and what samples were affected. This CAR form is filed with the data and is also useful for production of case narratives that are issued with final data reports.

15.4 The Table below outlines the data assessment, acceptance criteria, and corrective action procedures for out-of-control data.

Quality Control Acceptance Criteria and Corrective Action Plan

Quality Control Item	Frequency	Acceptance Criteria	Corrective Action
Initial Calibration	• Establish initially and when Continuing check standard fails criteria. • Calibration curve at 3 or 4 concentration levels. The surrogate calibration is a single point at 2ng/mL.	• %RSD≤20% for each relative response factor and a correlation coefficient ≥0.995 for each calibrated peak. • Calibration factors are to be calculated using area for each quantifiable peak with internal standard method and 1/X linear weighting, not forced through zero.	• Re-analyze the initial calibration curve and/or evaluate/correct instrument malfunction to obtain initial calibration that meets criteria. • Sample results above highest standard concentration require dilution and re-analysis.
Continuing Calibration Check Standard (CCC)	• Initially analyze a CCC immediately following a calibration curve. • After the initial CCC of the sequence, a CCC must be analyzed after every 10 samples. • Analytical sequence must end with analysis of a CCC.	• ≤ 30% difference based on "true" concentration for peaks 7, 116. • ≤ 15% difference based on "true" concentration for peaks 37, 47, 93, 102 and Total PCBs • Retention time of all quantitated peaks must be within RT window (reset with each initial CCC of a sequence) • The percent recovery for the internal standard (OCN) in the Continuing Calibration Check Standard must be within 50-150% of the average OCN area among the associated initial calibration standards. • All samples must be bracketed by CCCs that meet all criteria stated above	• If the reason for the failure of the CCC appears to be a poor injection (or a degraded standard solution), the CCC will be re-injected (or reprepared and re-injected) immediately following the failed CCC. This can only occur if the instrument is being attended by an analyst. If upon re-injection, the CCC meets all the acceptance criteria and there is no apparent impact on the sample data (*i.e.,* acceptable OCN areas and surrogate recoveries are observed), the analytical sequence will continue and samples will not be reanalyzed. The associated sample data will be reported. • If CCC failure was not due to a poor injection (or degraded standard solution) or the instrument was unattended at the time of the CCC failure, correct system, if necessary, and recalibrate. Initial calibration and CCC criteria must be met before sample analysis may begin. Samples that are not bracketed by complaint CCCs must be re-analyzed. • If acceptable CCCs are observed later in the sequence, samples bracketed by acceptable CCCs will be reported. Samples between the failed CCC and prior/ subsequent complaint CCC will be re-analyzed.

Quality Control Acceptance Criteria and Corrective Action Plan

Quality Control Item	Frequency	Acceptance Criteria	Corrective Action
Retention Time (RT) Windows	• Default RT window is ±0.07 minutes • RT windows are re-centered based on the initial CCC analyzed after calibration curve or if using the first CCC of the day to start a new sequence.	• RT of CCC peaks must be within established windows in the CCs analyzed for a sequence. • Re-centering windows is allowed only once per 24 hours.	• Adjust system, re-establish RT windows, and re-calibrate if necessary.
Retention Time (RT) shift	• Each CCC analysis: RT of all quantitated peaks in the CCC is evaluated against the initial CCC following the initial calibration curve. • Each sample analysis: Rely on RT windows to identify PCB congeners to report. Also use pattern recognition and professional judgment for peaks that shift from RT windows, because congener composition may shift RT for GC peaks.	• Each quantitated peak and surrogate peak should be with established windows.	• Inspect chromatographic system for malfunction, correct problem. Perform re-analysis if necessary.
Method Blank	• One per extraction batch of ≤20 samples of the same matrix per day. • Must be analyzed on each instrument used to analyze associated samples. • Must undergo all sample preparative procedures.	• Concentration does not exceed the total PCB method reporting limit (typically the MDL for aqueous samples). • Must meet surrogate criteria of 60 to 140 % recovery.	• Re-analyze method blank to determine if instrument contamination was the cause. If method blank re-analysis passes, then report samples. • If method blank is found to contain PCB contamination above total PCB reporting limit. Then re-extract and re-analyze all associated samples. If no sample exists for re-extraction, report data flagged to indicate method blank contamination or have client re-sample if possible.
Laboratory Control Spike (LCS)	• One per extraction batch of ≤20 samples per matrix per day. The LCS is typically Aroclor 1242 at approximately 20.0ng/L	• Percent recovery of Aroclor 1242 on a total PCB basis must be within method limits of 60 to 140% • Must meet surrogate criteria of 60 to 140% recovery.	• Re-analyze LCS to determine if instrument was the cause. If LCS passes, then report samples. • If LCS recovery is still out of limits, then re-extract and re-analyze all associated samples. If no sample exists for re-extraction, report data flagged to indicate LCS failed recovery or have client re-sample if possible.

Quality Control Acceptance Criteria and Corrective Action Plan

Quality Control Item	Frequency	Acceptance Criteria	Corrective Action
Matrix Spike/Matrix Spike Duplicate (MS/MSD)	• For aqueous samples, normal method procedure is to extract and analyze a matrix spike sample. One MS per extraction batch of ≤20 samples per matrix per day. The MS is typically Aroclor 1242 at approximately 20.0ng/L. • If requested, an MSD can be extracted an analyzed. The MSD would follow the above criteria as for the MS.	• Percent recovery for MS on a total PCB basis should be 60 to 140% • If MS/MSD is analyzed, relative percent difference (RPD) should be within 30%. • Must meet surrogate criteria of 60 to 140%(unless original unspiked sample is also outside of criteria).	• Re-analyze MS and/or MSD to determine if instrument was the cause. If MS and/or MSD pass, then report samples. • Check for errors such as calculations and spike preparation. • Check original unspiked sample results and surrogate recovery for indications of matrix effects. • If no errors are found, and the associated LCS is within 60 to 140 %, then sample matrix effects are likely the cause. Note exceedence in case narrative.
Surrogates	• 2,2',3,3',4,4',5,6,6'-Nonachlorobiphenyl is added to all samples and QC samples at a concentration of approximately 10ng/L.	• Percent recovery for the surrogate should be 60 to 140%	• Re-analyze the affected sample or QC sample to determine if instrument was the cause. If surrogate passes, then report samples. • Check for errors in surrogate calculations and surrogate solutions. • If no problem is found, then re-extract and re-analyze the sample. • If re-analysis is within limits and sample extract holding time, then report only the re-analysis. • If the re-analysis is within limits, but out of extraction holding time, then report both sets of data. • If the re-extraction produces surrogate recovery still out of limits, then report both sets of data. • If no sample exists for re-extraction, report data flagged to indicate surrogate failed recovery or have client re-sample if possible.

Quality Control Acceptance Criteria and Corrective Action Plan

Quality Control Item	Frequency	Acceptance Criteria	Corrective Action
Internal Standard	• Octachloronaphthalene (OCN) is added to all sample extracts, QC samples and calibration standards. For sample extracts, 4.5uL of 20.2ug/mL OCN is added to 5mL final extract volume. See text for OCN amounts in calibration standards.	• The internal standard area for samples and QC samples should be 50 to 150% of the average internal standard area among the associated initial calibration standards. • The internal standard area for CCCs must be 50 to 150% of the average internal standard area among the initial calibration standards.	• Re-analyze the affected sample or standard to determine if instrument was the cause. If internal standard passes, then report samples. • For Standards – If no problem is found, prepare new standards and re-test. If problem still exists, prepare new internal standard and then prepare new standard solutions and re-test. • For Sample Extracts – If no problem is found, then follow procedures outlined above for surrogate corrective action steps for re-extraction and re-analysis.

16.0 Contingencies for Handling Out-of-Control or Unacceptable Data:

16.1 Data that is detected to be out-of-control for any reason, when compared to method acceptance criteria, will addressed in the following manner:

16.1.1 If the problem exists with the gas chromatographic instrumentation, appropriate action will be taken to repair and perform maintenance to bring the instrument back to operating condition. Once the instrumentation is determined to be correctly operating analysis can begin again.

16.1.2 If the problem exists with calibration standard solutions, the analyst will prepare new standards and discard the standard solutions that are suspect. Instrument calibration can be performed and analysis can begin once system is in control.

16.1.3 If the problem exists with sample extraction and extract preparation, the extraction step that is producing the out-of-control situation will be diagnosed and rectified. Once the troubleshooting procedures correct the problem extraction can once again occur and analysis can continue.

16.2 In situations where data is reported under out-of-control conditions, the data will be annotated with data qualifiers and/or appropriate descriptive comments defining the nature of the excursion in the sample case narrative. If warranted, a corrective action report (CAR) will be issued to define the problem, steps to correct the problem, and final resolution.

17.0 Waste Management:

17.1 All applicable federal and state rules and regulations governing hazardous waste will be followed when disposing of laboratory waste generated during the execution of this method.

17.2 Please refer to standard operating procedures NE089 and NE054 regarding how hazardous waste is handled and disposed of by the laboratory.

18.0 References:

18.1 US EPA 40 CFR Part 136, "Guidelines Establishing Test Procedures for the Analysis of Pollutants," July, 1988.

18.2 Standard Methods for the Examination of Water and Wastewater, 19th Edition, Published by: American Public Health Association, American Water Works Association, Water Pollution Control Federation, 1995.

18.3 US EPA SW-846, "Test Methods for Evaluating Solid Waste Physical/Chemical Methods," Office of Solid Waste and Emergency Response, 3rd Edition, 1986 and its updates.

18.4 New York State Department of Health, "Environmental Laboratory Approval Program Certification Manual," Wadsworth Center for Laboratories and Research, 1988.

18.5 Mullin, M.D. 1985. PCB Workshop, US EPA Large Lakes Research Station, Grosse Ile, MI, June.

18.6 M. Zell, K. Ballschmiter, Baseline Studies of the Global Pollution, III. Trace Analysis of Polychlorinated Biphenyls (PCB) by ECD Glass Capillary Gas Chromatography in Environmental Samples of Different Trophic Levels, Fresenius Z. Anal. Chem., 304, 337-349, 1980.

18.7 M.D. Mullin, C.M. Pochini, S. McCrindle, M. Romkes, S.H. Save, "High-Resolution PCB Analysis: Synthesis and Chromatographic Properties of All 209 PCB Congeners," Environ. Sci. Technol., Vol 18, No. 6, pp 468-476, 1984.

18.8 D.L. Swackhamer, "Quality Assurance Plan, Green Bay Mass Balance Study, 1. PCBs and Dieldrin, US EPA Great Lakes National Program Office" Quality Assurance Coordinator, Field and Analytical Methods Committees, University of Minnesota, December 11, 1987.

18.9 George M. Frame, Robert E. Wagner, James C. Carnahan, John F. Brown, Jr., Ralph J. May, Lynn A. Smullen, and Donna L. Bedard, "Comprehensive, Quantitative, Congener-Specific Analyses of Eight Aroclors and Complete PCB

Congener Assignments on DB-1 Capillary GC Columns ", Chemosphere, Vol. 33, No. 4, pp. 603-623, 1996.

18.10 "Standard Operating Procedure for the Gas Chromatographic Analysis of Hydrophobic Organic Contaminant Extracts from Great Lakes Water Samples", USEPA Great Lakes National Program Office, 77 West Jackson Boulevard, Chicago, IL 60604-2590, GLNPO Organics SOP – 10, 6/1/94:Revision 2

18.11 "Biphenyls and Halogenated Pesticides by High Resolution Gas Chromatography", M.D. Mullin, Large Lakes Research Station, LLRS-SOP-ORG-013, revision 2, August 3, 1990, p 1-10.

18.12 Contract Laboratory Program – Statement of Work for Organic Analysis, Multi-Media, Multi-Concentration. Document OLM3.2, 1996.

APPENDIX A

Congener Composition of Mixed Aroclor Calibration Standard 1 (313.5ng/mL)

Congener Composition of Mixed Aroclor Calibration Standard 1(313.5ng/mL) (Aroclors 1232, 1248, 1262 in a ratio of 25:18:18)

file: S:/TEXT/SOP/ne207_appendix_A_Gbcalstd_313.5_ng_ml.DOC

DB-1 Peak Number [1]	IUPAC # [2]	Amount ng/mL
2	**001**	21.93
3	**002**	-
4	**003**	12.79
5	**004 010**	6.21
6	**007 009**	2.19
7	**006**	3.47
8	**005 008**	25.58
9	*014*	-
10	**019**	0.51
11	*030*	-
12	**011**	-
13	**012 013**	0.49
14	**015 018**	6.76
15	**017**	6.76
16	**024 027**	0.48
17	**016 032**	7.13
19	*023* **034** *054*	-
20	**029**	0.10
21	**026**	1.32
22	**025**	0.58
23	**031**	7.53
24	**028** *050*	9.64
25	**020** *021* **033 053**	7.26
26	**022 051**	5.30
27	**045**	1.63
28	*036*	-
29	**046**	0.73
30	*039*	-
31	**052** *069 073*	8.72
32	**043 049**	4.20
33	*038* **047**	1.83
34	**048** *075*	1.83
35	*062 065*	-
36	**035**	-
37	*104* **044**	7.86
38	**037 042 059**	4.75
39	**041 064 071** *072*	7.49
41	*068* **096**	-
42	**040**	1.72
43	**057** *103*	-
44	*058* **067** *100*	0.20
45	**063**	0.38
46	**074** *094 061*	3.47
47	**070**	6.21
48	**066** *076 098 080 093* **095 102** *088*	13.16

DB-1 Peak Number [1]	IUPAC # [2]	Amount ng/mL
49	*055* **091** *121*	0.93
50	**056 060**	6.40
51	**084 092** *155*	3.29
52	**089**	0.18
53	**090 101**	3.29
54	*079* **099** *113*	1.35
55	**119** *150*	0.05
56	*078* **083** *112 108*	0.27
57	**097** *152 086*	1.02
58	*081* **087** *117 125* **115** *145*	2.12
59	*111 116* **085**	1.28
60	*120* **136**	1.37
61	**077 110** *148*	3.89
62	*154*	-
63	**082**	0.80
64	**151**	3.11
65	**124 135**	0.53
66	**144**	1.10
67	*107* **109** *147*	0.24
68	*123*	-
69	*106* **118** *139* **149**	7.31
70	*140*	-
71	**114 134** *143*	0.37
72	**122 131 133** *142*	0.05
73	**146** *165 188*	0.71
74	**105 132** *161*	2.48
75	**153**	5.38
76	*127 168 184*	-
77	**141**	3.11
78	**179**	2.67
79	**137**	0.14
80	**130 176**	0.48
82	**138 163 164**	4.93
83	**158** *160 186*	0.46
84	*126* **129**	0.02
85	*166* **178**	2.01
87	**175** *159*	0.37
88	*182* **187**	6.58
89	**128** *162*	0.18
90	**183**	3.11
91	**167**	0.09
92	**185**	0.86
93	**174** *181*	5.85
94	**177**	3.11
95	**156 171**	1.44
96	**157 202**	0.12
98	**173**	0.07
99	**201**	0.71
100	**172** *204*	1.02
101	*192* **197**	0.20

DB-1 Peak Number [1]	IUPAC # [2]	Amount ng/mL
102	**180**	11.15
103	**193**	0.77
104	**191**	0.22
105	**200** *169*	0.79
106	**170**	2.34
107	**190**	0.77
108	**198**	0.22
109	**199**	7.68
110	**196 203**	7.86
111	**189**	0.07
112	**195**	1.01
113	**208**	0.45
114	*207*	0.17
115	**194**	3.29
116	**205**	0.20
117	**206**	1.24
118	*209*	0.02

1 - Note that 5 DB-1 peaks (PK18, PK40, PK81, PK86, PK97) have been removed from the DB-1 peak numbering scheme. The following low-level congeners that were designated as separately eluting peaks have been determined to co-elute with another congener. The DB-1 peak numbers are no longer required for these congeners, but the original DB-1 numbering system has remained intact for all other peaks.
PK 18 (23) now elutes in PK 19 (23,34,54)
PK 40 (68) now elutes in PK 41 (68,96)
PK 81 (176) now elutes in PK 80 (130,176)
PK 86 (166) now elutes in PK 85 (166,178)
PK 97 (157) now elutes in PK 96 (157,202)

2 - IUPAC congener numbers listed in boldface font were found to be present in at least one of the Aroclors at or above 0.05 weight percent. These congeners should be considered the primary congeners existing in a peak composed of co-eluting congeners. IUPAC congener numbers listed in italic font were absent or present below 0.05 weight percent.

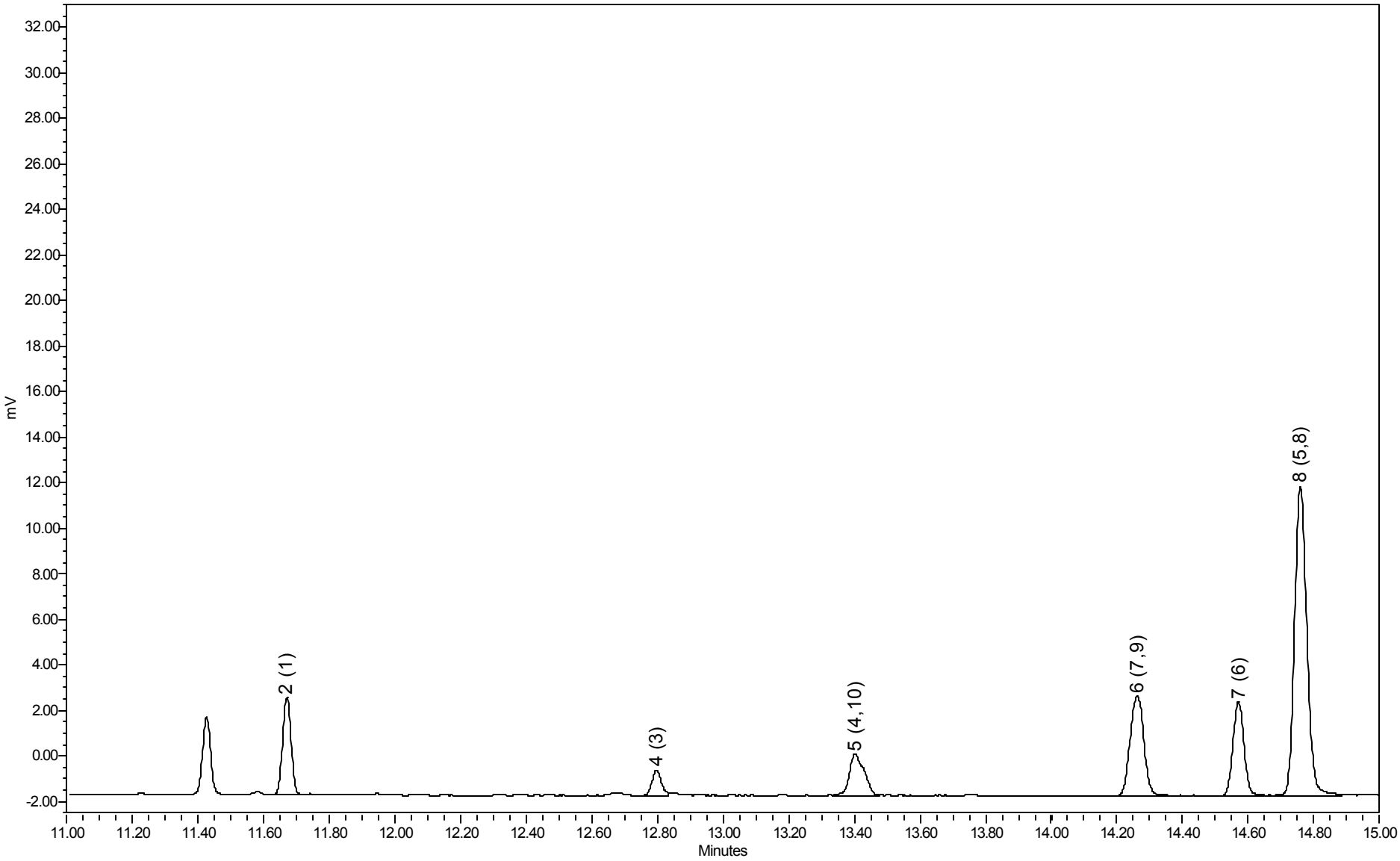
APPENDIX B

DB-1 Capillary GC/ECD Chromatograms:

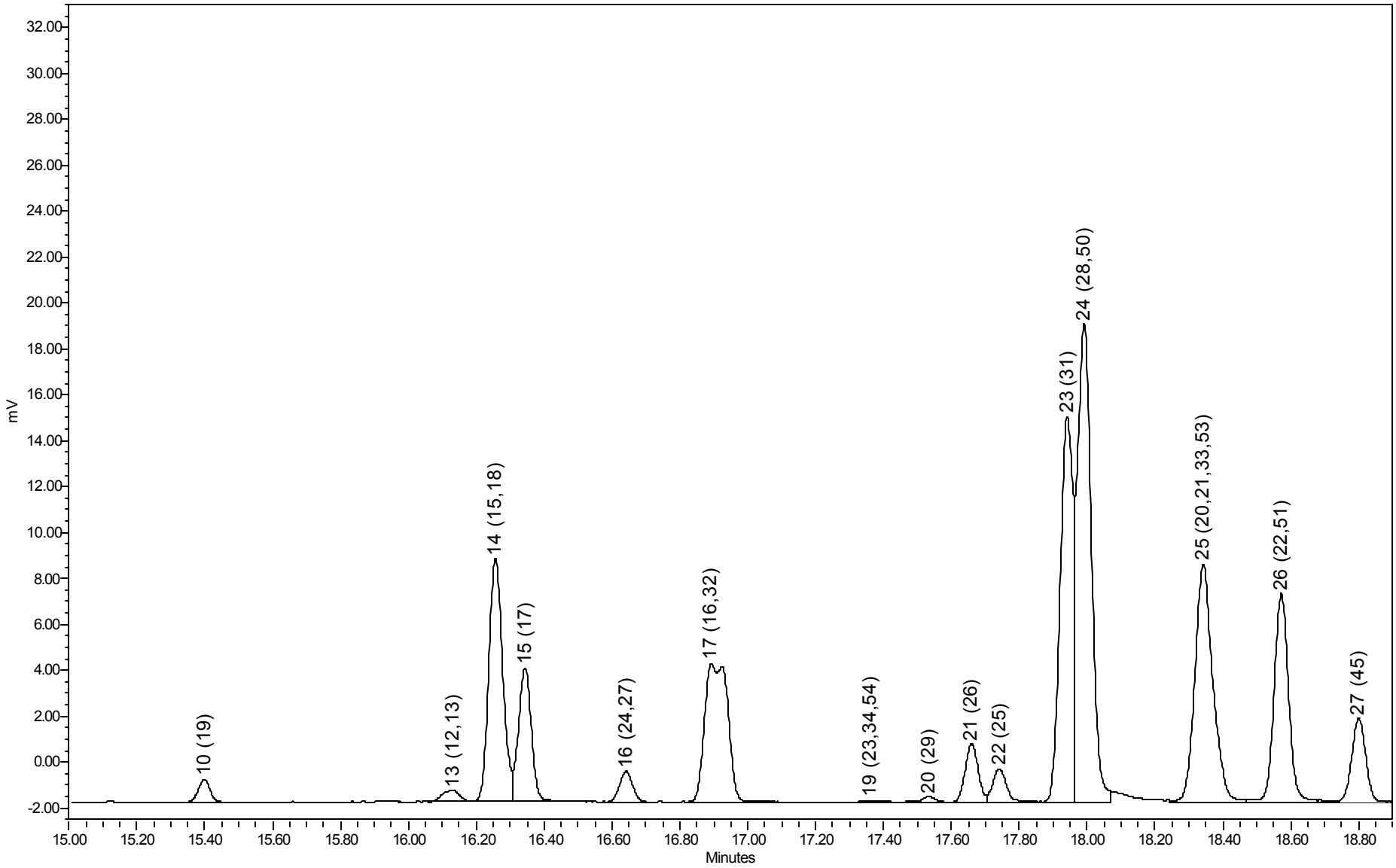
1 Initial Calibration Standard 1 (313.5ng/mL)

2 Supplemental Congener Standard: 3-chlorobiphenyl at 200ng/mL
All other PCB congeners at 5.00ng/mL

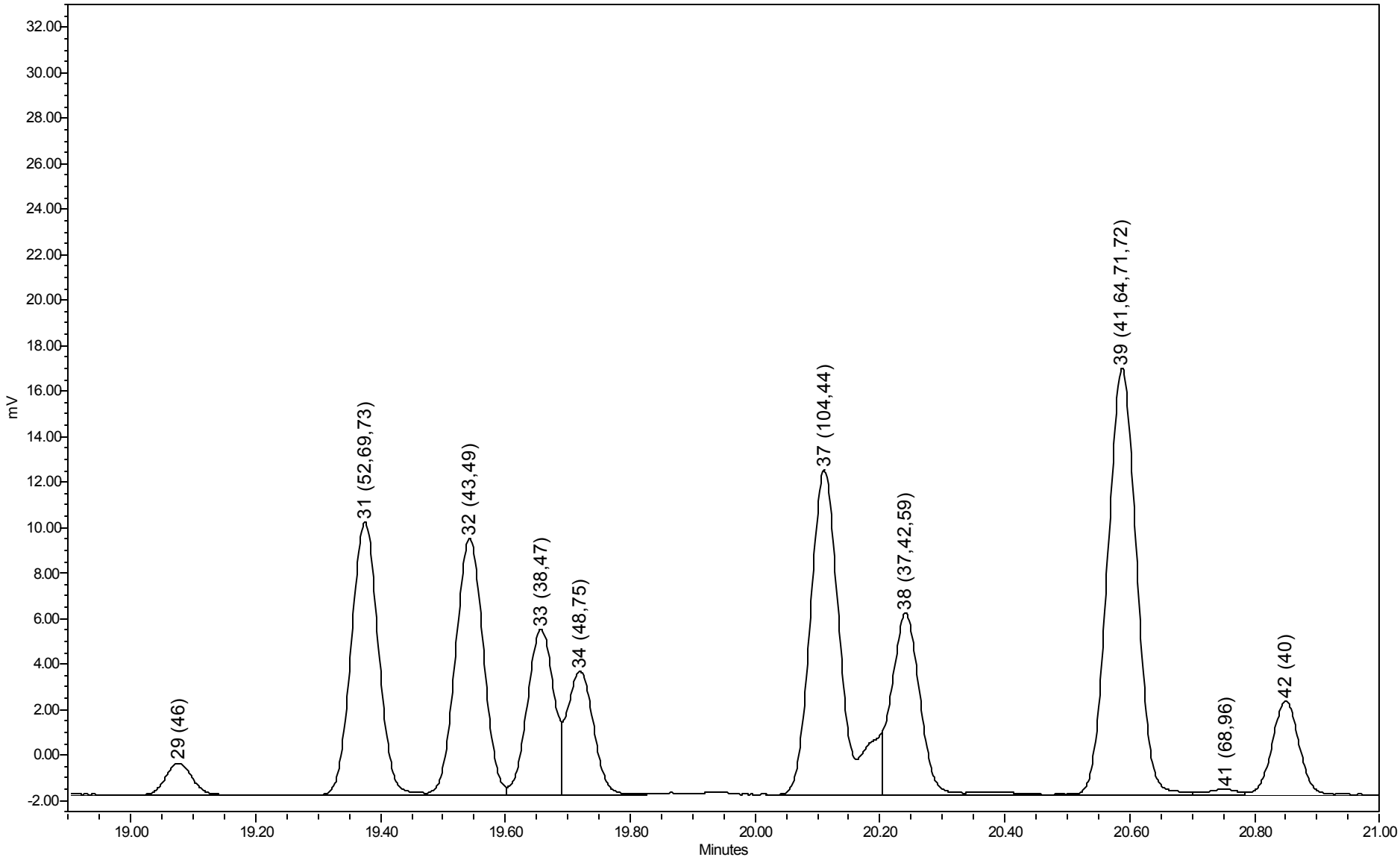
Congener Composition Chromatogram of Aroclor Calibration Mixture (314 ng/mL)



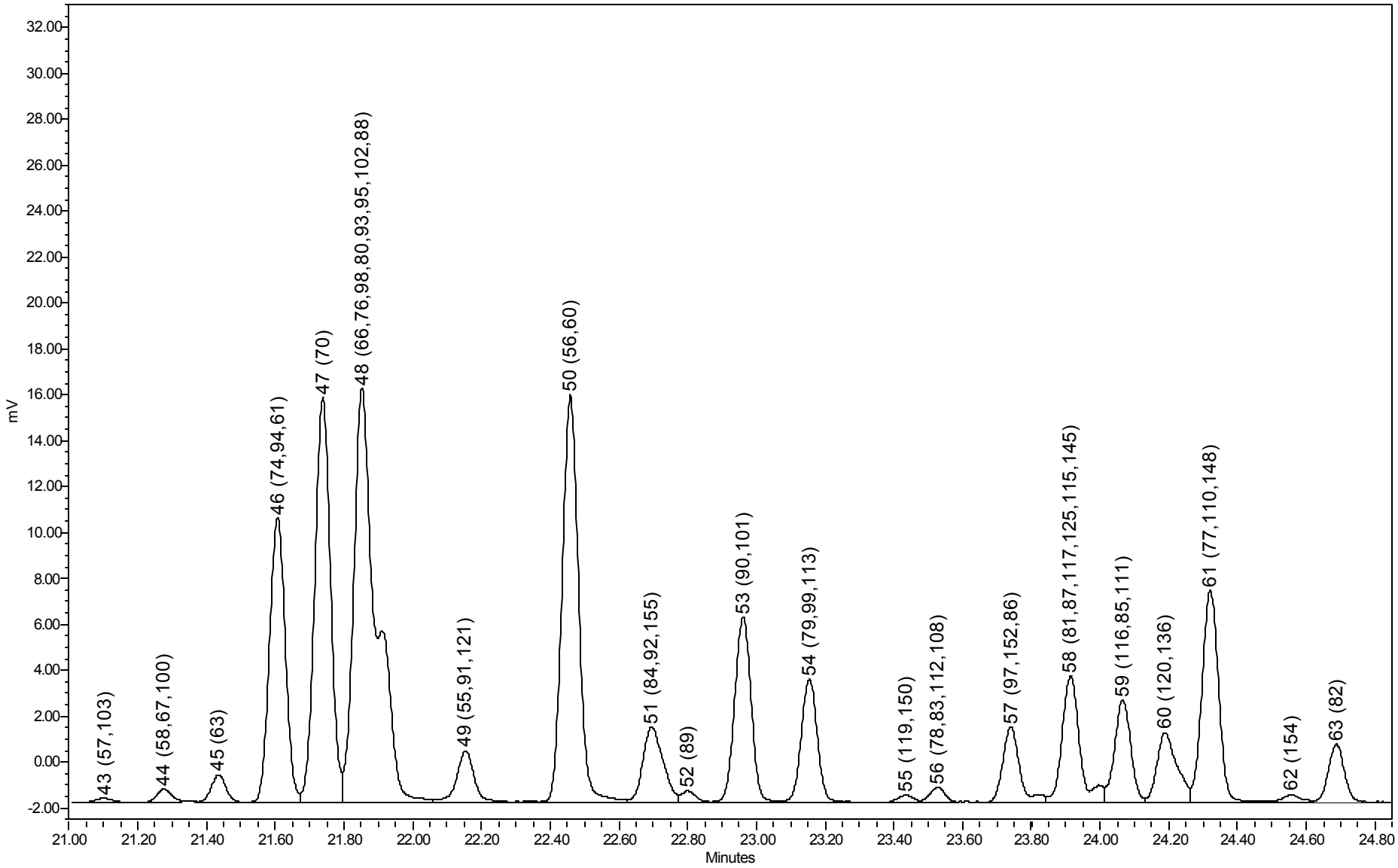
Congener Composition Chromatogram of Aroclor Calibration Mixture (314 ng/mL)



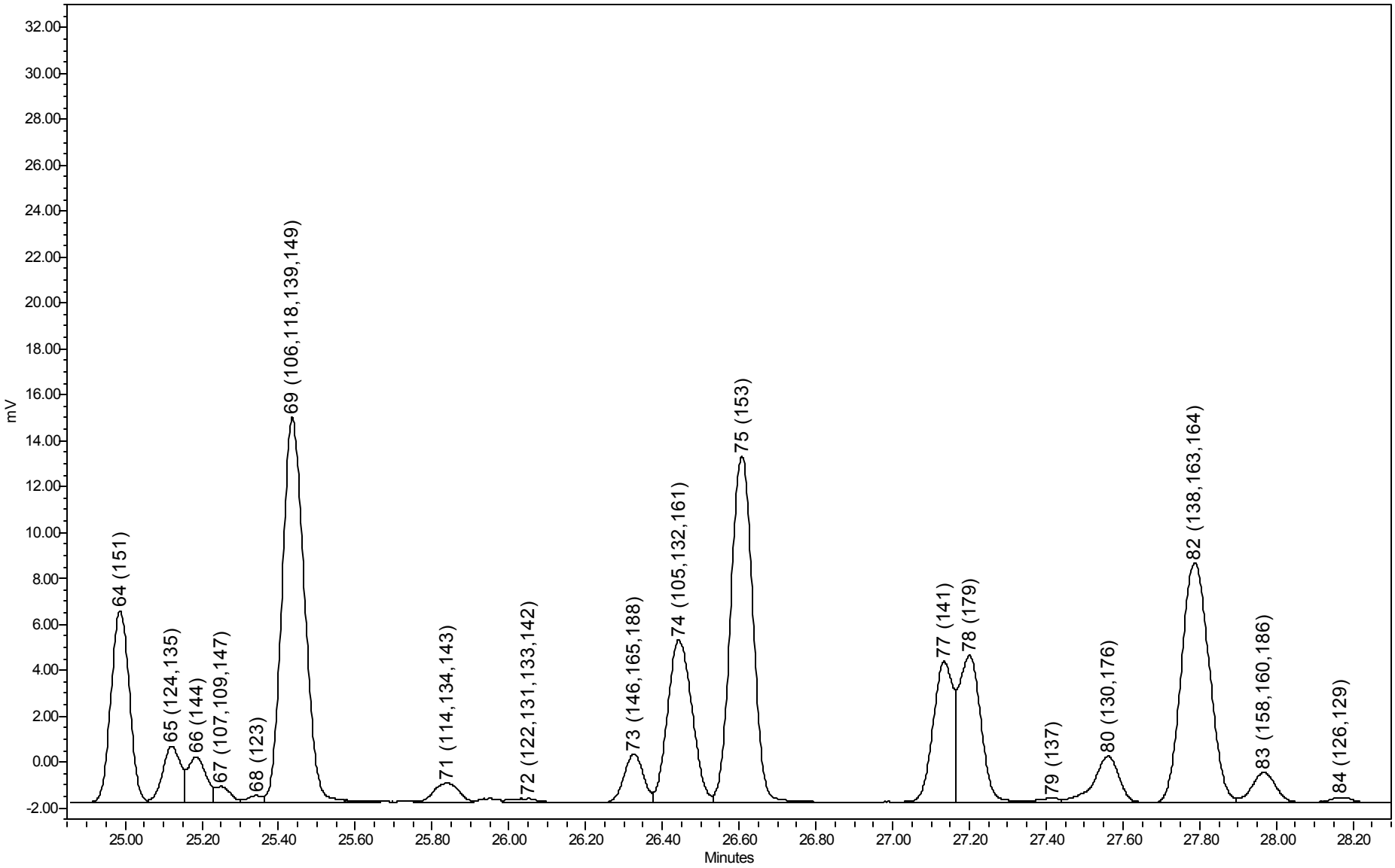
Congener Composition Chromatogram of Aroclor Calibration Mixture (314 ng/mL)



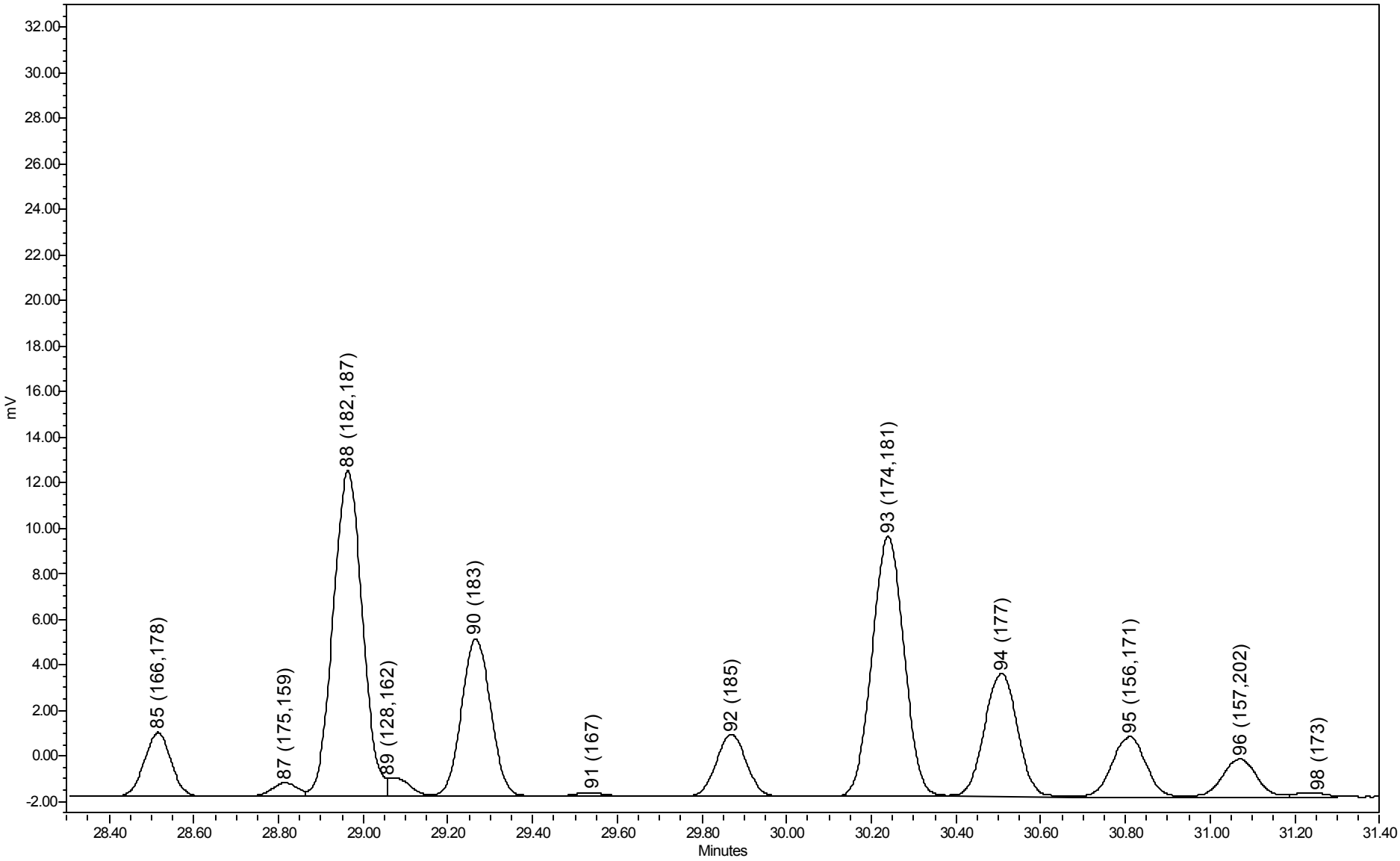
Congener Composition Chromatogram of Aroclor Calibration Mixture (314 ng/mL)



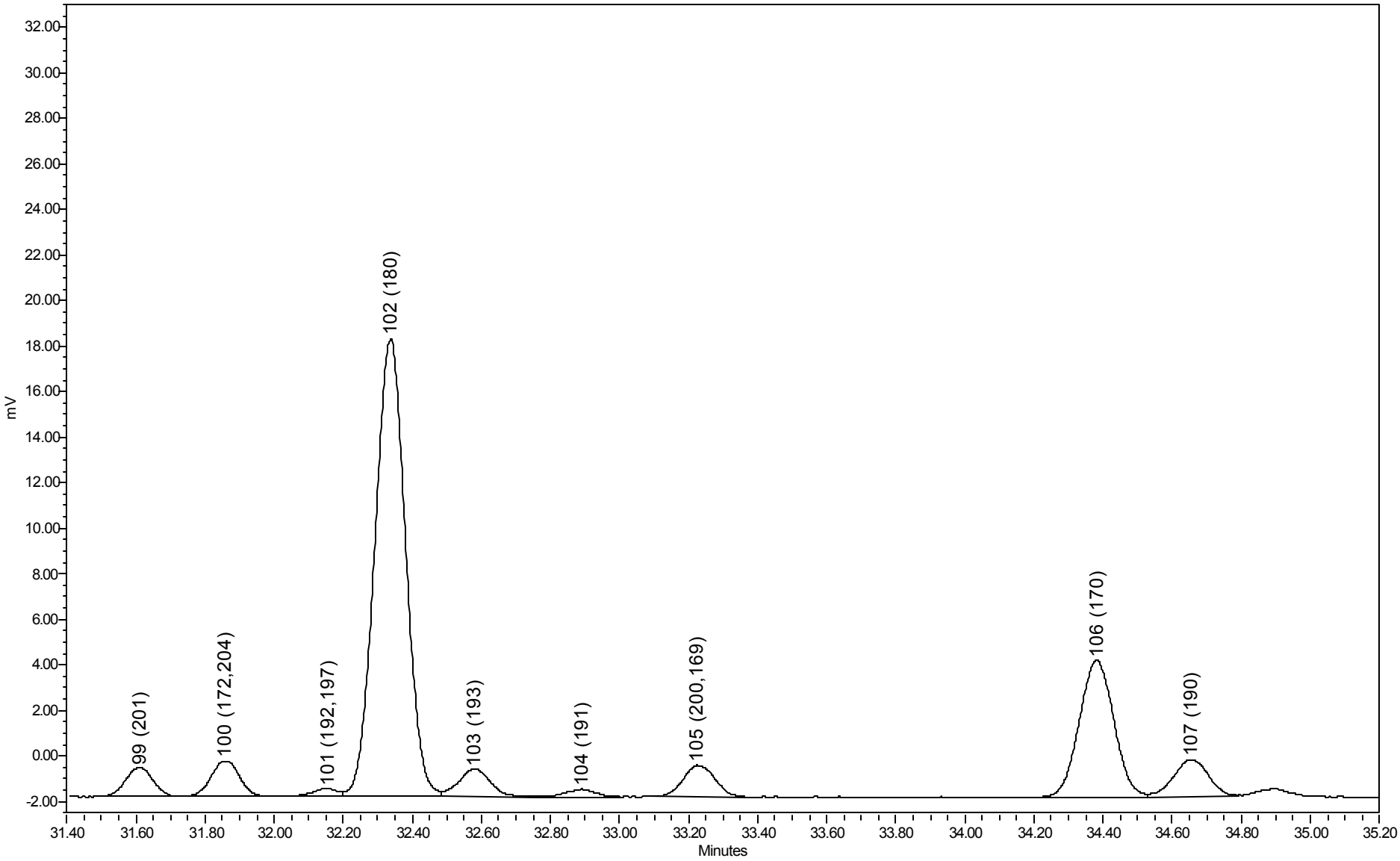
Congener Composition Chromatogram of Aroclor Calibration Mixture (314 ng/mL)



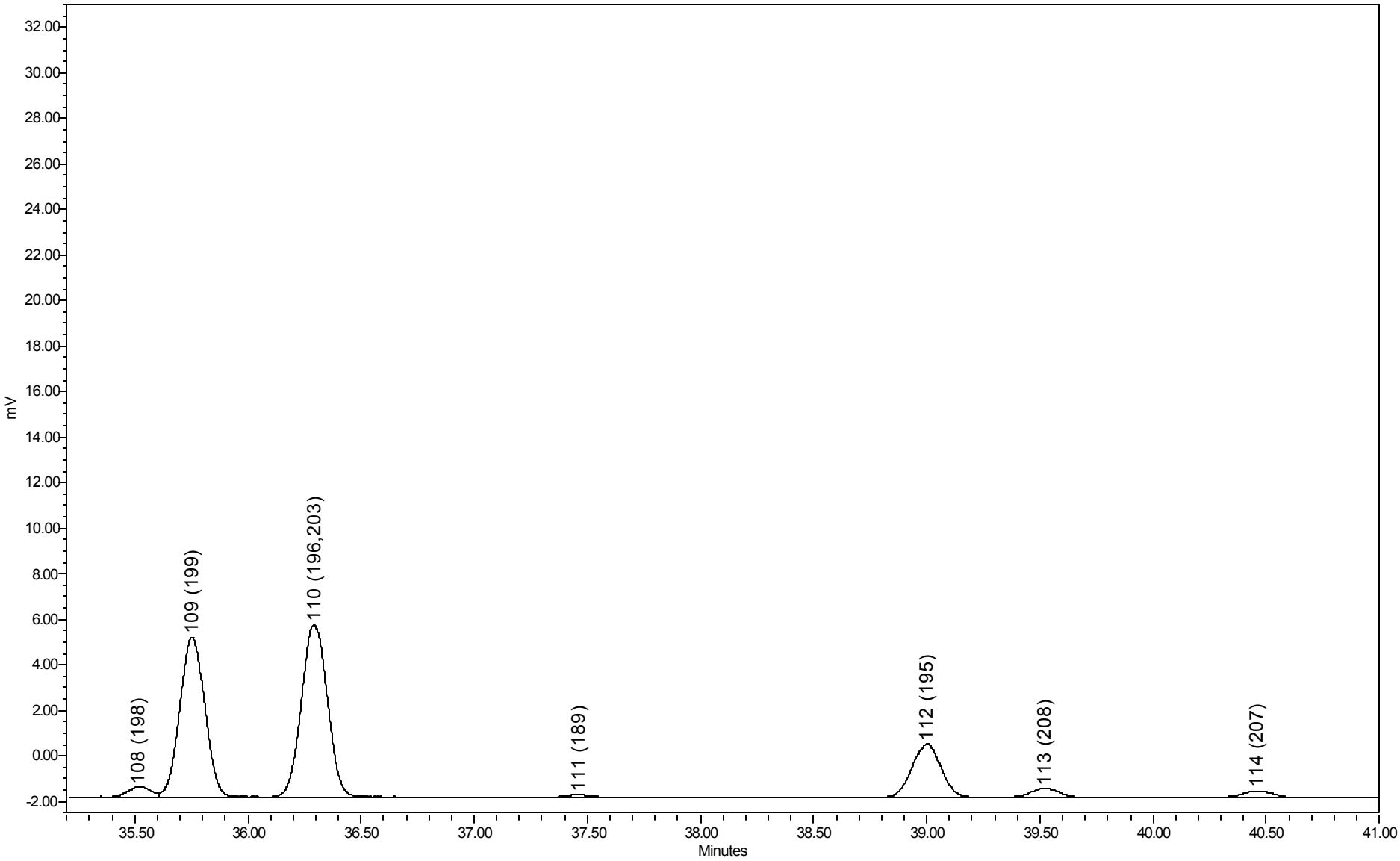
Congener Composition Chromatogram of Aroclor Calibration Mixture (314 ng/mL)



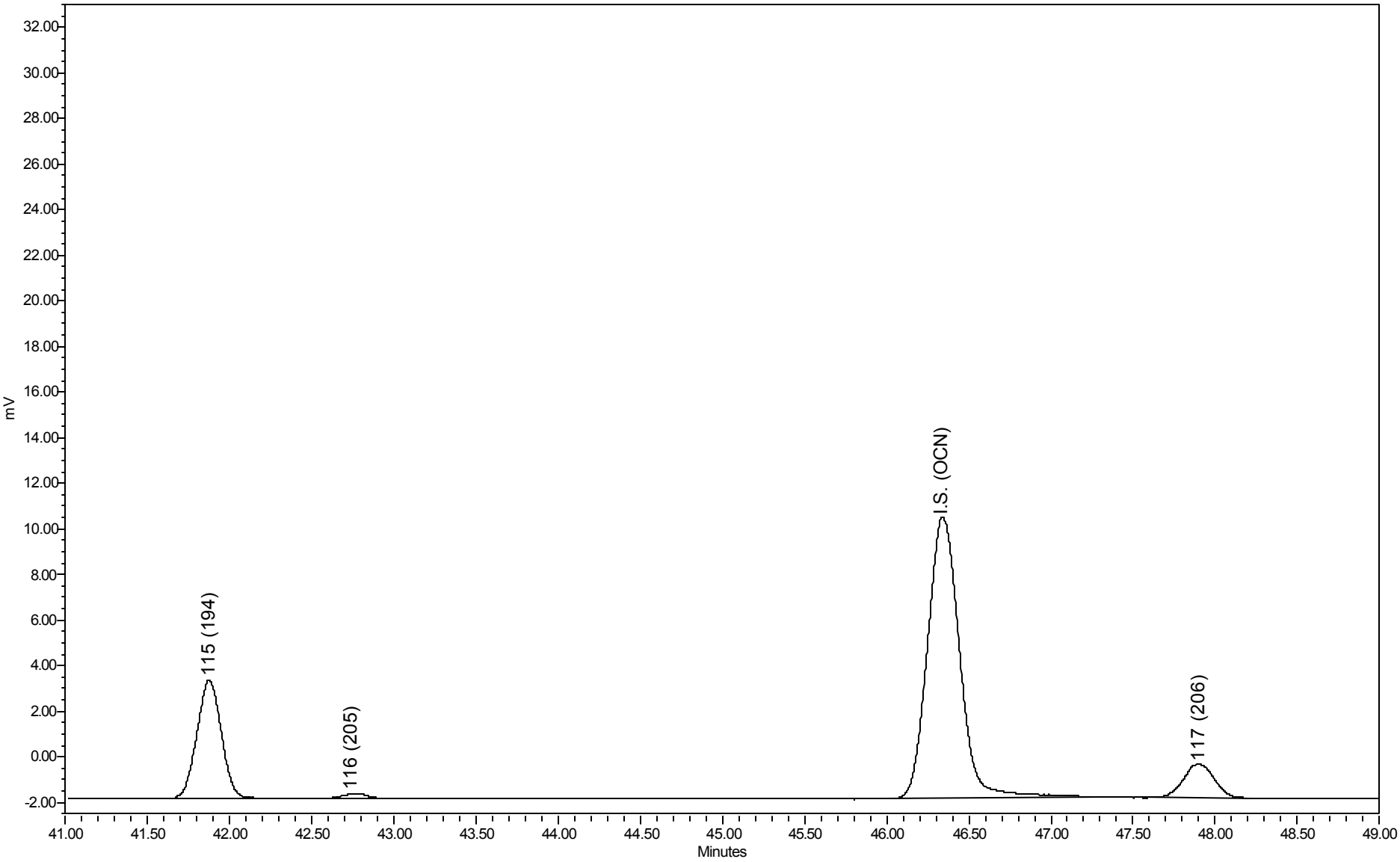
Congener Composition Chromatogram of Aroclor Calibration Mixture (314 ng/mL)



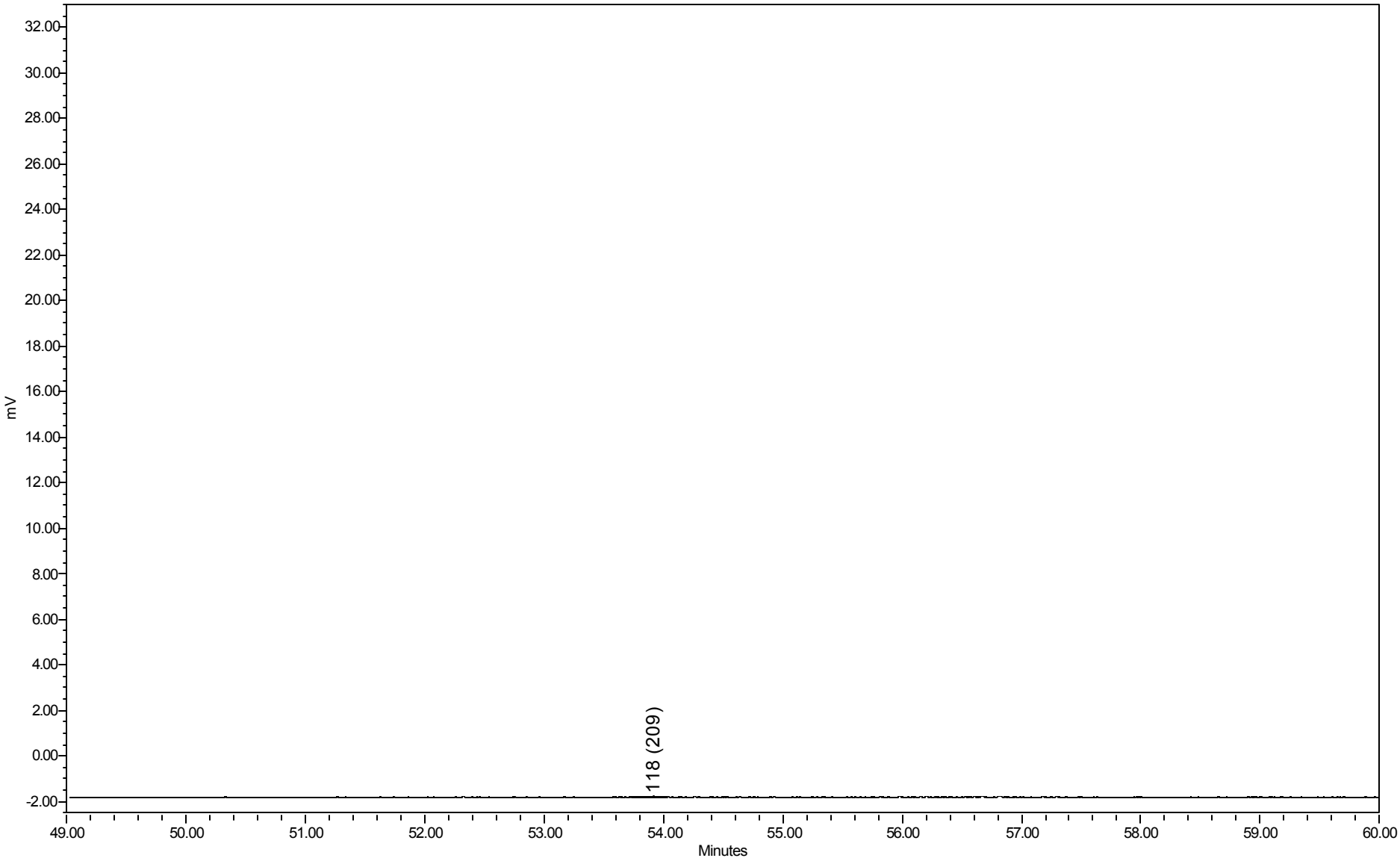
Congener Composition Chromatogram of Aroclor Calibration Mixture (314 ng/mL)



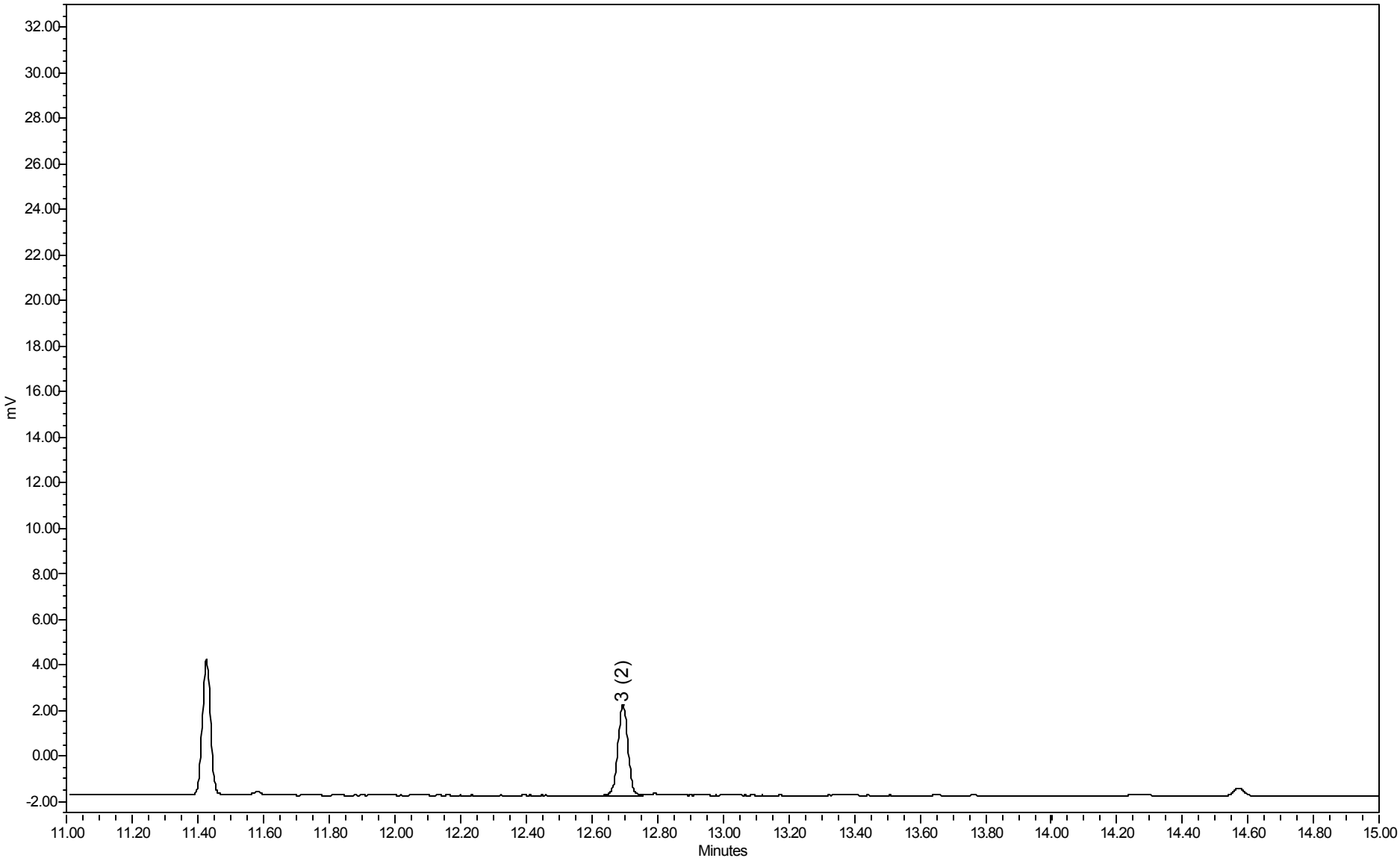
Congener Composition Chromatogram of Aroclor Calibration Mixture (314 ng/mL)



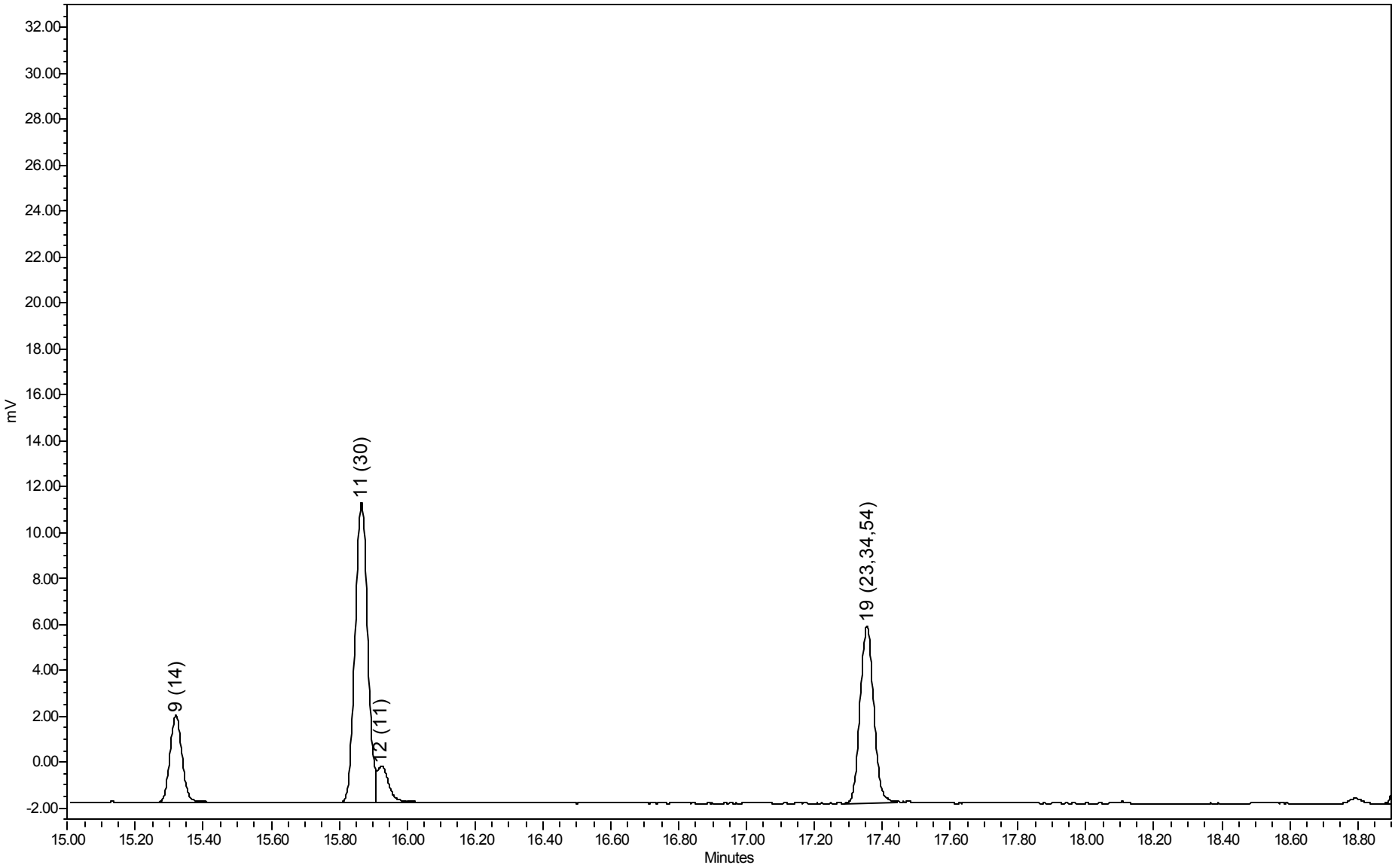
Congener Composition Chromatogram of Aroclor Calibration Mixture (314 ng/mL)



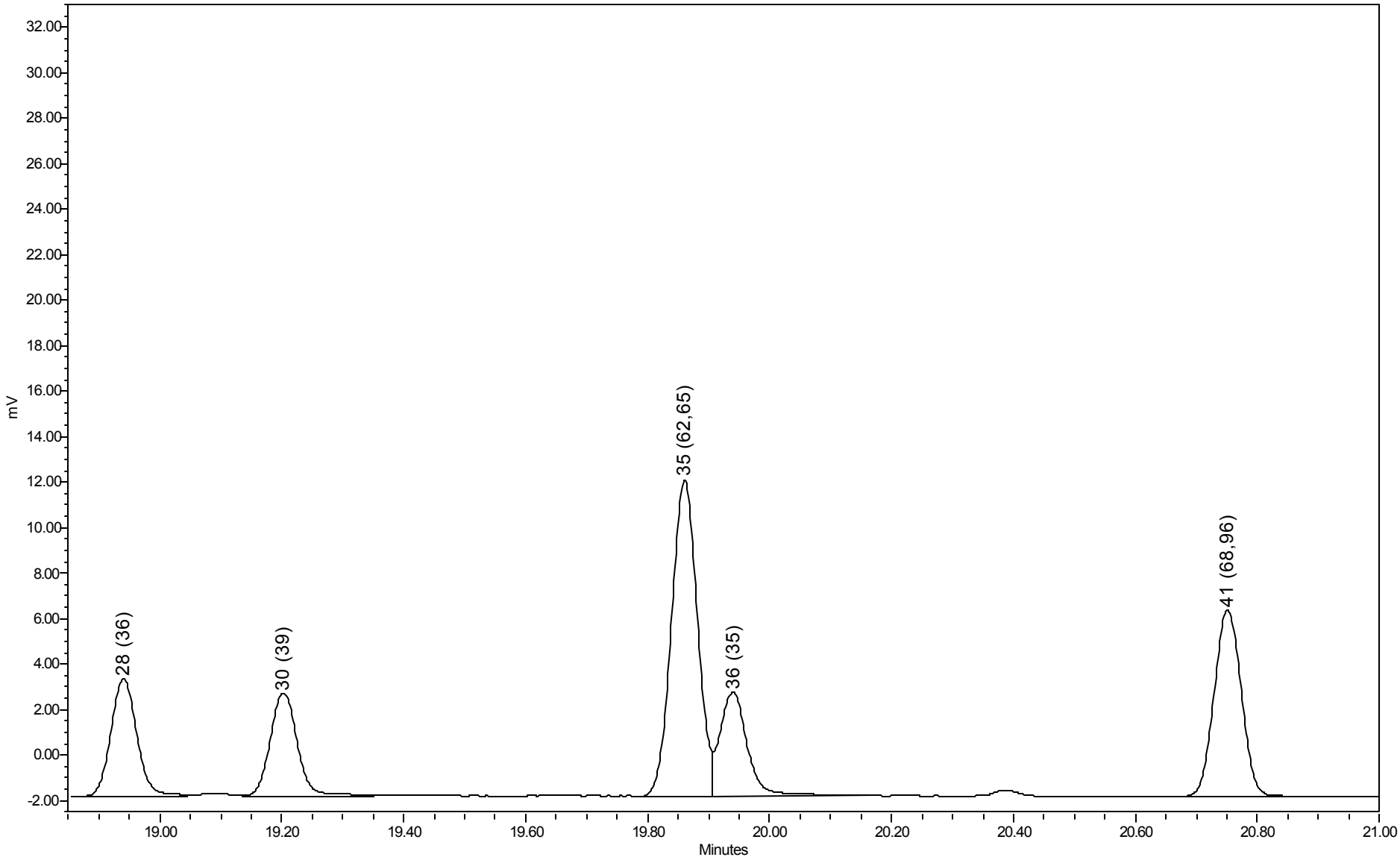
Composition Chromatogram of Supplemental Congener Standard (200 / 5.0 ng/mL)



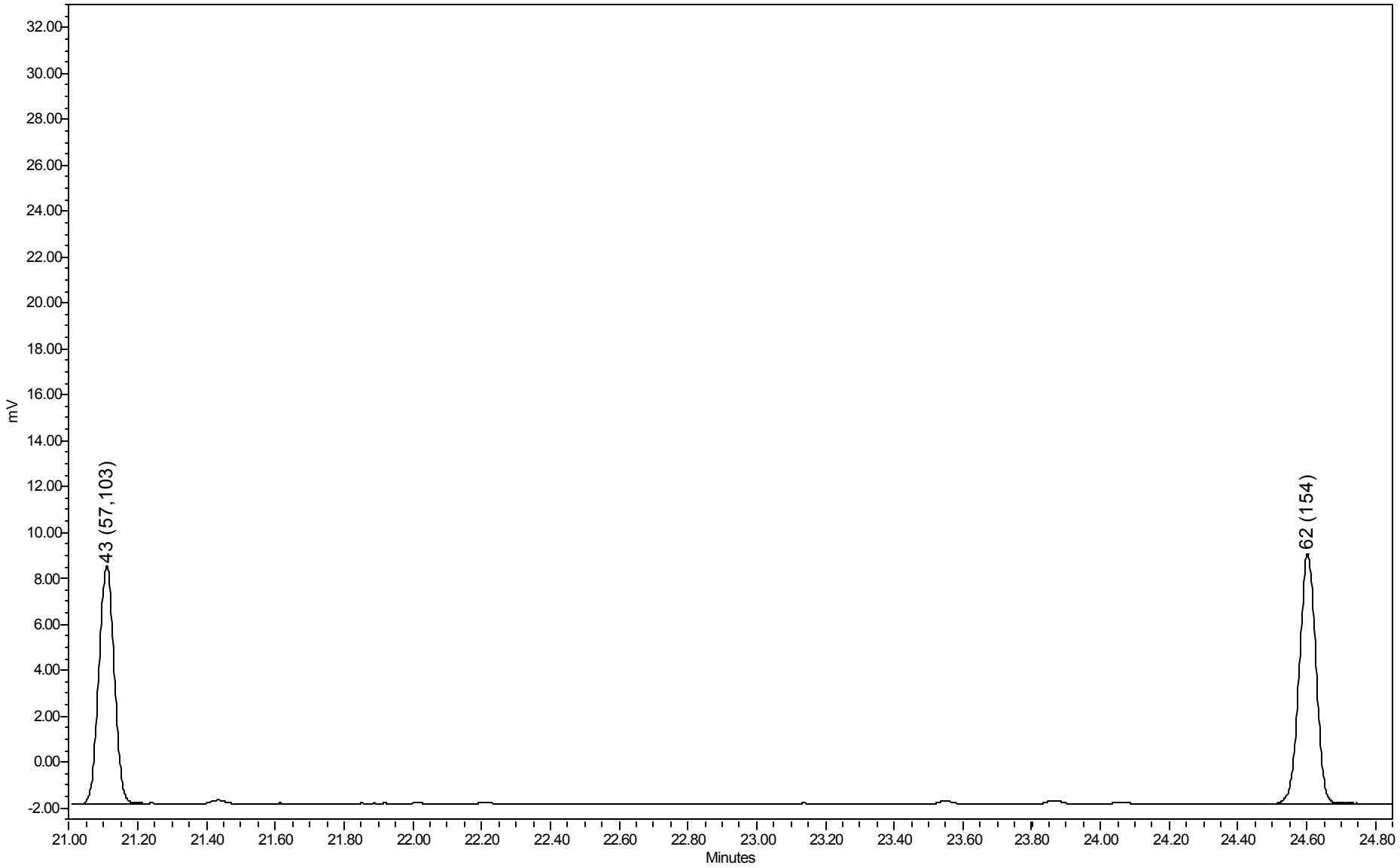
Composition Chromatogram of Supplemental Congener Standard (200 / 5.0 ng/mL)



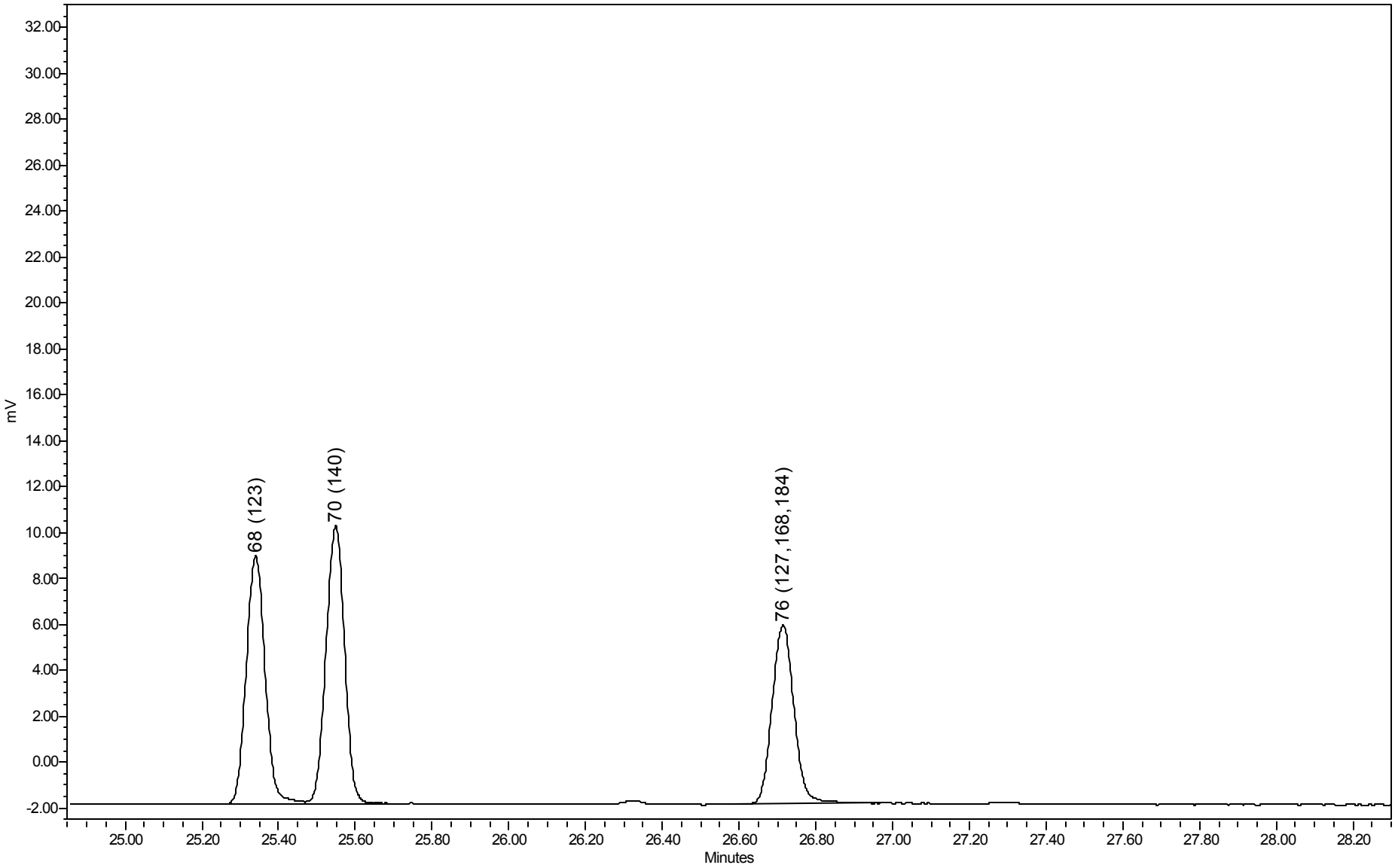
Composition Chromatogram of Supplemental Congener Standard (200 / 5.0 ng/mL)



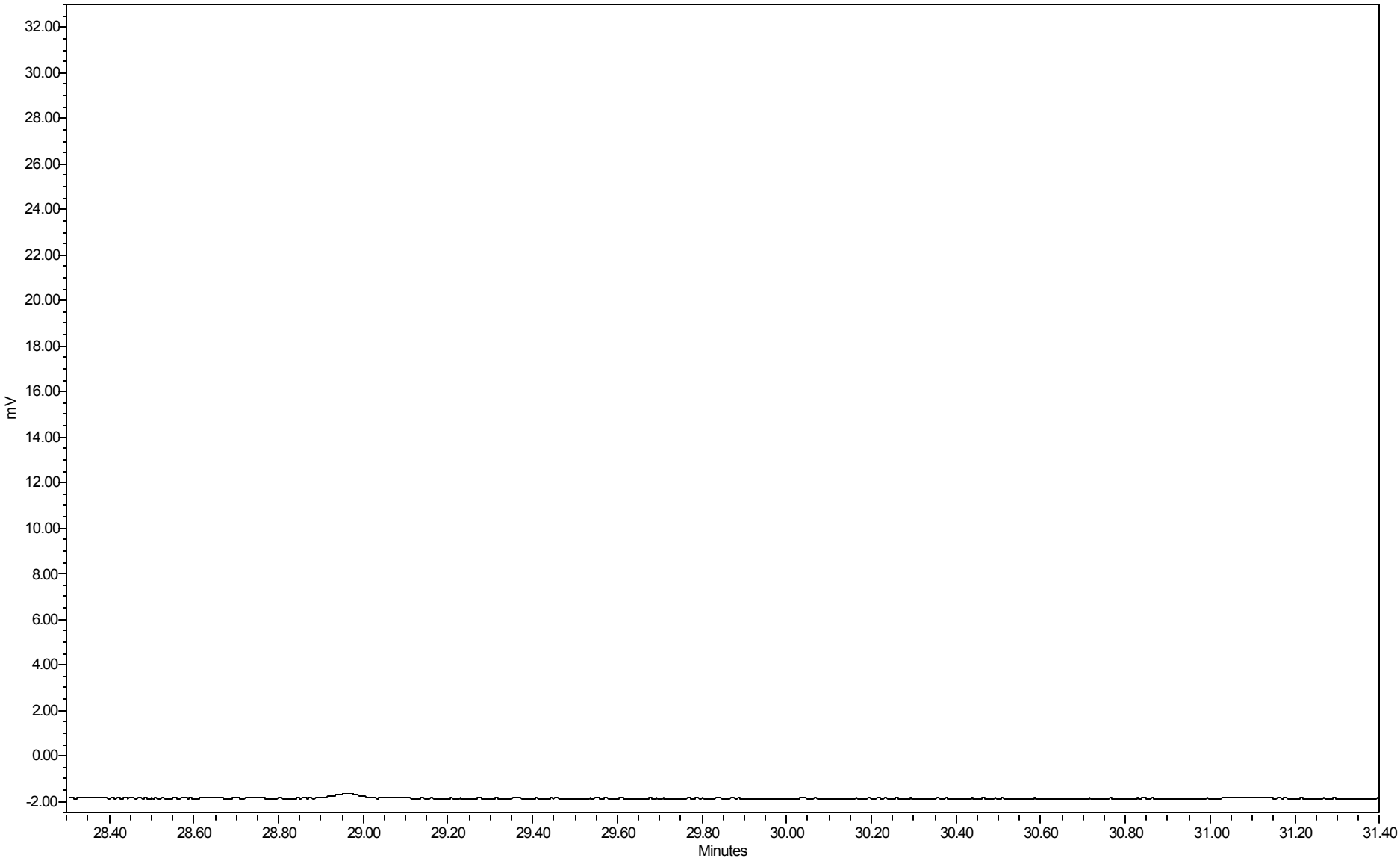
Composition Chromatogram of Supplemental Congener Standard (200 / 5.0 ng/mL)



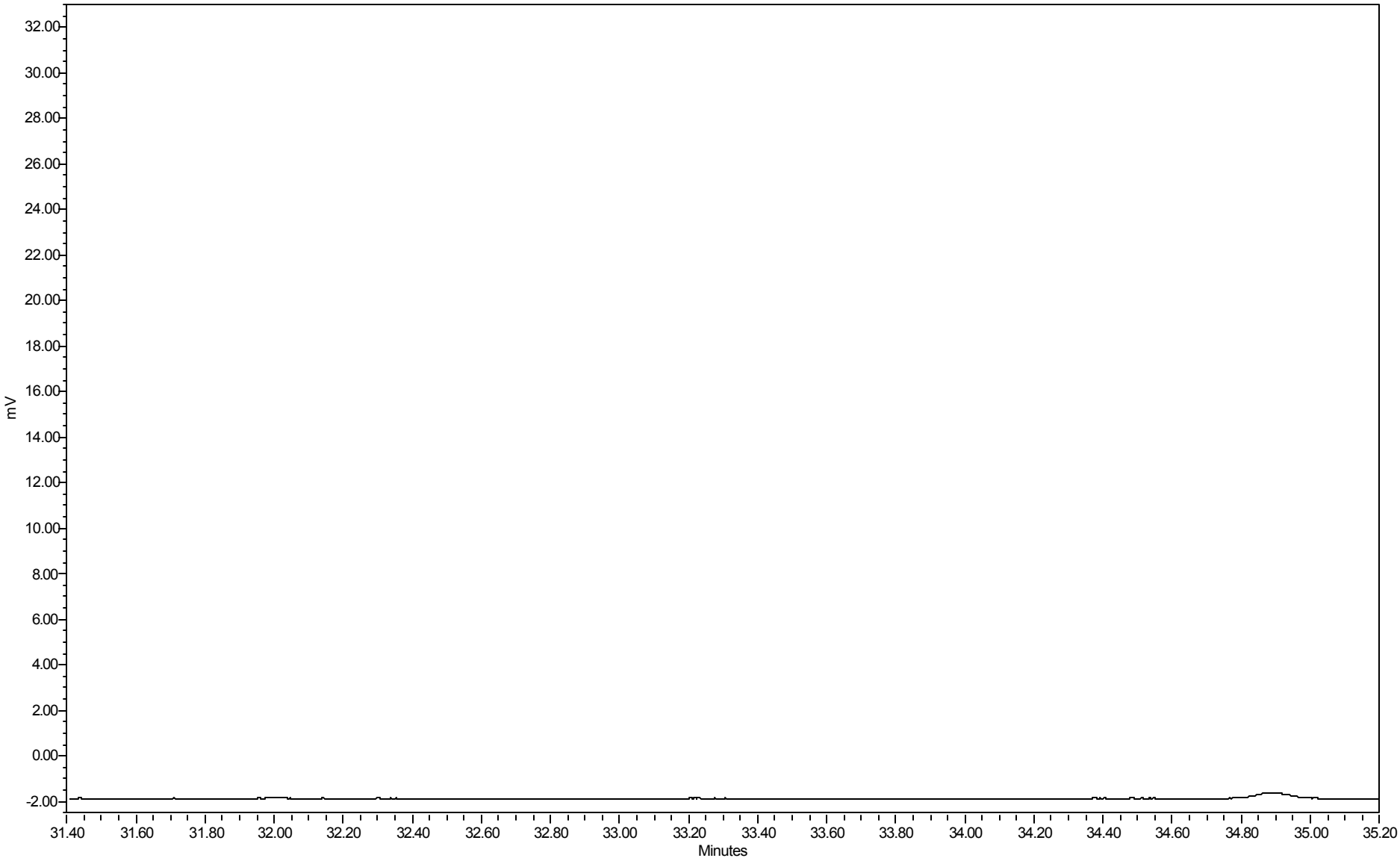
Composition Chromatogram of Supplemental Congener Standard (200 / 5.0 ng/mL)



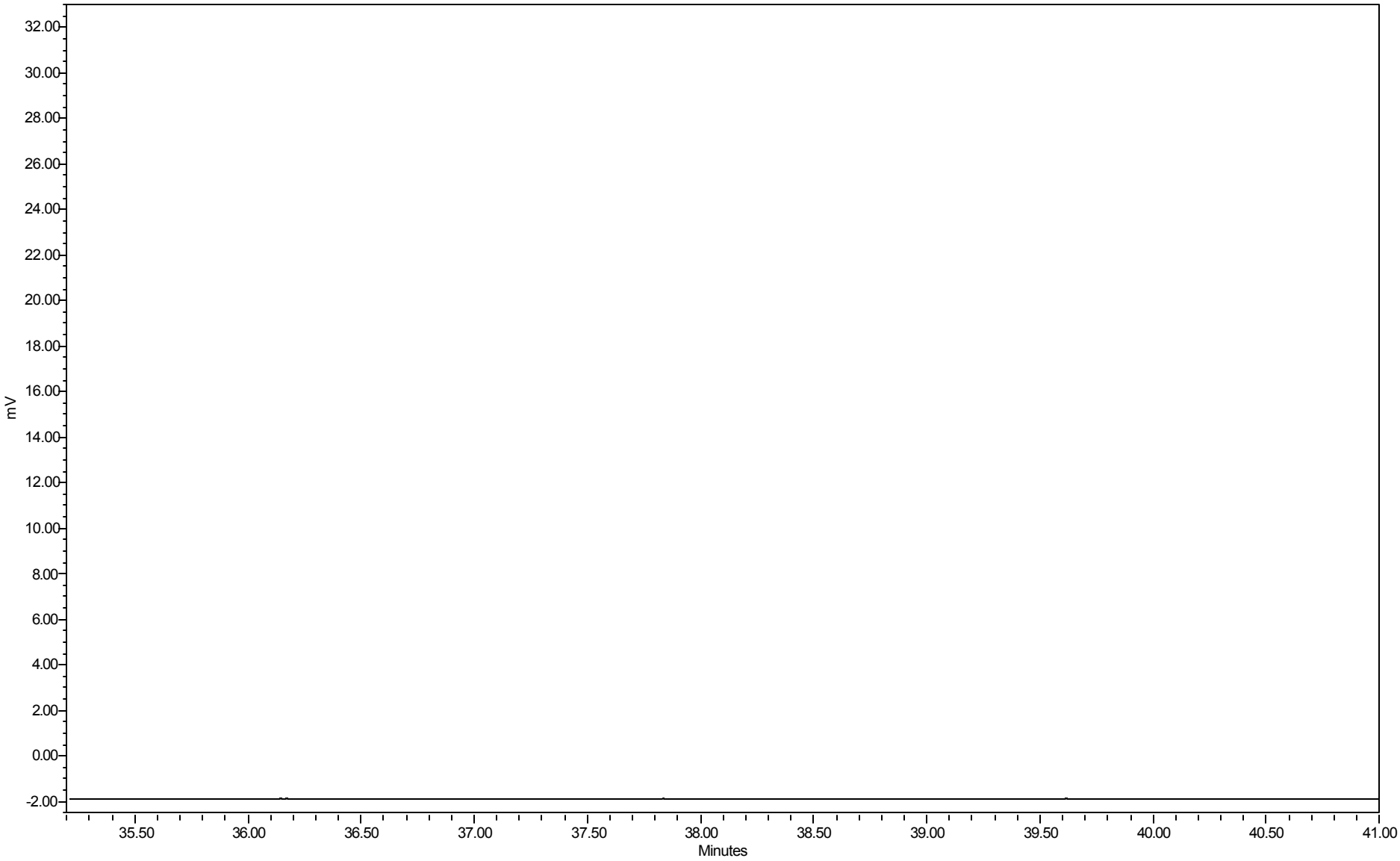
Composition Chromatogram of Supplemental Congener Standard (200 / 5.0 ng/mL)



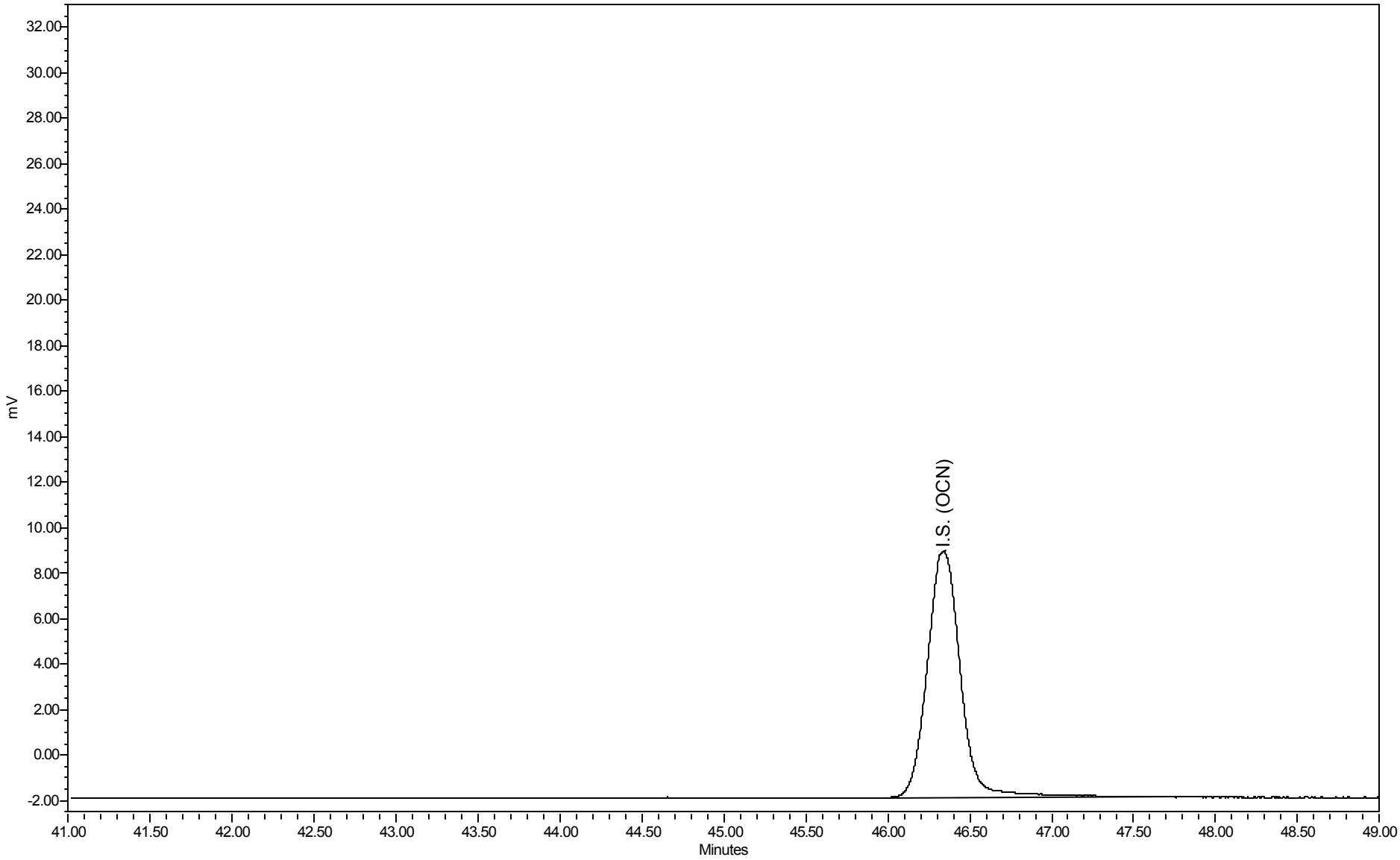
Composition Chromatogram of Supplemental Congener Standard (200 / 5.0 ng/mL)



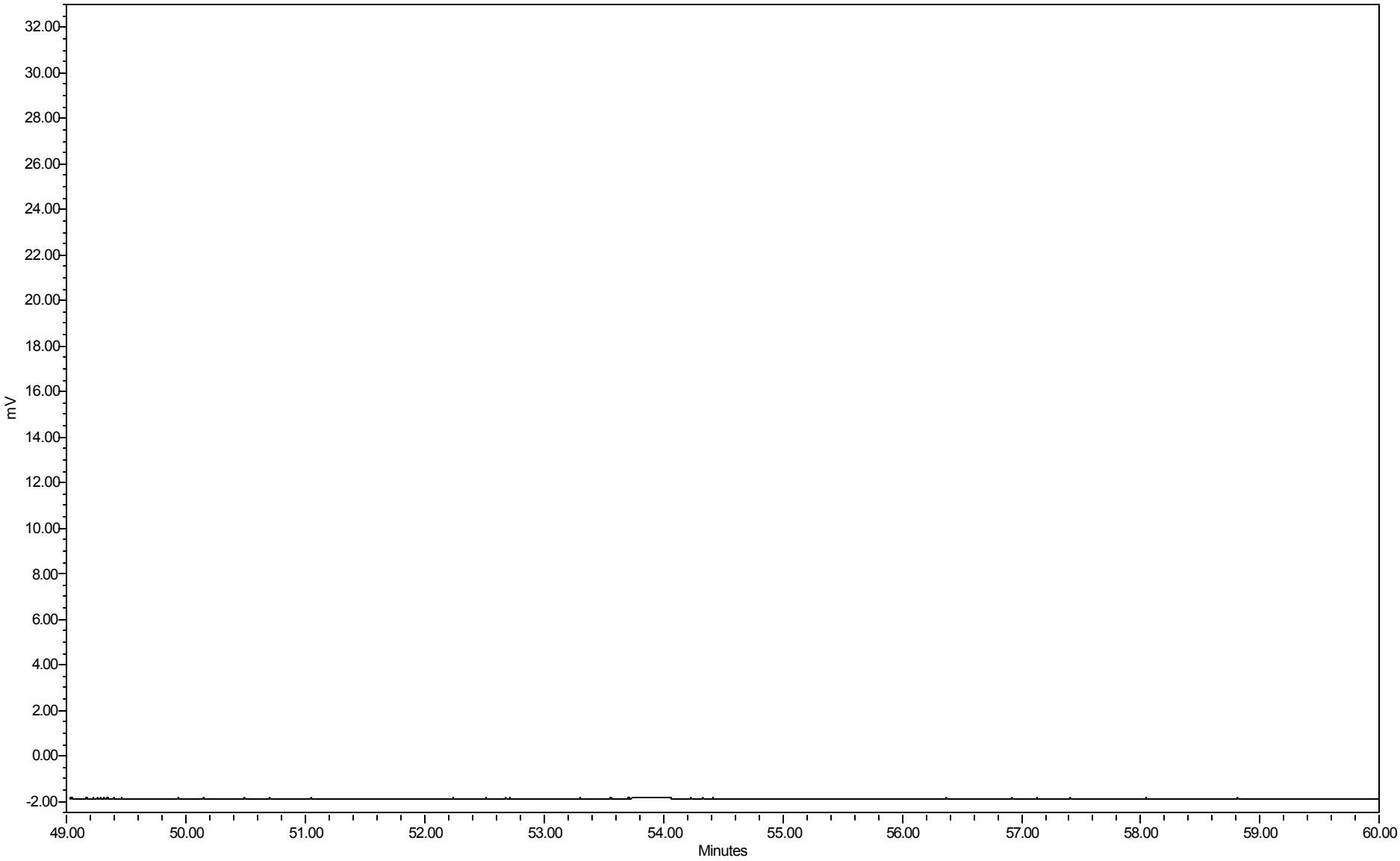
Composition Chromatogram of Supplemental Congener Standard (200 / 5.0 ng/mL)



Composition Chromatogram of Supplemental Congener Standard (200 / 5.0 ng/mL)



Composition Chromatogram of Supplemental Congener Standard (200 / 5.0 ng/mL)



APPENDIX C

Example of reporting format

Northeast Analytical Inc
2190 Technology Drive
Schenectady , NY 12308
(518) 346-4592 Fax (518) 381-6055

NEA File Name : M:\MIL2004\LIMSGC16\AH03735L.ARS

Customer : Client ID
Sample Description : Lab Control Spike

Comment : This is a comment line
Date Acquired : 04/26/2004 16:38:14

Total PCBs in sample = 175 ng/L

PCB Homolog Distribution

Homologs	Weight %	Mole %
Mono	0.00	0.00
Di	16.75	19.61
Tri	46.56	47.67
Tetra	31.07	28.19
Penta	4.95	4.03
Hexa	0.67	0.51
Hepta	0.00	0.00
Octa	0.00	0.00
Nona	0.00	0.00
Deca	0.00	0.00

Nominal 'Aroclor' Distribution

Aroclor	Indicator Peak (PK # / IUPAC #)	Amount ng/L	Percent Sediment	Percent Biota
A1221	2/001		0.0	0.0
A1242	23+24/31+28	22.7675	93.6	96.0
A1254SED	61/110	1.5444	6.4	
A1254BIO	***/###	0.9387		4.0
A1260	102/180		0.0	0.0
A1268	115/194		0.0	0.0

***/### : 69+75+82/149+153+138

Ortho Cl / biphenyl Residue = 1.44

Meta + Para Cl / biphenyl Residue = 1.74

TOTAL Cl / biphenyl Residue = 3.18

Northeast Analytical Inc
2190 Technology Drive
Schenectady , NY 12308
(518) 346-4592 Fax (518) 381-6055

PCB Congener Amount Report

NEA File Name : M:\MIL2004\LIMSGC16\AH03735L.ARS

Customer : Client ID
Sample Description : Lab Control Spike

Comment : This is a comment line
Date Acquired : 04/26/2004 16:38:14
Type for Mixed Peak Deconvolution = S

DB-1 Peak Number [1]	Retention Time	Molecular Weight	Peak Area	Amount ng/L	Picomoles/L Sample	MDL ng/L	RL ng/L	Qual
2	11.67	188.7				0.582	2.19	
3	12.70	188.7				25.1	1000	
4	12.80	188.7				0.318	1.28	
5	13.40	223.1	559	3.12	14.0	0.363	0.621	
6	14.26	223.1	816	0.685	3.07	0.0894	0.219	
7	14.57	223.1	1053	1.84	8.26	0.188	0.347	
8	14.76	223.1	5543	20.9	93.7	0.528	2.56	
9	15.32	223.1				0.845	25.0	
10	15.40	257.5	729	0.850	3.30	0.0660	0.102	
11	15.87	257.5				0.247	25.0	
12	15.93	223.1				0.347	25.0	
13	16.13	223.1				0.0617	0.0975	
14	16.25	249.0	9335	10.9	44.0	0.0978	0.676	
15	16.34	257.5	4867	11.1	43.2	0.142	0.676	
16	16.64	257.5	1192	0.858	3.33	0.0762	0.0762	
17	16.89	257.5	9035	12.0	46.7	0.165	0.713	
19	17.36	267.9				0.212	25.0	
20	17.53	257.5	185	0.124	0.480	0.0190	0.0194	
21	17.66	257.5	2242	2.30	8.94	0.0674	0.132	
22	17.74	257.5	1781	1.29	5.01	0.101	0.101	
23	17.94	257.5	11669	10.3	40.1	0.144	0.753	
24	17.99	257.5	15202	12.5	48.4	0.184	0.964	
25	18.34	259.5	11267	11.2	43.1	0.121	0.726	
26	18.57	258.7	7974	8.04	31.1	0.197	0.530	
27	18.80	292.0	2512	1.95	6.70	0.105	0.163	
28	18.94	257.5				0.181	25.0	
29	19.08	292.0	1154	1.03	3.51	0.117	0.117	
30	19.20	257.5				0.481	25.0	
31	19.37	292.0	5883	7.32	25.1	0.180	0.872	
32	19.54	292.0	5586	3.48	11.9	0.0508	0.420	
33	19.66	292.0	2196	0.983	3.37	0.0671	0.183	
34	19.72	292.0	2517	1.51	5.17	0.0562	0.183	
35	19.86	292.0				0.167	25.0	
36	19.94	257.5				0.200	25.0	

DB-1 Peak Number [1]	Retention Time	Molecular Weight	Peak Area	Amount ng/L	Picomoles/L Sample	MDL ng/L	RL ng/L	Qual
37	20.11	292.0	8183	6.71	23.0	0.122	0.786	
38	20.24	272.4	6080	6.04	22.2	0.126	0.475	
39	20.58	292.0	9758	6.21	21.3	0.148	0.749	
41	20.75	326.4	83			0.209	25.0	
42	20.84	292.0	2099	1.56	5.35	0.0990	0.172	
43	21.11	298.9	91			0.221	25.0	
44	21.28	298.9	448	0.270	0.905	0.0232	0.0402	
45	21.43	292.0	440	0.260	0.892	0.115	0.115	
46	21.60	292.0	4507	1.97	6.74	0.0478	0.347	
47	21.74	292.0	8334	4.69	16.1	0.108	0.621	
48	21.85	293.5	10065	8.25	28.1	0.267	1.32	
49	22.16	324.7	741	0.464	1.43	0.0278	0.0932	
50	22.45	292.0	8631	4.85	16.6	0.0865	0.640	
51	22.69	326.4	1097	1.40	4.29	0.209	0.329	
52	22.82	326.4	287	0.190	0.581	0.0328	0.0366	
53	22.95	326.4	1541	0.997	3.06	0.0548	0.329	
54	23.15	326.4	1042	0.444	1.36	0.0573	0.135	
55	23.42	326.4	62	0.0171	0.0525	0.0150	0.0150	
56	23.52	326.4	196	0.139	0.426	0.0373	0.0548	
57	23.74	326.4	922	0.434	1.33	0.0426	0.102	
58	23.91	326.4	1781	1.03	3.15	0.0799	0.212	
59	24.07	326.4	882	0.428	1.31	0.0525	0.128	
60	24.23	360.9	456	0.297	0.822	0.0511	0.137	
61	24.32	315.8	2330	1.54	4.89	0.0768	0.389	
62	24.56	360.9				0.373	25.0	
63	24.68	326.4	871	0.449	1.37	0.0978	0.0978	
64	24.99	360.9	118	0.0644	0.178	0.0502	0.311	J
65	25.13	350.5	70	0.0231	0.0659	0.0150	0.0530	J
66	25.15	360.9	58			0.0591	0.110	
67	25.25	336.8	132	0.0924	0.274	0.0396	0.0475	
68	25.34	326.4				0.135	25.0	
69	25.45	337.5	1662	0.819	2.43	0.106	0.731	
70	25.55	360.9				0.156	25.0	
71	25.84	347.8				0.0750	0.0750	
72	26.04	336.8				0.0129	0.0129	
73	26.32	360.9				0.0260	0.0713	
74	26.43	347.8	1362	0.630	1.81	0.0802	0.248	
75	26.60	360.9				0.126	0.538	
76	26.71	360.9				0.147	25.0	
77	27.13	360.9				0.0767	0.311	
78	27.20	395.3				0.0351	0.267	
79	27.40	360.9				0.0249	0.0274	
80	27.56	360.9				0.0169	0.0475	
82	27.77	360.9	269	0.120	0.331	0.118	0.493	J
83	27.96	360.9				0.0611	0.0611	
84	28.17	360.9				0.00672	0.00672	
85	28.51	395.3				0.0903	0.201	
87	28.81	395.3				0.0165	0.0731	
88	28.96	395.3				0.0926	0.658	
89	29.08	360.9				0.0335	0.0366	
90	29.26	395.3				0.0768	0.311	

DB-1 Peak Number [1]	Retention Time	Molecular Weight	Peak Area	Amount ng/L	Picomoles/L Sample	MDL ng/L	RL ng/L	Qual
91	29.53	360.9				0.0143	0.0179	
92	29.86	394.3				0.0265	0.0859	
93	30.24	394.3				0.130	0.585	
94	30.50	394.3				0.125	0.311	
95	30.80	382.2				0.0934	0.144	
96	31.07	429.8				0.00417	0.0121	
98	31.23	395.3				0.0799	0.0799	
99	31.61	429.8				0.0547	0.0713	
100	31.85	395.3				0.0563	0.102	
101	32.15	429.8				0.110	0.110	
102	32.33	395.3				0.163	1.11	
103	32.58	395.3				0.0731	0.0768	
104	32.88	395.3				0.0395	0.0438	
105	33.23	429.8				0.0247	0.0786	
106	34.38	395.3				0.0576	0.234	
107	34.65	395.3				0.0426	0.0768	
108	35.52	429.8				0.0443	0.0443	
109	35.75	429.8				0.244	0.768	
110	36.28	429.8				0.185	0.786	
111	37.45	395.3				0.0340	0.0340	
112	38.99	429.8				0.0492	0.101	
113	39.51	464.2				0.0532	0.0902	
114	40.45	464.2				0.0236	0.0340	
115	41.87	429.8				0.108	0.329	
116	42.76	429.8				0.0623	0.0623	
117	47.90	464.2				0.118	0.124	
118	53.86	498.6				0.0236	0.0236	

Concentration = 175 ng/L

Total Nanomoles = 0.662

Average Molecular Weight = 263.7

Number of Calibrated Peaks Found = 54

Internal Standard Retention Time = 46.33 Minutes

Internal Standard Peak Area = 158798.0

Northeast Analytical Inc
2190 Technology Drive
Schenectady , NY 12308
(518) 346-4592 Fax (518) 381-6055

Congener Weight and Mole Report

NEA File Name : M:\MIL2004\LIMSGC16\AH03735L.ARS

Customer : Client ID
Sample Description : Lab Control Spike

Comment : This is a comment line
Date Acquired : 04/26/2004 16:38:14

Type for Mixed Peak Deconvolution = S

DB-1 Peak Number [1]	Retention Time	T-CL:O-CL	IUPAC # [2]	RRT	Congeners [3]	Weight Percent	Mole Percent	DB-1 Peak Number [1]
2	11.67	1:1	**001**	0.3567	2	-	-	2
3	12.70	1:0	**002**	0.3853	3	-	-	3
4	12.80	1:0	**003**	0.3880	4	-	-	4
5	13.40	2:2	**004 010**	0.4039	2-2 ; 26	1.785	2.111	5
6	14.26	2:1	**007 009**	0.4236	24 ; 25	0.392	0.463	6
7	14.57	2:1	**006**	0.4304	2-3	1.055	1.247	7
8	14.76	2:1	**005 008**	0.4346	23 ; 2-4	11.960	14.139	8
9	15.32	2:0	*014*	0.4462	35	-	-	9
10	15.40	3:3	**019**	0.4474	26-2	0.487	0.498	10
11	15.87	3:2	*030*	0.4572	246	-	-	11
12	15.93	2:0	**011**	0.4584	3-3	-	-	12
13	16.13	2:0	**012 013**	0.4622	34 ; 3-4	-	-	13
14	16.25	2:0 3:2	**015 018**	0.4650	4-4 ; 25-2	6.265	6.636	14
15	16.34	3:2	**017**	0.4668	24-2	6.370	6.524	15
16	16.64	3:2	**024 027**	0.4721	236 ; 26-3	0.491	0.503	16
17	16.89	3:2	**016 032**	0.4783	23-2 ; 26-4	6.878	7.045	17
19	17.36	3:1 4:4	*023* **034** *054*	0.4856	235 ; 35-2 ; 26-26	-	-	19
20	17.53	3:1	**029**	0.4889	245	0.071	0.072	20
21	17.66	3:1	**026**	0.4912	25-3	1.318	1.349	21
22	17.74	3:1	**025**	0.4926	24-3	0.738	0.756	22
23	17.94	3:1	**031**	0.4965	25-4	5.903	6.046	23
24	17.99	3:1 4:3	**028** *050*	0.4969	24-4 ; 246-2	7.128	7.301	24
25	18.34	3:1 4:3	**020** *021* **033 053**	0.5031	23-3 ; 234 ; 34-2 ; 25-26	6.403	6.508	25
26	18.57	3:1 4:3	**022 051**	0.5074	23-4 ; 24-26	4.602	4.692	26
27	18.80	4:3	**045**	0.5109	236-2	1.119	1.011	27
28	18.94	3:0	*036*	0.5135	35-3	-	-	28
29	19.08	4:3	**046**	0.5157	23-26	0.587	0.530	29
30	19.20	3:0	*039*	0.5172	35-4	-	-	30
31	19.37	4:2	**052** *069 073*	0.5209	25-25 ; 246-3 ; 26-35	4.188	3.783	31
32	19.54	4:2	**043 049**	0.5236	235-2 ; 24-25	1.992	1.800	32
33	19.66	4:2	*038* **047**	0.5262	345 ; 24-24	0.563	0.508	33
34	19.72	4:2	**048** *075*	0.5267	245-2 ; 246-4	0.865	0.781	34
35	19.86	4:2	*062 065*	0.5289	2346 ; 2356	-	-	35
36	19.94	3:0	**035**	0.5302	34-3	-	-	36
37	20.11	5:4 4:2	*104* **044**	0.5333	246-26 ; 23-25	3.838	3.467	37
38	20.24	3:0 4:2	**037 042 059**	0.5352	34-4 ; 23-24 ; 236-3	3.458	3.348	38
39	20.58	4:2	**041 064 071** *072*	0.5406	234-2 ; 236-4 ; 26-34 ; 25-35	3.555	3.211	39
41	20.75	5:4	*068* **096**	0.5435	24-35 ; 236-26	-	-	41
42	20.84	4:2	**040**	0.5446	23-23	0.894	0.807	42
43	21.11	4:1 5:3	**057** *103*	0.5489	235-3 ; 246-25	-	-	43
44	21.28	4:1 5:3	*058* **067** *100*	0.5517	23-35 ; 245-3 ; 246-24	0.155	0.137	44
45	21.43	4:1	**063**	0.5534	235-4	0.149	0.135	45
46	21.60	4:1 5:3	**074** *094 061*	0.5570	245-4 ; 235-26 ; 2345	1.127	1.018	46

DB-1 Peak Number [1]	Retention Time	T-CL:O-CL	IUPAC # [2]	RRT	Congeners [3]	Weight Percent	Mole Percent	DB-1 Peak Number [1]
47	21.74	4:1	**070**	0.5595	25-34	2.684	2.424	47
48	21.85	4:1 5:3	**066** *076 098 080 093* **095 102** *088*	0.5609	24-34 ; 345-2 ; 246-23 ; 35-35 ; 2356-2 ; 236-25 ; 245-26 ; 2346-2	4.722	4.243	48
49	22.16	4:1 5:3	*055* **091** *121*	0.5658	234-3 ; 236-24 ; 246-35	0.266	0.216	49
50	22.45	4:1	**056 060**	0.5701	23-34 ; 234-4	2.776	2.507	50
51	22.69	5:3 6:4	**084 092** *155*	0.5739	236-23 ; 235-25 ; 246-246	0.802	0.648	51
52	22.82	5:3	**089**	0.5761	234-26	0.108	0.088	52
53	22.95	5:2	**090 101**	0.5788	235-24 ; 245-25	0.571	0.461	53
54	23.15	5:2	*079* **099** *113*	0.5814	34-35 ; 245-24 ; 236-35	0.254	0.205	54
55	23.42	5:2 6:4	**119** *150*	0.5860	246-34 ; 236-246	0.010	0.008	55
56	23.52	5:2	*078* **083** *112 108*	0.5874	345-3 ; 235-23 ; 2356-3 ; 2346-3	0.080	0.064	56
57	23.74	5:2 6:4	**097** *152 086*	0.5903	245-23 ; 2356-26 ; 2345-2	0.248	0.201	57
58	23.91	5:2	*081* **087** *117 125* **115** *145*	0.5929	345-4 ; 234-25 ; 2356-4 ; 345-26 ; 2346-4 ; 2346-26	0.589	0.476	58
59	24.07	5:2	*116* **085** *111*	0.5953	23456 ; 234-24 ; 235-35	0.245	0.198	59
60	24.23	6:4	*120* **136**	0.5971	245-35 ; 236-236	0.170	0.124	60
61	24.32	4:0 5:2	**077 110** *148*	0.5998	34-34 ; 236-34 ; 235-246	0.884	0.738	61
62	24.56	6:3	*154*	0.6039	245-246	-	-	62
63	24.68	5:2	**082**	0.6055	234-23	0.257	0.207	63
64	24.99	6:3	**151**	0.6101	2356-25	0.037	0.027	64
65	25.13	5:1 6:3	**124 135**	0.6129	345-25 ; 235-236	0.013	0.010	65
66	25.15	6:3	**144**	0.6139	2346-25	-	-	66
67	25.25	5:1 6:3	*107* **109** *147*	0.6152	234-35 ; 235-34 ; 2356-24	0.053	0.041	67
68	25.34	5:1	*123*	0.6166	345-24	-	-	68
69	25.45	5:1 6:3	*106* **118** *139* **149**	0.6186	2345-3 ; 245-34 ; 2346-24 ; 236-245	0.469	0.366	69
70	25.55	6:3	*140*	0.6202	234-246	-	-	70
71	25.84	5:1 6:3	**114 134** *143*	0.6256	2345-4 ; 2356-23 ; 2345-26	-	-	71
72	26.04	5:1 6:3	**122 131 133** *142*	0.6289	345-23 ; 2346-23 ; 235-235 ; 23456-2	-	-	72
73	26.32	6:2	**146** *165 188*	0.6342	235-245 ; 2356-35 ; 2356-246	-	-	73
74	26.43	5:1 6:3	**105 132** *161*	0.6364	234-34 ; 234-236 ; 2346-35	0.361	0.274	74
75	26.60	6:2	**153**	0.6393	245-245	-	-	75
76	26.71	6:2	*127 168 184*	0.6412	345-35 ; 246-345 ; 2346-246	-	-	76
77	27.13	6:2	**141**	0.6488	2345-25	-	-	77
78	27.20	7:4	**179**	0.6499	2356-236	-	-	78
79	27.40	6:2	**137**	0.6537	2345-24	-	-	79
80	27.56	6:2 7:4	**130 176**	0.6565	234-235 ; 2346-236	-	-	80
82	27.77	6:2	**138 163 164**	0.6605	234-245 ; 2356-34 ; 236-345	0.068	0.050	82
83	27.96	6:2	**158** *160 186*	0.6639	2346-34 ; 23456-3 ; 23456-26	-	-	83
84	28.17	6:2	*126* **129**	0.6674	345-34 ; 2345-23	-	-	84
85	28.51	7:3	*166* **178**	0.6735	23456-4 ; 2356-235	-	-	85
87	28.81	7:3	**175** *159*	0.6790	2346-235 ; 2345-35	-	-	87
88	28.96	7:3	*182* **187**	0.6816	2345-246 ; 2356-245	-	-	88
89	29.08	6:2	**128** *162*	0.6838	234-234 ; 235-345	-	-	89
90	29.26	7:3	**183**	0.6871	2346-245	-	-	90
91	29.53	6:1	**167**	0.6919	245-345	-	-	91
92	29.86	7:3	**185**	0.6980	23456-25	-	-	92
93	30.24	7:3	**174** *181*	0.7046	2345-236 ; 23456-24	-	-	93
94	30.50	7:3	**177**	0.7094	2356-234	-	-	94
95	30.80	6:1 7:3	**156 171**	0.7149	2345-34 ; 2346-234	-	-	95
96	31.07	8:4	**157 202**	0.7195	234-345 ; 2356-2356	-	-	96
98	31.23	7:3	**173**	0.7226	23456-23	-	-	98
99	31.61	8:4	**201**	0.7294	2346-2356	-	-	99
100	31.85	7:2	**172** *204*	0.7339	2345-235 ; 23456-246	-	-	100
101	32.15	8:4	*192* **197**	0.7392	23456-35 ; 2346-2346	-	-	101
102	32.33	7:2	**180**	0.7427	2345-245	-	-	102
103	32.58	7:2	**193**	0.7471	2356-345	-	-	103
104	32.88	7:2	**191**	0.7527	2346-345	-	-	104
105	33.23	8:4	**200** *169*	0.7588	23456-236 ; 345-345	-	-	105
106	34.38	7:2	**170**	0.7799	2345-234	-	-	106
107	34.65	7:2	**190**	0.7850	23456-34	-	-	107
108	35.52	8:3	**198**	0.8007	23456-235	-	-	108

DB-1 Peak Number [1]	Retention Time	T-CL:O-CL	IUPAC # [2]	RRT	Congeners [3]	Weight Percent	Mole Percent	DB-1 Peak Number [1]
109	35.75	8:3	**199**	0.8050	2345-2356	-	-	109
110	36.28	8:3	**196 203**	0.8149	2345-2346 ; 23456-245	-	-	110
111	37.45	7:1	**189**	0.8365	2345-345	-	-	111
112	38.99	8:3	**195**	0.8647	23456-234	-	-	112
113	39.51	9:4	**208**	0.8743	23456-2356	-	-	113
114	40.45	9:4	*207*	0.8909	23456-2346	-	-	114
115	41.87	8:2	**194**	0.9177	2345-2345	-	-	115
116	42.76	8:2	**205**	0.9342	23456-345	-	-	116
117	47.90	9:3	**206**	1.0294	23456-2345	-	-	117
118	53.86	10:4	*209*	1.1406	23456-23456	-	-	118

Concentration = 175 ng/L

Total Nanomoles = 0.662

Average Molecular Weight = 263.7

Number of Calibrated Peaks Found = 54

[1] - Note that 5 DB-1 peaks (PK18, PK40, PK81, PK86, PK97) have been removed from the DB-1 peak numbering scheme. The following low level congeners that were designated as separately eluting peaks have been determined to co-elute with another congener. The DB-1 peak numbers are no longer required for these congeners, but the original DB-1 numbering system has remained intact for all other peaks.

PK 18 (23) now elutes in PK 19 (23,34,54)
PK 40 (68) now elutes in PK 41 (68,96)

PK 86 (166) now elutes in PK 85 (166,178)
PK 97 (157) now elutes in PK 96 (157,202)

[2] - IUPAC congener numbers listed in **boldface** font were found to be present in at least one of the Aroclors at or above 0.05 weight percent. These congeners should be considered the primary congeners existing in a peak composed of co-eluting congeners. IUPAC congener numbers listed in *italic* font were absent or present below 0.05 weight percent.

[3] - PCB congener identification is denoted by position of the chlorine atoms on each ring of the biphenyl molecule. Designation used in this report has unprimed chlorines separated from prime chlorines by a hyphen that represents separation of the biphenyl rings.

[4] - DB-1 peaks may include one or more coeluting PCB congeners. In the case of some peaks, the congeners assigned to the peak consist of coeluting congeners and a congener that is resolved or is just slightly out of the normal retention time window of ± 0.07 minutes. If detection of one of the resolved congeners occurs, a comment will be included in the report narrative indication the assigned DB-1 peak includes the presence of the resolved congener. The DB-1 peaks consisting of coeluting congeners and a congener that is resolved are as follows:

DB-1 Peak	Resolved Congener (IUPAC #)
37 (**44**, *104*)	*104*
48 (**66**, *76, 98, 80, 93*, **95**, **102**, *88*)	*80, 88, 93*
56 (*78,* **83***, 112, 108)*	*108*
61 (**77, 110**, *148*)	**77**
72 (**122**, *131, 133, 142*)	**122**
89 (**128**, *162*)	*162*
105 (**200**,*169*)	*169*

STANDARD OPERATING PROCEDURE REVIEW

SOP Name	Reviewers	Title	QAO Approval	Effective Date
NE207_03	Christina L. Braidwood Robert E. Wagner	GC Manager Lab Director	Christina Braidwood	08/05/08

APPENDIX 29
SOP FOR DETERMINATION OF TOTAL SUSPENDED SOLIDS BY STANDARD METHOD 2540D (MODIFIED TO BE CONSISTENT WITH ASTM METHOD 3977-97)
(LANCASTER LABORATORIES, INC.)

Uncontrolled Copy

Total Suspended Solids

Approvals:

Prepared by: _____ Date: 3/20/09
Manager

Approved by: Kenneth A Bell Date: 3/20/09
Water Quality Management

Approved by: _____ Date: 3/20/09
Quality Assurance

Uncontrolled Copy

Revision Log:

Revision: 01		Effective Date:	This version
Section	**Justification**		**Changes**
			New

10457_01.DOC
032009

Reference:

1. *Standard Methods for the Examination of Water and Wastewater*, 20th Edition, 1998, 2540 D. p. 2-57 to 2-58.

2. ASTM D 3977-97 Standard Test Methods for Determining Sediment Concentration in Water Samples, Test Method B.

3. *Chemical Hygiene Plan*, Lancaster Laboratories, current version.

Cross Reference:

Document	Document Title
LOM-SOP-ES-203	Determining Method Detection Limits and Limits of Quantitation
LOM-SOP-ES-225	Reagents and Standards
LOM-SOP-LAB-208	Laboratory Balances
LOM-SOP-LAB-220	Laboratory Notebooks, Logbooks, and Documentation
MC-WQ-009	Equipment Muffle Furnaces and Ovens
MC-WQ-012	Maintenance of Desiccators
SOP-WQ-014	Instructions for Collecting Data on the LLENS System
SOP-WQ-017	Outlier Quality Control Data

Scope:

This method is applicable for the determination of suspended solids in potable, surface and saline water, as well as domestic and industrial wastewater.

The reporting limit for this analysis varies with the sample volume. LIMS may round the reporting limit during the calculation routine.

Basic Principles:

A well-mixed sample is filtered through a glass fiber filter and the residue on the filter is dried for at least one hour in an oven at 103 ° to 105°C. The increase in weight of the filter represents the total suspended solids (TSS).

Reference Modifications:

The SM 2540 D has been modified to be consistent with the ASTM D 3977 procedure by changing the drying process for each sample to be one single drying cycle of at least one hour in length as opposed to multiple drying cycles to verify a constant weight after drying.

Interferences:

Samples high in dissolved solids may yield positive interferences.

Safety Precautions and Waste Handling:

See *Chemical Hygiene Plan* for general information regarding employee safety, waste management, and pollution prevention.

Personnel Training and Qualifications:

Analysts are considered proficient when they have successfully completed a quad study for the analysis. A quad study consists of four laboratory control standards that are carried through all steps of the analysis and that meet the acceptance criteria for the LCS. Documentation for these studies is in each individual's training records.

Sample Handling:

Samples for total suspended solids should be kept unpreserved, refrigerated at 2° to 4°C and analyzed within 7 days of collection to minimize microbiological decomposition of the solids.

Non-representative, nonhomogeneous materials, such as leaves and sticks, may be excluded from the analysis if their inclusion is not desired in the final result.

Apparatus and Equipment:

1. ProWeigh Filters from Environmental Express – pre-weighed 47 mm glass fiber filters

2. Filtration apparatus

3. Desiccators, or equivalent. Refer to MC-WQ-012.

4. Oven maintained at 103° to 105°C. Adjust as needed to stay in this range. Refer to MC-WQ-009.

5. Analytical balance or equivalent. Refer to LOM-SOP-LAB-208.

Reagents and Standards:

Alternate weights and volumes may be used as long as final concentrations remain the same. Refer to LOM-SOP-ES-225 for the proper labeling and documentation of reagent preparation.

TSS Working Standard (150 mg/L) – Dry Naphthalimide for approximately 1 hour at 103° to 105°C. Desiccate approximately 1 hour. Dissolve 0.1500 ± 0.005 g Naphthalimide in approximately 700-mL of deionized water in a 1000-mL volumetric flask. **Mix very well.** Dilute to 1000 mL with deionized water. Store at room temperature. Stable 30 days. Naphthalimide can be weighed out and stored prior to use.

Procedure:

NOTE: LLENS is a computer program that integrates a PC with an analytical balance to collect data directly from the balance. It also organizes the data, performs calculations and transmits the final results to LIMS.

LLENS should be used for TSS whenever possible to facilitate data transfers according to the most recent version of SOP-WQ-014. However, data may also still be recorded traditionally in a raw data logbook using LOM-SOP-LAB-220.

1. Batch samples for analysis in the LLENS system. Assign a pre-washed, pre-weighed filter to each client sample and each QC sample on the batch.

2. Assemble filtration apparatus, and remove the assigned filter from its aluminum carrying dish and place on the filtration unit. Apply vacuum to the filtration apparatus.

3. The entire sample volume will be used for the analysis. Mark the water meniscus on the sample bottle. Shake the bottle and pour the entire into the filtration unit. While continuing the suction, rinse the inside of the sample container with deionized water and transfer the water to the filtration apparatus. Rinse sufficiently to ensure all of the solids inside the bottle are transferred to the filtration apparatus.

4. After the sample bottle is flushed, fill the bottle with water to the meniscus mark and then measure the sample volume using a graduated cylinder. Record this volume on the datasheet.

5. As the filtering proceeds, inspect the filtrate. If the filtrate is turbid, pour the filtrate back through the filter a second or possibly a third time. If the filtrate is still turbid, the filter may be leaking. In this case, the process should be repeated using a new filter. If the filtrate is transparent but discolored, a natural dye is present and refiltration is not necessary.

6. Transfer the filter back into its aluminum carrying dish and place in an oven maintained at 103°C to 105°C.

7. Dry the filter for at least one hour.

8. After the drying time, transfer the aluminum dish into a desiccator for at least 30 minutes. After cooling, record the oven dried weight of the filter.

Calculations:

$$mg\ Total\ Suspended\ Solids\ /\ L = \frac{(A-B)\times 1000\times 1000}{Sample\ Volume\ (mL)}$$

Where:

A = Weight of filter, (in grams) after drying

B = Tare weight of filter (in grams)

Statistical Information/Method Performance:

Refer to LOM-SOP-ES-203.

Quality Assurance/Quality Control:

Balances are calibrated each day before use.

One method blank and a 150-mg/L LCS must be run with each batch. Batch size is limited to 20 samples or less.

When sample volume permits, a sample matrix duplicate must be run with each group of not more than 10 samples. If there is not sufficient sample volume for the matrix duplicate, a LCSD should be analyzed.

The maximum residue limit is 0.2 gram.

See LIMS for current quality control (QC) acceptance windows. Follow guidelines in SOP-WQ-017 for outlier QC data.

APPENDIX 30
SOP FOR DETERMINATION OF TOTAL SUSPENDED SOLIDS BY STANDARD METHOD 2540D (MODIFIED TO BE CONSISTENT WITH ASTM METHOD 3977-97) (NE117_05)

STANDARD OPERATING PROCEDURE

NORTHEAST ANALYTICAL INC.

NE117_05.DOC

REVISION NUMBER: 5

DETERMINATION OF NON-FILTERABLE RESIDUE

(TOTAL SUSPENDED SOLIDS)

ACCORDING TO STANDARD METHODS SM 19 2540D

COPY # _____

NORTHEAST ANALYTICAL, INC
2190 TECHNOLOGY DRIVE
SCHENECTADY, NY 12308

(518) 346-4592

STANDARD OPERATING PROCEDURE

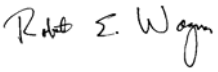
LABORATORY PROCEDURE NE117_05.DOC

REVISION 4 (02/195 (03/31/2009)

Author: Marsha Qian

Marsha Qian
Inorganics Department Manager

Reviewed by:



Robert E. Wagner
Laboratory Director

Approved by:

Christina L. Braidwood
Quality Assurance Officer

TABLE OF CONTENTS

1.0 IDENTIFICATION OF TEST METHOD

1.1 This SOP describes the procedures for determination of total filterable residue or total suspended solids (TSS) in drinking, surface, saline, and waste waters according to SM2540D from APHA.

2.0 APPLICABLE MATRIX AND MATRICES

2.1 This method is applicable to drinking, surface, saline, and waste waters.

3.0 DETECTION LIMIT

3.1 The practical range of determination of TSS is 4 to 20,000 mg/L. The detection limit for the instrument is contingent on the sample volume and the accuracy of the scale. A 1000 ml sample is regularly applied, with the scale weighing capability of 1 mg. The detection limit is 1 mg/L under this circumstance.

4.0 SCOPE AND APPLICATION

4.1 This SOP covers the non-filtered residue which does not pass through a glass fiber filter and dried to a constant weight at 103-105 ° C. The concentration of the non-filterable residue is calculated by the difference between the residue weight from filter weight, then dividing by the volume of sample filtered.

5.0 SUMMARY OF TEST METHOD

5.1 A well-mixed sample is filtered through a standard glass-fiber filter. The residue left on the filter is dried to a constant weight at 103–105 °C.

5.2 The reporting unit for non-filtered residue is mg/L.

5.3 The filtrate from this method may be used for filterable test (TDS).

6.0 DEFINITIONS

Residue, Non-filterable -- is defined as those solids which are retained by a glass fiber filter and dried to constant weight at 103-105ºC.

Method Blank (MB) - An aliquot of RO water that is analyzed exactly like a sample.

Lab Control Sample (LCS) -- A known concentration of sample is tested exactly as a sample.

Duplicate – A second aliquot of a sample that is treated exactly like a sample. Duplicate samples are analyzed to provide an indication of analytical precision. Samples must have a measurable concentration for a precision calculation to be meaningful.

Relative Percent Difference (RPD) -- to compare two values, the relative percent difference is based on the mean of the two values, and reported as absolute value.

Percent Recovery (%R) — the percentage of real value compare to the true value.

7.0 INTERFERENCES

7.1 Filtration apparatus, filter material, pre-washing, post-washing, and drying temperature are specified since these variables have been shown to affect the results.

7.2 Samples high in TDS, such as saline waters, brines and some wastes, may bring positive interference. Extra rinse is necessary after the filtration of samples in order to remove dissolved solids, which are possibly residing on the filter.

7.3 Exclude any large floating particles or submerged agglomerates of nonhomogenous materials from the sample if it is determined that their inclusion is not desired in the final result.

7.4 Limit the sample size to that yielding no more than 200 mg residue since excessive residue on the filter may form a water-entrapping crust.

7.5 Prolonged filtration times resulting from filter clogging may produce high results owing to increased colloidal materials captured on the filter.

8.0 SAFETY

8.1 Safety glasses and gloves are required. A lab coat or apron is strongly recommended. If samples contain known quantities of hazardous material, the dried sample and filters are classified as hazardous waste and are subject to the procedures listed in NE054.SOP.

9.0 EQUIPMENT AND APPARATUS

9.1 Analytical balance. Mettler AG204

9.2 Drying oven. VWR model 1370FM. Capable of maintaining 103-105 °C.

9.3 Large vacuum pump.

9.4 500 ml Erlenmeyer vacuum flasks with crucible holder and glass insert.

9.5 Glass fiber filters. (Whatman p/n 1827024).

9.6 Tweezers.

9.7 Rinse bottle. Filled with laboratory grade water.

9.8 1000, 500, 250 and 100 ml graduated cylinders.

9.9 40 ml Gooch crucibles. (Baxter p/n C8470-7).

9.10 Portable desiccator.

10.0 REAGENTS AND STANDARDS

10.1 Laboratory grade water (RO water). Located near front door of building.

10.2 Laboratory Control Sample (LCS): 100 mg/L of TSS made by analysts: 0.2g of cellulose Talc (USP, Fisher Scientific or other vendor) in 2000ml lab reagent grade water.

11.0 SAMPLE COLLECTION, PRESERVATION, SHIPMENT AND STORAGE

11.1 Analyst will be familiar with NE227.SOP *SAMPLE RECEIVING LOGIN AND STORAGE PROCEDURES.*

11.2 Samples require no preservation prior to analysis other than storage at 4º C in the walk-in cooler.

11.3 The holding time for TSS samples is seven days.

12.0 QUALITY CONTROL

12.1 Method Detection Limit study (MDL). Seven or eight MDLs samples (use ERA control samples or other acceptable standards) should be determined annually at a concentration of two to three times the estimated instrument detection limit for the analytes of interest. Analyze the samples according to the procedures set forth in this document. Calculate the MDL by multiplying the standard deviation of seven MDL measurements by 3.14. For the MDL to be valid, it must be greater than 1/10 the amount spiked but not greater than the amount spiked.

12.2 Precision and Accuracy (P&A) studies. Each analyst must demonstrate the ability to generate acceptable results with this method using the following procedure:

12.2.1 Spike four precision and accuracy samples for the analytes of interest at a level at least ten times the PQL level. Recovery must meet laboratory established acceptance criteria.

12.3 Analyst must read, understand, and use the latest version of the laboratory's SOP's that relate to their job responsibilities. The standard operating procedure must be read during their initial training, annually, and when the standard operating procedure is revised. Familiarity with the operation of the drying oven located in the Inorganics laboratory Familiarity with the maintenance of the portable desiccators Familiarity with the operation and maintenance of the vacuum pump.

12.4 A method blank sample is analyzed once every batch of twenty samples or less. 1000 ml of RO water should be used. The blank result must be less than reporting limit which is 1 mg/L currently.

12.5 A laboratory control sample is analyzed once every batch of twenty samples or less. From the certified value given or prepared standard of true value, filter enough sample for accurate determination. % LCS can be calculated as seen in Section 15.0.

12.6 A sample duplicate is analyzed once every batch of twenty samples or less. If additional sample is unavailable for duplicate analysis, analyze the laboratory control a second time. Calculate the relative percent difference (RPD) as seen in Section 15.0.

12.7 This section outlines the necessary quality control samples that need to be generated at the time of sample extraction. The results of the quality control measurement samples document the quality of the data generated. The following table lists the Quality Control samples required for total suspended solids.

Quality Control Requirements

QC Sample	Frequency
Method Blank	Analyzed with each sample batch (up to 20 samples). 1000 mL of water should be applied. Method blank must be less than reporting limit, which is 1 mg/L.
Lab Control Spike	Analyzed with each sample batch (up to 20 samples). Apply the certified value or prepared standard true value. Filter the sample for accurate determination. See LCS calculation in Section 15.0.
Laboratory Duplicate	Analyzed with each sample batch (up to 20 samples). If additional sample is unavailable, analyze the laboratory

control spike sample again. Calculate the relative percent difference (RPD), refer to Section 15.0.

12.8 Method Blank:

12.8.1 With each batch of samples to be extracted a method blank is processed. The method blank is carried through all stages of sample preparation and measurement steps. For water samples and organic-free reagent water blank is processed. The method blank must exhibit TSS levels less than the matrix defined reporting limit (RL). If the method blank exhibits contamination above the reporting limit, the samples associated with the contaminated blank should be re-analyzed. If there is no original sample available for re-analysis, then the results should be flagged with a "B" indicating blank contamination. The value measured in the blank is reported for those samples associated with the particular blank out of criteria.

12.9 Laboratory Control Spike:

12.9.1 A Laboratory Control Spike (LCS), also referred to as a QC reference check standard, is extracted with each batch of samples at a rate of one per 20 samples. For water sample, spike one liter of laboratory organic free water, extract and analyze. If the percent recovery for the LCS is out of criteria, (85%-115%) the analysis is out of the control for that analyte and the problem should be immediately corrected. If there is sufficient sample, the samples associated with the Laboratory Control Spike that failed must be re-analyzed. If no more sample material is available, the data must be flagged to indicate low or high Control Spike recovery.

12.10 Laboratory Duplicate Analysis:

12.10.1 Duplicate analysis of the same sample is performed to assess method precision. A duplicate can also be performed as a blind duplicate, so that identification with original sample is withheld. The analysis of a duplicate sample precludes that TSS are to be found at appreciable levels in samples. The relative percent difference must be less than or equal to 20%.

13.0 CALIBRATION AND STANDARDIZATION

13.1 Balance is NIST calibrated annually, and daily checks of balance are implemented.

13.2 Thermometer must be calibrated yearly and the tolerance has to be met. NIST traced thermometer with annual calibration certificate has to be used. Corrected values have to be applied.

14.0 PROCEDURE

14.1 Vacuum Pump, Oven and Dessicator Operations.

14.1.1 Refer to NE087.SOP Section 14.0 (Set oven temperature at 104 ± 1ºC).

14.2 Begin Batch Sample Preparation

14.2.1 Log into LIMS and create a logbook with all QC samples in Wetlab page.

14.3 Crucible Preparation

14.3.1 Place glass fiber filter in Gooch crucible. Handle filter with tweezers only.

14.3.2 Place crucible on filtration apparatus and apply vacuum.

14.3.3 Wash the filter with 20 ml volumes of deionized water. Discard washings.

14.3.4 Dry crucible at 104 ± 1°C for 1 hour.

14.3.5 Remove crucible from oven and place in dessicator for at least 1 hour or until crucible cools to room temperature, or store until needed.

14.3.6 Weigh crucible. If weight is not constant, put back in dessicator for at least ten more minutes and re-weigh. Repeat until a constant weight is obtained or until weight loss is less than 0.5 mg. Input crucible weight into LIMS.

14.4 Sample Filtration and Drying Process

14.4.1 Place crucible with filter on filtration apparatus and apply vacuum (Refer to Section 14.3 for crucible preparation procedure). Wet the filter paper with deionized water to seat in crucible.

14.4.2 Shake sample bottle to maintain homogeneity.

14.4.3 While maintaining vacuum, pour contents of cylinder over filter into Erlenmeyer vacuum flask. Continue to apply vacuum for several minutes or until all sample passes through filter.

14.4.4 Rinse cylinder with deionized water to remove all traces of the sample and pour into crucible.

14.4.5 Rinse filter with approximately 10 ml of deionized water to remove trace residue. Swirl and allow filtrate to empty into flask. Repeat two more times.

14.4.6 Once all filtrate is removed by suction, remove the vacuum.

14.4.7 Place crucible with residues in oven for at least 1 hour at 103-105 °C.

14.4.8 Place in dessicator for at least an hour or until crucible cools to room temperature, then weigh. Repeat the drying cycle until a constant weight is obtained (weight loss is less than 0.5 mg).

14.4.9 Record final weights into LIMS and calculate the TSS as in Section 15.0.

14.5 Documentation

14.5.1 Finalize logbook in LIMS by filling out all required areas.

14.5.2 Create a Certificate of Analysis in LIMS.

15.0 CALCULATIONS

15.1 Calculation for Sample result:

$$\text{TSS, mg/L} = \frac{\text{Final dish weight with residue, mg} - \text{Initial dish weight, mg}}{\text{Sample volume (L)}}$$

15.2 Calculation for LCS Recovery:

$$\%\text{Recovery} = (\text{Found value}/\text{True value}) \times 100$$

15.3 Calculation for Duplicate:

$$\%RPD = \frac{(\text{sample result - duplicate result})}{(\text{sample result + duplicate result})} \times 200$$

16.0 METHOD PERFORMANCE

16.1 Each analyst must pass a Proficiency and Accuracy Test in order to perform this analysis. Records are maintained by QA Office.

16.2 Method Detection Limit: A method detection limit will be determined for this method whenever major modification to the analysis procedures are made or at a minimum annual frequency. Seven or eight MDLs samples (use ERA control samples or other acceptable standards) should be determined annually at a concentration of two to three times the estimated instrument detection limit for the analytes of interest. Analyze the samples according to the procedures set forth in this document.

MDL = S * t(n-1, 1-alpha=0.99)
Where:

S = Standard deviation of the replicate analyses
n = Number of replicates
t(n-1, 1-alpha=0.99) = Student's t value for the 99% confidence level with n-1

For example: t for 8 replicates = t(7,0.99) = 2.998

16.2.1 The determined MDL must be less than the concentration spiked, but greater than one tenth (1/10) the spiked concentration. If not, repeat the MDL determination at an appropriate spike concentration for affected analytes.

16.3 Precision and Accuracy Determination: Precision and accuracy data is obtained for the method by analyzing four laboratory control spikes at least 10 X the PQL level or a blind proficiency test sample within the acceptable range of the PT provider. The analyte will be added to a laboratory organic free water sample, and taken through all analytical procedures. An initial Precision and Accuracy Demonstration of Capability is required for each analyst/technician combination.

16.3 Analyst must read, understand, and use the latest version of the laboratory's SOPs that relate to their job responsibilities. The standard operating procedure must be read during their initial training, annually, and when the standard operating procedure is revised. The analyst must have familiarity with the operation of the drying oven located in the Inorganics laboratory and familiarity with the maintenance of the portable desiccators.

17.0 POLLUTION PREVENTION

17.1 Pollution prevention is practiced in the laboratory by minimizing usage of solvents and chemicals, so that disposal of waste generated is held to the smallest amount possible. This is directly linked to the types of analytical procedures in place at the laboratory to reduce the volumes of solvents used for our analytical procedures.

17.2 Pollution prevention also relies on minimizing to the best extent the chemicals and solvents required to perform analytical procedures. The laboratory personnel strive to purchase chemicals and standards that will be consumed based on anticipated workload. For additional information about laboratory pollution prevention, please refer to laboratory SOP NE168.

18.0 DATA ASSESSMENT AND ACCEPTANCE CRITERIA FOR QUALITY CONTROL MEASURES

18.1 The analyst is responsible for generating the data and also is the initial individual to review the data. This would include inspection of the data, processing the raw data, producing all required data forms, inspection of calibration curves for compliance, laboratory control spike recovery, and spike duplicate recovery. See Table 1 for Acceptance Criteria.

18.2 Once the initial review of the data is performed by the analyst, decisions are made at that time to accept the data if all criteria are met or to reject sample data if any of the quality control parameters or limits are out of control. Depending on the situation, samples requiring re-analysis will be notified to the appropriate personnel,

18.3 The analyst may also consult with the quality control officer as to the best form of action to take, or if the situation warrants corrective action beyond routine practices. If no recourse is available and the data is to be reported out of criteria, a Case Narrative Report is generated and the deviation is documented and reported to the client. The Case Narrative Report is filed with the data and is also useful for production of case narratives that are issued with the final data reports. If a problem exists that requires follow-up to rectify, a Corrective Action Report (CAR) is issued to document the problem found, steps taken to resolve the problem, and what samples were affected. This CAR form is filed by the quality control officer and reviewed by management to verify that appropriate actions have been taken to correct the problem.

Table 1. Acceptance Limits and Corrective Actions for QC Requirements

QC Requirement	Acceptance Limits	Corrective Action
Method Blank	The level of target analyte in the method blank must be less than the reporting limit.	If the Method Blank is greater than the reporting limit, the only associated samples that can be reported are the ones below the reporting limit, or more than 10X the level of the Method Blank.
Lab Control Sample	LCS recovery must be within limits of 85-115%.	1) If the recovery is above the limit, only accept sample results that are below the reporting limit. 2) If the recovery is below the limit, no associated sample results can be accepted.
Duplicate	Duplicate analysis must be within limits The RPD is 20%.	1) When the sample level is more than 5X the reporting limit, and the RPD exceeds limit, re-analyze sample and duplicate if samples are not consumed. 2) When the level of the sample is less than 5X the reporting limit, the absolute difference between the sample and duplicate should be less than 2X the reporting limit. If either sample or duplicate is below the reporting limit, no limit is used.

19.0 CONTINGENCIES FOR HANDLING OUT OF CONTROL OR UNACCEPTABLE DATA

19.1 After completion of the analysis run, the analyst reviews the LIMS logbook and analytical data for completion and prints the required documentation. The supervisor reviews the LIMS logbook and records their initials and review dates on the appropriate documents.

19.2 If QC values fall outside the acceptable range and data need to be reported, then the following procedures will be implemented:

19.2.1 Re-analyze sample.
19.2.2 Recheck calculations.

19.3 If the above cannot be performed:

19.3.1 The Quality Assurance officer must be notified.
19.3.2 The data must be flagged with the appropriate qualifiers and case narrative.
19.3.3 The client must be notified about the data.

21.0 WASTE MANAGEMENT

21.1 All applicable federal and state rules and regulations governing hazardous waste will be followed when disposing of laboratory waste generated during the execution of this method.

21.2 Please refer to standard operating procedures NE054 regarding how hazardous waste is handled and disposed of by the laboratory.

22.0 REFERENCES

22.1 "Methods of Chemical Analysis of Water and Wastes'," EPA-60/4-79-020, revised March 1983. Method # 160.2

22.2 NYSDOH Environmental Laboratory Approval Program Manual Item # 271.

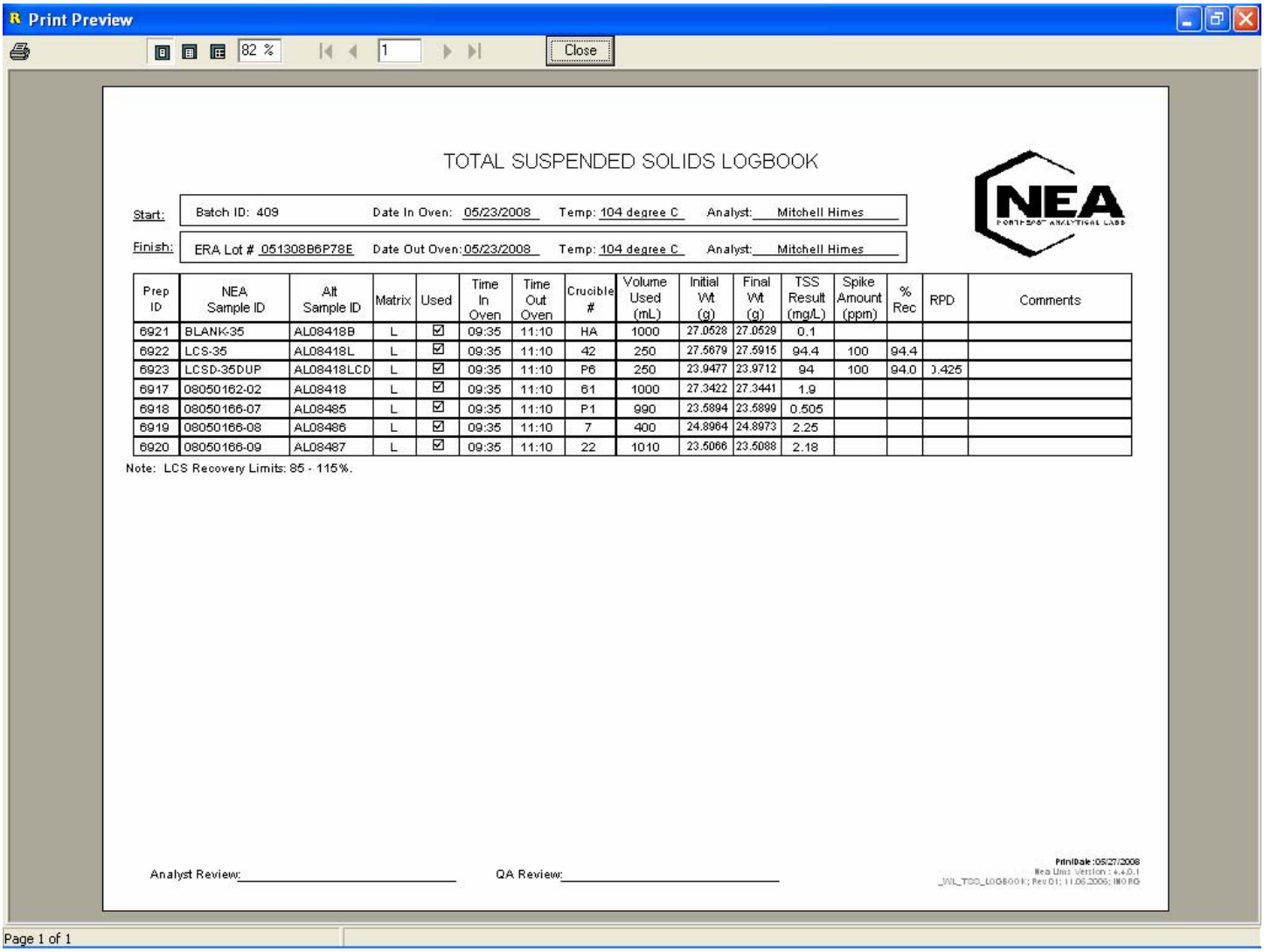
22.3 Standard Methods for the Examination of Water and Wastewater, SM 2540D, 19th, 1995, APHA.

23.0 TABLES, DIAGRAMS, FLOWCHARTS AND VALIDATION DATA

23.1 Appendix A: Example of TSS Logbook

23.2 Appendix B: Example of TSS Certification

APPENDIX A
Example of TSS Logbook



Prep ID	NEA Sample ID	Alt Sample ID	Matrix	Used	Time In Oven	Time Out Oven	Crucible #	Volume Used (mL)	Initial Wt (g)	Final Wt (g)	TSS Result (mg/L)	Spike Amount (ppm)	% Rec	RPD	Comments
6921	BLANK-35	AL08418B	L	☑	09:35	11:10	HA	1000	27.0528	27.0529	0.1				
6922	LCS-35	AL08418L	L	☑	09:35	11:10	42	250	27.5679	27.5915	94.4	100	94.4		
6923	LCSD-35DUP	AL08418LCD	L	☑	09:35	11:10	P6	250	23.9477	23.9712	94	100	94.0	0.425	
6917	08050162-02	AL08418	L	☑	09:35	11:10	61	1000	27.3422	27.3441	1.9				
6918	08050166-07	AL08485	L	☑	09:35	11:10	P1	990	23.5894	23.5899	0.505				
6919	08050166-08	AL08486	L	☑	09:35	11:10	7	400	24.8964	24.8973	2.25				
6920	08050166-09	AL08487	L	☑	09:35	11:10	22	1010	23.5066	23.5088	2.18				

Note: LCS Recovery Limits: 85 - 115%.

APPENDIX B
Example of TSS Certificate

NEA
NORTHEAST ANALYTICAL LABS

CERTIFICATE OF ANALYSIS
04/20/2009
XYZ Company
1234 Main Street
Anywhere, NY 12345
CONTACT: MARK LARUE

CELEBRATING 20 YEARS 1989 NEA 2009

MATRIX:	WATER		**PROJECT:**	ADD PROJECT NAME HERE	
DATE RECEIVED:	04/15/2009	**TIME:** 09:55	**LOCATION:**	ADD SAMPLING LOCATION HERE	
SAMPLED BY:	.		**LAB ELAP#:**	11078	
CUSTOMER PO:	N/A		**NEA LRF:**	09040127	

NEA ID	CUSTOMER ID	METHOD	DATE-TIME SAMPLED	RESULTS	PQL	FLAG	UNITS	DATE ANALYZED
Total Suspended Solids								
AM04135	SAMPLE 1	SM 2540D	04/14/2009 14:10	ND	1.00	U	mg/L	04/20/2009

Notes: ND (Not Detected). Denotes analyte not detected at a concentration greater than the PQL.
PQL (Practical Quantitation Limit). Denotes lowest analyte concentration reportable for the sample.

AUTHORIZED SIGNATURE:

William A. Kotas
Sr. Laboratory Representative

Robert E. Wagner
Laboratory Director

 Page 1 of 1

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STANDARD OPERATING PROCEDURE REVIEW

SOP Name	Review Number	Reviewers	Title	QAO Approval	Effective Date
NE117_05	00	Marsha Qian Christina L. Braidwood Robert E. Wagner	Inorganic Supervisor QAO Lab Director	Christina Braidwood	03/31/09

APPENDIX 31
SOP FOR DETERMINATION OF POC AND DOC BY STANDARD METHOD 5310B (NE128_06)

STANDARD OPERATING PROCEDURE

NORTHEAST ANALYTICAL INC.

NE128_06.DOC

REVISION NUMBER: 6

DETERMINATION OF TOTAL ORGANIC CARBON (TOC), PARTICULATE (POC), AND DISSOLVED TOTAL ORGANIC CARBON (DTOC) IN WATER

COPY # ____

Property of Northeast Analytical Inc.

NORTHEAST ANALYTICAL, INC
2190 TECHNOLOGY DRIVE
SCHENECTADY, NY 12308

(518) 346-4592

STANDARD OPERATING PROCEDURE

LABORATORY PROCEDURE NE128_06.DOC

REVISION: 6 (03/31/09)

Author: Nicole Morroni

Nicole Morroni
Inorganics Technician

Reviewed by:

Robert E. Wagner
Laboratory Director

Approved by:

Christina L. Braidwood
Quality Assurance Officer

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1.0 IDENTIFICATION OF TEST METHOD

1.1 This method outlines the determination of Total Organic Carbon (TOC), Particulate Organic Carbon (POC) and Dissolved Total Organic Carbon (DTOC) in waters by high temperature combustion.

1.2 This SOP describes TOC and DTOC procedures using Standard Method 5310 B (19th Edition).

1.3 POC test uses modified Standard Method 5310 B (19th Edition), and uses EPA Lloyd Kahn Method (1988) as a guide.

2.0 APPLICABLE MATRIX OR MATRICES

2.1 This SOP applies to drinking water, surface and saline waters, and domestic and industrial waste waters.

3.0 DETECTION LIMIT

3.1 The detection limit for DTOC/TOC in water is set at the level of the lowest calibration standard, which is 0.5 ppm currently at NEA.

3.2 The POC is analyzed in the same manner as soils, and therefore the detection limit is at the level of the minimum detected carbon in μg based on the individual instrument. The POC detection limit is reported with the unit of mg/L after the sample volume is adjusted.

4.0 SCOPE AND APPLICATION

4.1 The usefulness of the carbon measurement is to assess the potential oxygen demanding load of organic material on a receiving stream.

4.2 This Standard Operating Procedure outlines the sample preparation, instrument calibrations, and total organic carbon analysis by two different instruments, which are DC-190 and Shimadzu TOC-V with ASI or SSM.

4.3 Rosemont Dohrmann DC-190 and Shimadzu TOC-V with SSM can be used for POC analysis.

4.4 Shimadzu TOC-V Analyzer with ASI is used for the analysis of DTOC and TOC.

5.0 SUMMARY OF TEST METHOD

5.1 The centrifuge technique is used to separate particles from water. TOC in particles and TOC in a clear aqueous sample (POC and DTOC).

5.2 The fractions of Total Carbon (TC) can be defined as follows:

5.2.1 Inorganic Carbon (IC) is the carbonate, bicarbonate, and dissolved CO_2 in the sample.

5.2.2 Total organic Carbon (TOC) is the amount of carbon bonded to organic compounds in the sample.

5.2.3 Dissolved Total Organic Carbon (DTOC) is the TOC of the top portion of the water sample after the centrifugation.

5.2.4 Particulate Organic Carbon (POC) is the TOC of the bottom particles of the water sample after the centrifugation.

5.3 Organic carbons (TOC, DTOC, and POC in water samples) are measured by high-temperature combustion followed by infrared detection. Organic carbon is converted to carbon dioxide (CO_2) by catalytic combustion. The CO_2 formed can be measured directly by an infrared detector. The amount of CO_2 is directly proportional to the concentration of carbonaceous material in the sample.

5.4 POC can be a measured combustion-infrared method. The sample is homogenized by shaking, and then a portion is measured and centrifuged to allow the particulates to gravitate to the bottom of the vial. The top aqueous layer, which is used for DTOC analysis, is then carefully removed, and the remaining sample is dried in a boat. The sample is then treated with acid and dried at 104 ºC to remove IC. The treated sample is placed onto a boat holder and then pushed into a reaction chamber packed with an oxidative catalyst such as cobalt oxide, and heated to 900^{O}C. The organic carbon is oxidized to CO_2 and H_2O in the oxygenated atmosphere, so that the dried solid particulates can be analyzed.

* Filtration is not utilized in the sample preparation for POC and DTOC because studies at NEA lab have shown that results are not accurate at low DTOC levels (0.5 ppm) for water samples. Centrifuging water samples have provided better results based on NEA research.

5.5 TOC and DTOC are measured by injection, combustion, and detection. The sample is placed in a vial positioned on an autosampler. The sample is drawn up by a syringe equipped in the instrument, then acidified and sparged to remove IC. The treated sample is then sent into a reaction chamber packed with an oxidative catalyst such as platinum, which is heated to 680 ^{O}C. The organic carbon is oxidized to CO_2 and H_2O and is then analyzed using an infrared detector.

6.0 DEFINITIONS

6.1 **Analytical Batch** – The analytical batch is defined as a group of samples which are analyzed sequentially and use the same calibration curve and quality control checks.

6.2 **Calibration** – The establishment of an analytical curve is based on the area counts against the concentration of known standards. The calibration standards should be prepared using the same type of acid and/or reagents with the same concentration of acids and reagents used in the sample preparation.

6.3 **Calibration Blank** - A volume of reagent water that acts as a zero standard and is used to calibrate the instrument.

6.4 **Calibration Standard (CAL)** - A solution prepared from the dilution of stock standards solutions. The CAL solutions are used to calibrate the instrument response with respect to the organic carbon concentration.

6.5 **Calibration Curve –** A plot of the area counts of known standard solutions against the concentration of the known standards. This allows for a correlation to be made and for the analyst to then interpolate the concentration of samples based upon the area counts calculated by the instrument.

6.6 **Correlation Coefficient (r^2)** – The correlation coefficient for the calibration curve must be greater than or equal to 0.995 according to NYSDOH requirements.

6.7 **Continuing Check Blank (CCB)** - Carbon free water obtained from NEA's water system can be used as a CCB. Analyze the CCB solution after each CCV solution. If the absolute value of the CCB is less than the first standard, stop the analysis, correct the problem, recalibrate the instrument if necessary, and reanalyze all samples since the last compliant CCB.

6.8 **Continuing Calibration Verification (CCV)** – A solution of known as the organic carbon concentration, which is from a different source than the CAL standards. This evaluates the performance of the instrument

6.9 **Duplicate (DUP)** – A second aliquot of a sample that is treated in the same manner as the original.

6.10 **Matrix** – The predominant material of the sample composition.

6.11 **Matrix Spike (MS)** – An aliquot of the sample is spiked with a known concentration of organic carbon. The spiking occurs after the sample preparation but prior to analysis. A matrix spike is used to document the bias of a method in a given matrix.

6.12 **Method Detection Limit (MDL)** – The minimum concentration of organic carbon that can be identified, measured, and reported within a 99% confidence that the organic carbon concentration is greater than zero.

6.13 **Material Safety Data Sheet (MSDS)** – OSHA has established guidelines for the descriptive data that should be concisely provided on a data sheet to serve as the basis for written hazard communication programs. The thrust of the law is to have those who make, distribute, and use hazardous materials responsible for effective communication.

6.14 **Preparation Blank (PB)** – This is a sample of reagent water that goes through the same treatment as the samples do. It allows the analyst to be sure there is no contamination during the preparation steps.

6.15 **Practical Quantitation Limit (PQL)** – This is the lowest level that can be reliably achieved within specified limits of precision and accuracy during routine laboratory operating conditions.

6.16 **Relative Standard Deviation (RSD)** – To compare two or more values; the relative standard deviation is based on the mean of the values and the standard deviation of the values. RSD is reported as an absolute value, i.e., always expressed as a positive number or zero.

6.17 **Lab Reagent Water (LRG)** – Water in which the interference is not observed at or above the minimum quantitation limit of the parameters of interest.

6.18 **Rounding Rules** – If the figure following those to be retained is less than 5, the figure is dropped, and the retained figures are kept unchanged. If the figure following those to be retained is greater than 5, the figure is dropped, and the last retained figure is raised by one. If the figure following those to be retained is 5, and if there are no figures other than zeros beyond the five, the figure 5 is dropped, and the last-place figure retained is increased by one if it is an odd number, or it is kept unchanged if it is an even number.

6.18.1 If a series of multiple operations is to be performed (add, subtract, divide, multiply), all figures are carried through the calculations. Then the final answer is rounded to the proper number of significant figures.

6.19 **Sample Delivery Group (SDG)** – A unit within a single case that is used to identify a group of samples for delivery. An SDG is a group of 20 or fewer field samples within a case, received

over a period of up to 14 calendar days (7 calendar days for 14-day data turnaround contracts). Data from all samples in an SDG are due concurrently.

6.20 **Stock Standard solution**- A concentrated solution containing organic carbon prepared in the laboratory or purchased from a reputable commercial source.

7.0 INTERFERENCES

7.1 IC interference can be eliminated by acidifying the samples with HCl to a pH of 2 in order to convert it to CO_2. Subsequently sparging of the sample with a purified gas removes the CO_2.

7.2 The TOC procedure is limited by the maximum size of particles that can pass through the opening end of the needle of the instrument and is only applicable to homogeneous samples.

7.3 This procedure is only applicable to homogenous samples which can be injected into the apparatus reproducibly by means of a microliter type syringe or pipette for TOC. The opening of the syringe or pipette limits the maximum size of particles which may be included in the sample.

8.0 SAFETY

8.1 Safety glasses and disposable gloves must be worn when handling chemicals and samples. A lab coat or apron is recommended.

8.2 Personnel should familiarize themselves with the necessary safety precautions by reading the MSDS information covering any chemicals used to perform this SOP.

8.3 Each chemical should be regarded as a potential health hazard and exposure to these compounds should be as low as reasonably achievable. Specifically, concentrated phosphoric and hydrochloric acids present various hazards and are moderately toxic and extremely irritating to skin and mucous membranes. Use these reagents in a fume hood and if skin contact occurs, flush with large volumes of water.

8.4 Both instruments operate at high temperatures and care should be taken to avoid direct contact with the furnace or parts that enter or are near the furnaces.

9.0 EQUIPMENT AND APPARATUS

9.1 Rosemont-Dohrmann DC-190 IR-I NDIR detector module and TOC Boat Sampler Model 183.

9.2 Shimadzu TOC-V Analyzer with Solid Sample Module SSM-5000A and Autosampler ASI.

9.3 Quartz boats. Dohrmann (p/n 899-624).

9.4 Quartz boats for Shimadzu, customer made.

9.5 Quartz wool. Dohrmann (p/n 511-735).

9.6 VWR Model 1370FM drying oven set at 104 ^{o}C.

9.7 Muffle oven.

9.8 Tweezers large and small.

9.9 Magnet.

9.10 40 ml VOA Vials, unpreserved for DTOC and, preserved for TOC.

9.11 50 ml graduated cylinders, class A.

9.12 Centrifuge.

9.13 Aluminum weigh dishes.

9.14 White sample racks.

9.15 pH paper.

9.16 9” Pasteur glass pippettes.

9.17 White bulb.

9.18 10ml glass pipettes.

9.19 Black bulb.

9.20 10, 25, 50, 100, 500 mL Class A volumetric flasks.

9.21 Oxygen tank (2.6 purity or higher) with regulator.

9.22 Gray septum. Dohrmann (p/n 517-807).

9.23 Red/White septum. Dohrmann (p/n 511-914).

9.24 Cobalt catalyst. Dohrmann (p/n 511-883).

9.25 20-mesh tin. Dohrmann (p/n 511-876).

9.26 Copper. Dohrmann (p/n 511-895).

9.27 Pyrex wool. Dohrmann (p/n 511-895).

9.28 Platinum catalyst. Shimadzu (p/n 017-42801-01).

9.29 Platinum mesh. Shimadzu (p/n 630-00105-01).

9.30 Cobalt oxide catalyst. Shimadzu (p/n 630-00566).

9.31 Metal screen for catalyst. Shimadzu (p/n 638-58102).

9.32 Pyrex baking dish.

9.33 Sonicator in biota room.

9.34 Alconox soap.

10.0 REAGENTS AND STANDARDS

10.1 **LRG water**: Carbon-free water obtained from NEA's water system to be used as CCB. Laboratory research grade water system from U.S. Filter Water Systems Corporation.

10.2 Concentrated Nitric acid, 68-70 %, ACS grade, from EMD (p/n A200SI-212) or different vendor.

10.3 1:1 Nitric Acid (7.9 N). Dilute 50mL of concentrated nitric acid to a final volume of 100 mL with LGR water. (Use for POC sample acidification by DC-190).

10.4 Concentrated Hydrochloride acid, 36.5-38.0 %, from J.T.Baker (p/n A144SI-212) or different vendor.

10.5 1:5 Hydrochloric Acid (2.4 N). Dilute 20mL of concentrated hydrochloric acid to a final volume of 100mL with LGR water. (Use for POC sample acidification by Shimadzu).

10.6 2 N Hydrochloric acid: dilute 166 ml of concentrated hydrochloric acid to a final of 1000 ml with LGR water. (Use for boat cleaning).

10.7 Phosphoric Acid: Concentrated, ACS grade (p/n 215104-500G).

10.8 ERA Demand TOC stock standard (p/n 516)

10.9 High Purity Standards TOC stock standard (p/n CWW-TOC-G)

10.10 High purity solid Potassium Hydrogen Phthalate from Shimadzu (p/n 630-00635-01), VWR (BDH0260-500G) or other vendor

10.11 40,000 ppm stock TOC standard solution: dry solid potassium hydrogen phthalate at 104 ^{o}C for at least an hour. Cool in the desiccators to room temperature. Weigh 2.1272 g in a 25 ml of volumetric flask, and fill up to the line with LGR water.

10.12 Spiking standard solution (5000 ppm TOC): diluted from stock standard solution.

10.13 Calibration Standards for DC-190: Prepare 6 standards of different concentrations ranging from ~70 ppm - ~11430 ppm from stock standard solution. Add a drop of concentrated phosphoric acid to each 25 ml.

10.14 Calibration Standards for Shimadzu: Prepare 5 standards of different concentrations ranging from ~100 ppm - ~ 400,000 ppm. Add a drop of concentrated phosphoric acid to each 25 ml.

10.15 Organic Carbon Standard at 1000mg/L from two sources, for example VWR (p/n VW3880-2), Ultra Scientific or other vendor. Use as CCV check standard for POC on DC-190, calibration standard source and check standard source for TOC-V, the spiking solution for POC on the DC-190.

10.16 DTOC/TOC Calibration Standards: Prepare 2 standards at the concentrations of 5 ppm and 50 ppm from one source of 1000 ppm stock standard solution by making dilutions with fresh LRG water. Add phosphoric acid to standard to achieve pH of 2, about 2-3 drops to each 100 ml.

10.17 5 ppm TOC CCV check standard: pipette 0.5 ml 1000 ppm stock standard (which should be different from the calibration standard source) to 100 ml volumetric flask, acidify with phosphoric acid to a pH of about 2, and then dilute with fresh LGR water.

10.18 **Sparging Fluid for DC-190:** Fill a volumetric flask with LRG water and then add a drop of Phosphoric Acid and test pH. If the pH is not equal to or less than 2, continue adding a drop until it has a pH of 2 or less.

10.19 **Acidifying Solution for the TOC-V**: 25% Phosphoric Acid – Dilute 125 ml of Phosphoric Acid to a final volume of 500ml using LRG water.

11.0 SAMPLE COLLECTION, PRESERVATION, SHIPMENT AND STORAGE

11.1 Analyst must be familiar with SOP NE227 *STANDARD OPERATING PROCEDURE FOR SAMPLE RECEIVING, LOG-IN, AND STORAGE PROCEDURES.*

11.2 Samples for TOC in water should be preserved with 1:1 HCl, stored at 4 $\pm$ 2 ^{o}C, and have a holding time of 28 days. 28 days is recommended by the Environmental Protection Agency (EPA).

11.3 Samples for DTOC and POC can be taken from the same unpreserved sample. They must be stored at 4 $\pm$ 2 ^{o}C and have a holding time of 14 days.

11.4 Because of the possibility of oxidation or bacterial decomposition of some components of aqueous samples, the lapse of time between collection and start of analysis should be kept to a minimum. Samples should be protected from sunlight and atmospheric oxygen by preservation in NEA's refrigerator at 4 $\pm$ 2 ^{o}C; therefore, amber bottles are recommended.

12.0 QUALITY CONTROL

12.1 This section outlines the necessary quality control samples that need to be generated at the time of sample extraction. The results of the quality control measurement samples document the quality of the data generated. The following table lists the Quality Control samples required for this procedure.

Quality Control Requirements

QC Sample	Frequency
Continuing Calibration Verification	Analyzed immediately after calibration of instrument. Analyzed with each sample batch (up to 10 samples).
Continuing Calibration Blank	Analyzed immediately after the CCV.
Method Blank	POC ONLY: Analyzed with each sample batch (up to 20 samples). 80 or 160 mL of water should be applied. Method blank must be less than reporting limit.
Duplicate	Analyzed with each sample batch (up to 20 samples).
Matrix Spike	Analyzed with each sample batch (up to 20 samples).

12.2 The CCV should be analyzed immediately after calibration of an instrument. The CCV should be produced from a different source than the CAL standards. Currently POC uses a CCV solution that is 1000ppm from RICCA, and DTOC/TOC uses the Ultra Scientific standard solution diluted down to 5 ppm.

12.3 CCB is a blank that is analyzed immediately after every CCV. The CCB result should be lower than the low level standard.

12.4 Method Blank (MB) should be analyzed with each batch of POC samples by using an aliquot of reagent water and passing it through the same procedures as the other samples. Its concentration should be less than the first standard.

12.5 A Duplicate Sample (DUP) is usually analyzed on the first sample of a SDG or the sample that is specified by the client. It is prepared and treated in the same way as the original sample. The RPD% should be less than 20%, unless the sample concentration is less than 5 times the PQL.

12.6 Matrix Spike is run once every 20 samples, and is usually run on the same sample as the Duplicate.

12.6.1 For POC by DC-190: spike 250 ul of 1000 ppm CCV solution

12.6.2 For POC by TOC-V: spike 100 ul of a 5000ppm spiking solution

12.6.3 For DTOC/TOC: spike 0.303 ml 1000 ppm stock standard from the CCV check standard source to a 30 ml sample.

12.6.4 Spiking amount can be adjusted based on the sample's concentration.

13.0 CALIBRATION AND STANDARDIZATION

13.1 Calibration of the DC-190 for POC

13.1.1 A new calibration should be run every four months. It should be run sooner if CCV is repeatedly outside of limits or if the instrument has had major repairs done.

13.1.2 The calibration curve is based on 'ug of carbon' versus 'area'.

13.1.3 A calibration blank should be obtained as well as the calibration standards. Prepare standards at concentration levels at approximately 5, 10, 100, 250, 500, 800 ug of carbon after 70 ul are injected. Refer to SOP of NE205 attachment 23.2 for the preparation of standards.

13.1.4 The calibration blank and each standard should be run in duplicate. Each standard should be repeated until the standards are reproducible within 10% of each other. The procedures for running each sample can be found in Section 14.0.

13.1.5 The blank area should be subtracted from the average area of each calibration standard.

13.1.6 Each calibration should begin with a quartz boat filled with new quartz wool and should be freshly burned in the furnace until the baseline has been stabilized.

13.1.7 The area counts obtained for each replicate of each standard should be entered into the excel spreadsheet S:\Lab Data\Metals\TOC\Data (year)\tocDC190calibration (date).

The 'Calculate Curve Click Here' tab should then be pressed. Be sure the R squared is >0.995, the recovery of each standard is 90-110%, and the RPD is < 10% for each standard (the low level standard can be within 80-120%).

13.1.8 The curve is then entered into LIMS by going to the Wetlab department and selecting POC. In the Prep Book tab, create a new batch for the day and select the DC-190 as the instrument. Press the Blank button twice and then the ICx button, which then adds the standards into the Prep Book. Enter the area counts into the system as well as Std Lot, Blank Area, Slope, Low Std Concentration, and Calibration Date. To finalize the calibration in LIMS select all injections and press the 'calculate and send' button on top (a hand with a paper in it).

13.2 Calibration of the Shimadzu TOC-V with SSM for POC

13.2.1 A new calibration should be analyzed every four months. If the CCV is repeatedly outside of limits, or if the instrument has had major repairs, a new calibration should be completed.

13.2.2 The calibration curve is based on 'ug of carbon' versus 'area'.

13.2.3 A Calibration blank should be obtained as well as preparing the Potassium Hydrogen Phthalate standard at 40,000 ppm. The standard is then diluted appropriately in a volumetric to concentrations of 100 ppm, 400 ppm and 4,000 ppm. Clean boats are then injected with different volumes of the 100 ppm, 400 ppm, 4,000 ppm, and 40,000 ppm standards and analyzed. The final concentrations analyzed are 10, 40, 400, 4,000, and 40,000 ug of carbon. Please see details in SOP of NE205 Attachment 23.2.

13.2.4 To run the curve on the Shimadzu SSM, create a new Sample Run and save it as (date) TOC. Then select Insert – Calibration Curve. Select new curve.cal and then run according to Section 14.0.

13.2.5 The program will automatically zero shift the curve.

13.2.6 Each calibration should begin with a ceramic boat filled with new ceramic fibers and should be freshly burned in the furnace until the baseline has been stabilized.

13.2.7 The curve is then entered into LIMS by going to the Wetlab department and selecting POC. In the Prep Book tab create a new batch for the day and select the TOC-V as the instrument. Press the Blank button twice and then the ICx button, which then adds the standards into the Prep Book. Enter the area counts into the system as well as Std Lot, Blank Area, Slope, Intercept, Low Std Concentration, and Calibration Date. To finalize the calibration in LIMS, select all injections and press the 'calculate and send' button on top (a hand with a paper in it).

13.3 Calibration of the Shimadzu TOC-V with ASI for DTOC and TOC

13.3.1 A new calibration should be analyzed daily only if the CCV is outside of limits, or if the instrument has had major repairs completed.

13.3.2 The calibration curve is based on 'ug of carbon' versus 'area'.

13.3.3 Fresh LGR water is used as the calibration blank

13.3.4 5 and 50 ppm standards are used to create the calibration curve with six points; 0, 0.5, 1, 5, 10, and 50 ppm.

13.3.5 Place three clean VOA Vials with the blank, 5 ppm and 50 ppm standards in the appropriate position on the ASI sample tray.

13.3.6 To create the calibration curve on the TOC-V, generate a new Sample Run for the TOC-V Reg Sensitivity module and save it as (date) DTOC. Then select Insert – Calibration Curve. Select NPOC Reg Catalyst.cal, when prompted, and enter the appropriate tray positions in the Vial column, according to Section 14.0.

13.3.7 The program will automatically analyze the samples by acidifying, sparging, and then applying two analyses on each calibration point. 0.5 and 1 ppm standard will be diluted from 5 ppm vial , and 10 ppm will be diluted from 50 ppm vial. The instrument does the dilution automatically. If the SD for the two analyses is not less than 0.1, then a third analysis is completed. The pair with the smallest SD is averaged together and accepted as the result.

13.3.8 The calibration curve is not entered into LIMS but the curve data is entered into the Logbook portion of LIMS so that the data can be calculated. Begin by double-clicking on the calibration curve on the Explorer menu on the right side of the screen. A box should pop up and then select Print. From the print out enter the average of the zero standard into the Blank Area column in LIMS as well as the slope and intercept into their respective columns in LIMS.

14.0 PROCEDURE

14.1 Preparation of DTOC water samples

14.1.1 Remove the samples from the refrigerator and allow them to come to room temperature.

14.1.2 Label 40 ml vials with sample IDs and a set of VOA vials. Be sure to include a DUP and MS as required.

14.1.3 Mix the sample well, and measure 40ml in a graduated cylinder. Pour into the appropriately labeled 40 ml vial, cap the sample, and place into a rack. Repeat for all the samples in your sample set.

14.1.4 Place the vials in the centrifuge and centrifuge for 6 minutes. Set speed to 3/4. Remove the samples from the centrifuge, being sure not to agitate them.

14.1.5 Use a 10ml pipette and the black bulb to remove the top 30ml of sample and place it in a new labeled VOA vial. Add a drop of concentrated phosphoric acid to each vial. Add more if pH is not below 2.

14.1.6 At this point, spike the MS sample with 0.303 ml of 1000 ppm TOC stock standard. The final spiking concentration will be 10 ppm.

14.1.7 If the samples are analyzed that day, then place them in the ASI sample tray and continue to the analysis section. If the samples are not analyzed that day, they should be stored in the refrigerator until analysis.

14.2 Preparation of POC water samples

14.2.1 Remove the samples from the refrigerator and allow them to come to room temperature.

14.2.2 Label 40 ml vials with sample IDs, and check there is two vials for each sample. Be sure to include the PB, DUP, and MS as required.

* POC sample is regularly analyzed by DC-190. Shimadzu TOC-V SSM will be used as a back up instrument. When analyzing a sample for POC by Shimadzu; the POC sample should be prepared from 160 ml instead of 80 ml since the detection limit of the Shimadzu is two times of the DC-190 detection limit. Four 40 ml vials will be required instead of two vials.

14.2.3 Mix the sample well, and measure 40 ml in a graduated cylinder. Pour into one of the appropriately labeled vials. Measure a second 40 ml aliquot and fill the second vial. Cap the vials, and place them in a rack. Repeat for all the samples in the batch.

14.2.4 Place the vials in the centrifuge and centrifuge for 6 minutes. Set speed at 3/4. Remove the samples from the centrifuge, being sure not to agitate them.

14.2.5 Use a 10ml pipette and pipette bulb to remove the top 20 ml of water in each vial. Be careful to allow the particulates to settle to the bottom of the vial, because you will need to analyze this. You can discard the extra water down the drain or place it in a VOA vial for DTOC analysis. Shake one vial of each sample well and combine into the second vial so that there is only one vial per sample.

* If the POC sample is analyzed by the Shimadzu, remove 10 ml of the top water from each vial to a DTOC vial. Discharge the residual top water from each vial and combine all four bottom solutions as the POC sample.

14.2.6 Place the POC sample vials in the centrifuge and centrifuge for 6 minutes at a set speed of 3/4. Remove the samples from the centrifuge, being sure not to agitate them.

14.2.7 Carefully pipette as much water out of your sample vial without disturbing the particulates settling to the bottom of the vial.

14.2.8 If you are analyzing samples on the DC-190, set up a row of quartz boats in aluminum weigh dishes in the drying oven; one for each sample. If you are analyzing samples on the Shimadzu SSM, set up a row of quartz boats in the drying oven.

14.2.9 Use the 1000 ul pipette, carefully pipette to a maximum of 600 ul of sample into its assigned quartz boat for DC-190. Higher volume samples can fit into the Shimadzu quartz boat. Close the door and wait ~10 mins for the entire sample to dry. Then continue pipetting sample into its assigned boat, until there is no sample left in the vial. Then pipette 600 ul of reagent water into each vial, gently stir, and pipette the rinse into the assigned boat.

14.2.10 Remove any inorganic carbon by adding two drops of acid to each boat by gently lifting the boat to check the acid coats the entire bottom. If analyzing on the DC-190, use 1:1 HNO_3; if analyzing on the Shimadzu SSM, use 1:5 HCl as the acid.

14.2.11 Remove boats or tray with dried samples from oven to a cart. Cover each sample with plastic cap to prevent contamination until analysis.

14.3 Preparation of TOC water samples

14.3.1 Remove the samples from the refrigerator and allow them to equilibrate to room temperature.

14.3.2 Check there is air space in the vial. If there is not, then mix the sample well, and pour off a small amount. If there is no air space in the vial, the instrument would create a vacuum when taking up a sample.

14.3.3 The samples should be ready for analysis and placed on the ASI sample tray.

14.4 Analysis of DTOC/TOC water samples by Shimadzu TOC-V ASI

14.4.1 To prepare the main unit TC catalyst:

14.4.1.1 Be sure the instrument is turned off and has cooled to room temperature. Open the door of the main unit and remove the small top panel.

14.4.1.2 Disconnect the carrier gas tubing on the right and loosen all the thumb screws and remove the injector block.

14.4.1.3 Gently remove the bottom end of the combustion tube from the nut and slowly pull the tube up and out of the furnace.

14.4.1.4 Remove the catalyst and clean the tube if necessary.

14.4.1.5 Place a platinum mesh screens on the bottom of the tube and add 5 mm of quartz wool.

14.4.1.6 Add 100mm of the regular sensitivity catalyst , which is platinum catalyst only. Tap gently to check it settled.

14.4.1.7 Replace the tube into the furnace and connect to bottom nut.

14.4.1.8 Reattach the injector block and check that it is centered over the catalyst tube. Reconnect the carrier gas tubing line.

14.4.1.9 Close the instrument top cover. Turn on instrument and allow the catalyst to burn off particles for 2-3 hours.

14.4.2 Turn on the main unit by pressing the button on the bottom right corner on the front of the main unit. The main unit has the NDIR Detector and should warm up in approximately an hour. This unit is generally left on and only shut off to reboot the instrument.

14.4.3 Leave the SSM unit either on or off. This unit is generally left on but can be shut off. Warm it up long enough for the temperature to rise to its set point and the baseline to settle. The baseline of the unit will affect the results of the ASI unit.

14.4.4 At the start of each day, check the moisturizer level to be sure it is within the fill range and the humidifier to verify the water level is above the end of the outlet tube on the main unit. Turn on the oxygen tank. Be sure the oxygen is set to 60psi on the regulator. On the SSM, check the drain separator on the right side of the system to be sure it is not bubbling; fill with water to stop bubbling.

14.4.5 Open the TOC-Control V program. Select the Sample Table Editor. Press the New button (piece of white paper) and select Sample Run. Select the TOCV REG SENSITIVITY as the instrument and name the file as the (date) dtoc. Press the connect button (lightning bolt) and select use settings on PC. The instrument will now connect with the computer and ASI. When it is fully initialized, watch the baseline by going to the Instrument and Background Monitor.

14.4.6 The instrument is ready to analyze samples when the lights at both SSM and TOC tabs on the Background Monitor window are green.

14.4.7 When the instrument and samples are ready to be analyzed, start by opening LIMS and entering into the Wetlab department. Select the DTOC tab on the left.

14.4.8 Create a new batch and select the TOC-V as the instrument. Add in your first sample by selecting it in the To Be Done tab. Right-click and append to Prep Book. In the Prep Book, be sure the sample is selected, add the SET (CCV and CCB). Move the set to the top, then select the sample and add the DUP and MS by pressing their respective buttons. Continue appending samples and adding SETs as needed.

14.4.9 When the entire run is entered, select all the samples in the batch, and press the Save button (a disk). Select the NPOC reg catalyst method and enter the file name as (date) dtoc.

14.4.10 Go back to the TOC Control-V program and select the line after the calibration curve by clicking on the number on the left. Go to Edit and select Import. Select the file that was just created. All the samples should appear in the sample table as they appear in LIMS.

14.4.11 Open the ASI cover, and place the samples in the tray. Be sure to note the numbers associated with each sample. Then close the ASI cover.

14.4.12 Be sure the rinse and dilution bottles are filled with fresh LGR water. Also check the waste bottle is empty. The waste is acidified waste and should be disposed of accordingly.

14.4.13 To start running samples, select the calibration curve and press the Run button (green stoplight).

14.4.14 A box will pop up that asks what to do with the instrument when it has finished running. Leave “Keep Running” selected and press the Standby button on the bottom of the box.

14.4.15 A box will pop up that shows all the samples that will be analyzed. Fill in the vial positions according to where you placed the samples in the ASI sample tray.

14.4.16 Then a “Start ASI Measurement” box pops up. Be sure to uncheck the “External Acid Addition” box so the instrument will then acidify the samples. Then press Start.

14.4.17 The program will automatically run the calibration curve by acidifying, sparging, and then running two analyses on each calibration point. If the SD for the two batches is not less than 0.1, then a third analysis is completed and the pair with the closed SD is accepted as the result. Once the curve is completed, it will continue onto the samples, by analyzing them in the same way. Check the instrument periodically during the analysis if you are not analyzing over night.

14.4.18 When the analysis is completed, be sure that it meets all QC requirements. Then print the calibration curve data and the sample run by selecting File, then Print, then Table. Change settings to landscape and print. Go into LIMS, highlight all samples, and acquire samples from the TOC-V, and press the 'calculate and send' button.

14.4.19 Select each CCV/CCB set and the following 10 samples. Right click and assign a blank ID. Then select all QC and right click. Save selected QC for each LRF. Set the parameters to 30 psi for oxygen flow, Low range, and 'NA'for baseline, and save parameters. Be sure that you have filled in the calibration information.

14.4.20 Select the analysis batch for the day in LIMS and print a logbook (printer button). Then create a Certificate of Analysis.

14.5 Analysis of POC water samples by DC-190

14.5.1 The main NDIR detector should be turned on by the switch on the back of the instrument and allow to stabilize for a few hours. This module is generally left running and only shut off for rebooting the instrument when necessary.

14.5.2 The Analysis Mode is set to TC and the Inlet Mode is set to Boat.

14.5.3 At the start of each day, carefully check all components of both the main unit and boat sampler for wear. Check the level of acidified water in the right flask to be sure it is above the sparging finger. Empty any fluid in the left flask into acid waste. Turn the power onto the TOC Boat Sampler so the furnace begins to heat up. Turn the oxygen tank on. Be sure the oxygen is set to 30 psi. Check the right flask to be sure a vigorous flow of gas is emitted from the sparging finger. If not, apply leak check slution to check lines for gas leaks.

14.5.4 The boat sampler must heat up until the Furnace light is green, the Carrier Gas light is green, and the baseline is stabilized at a number below 3, which is displayed in the lower right-hand side of the main unit's display screen.

14.5.5 When the instrument and samples are ready, the analysis begins by opening LIMS and entering into the Wetlab department. Selecting the POC tab on the left.

14.5.6 Create a new batch, and then select the DC-190 as the instrument. Add your first sample by selecting it in the To Be Done tab. Right-click and append to Prep Book. In the Prep Book, be sure the sample is selected, add the SET (which consists of a CCV and CCB) and move the set to the top. Add in the samples and QC samples as PB, DUP and MS by pressing the appropriate buttons. Place your cursor in the Area box of the sample you intend to analyze (when you start should be a CCV).

14.5.7 Follow the directions in NE205_02 Section 14.1.12 through 14.1.22. Ignore the references to the QUAD and be sure to run a new CCV/CCB set every 10 samples.

14.5.8 Print out a logbook and also create a Certificate of Analysis.

14.6 Analysis of POC samples by Shimadzu TOC-V SSM

14.6.1 Turn on the main unit, and press the button on the bottom right corner on the front of the main unit. The main unit has the NDIR Detector and should warm up for an hour or two. This unit is generally left on, and is only shut off to reboot the instrument.

14.6.2 Turn on the SSM using the switch on the right side towards the back. This unit is generally left on but can be shut off. Warm it up long enough for the temperature to rise to its set point and the baseline to settle.

14.6.3 At the start of each day, check the moisturizer level to verify it is within the fill range and check the humidifier to verify the water level is above the end of the outlet tube on the main unit. Turn on the oxygen tank. Be sure the oxygen is set to 60psi on the regulator. On the SSM check the drain separator on the right side of the system to be sure it is not bubbling; fill with water to stop bubbling.

14.6.4 Open the TOC-Control V program. Select the Sample Table Editor. Press the New button (piece of white paper) and select Sample Run. Select the TOC-V+SSM as the instrument and name the file as (date) poc. Press the connect button (lightning bolt) and select settings on the PC. The instrument will now connect with the computer and SSM. When it is fully initialized, you can watch the baseline by going to Instrument and Background Monitor.

14.6.5 The instrument is ready to analyze samples when the lights at both SSM and TOC tabs on the Background Monitor window are green.

14.6.6 When the instrument and samples are ready, the analysis is begun by opening LIMS and entering in the Wetlab department. Select the POC tab on the left.

14.6.7 Create a new batch and then select the TOC-V as the instrument. Add in you first sample by selecting it in the To Be Done tab. Right-click and append to Prep Book. In the Prep Book, check the sample is selected, add the SET (CCV and CCB) and move the set to the top. Then select the sample and add the DUP and MS by pressing the appropriate buttons.

14.6.8 When the entire batch is entered, select all the samples in the batch and press the Save button (a disk). Select the NPOC regular catalyst method and then press Yes for using soil samples. Enter the file name as (date) poc.

14.6.9 Go back to the TOC Control-V program, and go to Edit; select Import. Select the file that was created. All the samples should appear in the sample table as they appear in LIMS.

14.6.10 To start running samples, select the first sample and press the Run button (green stoplight). Place the boat in the boat holder and close the boat port. It will then ask you to enter the weight of the sample. If you are analyzing CCV or CCB, enter the volume (should be 100 ul) by un-checking the “By Weight” box. When analyzing POC samples, un-check the “By Weight” box and enter 160000 ul (for the 160 ml of sample you started with). Slide the boat in the instrument when the instrument is ready, by pushing the blue push bar.

14.6.11 After the sample is measured, a window will pop up, saying to move the boat back to the cooling position and then again to the stop point. Press Next to continue analyzing the next sample.

14.6.12 When it is time to analyze the MS (the sample with 100 ul of the 5000 ppm spiking solution) enter the volume of the sample into the volume box. The MS must be spiked prior to being placed in the instrument. Continue analysis like a sample.

14.6.13 When the entire analysis is completed, select File, then Print, then Table. Change settings to landscape, and print. Go into LIMS. Highlight all samples that have not previously been acquired into LIMS. Acquire samples from the Shimadzu, and press the 'calculate and send' button.

14.6.14 Select each CCV/CCB set and the following 10 samples, and right click and assign a blank ID. Then select all QC, and right click, and Save selected QC for each LRF. Set the parameters to 30 psi for oxygen flow, Low range, and '-'for baseline and save parameters. Check that the calibration information is correct.

14.6.15 Select the analysis run for the day in LIMS and print a logbook (printer button). Also create a Certificate of Analysis.

14.6.16 To clean the ceramic boats, start by obtaining all the ash from the boats by scraping. Then place the boats in a jar with 2M HCl and cap. Shake the jar gently, and let jar sit for a half hour. Carefully remove the boats from the jar with tweezers and rinse thoroughly with tap water and then DI water. Then place the boats in the drying oven to dry. Once dry, they can be placed in the muffle oven at 900° C for 20 minutes.

15.0 CALCULATIONS

15.1 Report results to 3 significant figures.

15.2 TOC/DTOC calculation for Shimadzu TOC-V:

$$\text{mg/L} = (\text{Sample Area} - \text{Intercept}) * \text{DF} / \text{Slope}$$

Intercept and slope values are derived from the daily calibration curve information.
DF is the dilution factor of sample.

15.3 RPD Calculation = $\dfrac{(\text{Sample1} - \text{Sample2})}{(\text{Sample1} + \text{Sample2})} * 200$

15.4 Spike Added Calculation = $\dfrac{(\text{Volume of spike}) * (\text{Spike concentration})}{(\text{Sample volume})}$

15.5 % Recovery of Spike = $\dfrac{(\text{POC concentration of MS}) - (\text{POC concentration of Sample})}{(\text{Spike added})} * 100$

15.6 POC Concentration Calculation for DC-190 = $\dfrac{(\text{Sample Area} - \text{Blank Area}) * (\text{Inverse Slope})}{(\text{Sample volume})}$

15.7 POC Concentration Calculation of TOC-V = $\dfrac{(\text{Sample Area} - \text{Intercept})}{(\text{Slope}) * (\text{Sample volume})}$

15.8 % Recovery of CCV = $\dfrac{(\text{TOC Concentration of CCV})}{(\text{True Value of CCV})} * 100$

16.0 METHOD PERFORMANCE

16.1 Method Detection Limits should be determined annually or when a change in instrument hardware or operating conditions dictates they need to be re-determined as judged by the analyst. It is

performed by running 8 replicates of the lowest standard. Follow the MDL rules, refer to SOP of NE021. There is an MDL value for the DC-190 instrument and a global MDL for the Shimadzu instruments (TOC-V & TOC-V2)

16.2 Analysts must read, understand, and use the latest version of the laboratory's SOPs that relate to their job responsibilities. The SOPs must be read during their initial training, annually, and when the SOPs are revised.

16.3 For DTOC/TOC a Precision and Accuracy test should be performed annually by the analyst to demonstrate their ability to reproduce a known sample four times accurately while following the SOP for each applicable matrix, or a blind proficiency test sample, within acceptable PT limits. All recoveries should have a recovery between 80-120% of the known concentration and the RSD should be less than 20%. Initial demonstrations must be performed on each instrument, to demonstrate capability with different matrices.

17.0 POLLUTION PREVENTION

17.1 Pollution prevention is practiced in the laboratory by minimizing usage of solvents and chemicals, so that disposal of waste generated is held to the smallest amount possible. This is directly linked to the types of analytical procedures in place at the laboratory to reduce the volumes of solvents used for our analytical procedures.

17.2 Pollution prevention also relies on minimizing to the best extent the chemicals and solvents required to perform analytical procedures. The laboratory personnel strive to purchase chemicals and standards that will be consumed based on anticipated workload. For additional information about laboratory pollution prevention, please refer to laboratory SOP NE168.

18.0 DATA ASSESSMENT AND ACCEPTANCE CRITERIA FOR QUALITY CONTROL MEASURES

18.1 The analyst is responsible for generating the data and also is the initial individual to review the data. This would include inspection of the data, processing the raw data, producing all required data forms, inspection of calibration curves for compliance, CCB, and CCV recovery. See Table 1.0 for Acceptance Criteria.

18.2 Once the initial review of the data is performed by the analyst, decisions are made at that time to accept the data if all criteria are met or to reject sample data if any of the quality control parameters or limits are out of control. Depending on the situation, samples requiring re-analysis will be notified to the appropriate personnel,

18.3 The analyst may also consult with the quality control officer as to the best form of action to take, or if the situation warrants corrective action beyond routine practices. If no recourse is available and the data is to be reported out of criteria, a Case Narrative Report is generated and the deviation is documented and reported to the client. The Case Narrative Report is filed with the data and is also useful for production of case narratives that are issued with the final data reports. If a problem exists that requires follow-up to rectify, a Corrective Action Report (CAR) is issued to document the problem found, steps taken to resolve the problem, and what samples were affected. This CAR form is filed by the quality control officer and reviewed by management to verify that appropriate actions have been taken to correct the problem.

18.4 Calibration Assessment (Refer to Table 1.0 for the Calibration Procedures and Acceptance Criteria for TOC/DTOC)

18.4.1 All standards are run in duplicate with RPD <10% (except the lowest standard with RPD< 20%)

18.4.2 Refer to NE205 for POC calibration acceptance criteria.

Table 1.0 Calibration Procedures and Acceptance Criteria for TOC and DTOC

Calibration Element	Frequency	Acceptance Criteria
Initial Calibration (minimum blank + 5 points)	Daily	R^2 > 0.995
Initial and Continuing Calibration Verification (CCV) (Separate source from ICAL Standards)	Daily, prior to sample analysis, immediately following ICAL. every 10 samples and at the end of run	± 15% from expected concentration
Calibration Blank Verification (CCB)	After each CCV	Area reading lower than the lowest cal standard area

18.5 Analysis quality control criteria (Refer to Table 2.0 for Quality Control Procedures for TOC/DTOC).

18.5.1 % RPD for aqueous TOC/ DTOC samples and duplicates is less than 20% if sample concentration is 5x higher than the PQL. % RPD for POC samples and duplicates is less than 40% if sample concentration is 5x higher than the PQL.

18.5.2 MS recovery should be within 60-140% for POC, DTOC and TOC.

18.5.3 All samples should have area counts lower than the mean area count of the highest calibration standard.

Table 2.0 Quality Control Procedures for TOC and DTOC

QC Element	Frequency	Acceptance Criteria
Duplicate Sample (DUP)	One per batch or SDG	RPD < 20% for TOC/DTOC and 40% for POC when sample concentrations >5X CRDL.
Matrix Spike (MS)	One per batch or SDG	± 40% from expected value
Sample Result		Within Calibration range

***** An exception to this rule is granted in situations where the sample concentration exceeds the spike concentration by a factor of 4. In such an event to data shall be reported unflagged.

19.0 CORRECTIVE ACTIONS FOR OUT-OF-CONTROL DATA

19.1 Calibration must meet all requirements in Section 18.0. (Refer to Table 3.0 for Calibration Procedures and Corrective Actions for TOC/DTOC)

19.1.1 For POC if it does not meet the requirements the analyst can re-analyze a standard that is believed to be off the curve once and remake the solution and re-analyze as well. If requirements are still not met begin troubleshooting for mechanical issues. Start with air flow check and catalyst performance.

19.1.2 For DTOC/TOC the calibration must be completely re-analyzed if the curve is not compliant. Solutions can be remade prior to starting a new calibration curve. If it still does not meet requirements be sure the syringe is not leaking and that the sample is being correctly injected into the catalyst tube.

19.1.3 CCV does not fall within accepted range.

19.1.3.1 For POC: If the CCV does not pass, the boat should be burned in the furnace for 5 minutes and then cooled. Retry the CCV and if it still does not pass and there are no pipette issues (tip not on tightly, air bubble when solution sucked into tip) new solution should be obtained and run. If it still does not pass then air flow should be checked. If the recovery is too high then there is too little flow or a catalyst issue; and if the recovery is too low consistently then it may be a catalyst issue. Refer to Table 3.0 for further instructions.

19.1.3.2 For DTOC/TOC: If the CCV does not pass check that the volume of the solution to be sure that it has changed with fresh one, check the oxygen flow, and then rerun the sample once. If it still does not pass then a new calibration curve should be completed. If the samples were run over night and the CCV did not pass all samples will have to be re-run.

19.1.4 CCB does not meet requirements

19.1.4.1 For POC: If CCB does not pass the boat should be burned in the furnace for 5 minutes and then cooled. Retry the CCB and if it still does not pass then air flow should be checked as well as catalyst performance.

19.1.4.2 For DTOC/TOC: If CCB does not pass the vial should be filled with fresh water and the rinse bottle should be checked to be sure it is filled. The CCB should then be reanalyzed once. If it still does not pass the calibration curve should be rerun if no other major instrument issues are apparent. All the associated samples need to be reanalyzed.

19.2 Table 3 for QC Procedures and Corrective Actions for TOC/DTOC:

19.2.1 %RPD is over the limit:

19.2.1.1 For POC: If the %RPD is over the limit check that the sample is at least 5X greater than the PQL. If it is greater than 5X the PQL, reprepare a sample and duplicate and reanalyze. If it is less than 5X the PQL, write a narrative stating this and continue with your run.

19.2.1.2 For DTOC/TOC: If the %RPD is over the limit, the samples should be reanalyzed once if the samples have a concentration greater than the lowest standard. If they still do not meet the limit, they should be reprepared and reanalyzed.

19.2.2 MS Recovery is outside of the limits

19.2.2.1 For POC: If the MS does not pass then check that the amount being spiked with is at least 25% of the total carbon in the sample. If it is greater than 25% then re-prepare an MS sample and rerun, if it fails again then write up a case

narrative explaining this. If it is less than 25% then write up a case narrative explaining this and continue on with the run.

19.2.2.2 For DTOC/TOC: If the MS does not pass then check that the amount being spiked with is at least 25% of the total carbon in the sample. If it is greater than 25% then re-prepare an MS sample and rerun, if it fails again then write up a case narrative explaining this. If it is less than 25% then write up a case narrative explaining this and continue on with the run.

19.2.3 For POC, if the PB is not lower than the first standard it should be reprepared using fresh acid, fresh reagent water and reanalyzed.

19.2.4 If a sample is found to be over the range of the calibration area count then the sample should be re-prepared with a dilution (for DTOC/TOC) or a smaller volume (for POC), which would proportionally bring it into the range of the curve.

Table 3.0 Quality Control Procedures for TOC and DTOC

QC Element	Acceptance Criteria	Corrective Action
Method Blank (PB)	PB Area < lowest standard area	1. If lowest sample concentration is more than 10X the blank conc., no action. 2. If samples are non-detected, no action. 3. If detected sample concentrations are less than 10X blank conc., all associated samples must be prepared again with another method blank and reanalyzed.
Duplicate Sample (DUP)	RPD < 20% for TOC/DTOC and 40 % for POC samples >5X PQL.	Flag associated data.
Matrix Spike (MS)	± 40% from expected value*	Flag associated data.
Sample Result	Within Calibration range	Dilute sample and re-analysis

*****An exception to this rule is granted in situations where the sample concentration exceeds the spike concentration by a factor of 4. In such an event, data shall be reported unflagged.

20.0 CONTINGENCIES FOR HANDLING OUT OF CONTROL OR UNACCEPTABLE DATA

20.1 If the acceptance criteria for QC measures has been exceeded or is under the limits and the data is to be reported, the following procedures must be implemented.

20.1.1 The Quality Assurance officer must be notified.

20.1.2 The data must be flagged with the appropriate qualifiers and a case narrative must be written.

20.1.3 The client must be notified about the data.

21.0 WASTE MANAGEMENT

21.1 All applicable federal and state rules and regulations governing hazardous waste will be followed when the disposal of laboratory waste is generated during the execution of this method.

21.2 Please refer to standard operating procedure NE054 regarding how hazardous waste is handled and disposed of by the laboratory.

22.0 REFERENCES

22.1 Standard Methods 19th Edition "For the Examination of Water and Wastewater", Method 5310B Combustion-Infrared Method, 1995.

22.2 "Determination of Total Organic Carbon in Sediment," Lloyd Kahn, U.S.E.P.A. Region II, Edison, NJ 1988.

22.3 "DC-190 High-Temperature TOC Analyzer Operation Manual," Rosemont, Inc. 1990, 1991 Rev. C.

22.4 "TOC-V CPH/CPN & TOC-Control Software User Manual," Shimadzu Corporation 2004.

23.0 ATTACHMENTS

23.1 DTOC/TOC MDL

23.2 TOC/POC MDL for TOC-V

23.3 TOC/POC MDL for DC-190

23.4 DTOC Logbook Example

23.5 POC Logbook Example

Attachment 23.1
DTOC/TOC MDL

Northeast Analytical Inc.

Date: 3/26/09

Quality Assurance/Quality Control

Method Detection Limit Study

Analysis	Total Organic Carbon in Water	Spike Concentrat	0.5 ppm Organic Carbon Standard
Method	SM 5310B	TOC standard	032509B7P25C
Instrument	Shimadzu TOC-Vsch/ ASI-V	LIMS Batch	180
		LRF	9030140

Analyte	AM02933	AM02934	AM02935	AM02936	AM02937	AM02938	AM02939	AM02940	Ave. Conc.	Theo. Conc.	Ave. Rec	Std. Dev.	RSD	MDL	Valid
	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	%	ppm	%	ppm	?
TOC	0.676	0.728	0.703	0.689	0.684	0.680	0.733	0.671	0.696	0.500	139%	0.024	0.034	0.071	Y

Preparation Chemist: _____ Date: 3/26/09

Analyst: _____ Date: 3/26/09

QA/QC Officer: _____ Date: 3/26/09

Laboratory Director: _____ Date: 3/26/09

PQL=5xmdl

Method Detection Limit (MDL) calculations as based on procedures outlined in 40 CFR, part 136 App B; 1-July-85.

Attachment 23.2
TOC/POC MDL for TOC-V

Northeast Analytical, Inc.

Method Detection Limits

File Name: S:\QA\MDL\2008\Inorganics\TOC\[091608MDL_TOC_TOCV.XLS]A

Date: 16-Sep-08

Compound:	Total Organic Carbon		Analysis:	EPA Lloyd Kahn
Matrix:	Soil/Solid		Instrument:	TOC-V
Spike conc:	100	mg/kg	Method:	Boat Injection/IR

LIMS Batch 359

NEA Sample ID	Preparation Date	File Name	Analysis Date	Measured Concentration mg/kg	Percent Recovery (%)
AL09418	09/16/08	Run #1	09/16/08	171	171%
AL09419	09/16/08	Run #2	09/16/08	107	107%
AL09420	09/16/08	Run #3	09/16/08	161	161%
AL09421	09/16/08	Run #4	09/16/08	121	121%
AL09422	09/16/08	Run #5	09/16/08	154	154%
AL09423	09/16/08	Run #6	09/16/08	100	100%
AL09424	09/16/08	Run #7	09/16/08	132	132%
AL09425	09/16/08	Run #8	09/16/08	131	131%

Number (n):	8	
AVG:	134.7	mg/kg
STDEV (s):	25.4	mg/kg
%RSD:	18.8%	
MDL:	76.0	mg/kg
VALID ?:	Y	

One sided Student's t values (t) at the 99% confidence level.

Number (n)	(t) value
7	3.143
8	2.998

Sample Preparation Chemist: ______________ Date: 09/16/08

Instrument Analyst: ______________ Date: 09/16/08

QA/QC Officer: ______________ Date: 09/16/08

Attachment 23.3
TOC/POC MDL for DC-190

Northeast Analytical, Inc.

Method Detection Limits

File Name: S:\QA\MDL\2008\Inorganics\TOC\[061108MDL_TOC_DC190.XLS]A
Date: 11-Jun-08

Compound:	Total Organic Carbon	Analysis:	EPA Lloyd Kahn
Matrix:	Soil/Solid	Instrument:	DC 190
Spike conc:	72.0 mg/kg	Method:	Boat Injection/IR
		LIMS Batch	352

	NEA Sample ID	Preparation Date	File Name	Analysis Date	Measured Concentration mg/kg	Percent Recovery (%)
1	AL09418	06/10/08	Run #1	06/11/08	92.9	129%
2	AL09419	06/10/08	Run #2	06/11/08	83.3	116%
3	AL09420	06/10/08	Run #3	06/11/08	87.6	122%
4	AL09421	06/10/08	Run #4	06/11/08	74.8	104%
5	AL09422	06/10/08	Run #5	06/11/08	66.2	91.9%
6	AL09423	06/10/08	Run #6	06/11/08	70.5	97.9%
7	AL09424	06/10/08	Run #7	06/11/08	64.0	88.9%
8	AL09425	06/10/08	Run #8	06/11/08	76.7	107%

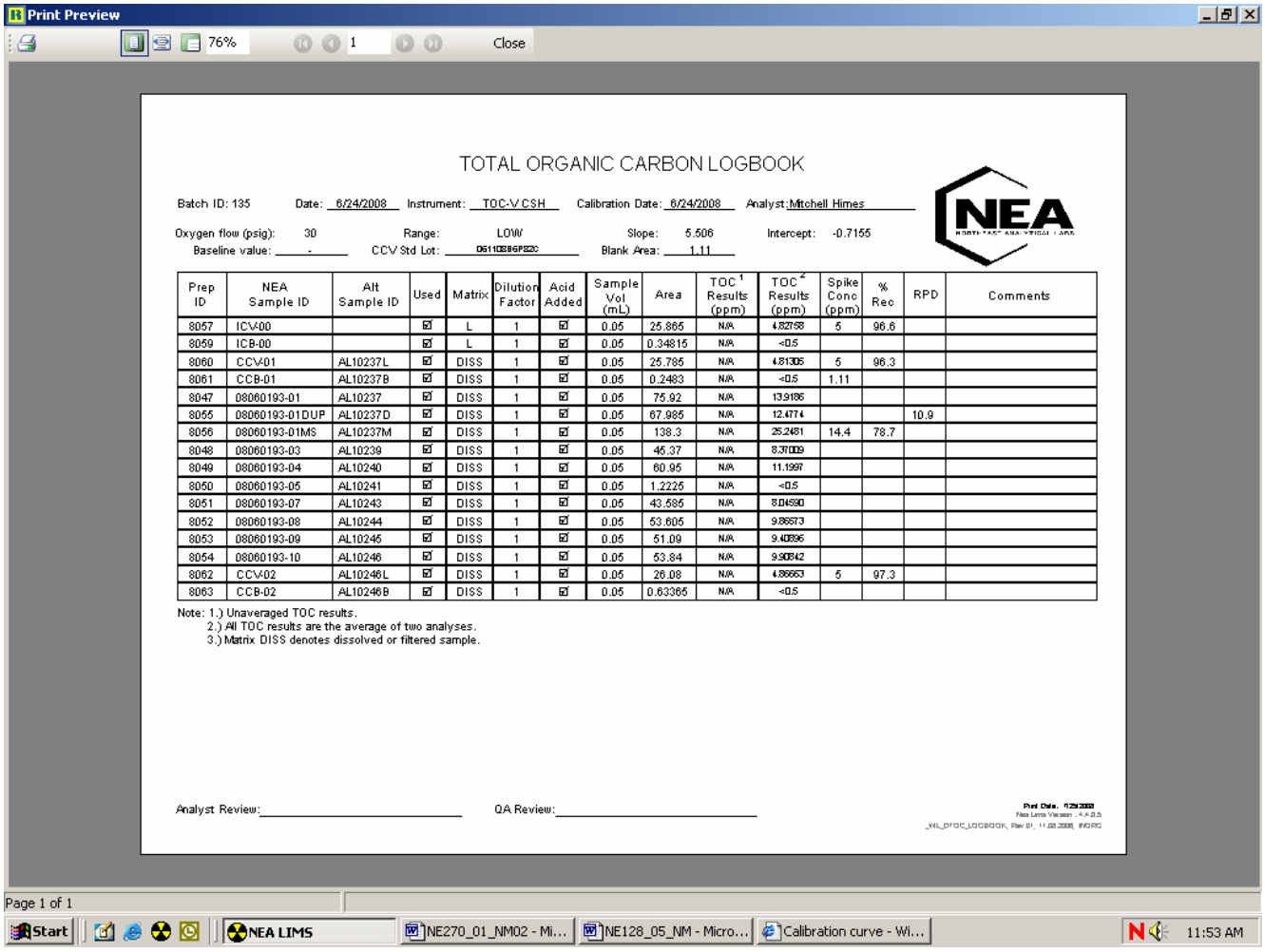
		Number (n):	8
One sided Student's t values (t)		AVG:	77.0 mg/kg
at the 99% confidence level.		STDEV (s):	10.3 mg/kg
Number (n)	(t) value	%RSD:	13.3%
7	3.143	MDL:	30.8 mg/kg
8	2.998	VALID ?:	Y

Sample Preparation Chemist: _____ Date: 06/10/08

Instrument Analyst: _____ Date: 06/11/08

QA/QC Officer: Christine L. Brinkman Date: 06/11/08

Attachment 23.4
DTOC Logbook Example

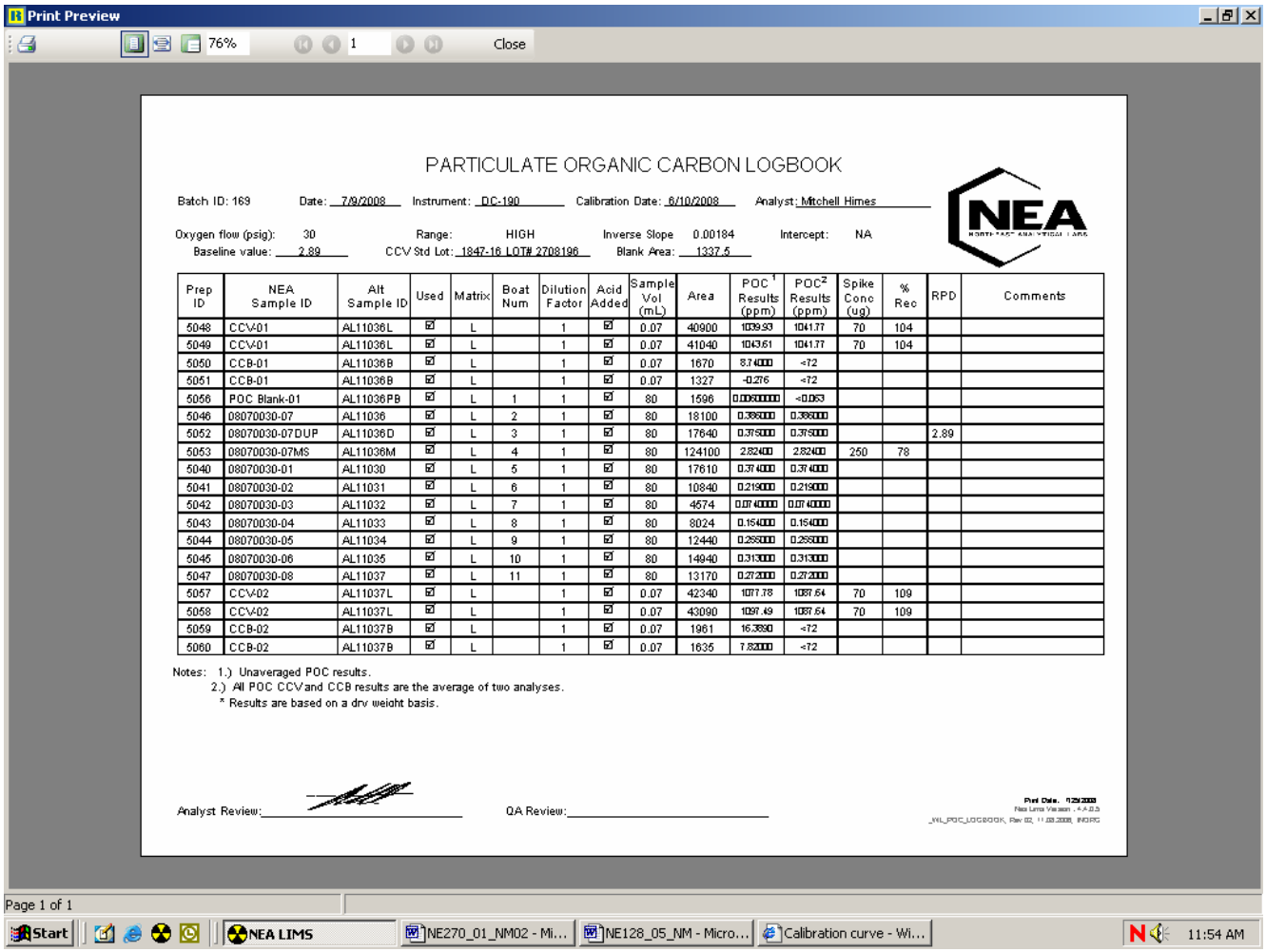


Prep ID	NEA Sample ID	Alt Sample ID	Used	Matrix	Dilution Factor	Acid Added	Sample Vol (mL)	Area	TOC [1] Results (ppm)	TOC [2] Results (ppm)	Spike Conc (ppm)	% Rec	RPD	Comments
8057	ICV-00		☑	L	1	☑	0.05	25.865	N/A	4.82758	5	96.6		
8059	ICB-00		☑	L	1	☑	0.05	0.34815	N/A	<0.5				
8060	CCV-01	AL10237L	☑	DISS	1	☑	0.05	25.785	N/A	4.81305	5	96.3		
8061	CCB-01	AL10237B	☑	DISS	1	☑	0.05	0.2483	N/A	<0.5	1.11			
8047	08060193-01	AL10237	☑	DISS	1	☑	0.05	75.92	N/A	13.9186				
8055	08060193-01DUP	AL10237D	☑	DISS	1	☑	0.05	67.985	N/A	12.4774			10.9	
8056	08060193-01MS	AL10237M	☑	DISS	1	☑	0.05	138.3	N/A	25.2481	14.4	78.7		
8048	08060193-03	AL10239	☑	DISS	1	☑	0.05	45.37	N/A	8.37009				
8049	08060193-04	AL10240	☑	DISS	1	☑	0.05	60.95	N/A	11.1997				
8050	08060193-05	AL10241	☑	DISS	1	☑	0.05	1.2225	N/A	<0.5				
8051	08060193-07	AL10243	☑	DISS	1	☑	0.05	43.585	N/A	8.04590				
8052	08060193-08	AL10244	☑	DISS	1	☑	0.05	53.605	N/A	9.86573				
8053	08060193-09	AL10245	☑	DISS	1	☑	0.05	51.09	N/A	9.40896				
8054	08060193-10	AL10246	☑	DISS	1	☑	0.05	53.84	N/A	9.90842				
8062	CCV-02	AL10246L	☑	DISS	1	☑	0.05	26.08	N/A	4.86663	5	97.3		
8063	CCB-02	AL10246B	☑	DISS	1	☑	0.05	0.63365	N/A	<0.5				

Note: 1.) Unaveraged TOC results.
2.) All TOC results are the average of two analyses.
3.) Matrix DISS denotes dissolved or filtered sample.

Analyst Review:_____ QA Review:_____

Attachment 23.5
POC Logbook Example



STANDARD OPERATING PROCEDURE REVIEW

SOP Name	Review Number	Reviewers	Title	QAO Approval	Effective Date
NE128_0506	00	Marsha Qian Christina L. Braidwood Robert E. Wagner	Inorganics Supervisor QAO Lab Director	Christina Braidwood	02/1903/31/09

APPENDIX 32
SOP FOR THE ACID DIGESTION OF AQUEOUS SAMPLES BY SW846 METHODS 3005A, 3010A, AND MCAWW METHOD 200.7 AND 200.8 (PT_IP_003_R7.1)(TEST AMERICA–PITTSBURGH)

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

Title: ACID DIGESTION OF AQUEOUS SAMPLES

Method(s): SW846 Methods 3005A and 3010A and EPA Methods 200.7 and 200.8

Approvals (Signature/Date):

10/12/07	10/15/07
William Reinheimer Date	Steve Jackson Date
Technical Manager	Health & Safety Manager / Coordinator
10/12/07	10/12/07
Nasreen DeRubeis Date	Larry Matko Date
Quality Assurance Manager	Laboratory Director

This SOP was previously identified as SOP No. PITT-IP-0003, Rev. 7.

1. SCOPE AND APPLICATION

1.1. This procedure describes the preparation of aqueous samples for the analysis of certain metals by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP) and ICPMS using the MCAWW Method 200.7 (NPDES), EPA Method 200.8 and SW846 Methods 3005A and 3010A (RCRA).

1.2. The applicability of each of these preparation protocols to specific analytes is detailed in Tables I and II (Appendix A). Additional elements may be analyzed following digestion by these protocols provided that the method performance criteria specified in Section 13.0 of this SOP are met.

1.3. This SOP provides procedures applicable to the preparation of dissolved, total recoverable and total elements in surface water, ground water, aqueous samples, leachates/extracts.

1.4. SW-846 Method 3005A is used to prepare surface and groundwater samples for total recoverable and dissolved metals determination by ICP or ICPMS.

1.5. ICP Method 200.7 and ICPMS Method 200.8 are used to prepare surface water, domestic and industrial waste samples for total recoverable and dissolved metals.

1.6. SW-846 Method 3010A is used to prepare aqueous samples, EP and mobility-procedure extracts, and wastes that contain suspended solids for total metals analysis by ICP or ICPMS.

1.7. All matrices require digestion prior to analysis with the exception of analyses for dissolved metals in filtered and acidified aqueous samples. Although digestion is not specifically required by the method, some clients and regulators do require digestion of dissolved samples and this must be clarified before project initiation.

2. SUMMARY OF METHOD

2.1. Method 3005A/ Method 6010B ICP or 6020 ICPMS - Preparation for Total Recoverable or Dissolved Metals Analysis.

2.1.1. A representative aliquot of sample is heated with nitric and hydrochloric acids (concentrations and volumes differ between methods) and substantially reduced in volume. The digestate is filtered (if necessary) and diluted to volume.

2.2. Method 3010A - Preparation for Total Metals Analysis by Method 6010B ICP or 6020 ICPMS.

2.2.1. A representative aliquot of sample is refluxed with nitric acid. This step is repeated until the digestate is light in color or until its color has stabilized. After the digestate has been reduced to a low volume, it is refluxed with hydrochloric acid, filtered (if necessary) and brought up to volume.

2.3. Methods 200.7 and 200.8 have method specific preparations.

2.4. Digestion Procedures

2.4.1. The laboratory performs all the digestion procedures listed in the SOP, depending on the project requirements.

2.5. Refer to PITT-QA-0024 for subsampling procedures.

3. DEFINITIONS

3.1. Dissolved Metals: Those elements that pass through a 0.45 um membrane. (Sample is acidified after filtration).

3.2. Suspended Metals: Those elements which are retained by a 0.45 um membrane.

3.3. Total Metals: The concentration determined on an unfiltered sample following digestion.

3.4. Total Recoverable Metals: The concentration determined on an unfiltered sample following treatment with hot, dilute mineral acid.

3.5. Additional definitions of terms used in this SOP may be found in the glossary of the LQM.

4. INTERFERENCES

4.1. There are numerous routes by which samples may become contaminated. Potential sources of trace metals contamination include: metallic or metal-containing labware (e.g., talc gloves which contain high levels of zinc), containers, impure reagents, dirty glassware, improper sample transfers, dirty work areas, atmospheric inputs such as dirt and dust, etc. Be aware of potential sources of contamination and take appropriate measures to minimize or avoid them.

4.2. The entire work area, including the bench top and fume hood, should be thoroughly cleaned on a routine schedule in order to minimize the potential for environmental contamination. Refer to Appendix C for additional contamination control guidelines.

4.3. Boron and silica from the glassware will migrate into the sample solution during and following sample processing. For critical low-level determinations of boron and silica, only quartz and/or plastic labware should be used.

4.4. Physical interference effects may contribute to inaccuracies in the determinations of trace elements. Oils, solvents and other matrices may not be digested using these methods if they are not soluble with acids. If physical interferences are present, they should be documented.

4.5. Visual interferences or anomalies (such as foaming, emulsions, precipitates, etc.) must be documented.

4.6. Allowing samples to boil or go dry during digestion may result in the loss of volatile metals. If this occurs the sample must be reprepared. Antimony is easily lost by volatilization from hydrochloric acid media.

4.7. Precipitation of silver chloride (AgCl) may occur when chloride ions and high concentrations of silver (i.e., greater than 1 mg/L) are present in the sample.

4.8. Specific analytical interferences are discussed in each of the determinative methods.

5. SAFETY

5.1. Employees must abide by the policies and procedures in the Corporate Safety Manual, Radiation Safety Manual and this document.

5.2. Samples that contain high concentrations of carbonates or organic material or samples that are at elevated pH can react violently when acids are added.

5.3. The acidification of samples containing reactive materials may result in the release of toxic gases, such as cyanides or sulfides. Acidification of samples should be done in a fume hood. The analyst should also be aware of the potential for a vigorous reaction.

5.4. The following is a list of the materials used in this method, which have a serious or significant hazard rating. NOTE: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table. A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Hydrochloric Acid	Corrosive Poison	5 ppm-Ceiling	Inhalation of vapors can cause coughing, choking, inflammation of the nose, throat, and upper respiratory tract, and in severe cases, pulmonary edema, circulatory failure, and death. Can cause redness, pain, and severe skin burns. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
Nitric Acid	Corrosive Oxidizer Poison	2 ppm-TWA 4 ppm-STEL	Nitric acid is extremely hazardous; it is corrosive, reactive, an oxidizer, and a poison. Inhalation of vapors can cause breathing difficulties and lead to pneumonia and pulmonary edema, which may be fatal. Other symptoms may include coughing, choking, and irritation of the nose, throat, and respiratory tract. Can cause redness, pain, and severe skin burns. Concentrated solutions cause deep ulcers and stain skin a yellow or yellow-brown color. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

5.5. Eye protection that protects against splash, laboratory coat, and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled. Cut resistant gloves must be worn doing any other task that presents a strong possibility of getting cut. Disposable gloves that have become contaminated will be removed and discarded; other gloves will be cleaned immediately.

5.6. The preparation of standards and reagents will be conducted in a fume hood with the sash closed as far as the operation will permit or under other means of mechanical ventilation.

5.7. All work must be stopped in the event of a known or potential compromise to the health and safety of a TestAmerica associate. The situation must be reported **immediately** to a laboratory supervisor and the EHSC.

6. EQUIPMENT AND SUPPLIES

6.1. Hot plate, hot block, or other adjustable heating source capable of maintaining a temperature of 90 - 95°C.

6.2. Thermometer that covers a temperature range of 0-150°C.

6.3. Hot Block Disposable Digestion Cups (from Environmental Express).

6.4. Watch glasses, plastic disposable.

6.5. Whatman No. 41 filter paper or equivalent.

6.6. Funnels or equivalent filtration apparatus.

6.7. Centrifugation equipment (if desired method of removing particulates is centrifugation).

6.8. Graduated cylinder or equivalent capable of measuring 50 mL within 3% accuracy.

6.9. Analytical balance capable of accurately weighing to the nearest 0.01 grams.

6.10. Repipetors or suitable reagent dispensers.

6.11. Calibrated automatic pipettes with corresponding pipet tips or Class A glass volumetric pipettes.

6.12. Class A volumetric flasks.

6.13. pH indicator strips (pH range 0 - 6).

6.14. Plastic digestate storage bottles.

7. REAGENTS AND STANDARDS

7.1. Reagent water must be produced by a Millipore DI system or equivalent. Reagent water must be free of the analytes of interest as demonstrated through the analysis of method blanks as defined in the determinative SOPs.

7.2. Laboratory Control Sample (LCS) and matrix spike (MS) solutions are purchased as custom TestAmerica solutions. All standards must be stored in FEP fluorocarbon or previously unused polyethylene or polypropylene bottles. Stock standard solutions must be replaced prior to the expiration date provided by the manufacturer. If no expiration date is provided, the stock solutions may be used for up to one year and must be replaced sooner if verification from an independent source indicates a problem.

7.3. Working ICP/ICPMS LCS/MS spike solution: The LCS/MS working spike solution is provided directly by the vendor, no further standard preparation is necessary.

7.4. The TCLP MS working spike solution is provided directly by the vendor, no further standard preparation is necessary.

7.5. The LCS and MS samples must contain all the elements designated for analysis in each batch of samples. If a non-routine element is required that is not contained in the custom TestAmerica solution, a solution must be purchased from the designated vendor that will cover the additional analyte(s) of interest and provide for a final spike concentration that is appropriate to the determinative method.

7.6. Aqueous laboratory control samples (LCSW) and matrix spike samples are prepared as described in Sections 9.5 and 9.6. Refer to Tables III and IV (Appendix A) for details regarding the stock, working standard and final digestate spike concentrations for ICP/ICPMS LCS and matrix spike preparations.

7.7. Nitric acid (HNO_3), concentrated, trace metal grade or better.

7.8. Nitric acid, 1:1 - dilute concentrated HNO_3 with an equal volume of reagent water.

Note: When preparing diluted acids always add acid to water. If the water is added to the acid a violent reaction may occur.

7.9. Hydrochloric acid (HCl), concentrated, trace metal grade or better.

7.10. Hydrochloric acid, 1:1 - dilute concentrated HCl with an equal volume of reagent water.

Note: When preparing diluted acids always add acid to water. If the water is added to the acid a violent reaction may occur.

8. SAMPLE COLLECTION, PRESERVATION, SHIPMENT AND STORAGE

8.1. Sample holding time for metals included under the scope of this SOP is 180 days from the date of collection to the date of analysis.

8.2. Aqueous samples are preserved with nitric acid to a pH of <2 and may be stored in either plastic or glass. If boron or silica is to be determined, plastic containers are preferred. Refrigeration is not required. Preservation must be verified prior to analysis.

8.3. For dissolved metals analysis, the samples should be filtered through a 0.45 um filter prior to preservation. Filtration must be done in the field or within 24 hours of collection.

Note: If a sample being analyzed for dissolved metals is found to contain sediment the analyst should contact their supervisor or group leader. The client should be notified of the problem to decide how to treat the sample.

9. QUALITY CONTROL

Table V (Appendix A) provides a summary of quality control requirements including type, frequency, acceptance criteria and corrective action.

9.1. Initial Demonstration of Capability

Prior to analysis of any analyte using any method contained within this SOP the following requirements must be met:

9.1.1. Method Detection Limit (MDL) - An MDL must be determined for each analyte/matrix prior to the analysis of any samples. The MDL is determined using seven replicates of reagent water, spiked with all the analytes of interest, which have been carried through the entire analytical procedure. MDLs must be redetermined on an annual basis in accordance with 40 CFR Part 136 Appendix B requirements as detailed in PITT-QA-007. The spike level should be between the calculated MDL and 10X the MDL to be valid. The result of the MDL determination must be below the TestAmerica reporting limit.

9.1.2. Initial Demonstration Study - This requires the analysis of four QC check samples. The QC check sample is a well-characterized laboratory generated sample used to monitor method performance, which should contain all the analytes of interest. The results of the initial demonstration study must be acceptable before analysis of samples may begin. The results of the initial demonstration study may be used to extend a method for the analysis of other elements provided all acceptance criteria are met.

9.1.2.1. Four aliquots of the check sample (LCS) are prepared and analyzed using the procedures detailed in this SOP and the determinative SOPs.

9.1.2.2. Calculations and acceptance criteria for QC check samples are given in the determinative SOPs (PITT-MT-0001 and PITT-MT-0020).

9.2. Preparation Batch - A group of up to 20 samples that is of the same matrix and is processed together using the same procedures and reagents. The preparation batch must contain a method blank, a LCS and a matrix spike/matrix spike duplicate (SW-846 Methods) or a matrix spike for every 10 or fewer sample (200.7). In some cases, at client request, it may be appropriate to process a matrix spike and sample duplicate in place of the MS/MSD. If clients specify specific samples for MS/MSD, the batch may contain multiple MS/MSD pairs.

9.3. Sample Count - Laboratory generated QC samples (method blanks, LCS, MS, MSD) are not included in the sample count for determining the size of a preparation batch.

9.4. Method Blank (MB) - One method blank must be processed with each preparation batch. The method blank consists of reagent water containing all reagents specific to the

method that is carried through the entire analytical procedure, including preparation and analysis. The method blank is used to identify any system and process interferences or contamination of the analytical system that may lead to the reporting of elevated analyte concentrations or false positive data. Criteria for the acceptance of blanks are contained within the individual analytical method SOP's. If the method blank does not meet the criteria contained within the analytical method SOPs, the blank and all associated samples in the batch must be redigested.

9.4.1. Aqueous method blanks are prepared by taking 50 mL or 50 g of reagent water through the appropriate procedure as described in Section 10.

9.4.2. TCLP method blanks are prepared by taking 50 mL or 50 g of leachate fluid through the appropriate procedure as described in Section 10.

9.5. Laboratory Control Sample (LCS) - One aqueous LCS (referred to as a Laboratory Fortified Blank in 200.7) must be processed with each preparation batch. The LCS must contain all analytes of interest and must be carried through the entire analytical procedure. The LCS is used to monitor the accuracy of the analytical process. On-going monitoring of the LCS results provides evidence that the laboratory is performing the method within acceptable accuracy and precision guidelines. Criteria for the acceptance of LCS results are contained within the individual analytical method SOP's. Corrective action when LCS results fail to meet control limits will be repreparation and reanalysis of the batch. Refer to Section 7.3 for instructions on preparation of the aqueous LCS spike solution.

9.5.1. The aqueous LCS is prepared by spiking a 50 mL aliquot of reagent water with 0.5 mL of the working LCS/MS spike solution (7.3). The LCS is then processed through the appropriate procedure as described in Section 10.

9.6. Matrix Spike/Matrix Spike Duplicate (MS/MSD) - One MS/MSD pair must be processed for each preparation batch of up to 20 samples (SW-846 Methods) or one matrix spike is processed for every 10 or fewer samples (200.7). A matrix spike (MS) is a field sample to which known concentrations of target analytes have been added (referred to as a Laboratory Fortified Matrix in 200.7). A matrix spike duplicate (MSD) is a second aliquot of the same sample (spiked identically as the MS) prepared and analyzed along with the sample and matrix spike. Some client specific data quality objectives (DQO's) may require the use of sample duplicates in place of or in addition to MS/MSD's. The MS/MSD results are used to determine the effect of a matrix on the precision and accuracy of the analytical process. Samples identified as field blanks cannot be used for MS/MSD analysis. If any analyte recovery or RPD falls outside the acceptance range, the recovery of that analyte must be in control for the LCS. If the recovery of the LCS is outside limits, corrective action must be taken. Corrective action will include repreparation and reanalysis of the batch. Corrective action when MS results fail to meet control limits does not include repreparation of samples unless the results indicate that a spiking error may have occurred.

9.6.1. The aqueous matrix spike sample is prepared by spiking a 50 mL aliquot of a sample with 0.5 mL of the working LCS/MS spike solution (7.3). The matrix spike sample is then processed as described in Section 10.

9.6.2. The TCLP matrix spike sample is prepared by spiking a 50 mL aliquot of a leachate with 0.5 mL of the working TCLP spike solution (7.4). The matrix spike sample is then processed as described in Section 10.

NOTE: The TCLP matrix spike must be added prior to preservation of the leachate.

9.6.3. If insufficient sample is available to process a MS/MSD, then a second LCS must be processed. The LCS pair is then evaluated according to the MS/MSD criteria.

9.7. Quality Assurance Summaries - Certain clients may require specific project or program QC, which may supersede the SOP requirements. Quality Assurance Summaries (QAS) should be developed to address these requirements.

10. PROCEDURE

10.1. Hotplate/hotblock temperature must be verified daily for each hotplate/hotblock used and must be recorded on either the metals preparation log or in a hotplate/hotblock temperature logbook. The hotplate/hotblock temperature should be verified by measuring the temperature of a beaker or an equivalent digestion sample container of reagent water placed on each hotplate/hotblock.

10.2. One time procedural variations are allowed only if deemed necessary in the professional judgment of supervision to accommodate variation in sample matrix, radioactivity, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using a Nonconformance Memo and is approved by a Technical Specialist and QA Manager. If contractually required, the client shall be notified. The Nonconformance Memo shall be filed in the project file.

10.3. Any unauthorized deviations from this procedure must also be documented as a nonconformance, with a cause and corrective action described.

10.4. All preparation procedures must be carried out in a properly functioning hood.

10.5. All samples are to be checked out of sample control with the chain of custody documentation filled out completely.

10.6. Proper sample identification is extremely important in any preparation procedure. Labeling of beakers and bottles must be done in a manner to ensure connection with the proper sample.

10.7. Samples are typically logged in as either waters or wastes. Wastes such as organic liquids or sludges and tissues (animal/vegetable) are usually logged in with solid test codes. When initiating prep examine the sample to see if the sample matches the matrix designation. If the sample is logged in as aqueous but it appears more like a waste (biphasic, sludge like, organic liquid, lots of sediment etc.) contact the lab supervisor or project manager for further instructions. In some cases it may be more appropriate to process these samples as solids.

10.8. If possible prepare all the samples of a project at the same time to minimize the QC required and streamline the flow of the project through the lab and reporting group.

10.9. Guidelines are provided in the appendices on procedures to minimize contamination of samples and standards.

10.10. The following procedure must be followed for all aqueous sample preparations:

10.10.1. Measure and record sample pH with pH paper on a separate aliquot of sample. This is typically verified and documented at sample receipt.

Note: If the sample pH is > 2 pH units, the client must be notified of the anomaly.

10.10.2. Mix sample by shaking the container.

10.10.3. Measure and transfer 50 mL or 50 g of the sample into a beaker.

Note: This SOP allows for samples to be weighed instead of measured volumetrically (See Section 18.1.2).

10.10.4. Measure extra aliquots of sample(s) selected for the MS or MS/MSD analysis. Spike each aliquot with 0.5 mL of spiking solution (7.3 or 7.4).

10.10.5. Measure and transfer 50 mL of reagent water into a beaker for the method blank.

10.10.6. Measure and transfer 50 mL of reagent water into a beaker for the LCS and add 0.5 mL of spiking solution (7.3)

10.11. Proceed to the appropriate Section for the desired method as follows:

Method 3005A	10.12
Method 3010A	10.13
Method 200.7	10.14
Method 200.8	10.15

10.12. **Method 3005A - Preparation for Total Recoverable or Dissolved Metals Analysis by ICP/ICPMS (See Figure 1)**

10.12.1. To the sample beaker, add 1 mL of concentrated HNO_3 and 2.5 mL of concentrated HCl.

10.12.2. Cover with disposable watch glass.

10.12.3. Heat at 90 - 95°C until volume is reduced to between 15 and 20 mL.

NOTE: DO NOT ALLOW SAMPLE TO BOIL OR GO DRY. Doing so will result in the loss of analyte and the sample must be reprepared.

10.12.4. Cool the beaker in a fume hood.

10.12.5. Wash down beaker walls and watch glass with reagent water.

10.12.6. Filter sample, if insoluble materials are present, though a prewashed (1% nitric acid) Whatman 41 filter paper or plunger filter into a disposable sample container.

Note: If any samples in a preparation batch are filtered, the method blank and LCS associated with that batch must also be filtered.

Note: In place of filtering, the samples, after dilution and mixing, may be centrifuged or allowed to settle by gravity overnight to remove insoluble material.

10.12.7. Rinse beaker and filter paper with reagent water to ensure complete sample transfer.

10.12.8. Adjust the final volume/mass to 50 mL or 50 g with reagent water. The sample is now ready for analysis

10.13. **Method 3010A - Preparation for Total Metals Analysis by ICP/ICPMS Spectroscopy (See Figure 2)**

10.13.1. To the sample beaker, add 1.5 mL of concentrated HNO_3.

10.13.2. Cover with disposable watch glass.

10.13.3. Place beaker on hotplate or hotblock (90-95 °C) and evaporate to low volume of 5 - 10 mL while ensuring that no portion of the bottom of the beaker is allowed to go dry.

NOTE: DO NOT ALLOW SAMPLE TO BOIL OR GO DRY. Doing so will result in the loss of analyte and the sample must be reprepared.

10.13.4. Cool the beaker in a fume hood.

10.13.5. Add another 1.5 mL portion of concentrated HNO_3 and re-cover the beaker.

10.13.6. Continue refluxing until the digestion is complete.

Note: Digestion is complete when the digestate is light in color or does not change in appearance. For most samples the addition of two nitric acid aliquots is sufficient, additional aliquots of nitric acid may be added if necessary.

10.13.7. Evaporate to low volume of 5 - 10 mL while ensuring that no portion of the bottom of the beaker is allowed to go dry.

10.13.8. Cool the beaker in a fume hood.

10.13.9. Add 5 mL of 1:1 HCl.

10.13.10. Cover and reflux for an additional 15 minutes to dissolve precipitate or residue.

10.13.11. Wash down beaker walls and watch glass with reagent water.

10.13.12. Filter sample, if insoluble materials are present, though a prewashed (1% nitric acid) Whatman 41 filter paper or plunger filter into a disposable sample container.

Note: If any samples in the QC batch are filtered the method blank and LCS associated with that batch must also be filtered.

Note: In place of filtering, the samples, after dilution and mixing, may be centrifuged or allowed to settle by gravity overnight to remove insoluble material.

10.13.13. Rinse beaker and filter paper with reagent water to ensure complete sample transfer.

10.13.14. Adjust final volume/mass to 50 mL or 50 g with reagent water. The sample is now ready for analysis.

10.14. **Method 200.7 - Preparation for Total Recoverable or Dissolved Metals Analysis by ICP (See Figure 3)**

10.14.1. To the sample beaker containing 50 mL of sample, add 1 mL of 1:1 HNO_3 and 0.5 mL of 1:1 HCl.

10.14.2. Heat at 80-85 °C until volume is reduced to between 15 and 20 mL.

NOTE: DO NOT ALLOW SAMPLE TO BOIL OR GO DRY. Doing so will result in the loss of analyte and the sample must be reprepared.

10.14.3. Cover with disposable watch glass.

10.14.4. Gently reflux for 30 minutes.

10.14.5. Cool the beaker in the fume hood.

10.14.6. Wash down beaker walls and watch glass with reagent water.

10.14.7. Filter sample, if insoluble materials are present, though a prewashed (1% nitric acid) Whatman 41 filter paper or plunger filter into a disposable sample container.

Note: If any samples in the QC batch are filtered the method blank and LCS associated with that batch must also be filtered.

10.14.8. Rinse beaker and filter paper with reagent water to ensure complete sample transfer.

10.14.9. Adjust the final volume/mass to 50 mL or 50 g with reagent water. The sample is now ready for analysis.

10.15. **Method 200.8 - Preparation for Total Recoverable or Dissolved Metals Analysis by ICPMS (See Figure 4)**

10.15.1. To the sample beaker containing 100 mL of sample, add 2 mL of 1:1 HNO_3 and 1.0 mL of 1:1 HCl.

10.15.2. Heat at 80-85 °C until volume is reduced to between 15 and 20 mL.

NOTE: DO NOT ALLOW SAMPLE TO BOIL OR GO DRY. Doing so will result in the loss of analyte and the sample must be reprepared

10.15.3. Cover with disposable watch glass.

10.15.4. Gently reflux for 30 minutes.

10.15.5. Cool the beaker in the fume hood.

10.15.6. Wash down beaker walls and watch glass with reagent water.

10.15.7. Filter sample, if insoluble materials are present, though a prewashed (1% nitric acid) Whatman 41 filter paper or plunger filter into a disposable sample container.

Note: If any samples in the QC batch are filtered the method blank and LCS associated with that batch must also be filtered.

10.15.8. Rinse beaker and filter paper with reagent water to ensure complete sample transfer.

10.15.9. Adjust the final volume/mass to 50 mL or 50 g with reagent water.

10.15.10. Take a 25 mL aliquot of the 50 mL sample volume and dilute up to 50 mL with de-ionized water.

10.16. Documentation and Record Management

10.16.1. The preparation benchsheet should, at a minimum, include the following information:

- Preparation date, analyst name, matrix, prep type), SOP reference.
- Sample ID, initial weight/volume and final weight/volume.
- Standards Documentation (source, lot, prep date, volume added).
- Analyst Signature.
- Reviewer's Signature and date.

11. CALCULATIONS / DATA REDUCTION

11.1. Not Applicable.

12. METHOD PERFORMANCE

12.1. Method performance is determined by the analysis of matrix spike and matrix spike duplicate samples as well as method blanks and laboratory control samples. In general, the matrix spike recovery should fall within +/- 25 % (SW-846 Methods) or +/- 30% (200.7) and the matrix spike duplicates should compare within 20% RPD. Method blanks must meet the criteria specified in determinative SOPs. The laboratory control samples should recover within 20% (SW-846 Methods) or 15% (200.7) of the true value until in house control limits are established. Acceptance criteria are given in the determinative SOPs. **Refer to PITT-QA-DoD-0001 for specific DoD QC requirements.**

12.2. The initial demonstration study as detailed in Section 9.1.2 must be acceptable before the analysis of field samples under this SOP may begin. The results of the initial demonstration study may be used to extend a method for the analysis of other elements provided all acceptance criteria are met.

12.3. Training Qualification:

The group/team leader has the responsibility to ensure that this procedure is performed by an associate who has been properly trained in its use and has the required experience.

13. POLLUTION CONTROL

13.1. All waste will be disposed of in accordance with Federal, State and Local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this method and the policies in section 13 of the Corporate Safety Manual for "Waste Management and Pollution Prevention.

13.2. This method allows for the proportional reduction of sample and reagent volumes to decrease waste generation.

14. WASTE MANAGEMENT

14.1. The following waste streams are produced when this method is carried out.

14.1.1. Acidic waste containing nitric acid generated by the digestion. This waste is collected in a waste container identified as "Acid Waste", Waste #33. This waste is neutralized to a final pH between 6 and 9 and discharged down into a lab sink.

14.1.2. Contaminated disposable materials utilized for the analysis. These items are placed in trash containers which are emptied in the general trash dumpster located near the shipping/receiving dock.

15. REFERENCES

15.1. Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, 3rd Edition, Final Update I, Revision 1, July 1992. Methods 3005A and 3010A.

15.2. Determination of Metals and Trace Elements in Water and Wastes by Inductively Coupled Plasma-Atomic Emission Spectrometry, Method 200.7, Revision 4.4, May 1994.

15.3. Methods for the Determination of Metals in Environmental Samples, Supplement 1 (EPA/600/R-94/111), Method 200.8, Determination of Trace Elements in Waters by Inductively Coupled Plasma - Mass Spectrometry, Revision 5.4, 1994

15.4. PITT-MT-0001, Inductively Coupled Plasma-Atomic Emission Spectroscopy, Spectrometric Method for Trace Element Analysis of Water and Wastes, Method 6010A and Method 200.7.

15.5. PITT-MT-0020, Analysis of Metals by Inductively Coupled Plasma/Mass Spectrometry (ICPMS) for Methods 200.8, 6020 & ILM05.2.

15.6. QA-003, TestAmerica QC Program.

15.7. QA-004, Rounding and Significant Figures.

15.8. PITT-QA-007, Method Detection Limits.

15.9. PITT-QA-0024, Subsampling.

15.10. PITT-QA-DoD-0001, Implementation of the DoD QSM Version 3.

16. ATTACHMENTS

16.1. Figure 1 – Method 3005A Flowchart

16.2. Figure 2 – Method 3010A Flowchart

16.3. Figure 3 – Method 200.7 Flowchart

16.4. Figure 4 – Method 200.8 Flowchart

16.5. Appendix A – Tables

16.5.1. Table I – Approved Preparation Method Analytes – SW846

16.5.2. Table II – Approved Preparation Method Analytes – NPDES

16.5.3. Table III – ICP/ICPMS Matrix Spike and Aqueous Laboratory Control Sample Levels

16.5.4. Table IV – TCLP Reporting Limits, Regulatory Limits and Matrix Spike Levels

16.5.5. Table V – Summary of Quality Control Requirements

16.6. Appendix B – Metals Prep Benchsheet

16.7. Appendix C – Contamination Control Guidelines

17. REVISION HISTORY

17.1. Revision 7, 8/24/07

17.1.1. Changed laboratory name to TestAmerica.

17.1.2. Changed the format of the SOP to correspond to the new Corporate SOP format.

17.1.3. Added a reference for the source method for EPA Method 200.8.

17.1.4. For Method 200.7, removed the addition of 2.25 mL of HCl after the digestion.

17.1.5. For Method 200.7, revised the amount of 1:1 HCl added from 2.5 mL to 0.5 mL.

17.1.6. For Method 200.8, removed the addition of 1 mL of HCl after the digestion.

17.2. Revision 7.1, 10/11/07

17.2.1. For Method 200.7, removed the addition of 2 mL of concentrated HNO_3 after the digestion.

17.2.2. For Method 3005A, removed the addition of 1.5 mL of concentrated HNO_3 after the digestion.

18. METHOD MODIFICATIONS

18.1. Modifications applicable to SW-846 reference methods.

18.1.1. Chapter 1 of SW-846 states that the method blank should not contain any analyte of interest at or above the MDL. This SOP states that the method blank must not contain any analyte of interest at or above the reporting limit. Common lab contaminants are allowed up to two times the reporting limit in the blank following consultation with the client. **Refer to PITT-QA-DoD-0001 for specific DoD QC requirements.**

18.1.2. This SOP allows for aqueous samples to be weighed instead of measured volumetrically. This assumes the density of the sample is close to 1.0 g/mL. Samples with large amounts of sediment or suspended solids, sludges, non-aqueous liquids must be processed volumetrically. Weighing samples directly into the digestion vessel minimizes the potential for cross contamination, offers

improved accuracy over the use of graduated cylinders (comparable to volumetric flask accuracy), uses less glassware and is more efficient.

18.1.3. The referenced methods as well as Table 3-1 of SW-846 refer to the use of a 100 mL aliquot for digestion. This SOP requires the use of a 50 mL sample size to reduce waste generation. The use of reduced sample volumes are supported in EPA's document "Response to Public Comments Background Document, Promulgation of the Second Update to SW-846, Third Edition" dated November 3, 1994. This document stated "..flexibility to alter digestion volumes is addressed and "allowed" by the table (3-1) and is also inherently allowed by specific digestion methods. Table 3-1 is only to be used as guidance when collecting samples..." EMSL-Ci has also taken the stance that "reduction in sample size and appropriate corresponding reduction in sample volume is not considered a significant change in the methodology." Additionally, in written correspondence from the Office of Solid Waste, Olliver Fordham stated " As a "representative sample" can be assured, scaling causes no loss of precision and accuracy in the analysis."

18.2. Modifications Specific to Method 3010A

18.2.1. Section 10.13.7 of this SOP requires the sample be reduced to a volume of 5 - 10 mL. Section 7.2 of Method 3010A states the volume should be reduced to 3 mL but also states that no portion of the bottom of the beaker should go dry. The SOP required volume is a closer approximation of the volume required to provide an adequate covering of the beaker so as to prevent the loss of critical analytes through volatilization.

18.2.2. The scope of 3010A has been expanded to include silver based on comparison studies with 7760A. Method 3010A consistently demonstrated improved accuracy and precision over Method 7760A in the matrices tested (reagent water, surface water and TCLP leachate) up to a concentration of 1 ppm silver.

FIGURE 1. METHOD 3005A

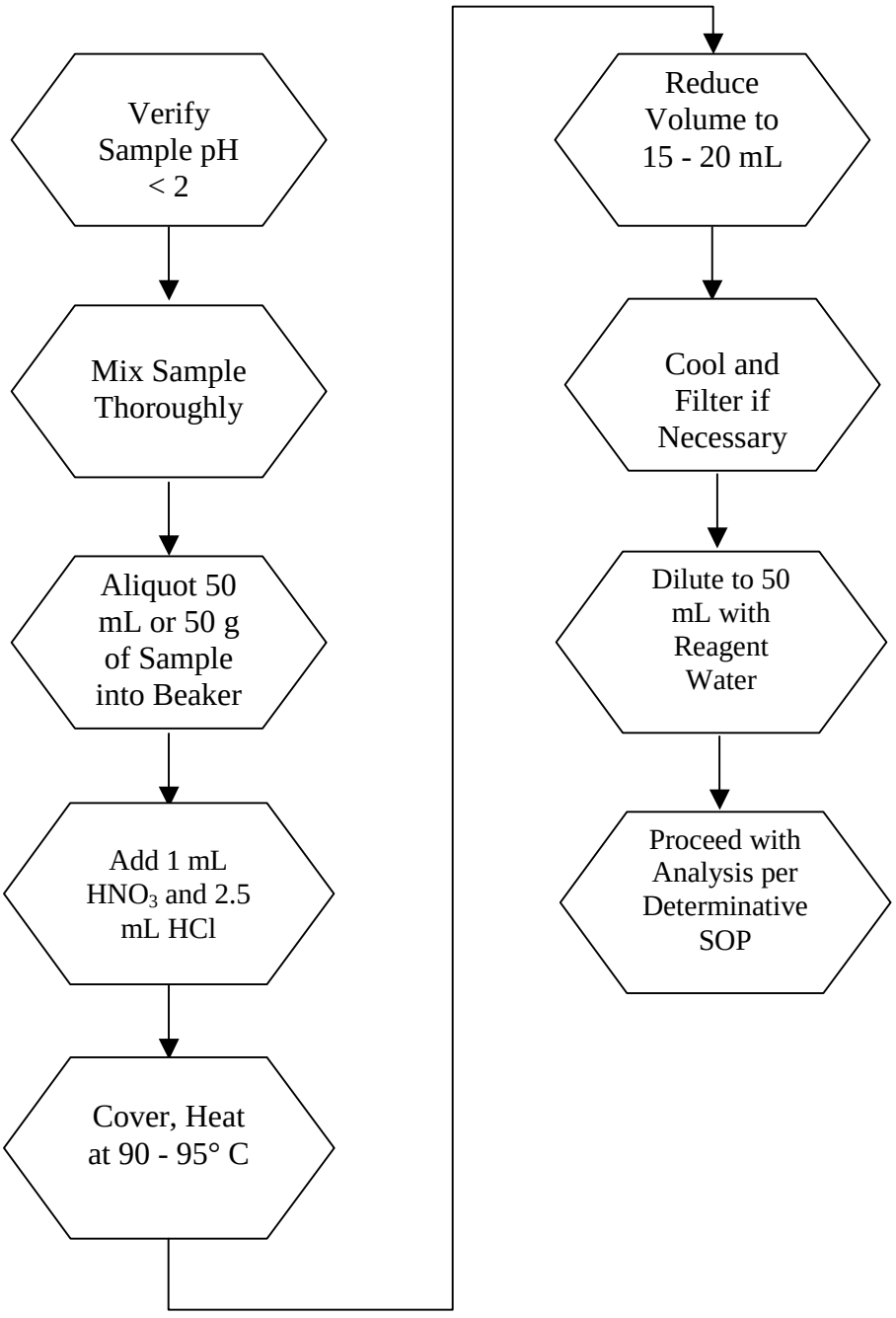


FIGURE 2. METHOD 3010A

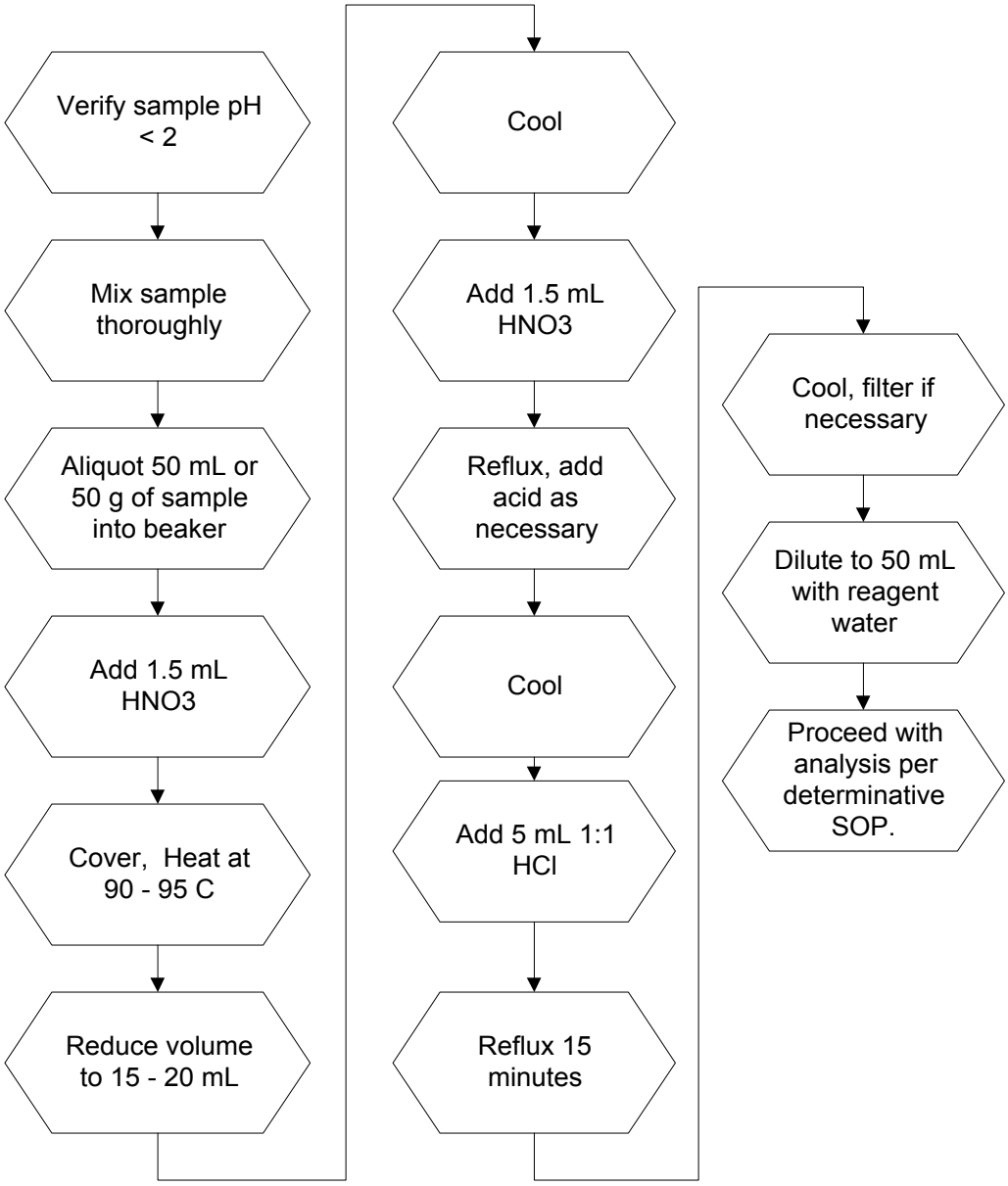


FIGURE 3. METHOD 200.7

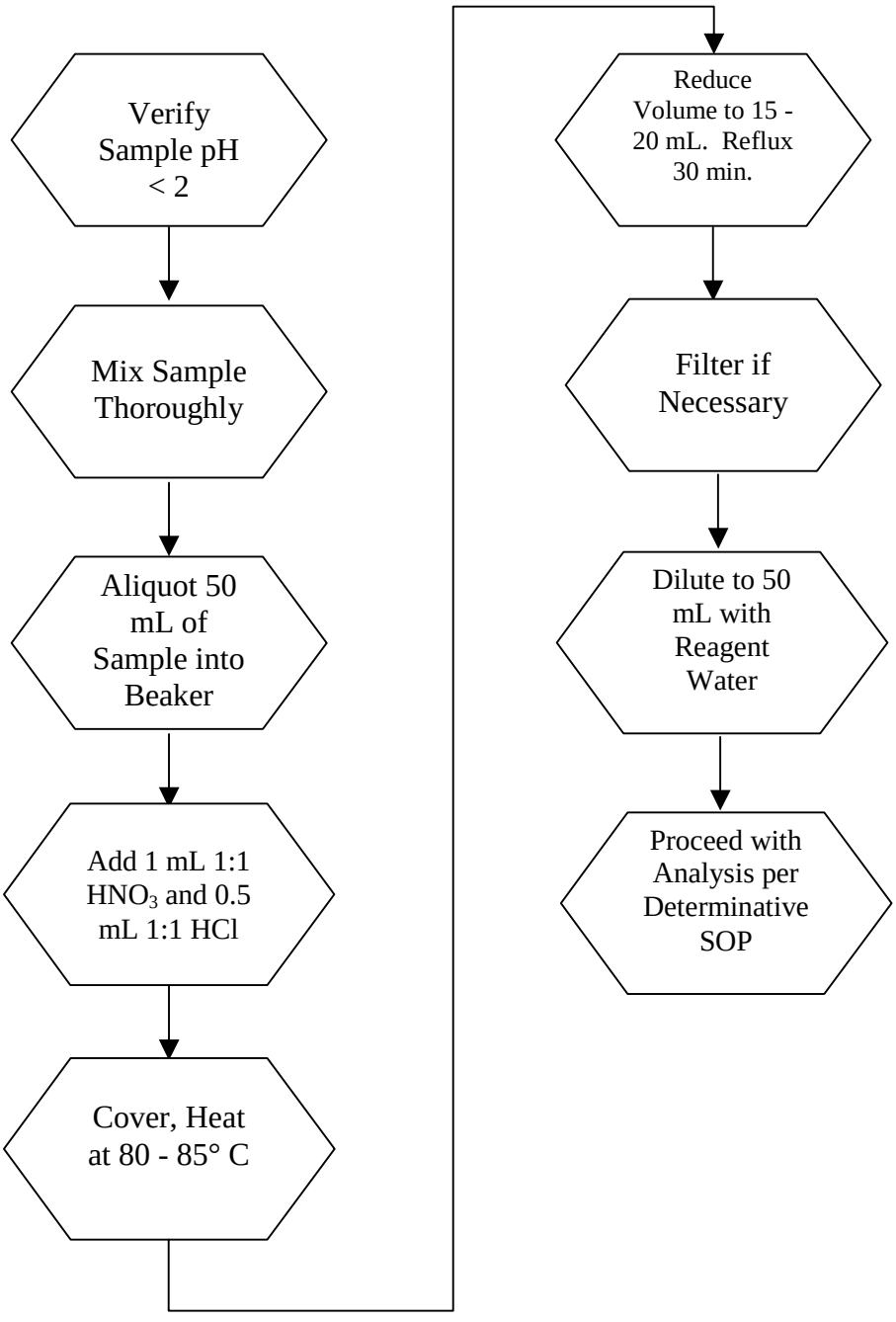
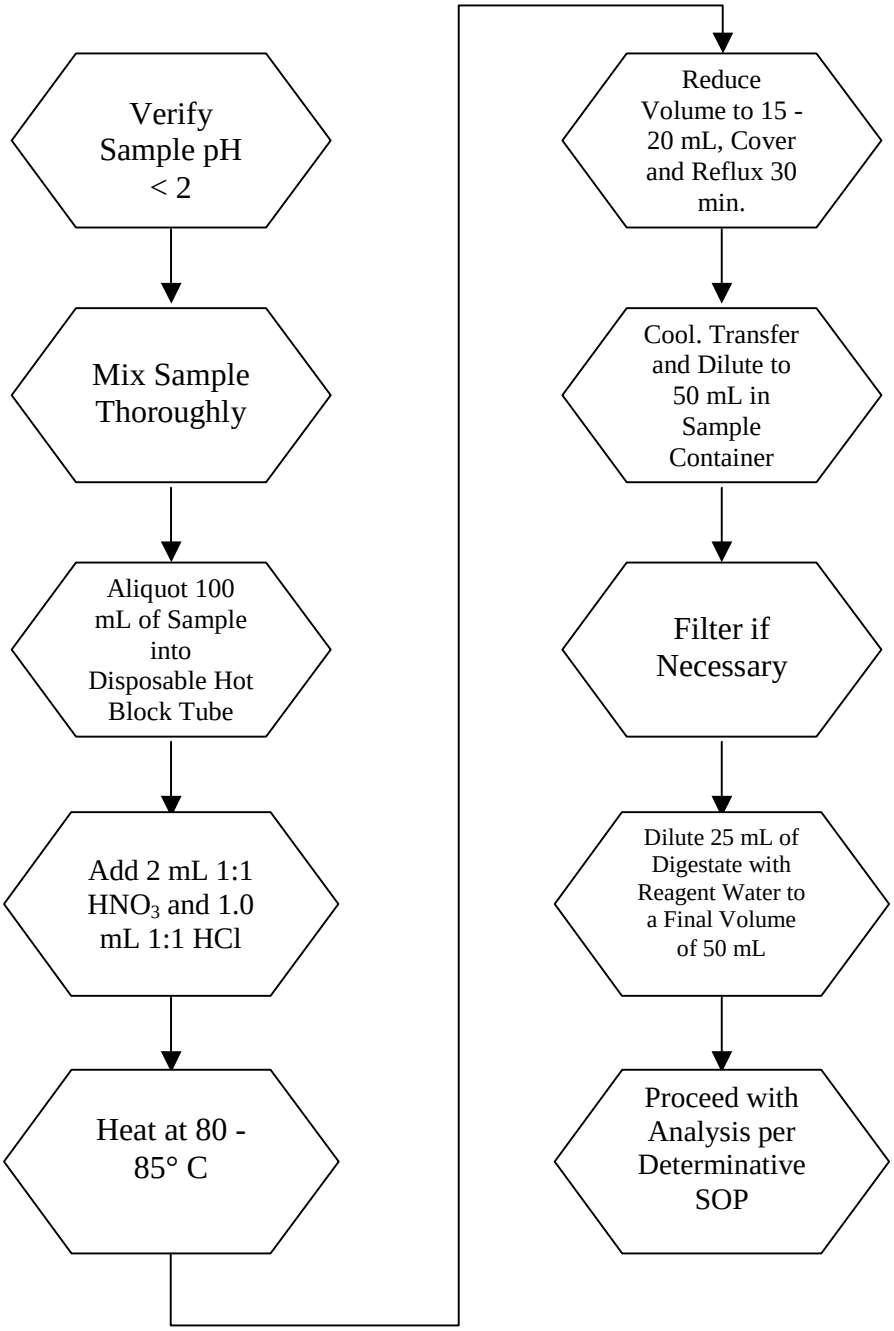


FIGURE 4. METHOD 200.8



APPENDIX A

TABLES

TABLE I
Approved Preparation Method Analytes - SW846

ELEMENT	Symbol	CAS Number	3005A	3010A
Aluminum	Al	7429-90-5	X	X
Antimony	Sb	7440-36-0	X	X
Arsenic	As	7440-38-2	X	X
Barium	Ba	7440-39-3	X	X
Beryllium	Be	7440-41-7	X	X
Cadmium	Cd	7440-43-9	X	X
Calcium	Ca	7440-70-2	X	X
Chromium	Cr	7440-47-3	X	X
Cobalt	Co	7440-48-4	X	X
Copper	Cu	7440-50-8	X	X
Iron	Fe	7439-89-6	X	X
Lead	Pb	7439-92-1	X	X
Magnesium	Mg	7439-95-4	X	X
Manganese	Mn	7439-96-5	X	X
Molybdenum	Mo	7439-98-7	X	X
Nickel	Ni	7440-02-0	X	X
Potassium	K	7440-09-7	X	X
Selenium	Se	7782-49-2	X	X
Silver	Ag	7440-22-4	X	X
Sodium	Na	7440-23-5	X	X
Thallium	Tl	7440-28-0	X	X
Vanadium	V	7440-62-2	X	X
Zinc	Zn	7440-66-6	X	X

X - Designates that the preparation method is approved for an element

Note: Additional elements may be analyzed following digestion by these protocols provided the method performance criteria specified in Section 12.0 of the SOP are met.

TABLE II
Approved Preparation Method Analytes - NPDES

ELEMENT	Symbol	CAS Number	200.7
Aluminum	Al	7429-90-5	X
Antimony	Sb	7440-36-0	X
Arsenic	As	7440-38-2	X
Boron	B	7440-42-8	X
Barium	Ba	7440-39-3	X
Beryllium	Be	7440-41-7	X
Cadmium	Cd	7440-43-9	X
Calcium	Ca	7440-70-2	X
Chromium	Cr	7440-47-3	X
Cobalt	Co	7440-48-4	X
Copper	Cu	7440-50-8	X
Iron	Fe	7439-89-6	X
Lead	Pb	7439-92-1	X
Magnesium	Mg	7439-95-4	X
Manganese	Mn	7439-96-5	X
Molybdenum	Mo	7439-98-7	X
Nickel	Ni	7440-02-0	X
Potassium	K	7440-09-7	X
Selenium	Se	7782-49-2	X
Silicon	Si	7631-86-9	X
Silver	Ag	7440-22-4	X
Sodium	Na	7440-23-5	X
Thallium	Tl	7440-28-0	X
Vanadium	V	7440-62-2	X
Zinc	Zn	7440-66-6	X

X - Designates that the preparation method is approved for an element

Note: Additional elements may be analyzed following digestion by these protocols provided the method performance criteria specified in Section 12.0 of the SOP are met.

TABLE III
ICP/ICPMS Matrix Spike and Aqueous Laboratory Control Sample Levels

ELEMENT	Working LCS/MS Standard (mg/L)	Aqueous LCS/ MS Level * (ug/l)
Aluminum	200	2000
Antimony	50	500
Arsenic	200 (ICP), 4 (ICPMS)	2000 (ICP), 40 (ICPMS)
Barium	200	2000
Beryllium	5	50
Cadmium	5	50
Calcium	5000	50000
Chromium	20	200
Cobalt	50	500
Copper	25	250
Iron	100	1000
Lead	50 (ICP), 2 (ICPMS)	500 (ICP), 20 (ICPMS)
Lithium	100	1000
Magnesium	5000	50000
Manganese	50	500
Molybdenum	100	1000
Nickel	50	500
Potassium	5000	50000
Selenium	200 (ICP), 1 (ICPMS)	2000 (ICP), 10 (ICPMS)
Silver	5	50
Sodium	5000	50000
Strontium	100	1000
Thallium	200 (ICP), 5 (ICPMS)	2000 (ICP), 50 (ICPMS)
Vanadium	50	500
Zinc	50	500
Boron	100	1000
Silica	1000	10000
Tin	200	2000
Titanium	100	1000

* Levels shown indicate the spike concentration in the final digestate of the aqueous LCS or matrix spike based on the addition of 0.5 mL working spike (7.3) to 50 mL of sample.

TABLE IV
TCLP Reporting Limits, Regulatory Limits and Matrix Spike Levels

ELEMENT	RL (ug/L)	Regulatory Limit (ug/L)	Spike Level (ug/L)
Arsenic	500	5000	5000
Barium	10000	100000	50000
Cadmium	100	1000	1000
Chromium	500	5000	5000
Lead	500	5000	5000
Selenium	250	1000	1000
Silver	500	5000	1000

TABLE V
Summary Of Quality Control Requirements

QC PARAMETER	FREQUENCY	ACCEPTANCE CRITERIA[1]	CORRECTIVE ACTION
Method Blank	One per sample preparation batch of up to 20 samples.	Refer to determinative SOPs: PITT-MT-0001 and PITT-MT-0020	Redigest and reanalyze samples associated with the method blank.
Laboratory Control Sample (LCS)	One per sample preparation batch of up to 20 samples.	Refer to determinative SOPs: PITT-MT-0001 and PITT-MT-0020	Redigest and reanalyze all samples associated with the LCS.
Matrix Spike	One per sample preparation batch of up to 20 samples (SW-846 Methods) or one per every 10 or fewer samples (200.7).	Refer to determinative SOPs: PITT-MT-0001 and PITT-MT-0020	Reprep not required unless preparation error suspected.
Matrix Spike Duplicate	See Matrix Spike	Refer to determinative SOPs: PITT-MT-0001 and PITT-MT-0020	See Corrective Action for Matrix Spike.

[1] **For specific DoD requirements, refer to PITT-QA-DoD-0001.**

APPENDIX B

METALS PREP BENCHSHEET

METALS PREP BENCHSHEET

TestAmerica Pittsburgh ***Metals Preparation Log*** Batch No. 7232156 Page 1 of 1

v1.0.6 - Last Revised 12/30/2005

Method 3050B	Matrix Solid	Start Time 0945	SDG -
Analyst example	Date 082007	Lot Numbers	
MS STLPA-MS-A, STLPA-MS-B, STLPA-MS-C		C7H030157	
Lab Lot # C7H030157			
Analyst Sign:			

Sample ID	Initial Wt/Vol g/mL	Final Vol mL	Comments
J3500			
J3501			
J3503			
J3505			
J3507			
J3509			
J350A			
J350C			
J350F			
J350H			
J350K			
J350N			
J350R			
J350W			
J351D			
J35X4			
J35X6			
J35X8			
J35X9			
J35XM			
J35XM S			
J35XM D			
J47LA B			
J47LA C			

SAMPLE CODING: B-Blank C-Check L-Check Duplicate S-Matrix Spike D-Matrix Spike Duplicate X-Sample Duplicate

NOTE: Samples marked with an asterisk (*) required filtration after digestion and prior to analysis
Samples marked with a plus sign (+) required additional Conc.HNO3 in digestion process, brown fumes were observed

Reagents: 10mL 1:1 HNO3, Met 4475-07, Standards Log
5 mL Conc.HNO3, 6623E20033, Mallinckrodt
10mL 30% H2O2, 42H15, Mallinckrodt
10mL Conc.HCl, 5587C47A01, Mallinckrodt

Minimum digestion times have been met (analyst initials):

Hot Plate/Block Temp	Correction Factor

Digestate(s)	Date	Time	(Received)	Analyst	Location	Date	Time	(Relinquished)	Analyst	Location

	Lot Number	Manufacturer	
Initial Digestion Vessel:	A603LP021	Environmental Express	Pipet #: J0450H
Final Digestion Vessel	070603	Corning	Balance #: C94817
Filter Paper:	G1822665	Whatman	Printed on: 24-Aug-07 1:36:47 PM

Reviewed By: Date: MET-86-7232156

APPENDIX C

CONTAMINATION CONTROL GUIDELINES

APPENDIX C
CONTAMINATION CONTROL GUIDELINES

The following procedures are strongly recommended to prevent contamination:

All work areas used to prepare standards and spikes should be cleaned before and after each use.

All glassware should be washed with detergent and tap water and rinsed with 1:1 nitric acid followed by deionized water.

Proper laboratory housekeeping is essential in the reduction of contamination in the metals laboratory. All work areas must be kept scrupulously clean.

Powdered or Latex Gloves must not be used in the metals laboratory since the powder contains silica and zinc, as well as other metallic analytes. Only vinyl or nitrile gloves should be used in the metals laboratory.

Glassware should be periodically checked for cracks and etches and discarded if found. Etched glassware can cause cross contamination of any metallic analytes.

The following are helpful hints in the identification of the source of contaminants:

Reagents or standards can contain contaminants or be contaminated with the improper use of a pipette.

Improper cleaning of glassware can cause contamination.

Separate glassware if an unusually high sample is analyzed and soak with nitric acid prior to routine cleaning.

APPENDIX 33
SOP FOR THE DETERMINATION OF TAL METALS BY EPA METHOD 200.8 (PT_MT_002_R5)(TEST AMERICA-PITTSBURGH)

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

Title: Analysis Of Metals By Inductively Coupled Plasma/Mass Spectrometry (ICPMS)

Method(s): EPA 200.8, SW-846 6020 & CLP ILM05.2

Approvals (Signature/Date):

William Reinheimer Technical Manager	05/22/08 Date	Steve Jackson Health & Safety Manager / Coordinator	05/27/08 Date
Nasreen K. DeRubeis Quality Assurance Manager	05/21/08 Date	Larry Matko Laboratory Director	05/20/08 Date

This SOP was previously identified as SOP No. PITT-MT-0020, Rev. 4.

1. SCOPE AND APPLICATION

1.1. This method is applicable to the determination of metals by inductively coupled plasma mass spectrometry (ICP-MS) by EPA Method 6020 and EPA Method 200.8.

1.2. This method is applicable to drinking, surface, and saline waters, soil, wipe, tissue and waste samples.

1.3. Reporting Limits

The standard reporting limits for metals analyzed by ICP-MS are listed in Table 1. Upon client request, results below the standard reporting limit but above the current method detection limit (MDL) may be reported and qualified as “estimated”.

1.4. Methods are based on the requirements of the US EPA Contract Laboratory Program (CLP) method ILM05.2D, and SW-846 methods 6020 and 6020. Instructions within this document that are general are given in BLACK, whilst those that apply only to 6020 are in BLUE and those that apply only to ILM05.2D are in RED.

1.5. Elements that may be determined using this procedure include: Al, Sb, As, Ba, Be, B, Cd, Cr, Co, Cu, Fe, Pb, Mn, Mo, Ni, Se, Si, Ag, Sr, Tl, Sn, Ti, V, Zn, Ca, Mg, K, P, Cs and Na.

Note: successful Ag analysis may require all solutions to be prepared as described, but with the addition of hydrochloric acid to 1% (v/v). This may degrade performance for As, Se and V.

1.6. For DoD QSM Version 3 requirements, refer to SOP PT-QA-025.

2. SUMMARY OF METHOD

2.1. The sample solution is introduced into a pneumatic nebulizer via a peristaltic pump. The nebulizer generates a fine aerosol by bringing the solution into contact with a high velocity flow of argon gas at its tip. The nebulized sample is sorted by droplet size in the spray chamber. Large droplets are rejected, whilst smaller particles are transported with the gas stream into the plasma.

2.2. The argon plasma operates with a continuously applied radio frequency (RF) field to give a high-energy discharge consisting of argon atoms, ions and electrons. The hottest part of the plasma can attain 6000-8000 K. In the plasma, aerosol droplets undergo evaporation, atomization and ionization. Ions are sampled through an aperture in a metal cone (sampler) at atmospheric pressure, into the expansion region at about 2 mbar and subsequently through an aperture in a second metal cone (skimmer) into the intermediate chamber.

2.3. An electrostatic ion lens system focuses the ion beam through a differential aperture into the analyser chamber, at about 10-7 mbar. The ions are filtered by mass-to-charge ratio in microsecond timescales by the quadrupole. The selected mass is detected by a discrete dynode electron multiplier. The multiplier has two simultaneous modes of operation: pulse count and analogue. The combination of these two modes allows seamless detection spanning 8 - 9 orders of magnitude. A detector “cross-calibration” is required for the analogue counts to be converted to equivalent pulse counts. The output from the detector is proportional to the concentration of the element in the aspirated solution, hence the concentration of unknown samples may be calculated when the instrument response is

calibrated with standards of known concentration.

2.4. The linear range may vary from instrument to instrument and is dependant upon the sensitivity determined by the optimization parameters. This should be determined by the individual laboratory. In the test study at TestAmerica Pittsburgh, the linear ranges listed in Table 1 (below) were obtained:

2.4.1. Table 1. Test study linear ranges for the X5 ICP-MS

Analytes	Linear Range (mg/L)
Sb, As, Ba, Be, Cd, Cr, Co, Cu, Pb, Mn, Ni, Se, Ag, Tl, V, Zn	0.20 – 20.0
Al, Ca, Mg, K Na, Fe	100 - 1500

2.5. Calibration standard concentrations are listed in Table 2 below.

2.5.1. Table 2. Calibration standard concentrations for analysis of water and waste

Analytes	Calibration Range (mg/L)
Al, Mn	1.0
Sb, As, Ba, Be, Cd, Cr, Co, Cu, Pb, Ni, Se, Ag, Tl, V, Zn	0.20
Ca, Mg, K Na, Fe	100
Fe	50
B, Mo, Sn, Sr, Ti	0.20
Si	10

3. DEFINITIONS

3.1. See the LQM for definitions of general terms

3.2. See appendix for Glossary of Abbreviations

4. INTERFERENCES

4.1. Isobaric interferences. Elemental isobaric interferences occur when different elements have isotopes at the same nominal mass, e.g. ^{114}Cd and ^{114}Sn. Problematic elemental isobaric interferences for these methods are listed in Table 3. The correction factors given in Table 3 are based on theoretical isotopic abundance ratios and may require adjustment.

Table 3 Isobaric Interferences and Correction Equations

m/z	Analyte	Interferent	Correction
58	Ni	Fe	58Ni=58M-0.0040*56Fe
64	Zn	Ni	64Zn=64M-0.0440*60Ni
82	Se	Kr	82Se=82M-1.0010*83Kr
114	Cd	Sn	114Cd=114M-0.0270*118Sn
115	In	Sn	115In=115M-0.0140*118Sn
123	Sb	Te	123Sb=123M-0.1240*125Te
138	Ba	Ce	138Ba=138M-0.0030*140Ce

4.2. Abundance Sensitivity - Abundance sensitivity is the ability of the quadrupole to separate a low intensity peak from an adjacent high intensity peak. An example of the requirement of this is the detection of low concentrations of manganese (m/z 55) in the presence of high concentrations of iron (m/z 56). Quadrupole resolution and bias can be adjusted during set-up to resolve these signals.

4.3. Isobaric Polyatomic Ion Interferences - Polyatomic ions are produced by chemical reaction in the plasma and the interface region. If these polyatomic ions have the same nominal mass to charge (m/z) ratio as an analyte a polyatomic interference is observed. The principle polyatomic species for this method are listed in Table 4. Some of the correction factors given in Table 4 are based on theoretical isotopic abundance ratios and may require adjustment. Other factors were derived empirically. The stability of the empirical factors was determined during the test study at Thermo Electron. It was found that the factors require little or no adjustment and can be transferred between similarly configured X5 instruments.

Table 4. Isobaric Polyatomic Interferences and Correction Equations

m/z	Analyte	Interferent	Correction
51	V	ClO	51V = 51M-3.0460*53ClO 53ClO = M53-0.114*52Cr
52	Cr	ArC, ClOH	52Cr = 52M-0.0050*13C
56	Fe	CaO	56Fe = 56M-0.1500*43Ca
56	Co	CaO, CaOH	59Co = 59M-0.0046*43Ca
60	Ni	CaO	60Ni = 60M-0.0020*43Ca
75	As	ArCl	75As = 75M-3.000*77ArCl 77ArCl = 77M-0.8000*82Se 82Se = 82M-1.0010*83Kr

m/z	Analyte	Interferent	Correction
111	Cd	MoO	111Cd = 111M-0.9820*108MoO 108MoO = 108M-0.712*106Cd

4.4. Physical Interferences - Physical interferences include transport effects, ionization effects and deposition effects in the sample introduction system, plasma and interface, which result in signal suppression and signal drift. Transport effects arise from variations in solution properties, e.g. viscosity or surface tension, which affect nebulization efficiency and aerosol droplet size. The concentration of dissolved matter will affect the ionization efficiency of the analytes in the plasma and will cause a mass-dependant suppression effect and contribute to space-charge effects. Dissolved matter may also condense on the cones, altering the ion beam profile. This normally manifests itself as a time-dependant downward signal drift. To reduce the severity of these effects it is advised that the total dissolved solids concentration of solutions aspirated should be limited to <0.05%. Samples known to contain higher dissolved solids concentrations should be diluted. Signal suppression and drift can be corrected, to a degree, with the use of internal standardization techniques. Since these effects can be mass-dependant and may be related to the ionization potential of the element, a multiple-element internal standard approach should be used.

4.5. Memory Effects - Memory effects occur when the signal for an analyte from a sample contributes to the signal of a subsequent sample. This effect can be severe for certain elements due to their physico-chemical properties, e.g. mercury. This effect is minimised by aspirating a wash solution between samples. A monitored wash can be used in order to ensure that analyte signals recover to the background level.

5. SAFETY

5.1. Employees must abide by the policies and procedures in the Corporate Environmental Health and Safety Manual (CW-E-M-001), Radiation Safety Manual and this document. This procedure may involve hazardous material, operations and equipment. This SOP does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, gloves, lab coats and closed-toe, nonabsorbent shoes are a minimum.

5.2. Specific Safety Concerns or Requirements

5.2.1. The ICP plasma emits strong UV light and is harmful to vision. All analysts must avoid looking directly at the plasma.

5.3. Primary Materials Used

The following is a list of the materials used in this method, which have a serious or significant hazard rating. **NOTE: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the

information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Nitric Acid	Corrosive Oxidizer Poison	2 ppm-TWA 4 ppm-STEL	Nitric acid is extremely hazardous; it is corrosive, reactive, an oxidizer, and a poison. Inhalation of vapors can cause breathing difficulties and lead to pneumonia and pulmonary edema, which may be fatal. Other symptoms may include coughing, choking, and irritation of the nose, throat, and respiratory tract. Can cause redness, pain, and severe skin burns. Concentrated solutions cause deep ulcers and stain skin a yellow or yellow-brown color. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
Hydrochloric Acid	Corrosive Poison	5 ppm-Ceiling	Inhalation of vapors can cause coughing, choking, inflammation of the nose, throat, and upper respiratory tract, and in severe cases, pulmonary edema, circulatory failure, and death. Can cause redness, pain, and severe skin burns. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

5.4. Eye protection that protects against splash, laboratory coat, and chemically resistant gloves must be worn while samples, standards, solvents, and reagents are being handled. Cut resistant gloves must be worn doing any other task that presents a strong possibility of getting cut. Disposable gloves that have been contaminated will be removed and discarded; other gloves will be cleaned immediately.

5.5. The waste pumped from the spray chamber is corrosive and must be handled with care, especially if large volume containers are used, as these may be heavy and awkward to carry. Empty the waste vessel daily to reduce the quantity that must be disposed each time and to keep weight to a minimum. Protective clothing, including hand and eye protection must be worn when handling this waste.

5.6. The wash solution is corrosive and must be handled with care. This solution must be prepared and stored in a vessel made of a robust acid-resistant material with a tight fitting lid that it is resistant to breakage if dropped. Large volumes of this solution will be heavy and may be awkward to carry. Ensure adequate provision for transporting the vessel, i.e. suitable handles on the vessel, minimum distance between the preparation area and the

instrument. Use a cart to transport the vessel where necessary or ask for assistance in carrying.

5.7. Many of the concentrated metal standard solutions are toxic and must be handled with care. Skin and eye protection should be worn when handling and inhalation of vapours must be prevented.

5.8. Fumes generated by the plasma can be hazardous and must be removed from the laboratory with an extraction system as detailed in the X Series site planning guide. If the extraction system is faulty do not attempt to use the instrument. The extraction system should be inspected on a regular basis.

5.9. The plasma emits strong UV light and is harmful to vision.

5.9.1. *WARNING:* AVOID looking directly at the plasma.

5.10. The plasma is a source of radio frequency (RF) radiation and intense, ultra-violet radiation that can damage the eyes. This radiation is normally contained by the system, but operators must be aware of the dangers. The instrument must be properly maintained by qualified service personnel. Never attempt to defeat hardware interlocks – they are there for your safety.

5.11. WARNING: People with pacemakers should not go near the instrument while in operation. DIAZOMETHANE is an extremely toxic gas with an explosion potential. Since the explosion potential is catalyzed by imperfections in glass, generation of diazomethane must be carried out in glassware free from etches, cracks, chips, and which does not have ground glass joints. Solutions of diazomethane will be kept at temperatures below 90°C. Diazomethane must be generated and handled in a fume hood.
Note: Diazomethane has not been classified as a carcinogen under the current OSHA definition.

5.12. Should the plasma need to be extinguished in an emergency, open the torch box door. This will immediately cut-off the power to the plasma RF generator, extinguishing the plasma. After extinguishing the plasma, the torch, torch box, cones and cone housing may remain very hot for some time. Operators must be aware of this fact and allow cooling time prior to handling these components.

5.13. There are high voltage components inside the instrument. Routine maintenance does not require access to any of the electronic components. If an electronic fault is suspected, a qualified service engineer must be called. Do not attempt to tamper with electronic components yourself.

5.14. Exposure to chemicals must be maintained as low as reasonably achievable, therefore, unless they are known to be non-hazardous, all samples must be opened, transferred and prepared in a fume hood, or under other means of mechanical ventilation. Solvent and waste containers will be kept closed unless transfers are being made.

5.15. The preparation of standards and reagents will be conducted in a fume hood with the sash closed as far as the operation will permit.

5.16. All work must be stopped in the event of a known or potential compromise to the health and safety of an associate. The situation must be reported immediately to a laboratory

supervisor and/or the EHSC.

6. EQUIPMENT AND SUPPLIES

6.1. Instrumentation

6.1.1. (2) X Series ICP-MSs fitted with Xi interface and Y-connector for on-line internal standard addition (supplied with this package).

6.1.2. (2) Cetac ASX-510 autosamplers.

6.2. Supplies

6.2.1. Ultrapure water system capable of delivering de-ionized, polished water of at least 18 MΩ cm

6.2.2. Yellow/orange tab peristaltic pump tubes (~0.5 mm ID)

6.2.3. White/white tab peristaltic pump tubes (~1 mm ID)

6.2.4. A range of adjustable pipettes, such as Rainin pipettes. Adjustable pipettes with a capacity of 0.1 mL, 1 mL, and 10 mL are recommended. These must be calibrated regularly to ensure accurate volumes are delivered.

7. REAGENTS AND STANDARDS

7.1. General Reagents

7.1.1. **Laboratory Water** - All laboratory water used in these procedures must be of very high quality, purified with a reverse osmosis system and polished with an ion exchange system to give a final product of resistivity >18 MΩ cm.

7.1.2. **Hydrochloric Acid** (sp. gr. 1.18) - Hydrochloric acid must be at least Romil "SPA", J.T. Baker "Instra Analyzed", BDH/Merk "Analar", Fisher "Optima" - grade or equivalent. Hazards – corrosive, causes severe burns.

7.1.3. **Nitric Acid** (sp. gr. 1.42) - Nitric acid must be at least Romil "SPA", J.T. Baker "Instra Analyzed", BDH/Merk "Analar", Fisher "Optima" - grade or equivalent. Hazards – oxidising and corrosive, causes severe burns.

7.1.4. **2 % (m/v) Nitric Acid** - This reagent is used for the calibration blank, ICB, CCB, sample dilution and solution preparation. Add 5 mL of Conc of HNO3 to DI water and dilute to 250 mL

8. SAMPLE COLLECTION, PRESERVATION, SHIPMENT AND STORAGE

8.1. Samples are to be collected in plastic or glass containers.

8.2. Aqueous samples are preserved with nitric acid to a pH of <2.

8.3. All soil and wipe samples must be refrigerated to 4°C ± 2°C.

8.4. Tissue samples are stored frozen until preparation.

8.5. The analytical holding time for metals by ICP-MS is 6 months.

8.6. Aqueous samples for total metals must be digested before analysis using an appropriate digestion procedure. Method 200.8 has its own digestion specifications that are followed by the laboratory. Method 3005A is used for total recoverable metals and dissolved and method 3010A is used for total metals by 6020. These are covered in the SOP PT-IP-003. Upon consultation with the client dissolved samples can forego digestion to help prevent contamination when very low detection limits are required.

8.7. Soil, wipe, tissue and waste samples should be digested before analysis using an appropriate digestion procedure. Method 3050B of SW846 is the appropriate digestion procedure. The SOP for 3050B is PT-IP-002.

9. QUALITY CONTROL

9.1. Sample QC

9.1.1. Quality Control Batch

The batch is a set of up to 20 field samples that are of the same matrix and are processed together using the same procedures and reagents. The batch must contain a method blank, an LCS and a matrix spike/matrix spike duplicate. (In some cases, at client request, it may be appropriate to process a matrix spike and sample duplicate in place of the MS/MSD). If clients specify particular samples for MS/MSD, the batch may contain multiple MS/MSDs. See policy QA-003 for further definition of the batch.

9.1.2. Insufficient Sample

If insufficient sample is available to process a MS/MSD, then a second LCS may be processed, if precision data is required by the client. The LCS pair is then evaluated according to the MS/MSD RPD criteria.

9.1.3. Method Blank

One method blank must be processed with each preparation batch. The method blank consists of reagent water containing all reagents specific to the method that is carried through the entire analytical procedure, including preparation and analysis. The method blank is used to identify any system and process interferences or contamination of the analytical system that may lead to the reporting of elevated analyte concentrations or false positive data. The method blank must not contain any analyte of interest at or above the reporting limit (except common laboratory contaminants, see below) or at or above 10% of the measured concentration of that analyte in the associated samples, whichever is higher. Certain programs, such as USACE, may require a more stringent evaluation of the method blank, for instance, that the blank not contain any analytes of interest at a concentration greater than ½ the reporting limit. **Refer to PT-QA-025 for specific DoD requirements for the method blank.**

- If the analyte is a common laboratory contaminant (copper, iron, zinc), the data may be reported with qualifiers if the concentration of the analyte in the method blank is less than five times the RL. Such action must be documented in the

NCM program.

- Re-preparation and reanalysis of any samples with reportable concentrations of analytes less that 10 times the value found in the method blank is required unless other actions are agreed with the client.
- If there is no target analyte greater than the RL in the samples associated with an unacceptable method blank, the data may be reported. This must be documented in the NCM program.
- If reanalysis of the batch is not possible due to limited sample volume or other constraints, the method blank is reported, all positive results in associated samples are flagged with a "J", and appropriate comments may be made in a narrative to provide further documentation.

9.1.3.1. Refer to the QC Program document (QA-003) for further details of the corrective actions.

9.1.3.2. For samples that have not been digested or matrix matched, a CCB result is reported as the method blank. The CCB analyzed immediately prior to the start of the dissolved sample analyses must be used for this purpose. No more than 20 samples can be associated with one CCB.

9.1.4. Laboratory Control Sample (LCS)

9.1.4.1. A laboratory control sample (LCS) is prepared and analyzed with every batch of samples. All analytes must be within established control limits. The LCS is spiked with the compounds listed in Tables 9 and 10 unless otherwise requested by the client.

9.1.4.2. If any analyte in the LCS is outside the laboratory established historical control limits, corrective action must occur:

- Check calculations,
- Check instrument performance,
- Reanalyze the LCS, and if still outside of control limits,
- Evaluate the data, and/or
- Re-prepare and reanalyze all samples in the QC batch.

9.1.4.3. Data may be reported with an anomaly in the following cases:

- The LCS recoveries are high and the analyte of concern is not detected in field samples,
- All target requested analytes are within control, but other LCS compounds are out of control,
- If no sample preparation is performed (eg., dissolved metals), the LCS may be reprepared and reanalyzed within the same sequence.

9.1.4.4. The analyst should evaluate the anomalous analyte recovery for possible

trends.

9.1.4.5. If the batch is not re-extracted and reanalyzed, the reasons for accepting the batch must be clearly presented in the project records and the report.

9.1.4.6. If re-extraction and reanalysis of the batch is not possible due to limited sample volume or other constraints, the LCS is reported, all associated samples are flagged, and appropriate comments are made in a narrative to provide further documentation.

9.1.4.7. For samples that have not been digested or matrix matched, a CCV result is reported as the LCS. The CCV run immediately prior to the start of the dissolved sample analyses must be used for this purpose. No more than 20 samples can be associated with one CCV.

9.1.5. Matrix Spike/Matrix Spike Duplicate (MS/MSD)

A matrix spike/matrix spike duplicate (MS/MSD) is prepared and analyzed with every batch of samples. The MS/MSD is spiked with the same analytes as the LCS (See Appendix 11). Compare the percent recovery and relative percent difference (RPD) to that in the historically generated limits. **Refer to PT-QA- 025 for specific DoD requirements for the MS.**

Note: Some programs require a Matrix Spike and Matrix Replicate in lieu of an MS/MSD. When a matrix spike/matrix replicate is performed the matrix spike is evaluated for accuracy (% recovery) and the matrix replicate is evaluated for precision (RPD).

- If any individual recovery or RPD falls outside the acceptable range, corrective action must occur. The initial corrective action will be to check the recovery of that analyte in the Laboratory Control Sample (LCS). Generally, if the recovery of the analyte in the LCS is within limits, then the laboratory operation is in control and analysis may proceed. The reasons for accepting the batch must be documented.

- If the recovery for any component is outside QC limits for both the matrix spike/spike duplicate and the LCS, the process is out of control and corrective action must be taken. Corrective action will normally include re-preparation and reanalysis of the batch.

- If a MS/MSD or MS/Dup is not possible due to limited sample, then a LCS duplicate should be analyzed. RPD of the LCS and LCSD are compared to the matrix spike limits.

- The matrix spike/duplicate must be analyzed at the same dilution as the unspiked sample, even if the matrix spike compounds will be diluted out.

9.1.5.1. If the amount of an analyte found in the unspiked sample is greater than 4 times the amount of spiked analyte added, then routine control limits do not apply and recoveries are not evaluated. Other analytes in the MS and MSD must still be reported. File an NCM stating that the 4X rule was applied, and report the recovery in the LIMS as “ND MSB”. This

NCM must be included in the final report.

9.1.5.2. For samples that have not been digested or matrix matched, a MS/MSD must be performed per batch of up to 20 samples by spiking two aliquots of the sample.

9.1.6. Post-Digestion Spike Samples (PDS)

9.1.6.1. For DoD samples, a post digestion spike will be run on a sample if the if the MS/MSD for the sample falls outside of % recovery criteria. A post digestion spike is a matrix spike on a sample, which is added after the sample preparation is completed. For 6020 the default matrix spike protocol is a "post digestion spike". However, TestAmerica Pittsburgh will perform a conventional matrix spike and spike duplicated as the default matrix QC. We will perform the "PDS" only where the conventional matrix spike fails. We believe that this approach will provide more complete matrix information than the default requirements. The spike recovery from the post digestion spiked sample should be within the range 75-125% where the spike value is greater than 25% of the indigenous analyte concentration. The software calculates this based on the following equation:

%Repeatability = 100 * (Spk-Orig)/Tru

where, Spk is the spiked sample result and Orig is the original sample result and Tru is the True spiked concentration value. If a result is outside the required range, the data should be assessed carefully and samples may require reanalysis.

9.1.7. Serial Dilution Samples (SER) - Some regulatory programs such as require a dilution test be performed for each matrix within an analytical batch determination. The results of the serial dilution sample(s) (SER) after dilution correction should be within the range 90-110% of the original sample, if the result for the original sample is greater than 50*IDL for CLP or greater than 50*MDL for 200.8 or 6020.

9.1.7.1. The software calculates this based on the following equation:

%Repeatability = 100 * Ser/Orig

where, SER is the dilution corrected serial diluted sample result and Orig is the original sample result. If a result is outside the required range, the data should be assessed carefully and samples may require reanalysis.

9.1.8. Duplicate Samples (DUP); %RPD = ±20%: Results of the duplicate sample(s) (DUP) must be within ±20% of the results of the original sample, where the result is greater than or equal to 5*CRQL for CLP or greater than 5*RL for 200.8 or 6020. The software calculates this based on the following equation:

%RPD = (S-D) / [(S+D)/2] * 100%

where, D is the duplicate sample result and S is the original sample result.

If a result is outside the required range, the data should be assessed carefully

and samples affected may need to be reanalyzed where the project requires it.

9.2. Instrument QC

9.2.1. Linear Range Verification (LR) - The linear range is determined semi-annually (2x/year) for each element on the standard list. See Section 13 for details of the linear range verification. The Linear Range study must be performed quarterly if doing ILM05.2.

9.2.2. The internal standard intensities in samples must be within 60 to 125% of the IS intensities for the Calibration Blank for method 200.8 and from 30% to 120% for method 6020. If this criterion is not met, the sample will be diluted and reanalyzed until the IS recoveries are within the limits. If the upper control limit is exceeded, the analyst should review the data for the presence possible contribution from the native sample. Narrate any findings.

9.2.2.1. For method 6020 the internal standard intensity in the ICV, ICB, CCV and CCB should be within 20% of the IS intensity in the calibration blank of the initial calibration. If not, the analyst should check for any instrument anomalies and continue if none are noted. For method 200.8 the IS acceptance range does not vary from the 60 to 125% noted above.

9.2.3. Interference Check Solutions (ICSAs) - The results of ICSA must be within ±3CRQL of the analytes "true" value or ±20% of the analytes "true" value, whichever is the greater. The "true" value will be taken as zero, unless otherwise indicated in the solution manufacturer's literature. The software automatically checks for compliance with the above, based on a "true" value of zero. If a result falls outside this range, the analysis must be terminated and the samples associated must be reanalyzed. **Refer to PT-QA-025 for specific DoD requirements for the ICSA.**

9.2.4. Interference Check Solution Spike Recoveries (ICSABs) - Results of ICSAB must be within ±20% of the analytes "true" value. The software automatically checks for compliance with the above, based on the values indicated in (Tables 4 and 5). If a result falls outside this range, the analysis must be terminated and the samples associated must be reanalyzed.

9.2.5. Initial Calibration Verification (ICV/ICB) - Calibration accuracy is verified by analyzing a second source standard (ICV). The ICV must fall within ± 10% of the true value for that solution. An ICB is analyzed immediately following the ICV to monitor low level accuracy and system cleanliness. The ICB result must fall within ± the reporting limit (RL) from zero. (Certain programs, may require a more stringent evaluation of ICB, for instance, that the blank not contain any analytes of interest at a concentration greater than ½ the reporting limit.) **Refer to PT-QA-025 for specific DoD requirements for the ICB.** If either the ICV or ICB fail to meet criteria, the analytical sequence should be terminated, the problem corrected, the instrument recalibrated and the calibration re-verified.

9.2.6. CRQL Check Standard (CRI)

FOR ILM05.2, THE RESULTS OF THE CRI MUST BE WITHIN THE RANGE 70-130% RECOVERY FOR ALL ANALYTES, EXCEPT CO, MN AND ZN, WHICH MUST BE IN THE RANGE 50-150% RECOVERY. THIS IS CHECKED BY THE SOFTWARE, BASED ON THE TRUE VALUES. IF ANY ANALYTE IS OUTSIDE THE RANGE INDICATED, THE SAMPLE MAY BE RE-RUN ONCE. IF THE RESULTS FALL WITHIN THE REQUIRED VALUES UPON RE-RUN, NO FURTHER CORRECTIVE ACTION NEED BE TAKEN. IF STILL OUTSIDE THE ACCEPTABLE RANGE, THE ANALYSIS SHALL BE TERMINATED, THE PROBLEM CORRECTED AND THE SAMPLES REANALYZED. **FOR NON-CLP METHODS** THE METHOD DOES NOT SPECIFY CRITERIA, HOWEVER THE LAB USES THE RANGE 50 – 150%. **REFER TO PT-QA-025 FOR SPECIFIC DOD REQUIREMENTS FOR THE CRI STANDARD.**

9.2.7. Continuing Calibration Verification (CCV/CCB) - Calibration accuracy is monitored throughout the analytical run through the analysis of a known standard after every 10 samples. Results for the CCV must be within the range 90-110% recovery. This is checked by the software, based on the true values. If outside this range, the analysis must be terminated, the problem corrected and the samples since the last valid CCV must be re-analyzed. The CCB result must fall within ± RL from zero. (Certain programs, may require a more stringent evaluation of the CCB, for instance, that the blank not contain any analytes of interest at a concentration greater than ½ the reporting limit. The analyst should refer to the project notes provided by the PM to identify when this is an issue and if so what the corrective actions to take for exceedances.) **Refer to PT-QA-025 for specific DoD requirements for the CCB.** Sample results may only be reported when bracketed by valid CCV/CCB pairs. If a mid-run CCV or CCB fails, the CCV or CCB may be reanalyzed once and accepted if there is a reason for the initial out-of-control event such as carryover from a high concentration sample. Otherwise, if the CCV or CCB fails, the analysis for the affected element must be terminated, the problem corrected, the instrument recalibrated, the calibration verified and the affected samples reanalyzed. (Refer to Section 10.9 for an illustration of the appropriate rerun sequence).

9.3. Nonconformance and Corrective Action:

Any deviations from QC procedures must be documented as a nonconformance, with applicable cause and corrective action approved by the QA Manager.

9.4. Quality Assurance Summaries:

Certain clients may require specific project or program QC that may supersede these method requirements. Quality Assurance Summaries should be developed to address these requirements.

9.5. QC Program:

Further details of QC and corrective action guidelines are presented in the QC Program document (QA-003). Refer to this document if in doubt regarding corrective actions.

10. PROCEDURE

10.1. Sample Preparation

10.1.1. Refer to SOPs PT-IP-002, PT-IP-003 and PT-IP-005.

10.2. Calibration

10.2.1. Instrument start-up

Follow the instrument start-up procedure outlined in the Thermo X-Series ICP-MS Operator's Manual.

10.2.2. Instrument Tuning

10.2.2.1. Aspirate a 20 ppb tuning solution containing all of the tuning elements. The 6020 tuning elements are Li, Co, In, and Tl. The instrument manufacturer monitors Mg, Ce, Be & Pb for instrument performance.

10.2.2.2. Mass calibration and resolution checks must be documented and included as part of the raw data package.

10.2.2.3. Resolution must be < 0.90 amu at 10% peak height for the 6 tuning (Be, Ce, Co, In, Mg, & Pb) for 6020. Resolution must be ≤ 0.75 amu at 5% of the peak height for ILM05.2. And the resolution must be ≤ 0.9 amu at 5% of the peak height for Method 200.8.

10.2.2.4. Mass calibration must be within ± 0.1 amu from the actual value for the 6 tuning elements (Be, Ce, Co, In, Mg, & Pb) or the mass calibration must be adjusted.

10.2.2.5. A "daily" performance check must be performed. This uses the same tuning solution as above. The 6 tuning elements must have RSDs below 5%. The oxides must be below 3.5%. If any of these conditions are not met repairs or optimization procedures must be performed until these specifications are met.

10.2.3. Initial Calibration

10.2.3.1. Calibration consists of a blank and the following calibration standards (STD1, STD 2X, and STD 3X see Table 2 for concentrations) in accordance with the manufacturer's procedure. Use the average of three integrations for both calibration and sample analyses.

10.2.3.2. Following the STD, STD2X & STD3X, an ICV/ICB pair is analyzed. The ICV must be within ± 10% of the true value to be acceptable.

10.2.3.3. For 6020 and ILM05.2, following the ICV/ICB pair, the CRI/RLV is run then the ICSA is analyzed.

10.2.3.4. For 6020 and ILM05.2, following the ICSA, analyze the ICSAB. The ICSAB must be within ± 20% of the true value.

10.2.3.5. Internal standards are added to all standards and samples by the instrument automatically prior to analysis.

10.2.4. Continuing Calibration:

10.2.4.1. Following every 10 samples (including lab QC), analyze a CCV/CCB pair. These must be within ± 10% of the true value for analysis to continue. For methods 6020 and ILM05.2, a CCV/CCB pair should also be analyzed immediately after the ICSAB.

10.2.4.2. All samples must be bracketed by an acceptable CCV/CCB pair. Where a CCV/CCB fails the samples preceding it back to the last acceptable CCV/CCB must be reanalyzed.

10.2.5. Instrument Set-up

10.2.5.1. Configure the X Series with the standard sample introduction equipment, i.e. a glass concentric nebulizer, glass impact bead spray chamber and a one-piece torch with 1.5mm ID injector tube. A Peltier spray chamber cooling unit is optional. Ensure that the Xi interface cones are fitted. These are standard with the X5 instrument and an option for the X7. They can be identified as follows:

Xi Sampler - 1.1 mm orifice, no nipple, no holes around the flat circumference

Xi Skimmer - Small pointed skimmer mounted in a copper adapter with two screws

Yellow/orange tab peristaltic pump tubes (6.2.2) should be used for sample and internal standard uptake. Connect the liquid output end of the peristaltic pump tubes to the 1.0 mm (OD) barbed fitting screwed into the Y connector. Note that the barbed fitting may require tightening with a pair of grips to ensure a good fluid-tight seal. The mixed output flow should be connected to the nebulizer. See diagram in Appendix 6 for plumbing schematic. A white/white tab peristaltic pump tube (6.2.3) should be connected to the spray chamber drain outlet at one end and to a tube running into a waste vessel at the other and wound on the pump to draw the waste liquid away from the spray chamber.

10.2.5.2. Perform the daily maintenance as outlined in Appendix 3.

10.2.5.3. Switch the instrument into the *Operate* state by clicking the *ON* button at the top of the screen. During the automated ignition sequence, the following processes occur:

i. Torch purge with argon gas

ii. RF power match

iii. Plasma ignition

iv. Slide valve open

v. Electronics on

This process takes about two minutes. Upon successful ignition, the software will display *Operate* in the *Instrument State* bar. If the event of unsuccessful ignition, the software will display an error message and/or place a message in the *Technician Event Log*. Upon unsuccessful ignition, inspect the sample introduction equipment and torch, ensuring a good gas-seal at each connection and ensuring the torch is not misaligned or damaged. If all appears satisfactory, the ignition may be attempted again. If the ignition process consistently fails, contact your local Thermo service agent for advice.

10.2.5.4. Once the instrument is in the *Operate* state, it should be left for 30 minutes to reach thermal equilibrium prior to starting analytical measurements. The optimization (tuning), performance testing and instrument set-up calibrations may be performed after 15 minutes. Ensure that the peristaltic pump is operated at a default analytical speed of 15%. This is done by clicking on *Instrument*, *Configurations*, *Configuration Editor*, *View Selected Accessories* (network icon), *Peristaltic Pump*, *Connect* (chain icon). Set pump speed to 15% using the slider bar and adjust the *Settle Time* to 10 seconds and click on *Apply*. Click *OK* to close the dialogue box.

10.2.5.5. During the initial 15 minutes, the system can be “conditioned” by aspirating the system thoroughly with 2% nitric acid + 1% HCL solution prior to continuing.

10.2.5.6. Instrument tuning (optimization) is performed using a 20 µg/L Tune Solution, aspirated through the sample uptake tube. Optimization may not be necessary from day to day if the sample introduction system and cones have not been adjusted in any way and if the instrument fulfils the performance requirements given below. If the instrument gives performance exceeding the requirements shown below, proceed to 10.2.5.7. Otherwise, tune the instrument manually or using *Autotune* while aspirating 20 µg/L Tune Solution through both the sample and internal standard uptake tubes. *Autotune*, using an appropriately defined sequence is advised (see Appendix 4).

The final conditions must give the following:

^{9}Be	>2000cps
^{115}In	>50000cps
^{208}Pb	>25000cps
$^{156}CeO/^{140}Ce$	<0.02

If the above criteria are met, proceed to 10.2.5.7. If the above criteria are not met, do not proceed. Check that the tune solution was prepared

properly and remake if necessary. If the sensitivity is below the minimum requirement, a new detector plateau may be required (see Appendix 6), the cones may require cleaning (see Appendix 8), or the nebulizer or sample uptake lines may have become blocked or may not be properly clamped on the peristaltic pump. If the CeO/Ce ratio is >0.025, the nebulizer gas flow can be reduced and/or the sampling depth increased, obtaining a corresponding reduction in oxide formation. Recheck the above parameters after taking any remedial action.

10.2.5.7. Save the satisfactory instrument settings by clicking on the disk icon on the Tune page. Note that this is not necessary if Autotune has been used, as the instrument settings are saved automatically (unless manual adjustments have been made after autotuning).

10.2.5.8. Set-up the resolution as described in Appendix 5.

10.2.5.9. Perform a cross-calibration (and mass-calibration and detector voltage setup if required) as explained in Appendix 6. Note that retuning may be necessary after performing this routine.

10.2.5.10. Aspirate Tune solution and run a *Performance Report* (see Appendix 4) to confirm the mass-calibration, resolution, minimum sensitivity and maximum cerium oxide requirement and to verify instrument stability. The performance report acquires five consecutive one-minute runs and calculates the percentage relative standard deviation (RSD) of the five measurements for each isotope. The RSD of the elemental analytes in the performance report must be <5%. If the performance report passes, proceed to (10.3). If the performance report fails, check:

a. Liquid uptake tubes for kinks or other damage

b. Condition and position of the peristaltic pump tubing

c. Tightness of the peristaltic pump clamp screws (these should be just tight enough to draw liquid through the tube smoothly)

d. Joints of all sample introduction components, ensuring a good seal

e. Nebulizer for blockage

f. Salt deposition on cones

Remedy the above as necessary and repeat the test. Note that retuning may be required if any sample introduction components are adjusted or replaced.

Note: Resolution set-up may require adjustment if the resolution check fails (see Appendix 5). Note that the quadrupole and hexapole bias strongly influence abundance sensitivity (Pole Bias should be kept >+4V and Hexapole Bias <-3V).

If the measured mass position for each mass in the performance report is not within ±0.1 amu of the nominal mass position, a new mass-calibration must be performed (see Appendix 6).

10.3. Sample Analysis

10.3.1. Open the method template by clicking on *Templates* and then <TESTAMERICA PITTSBURGH ICPMS ANALYSIS>. The method template will be opened. This contains all the saved analytical parameters and only the sample list need be amended.

10.3.2. Go to *Sample List*. This grid contains all the information about calibration, QC and samples to be run. The calibration and QC concentration information is already stored. Enter all unknown samples into the list in the appropriate order below the existing calibration and QC samples by overwriting the sample label fields. Delete any QC samples that do not apply to the required method. (If sample list changes are to be made permanent to the method, save the method as a *Template*, by going to *File*, *Save as Template*. Enter a new name to create an amended method, or use the same name to overwrite the current one.)

10.3.3. Once all the sample information is added, check the required autosampler positions have been correctly entered. Amend as necessary. To sequentially renumber positions, add the correct position required for the initiation of the sequence and right mouse click on the first correctly numbered cell. A pop-up menu will appear. Select *Renumber autosampler positions* from this. Ensure that all samples have one survey run and 3 main runs and a probe depth of 155mm.

10.3.4. Save the experiment run by clicking on the *File* menu, then *Save as*. Enter the required file name, e.g. *enviro090902* and click *Save*.

10.3.5. To print the sample list, go to *Reports* and check the *Sample List* box. Click the refresh icon. The sample list will be displayed in a printable format. Press the print icon. Note that this can only be done with PlasmaLab version 2.3 and above.

10.4. Loading the Autosampler

10.4.1. Pour the required samples into pre-cleaned 15ml polypropylene test tubes (5.1.4). To avoid contamination, a small amount of the solution to be analyzed can be poured into the tube and then discarded. This will rinse out any residual contamination.

10.4.2. Pour blanks, standards and QCs (positioned in rack 0) into pre-cleaned 50ml polypropylene tubes. To avoid contamination, a small amount of the solution to be analyzed can be poured into the tube and then discarded. This will rinse out any residual contamination. Note that **2% nitric acid** (7.1.4) is used as the calibration blank, ICB, and CCB.

10.4.3. For the **serial dilution** (“L”) sample(s), dispense 2.00±0.02 mL of the original sample into a pre-cleaned 15 mL polypropylene test-tube and add 8.00±0.08 mL of 2% nitric acid (7.1.4). Mix well. This is a 5-fold dilution.

10.4.4. Place the tubes for each sample into the appropriate position in the rack

according to the sample list. Note that the autosampler works on a two-dimensional grid position system by rack number (0-4). See Appendix 9 for autosampler position map.

10.5. Initiating Analysis

10.5.1. Place the sample probe into the autosampler arm and the internal standard probe into the internal standard solution.

10.5.2. Go to *Instrument*, *Tune* and click on the accessories dialog icon. Click on *Autosampler* and then on the chain icon to connect. The autosampler should initialize. Ensure that the probe is at the correct height by positioning it so that its tip just protrudes through the hole in the bottom of the arm. Click on the *Go to Wash* icon (faucet) to send the probe to the wash station. Ensure that the wash solution is being correctly delivered to the wash station via the peristaltic pump at the rear of the autosampler. Allow at least 2 minutes for the liquid to be delivered to the sample introduction system.

10.5.3. Click on the experiment to be run. Click the *Queue* icon and then *Append* and *OK*. The analysis has now been initiated.

10.5.4. To monitor the progress of the analysis, right-mouse click on the *MS* icon at the bottom-right of the screen and select *Open Service Window* from the pop-up menu. The Service Window hovers over the current application window until moved or closed and displays the current instrument activity. This window is also used **to stop an analysis** if required. This is done by clicking on the ***^{x}Q* icon**.

10.5.5. To view results as they are generated, click on the experiment icon and go to the *Results* tab. Click on the *Refresh* button or the refresh icon (green circular arrows on a page) to calculate the results from the data obtained.

10.5.6. To view calibration plots, click on the *Calibration Data* tab. The calibration for each analyte can be viewed by clicking on the required isotope in the *Analyte* box. Each subsequent set of calibrations (calibration block) can be displayed by selecting the required calibration block from the drop-down combo box, e.g. *FQ Block 1*, *FQ Block 2*, etc. FQ denotes a Fully-Quantitative calibration and SQ denotes a Semi-Quantitative calibration, i.e. a response curve generated from the *FQ* calibrations. The SQ response curve is used to calculate semi-quantitative concentrations if required.

10.5.7. To view data, click on the *Numerical Results* tab. The *Analyte Dilution Conc.* tab is a tabular display of the calculated corrected concentrations for each analyte. These values have been corrected for internal standardization, external drift correction (if used), and dilution (where entered). The *Mass Uncorrected ICPS* tab shows the uncorrected raw data for each measured mass in units of integrated counts per second (ICPS). The *Analyte ICPS* tab shows integrated counts per second data that has been mathematically corrected for blank deduction, internal standardization, drift correction (if used), and dilution (as appropriate). The *Survey* tabs show the data integrated from the survey scan for each sample. Any concentrations displayed in the survey page will be semi-quantitative only.

10.5.8. To edit the amount of data on screen (filter the results display), click on the filter icon (funnel and lightening). Alter the numerical values or the check boxes to select the required data to display and click on *OK*. To jump directly to a particular sample of interest, find the sample in the drop-down combo box at the top of the data display and click on it.

10.5.9. To display mass-spectra, click on the *Spectra* tab. Display the spectrum for a particular sample by double-clicking on the sample name in the selection box on the left of the screen. Note that several spectra may be overlaid by double-clicking on each sample to be displayed. To zoom into a particular area, click the zoom icon (magnifying glass) and click and drag on the spectral display to zoom into the required area. The dashed-lines represent data acquired in the analogue mode of the detector whilst the solid-lines represent pulse-count data. To remove the noise associated with analogue detection at low signal levels, point at the display and right-mouse click to bring up a menu. Go to *View Options* and then click on *Eliminate Analogue Noise*. To identify a peak, click on it and wait for the options for that mass to be displayed in the box above the spectral display. To fingerprint a spectrum, double click on the species to fingerprint in the options box. This will overlay the isotopic pattern for the selected species, based on the lowest relative intensity signal for the pattern masses. The spectra may be navigated by using the arrow buttons above the display. Allow the arrow cursor to hover over each button for an on-screen explanation of its function.

10.6. Post-Analysis Data Processing

10.6.1. Internal Standards

10.6.1.1. Check the internal standard recovery percentage for each internal standard isotope used for every sample. The percentage for each isotope must be within the range 30-120% for method 6020 and 60 – 125% for method 200.8.

10.6.1.2. If above 120%, check that the other internal standard isotopes show similar deviation. If not, this may be due to the presence of the internal standard element in the sample. This is particularly common with the isotopes of Li, Sc and Y in environmental materials. If this is the case, the affected internal standard isotope may be excluded for the sample affected, as follows. Go to the *Sample List*.

Find the sample affected and select it in the list by clicking on the box in the left-hand column. Click *Show Advanced* and go to *Internal Standards*. Click on *New Internal Standard Set*. Select the affected isotope(s) in the *Internal Standards* box on the right. Remove the affected isotope from the *Internal Standards* box by using the left hand arrow button (<<). Recalculate the results for this sample by going back to *Results* and clicking on *Refresh*.

10.6.1.3. If any internal standard isotope is outside the range 30-120% and all other internal standard isotopes show similar values for that sample, the instrument may have drifted, or the sample may be producing a

suppression or enhancement effect. Find the nearest blank following the sample in question and check its internal standard results. If these are similarly reduced or elevated, the instrument has drifted and the samples must be reanalyzed from the last compliant blank. If the blank does not exhibit similar drift, the sample must be producing a suppression or enhancement effect due to its matrix. In this case the sample must be re-analyzed after a five-fold (1+4) or a ten-fold (1+9) dilution to reduce the matrix effect.

10.7. General protocols

10.7.1. One time procedural variations are allowed only if deemed necessary in the professional judgment of supervision to accommodate variation in sample matrix, radioactivity, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using a Nonconformance Memo and is approved by a Technical Specialist and QA Manager. If contractually required, the client shall be notified. The Nonconformance Memo shall be filed in the project file.

10.7.2. Any unauthorized deviations from this procedure must also be documented as a nonconformance, with a cause and corrective action described.

10.7.3. An analytical run will consist of all customer samples and quality control samples analyzed under a daily initial calibration. Each new initial calibration will begin a new analytical run.

10.7.4. Type in the QC and sample information into the autosampler table.

10.7.5. In order to use the ICP-MS data upload program into LIMS, the following naming conventions must be followed:

- Samples are identified by the 5-character work order number
- Matrix spikes, duplicates, and matrix spike duplicates are identified by the 5-character work order number followed by S (matrix spike), D (matrix spike duplicate) or X (sample duplicate).
- Prep Blanks are identified by the 5-character work order number followed by B.
- LCSs are identified by the 5-character work order number followed by C (LCS) or L (LCS Duplicate).

10.8. Initial Calibration

10.8.1. Open a new dataset using the date and instrument in the title. For instance the first run (A) on instrument 2 on JAN 1, 2003 would be X30101A.

10.8.2. Open the appropriate method if one already exists or create a new one for the analytes to be quantitated in the run. Solicit the assistance of a senior ICP-MS operator in creating a new method.

10.8.3. See Tables 7, 8, and 9 for recommended isotopes and interference equations for

commonly analyzed elements.

10.8.4. If no recommended isotopes are given for the element to be analyzed, consult a senior ICP-MS operator or appropriate reference.

10.8.5. See Table 10 for commonly used internal standards.

10.8.6. All masses which could affect data quality should be monitored to determine potential interferences either simultaneously during an analytical run or in a separate scan.

10.8.7. Internal standards are added to all standards and samples by the instrument prior to analysis.

10.8.8. Use of an existing autosampler table is suggested. A read delay of 45 to 60 seconds is used between all analyses.

10.8.9. Calibration consists of a blank and a single calibration standard (STD1, see Table 2 for concentrations) in accordance with the manufacturer's procedure. Use the average of three integrations for both calibration and sample analyses.

10.9. The order of analysis for the initial QC samples and calibration should be:

1. Rinse
2. Performance Report (Tune Check)
3. STD1 (Calibration Standard)
4. STD2 (2x Calibration Standard)
5. STD3 (3X Calibration Standard)
6. ICV (Second source, must be ± 10% of true value)
7. ICB
8. CRI / RLV (Reporting Limit Verification Standard)
9. ICSA (Interference check solution.)
10. ICSAB (Interference check solution, ± 20% of true value)
11. CCV
12. CCB
13. Prep QC such as LCS or MB, followed by samples (up to 10 runs)
14. Rinse
15. CCV
16. CCB

10.9.1. To continue the analytical run, add an additional 10 runs followed by a rinse and

CCV/CCB, and repeat for up to 24 hours.

10.9.2. Analysis sequence when out-of-control QC is observed: Recalibrate and rerun all affected samples (including initial QC)

11. CALCULATIONS / DATA REDUCTION

11.1. All pertinent calculations are performed by the Plasma LAB software.

11.2. Reporting Requirements

11.2.1. Units are ug/L or mg/L for aqueous samples and mg/kg for soil samples and ug/wipe for wipe samples.

11.2.2. If dilutions were required due to insufficient sample, interferences, or other problems, the laboratory reporting limits are multiplied by the dilution factor.

11.2.3. For results less than 10, two significant figures will be reported. For results greater than or equal to 10, three significant figures will be reported. Refer to Policy QA-004 for additional information on significant figures and rounding.

11.2.4. Document any non-standard procedures or anomalies by using the anomaly program (Clouseau).

11.3. Data Package Requirements

11.3.1. A complete data package consists of: the daily tuning package, the method printout, run log, internal standard summary for 5.2 only, standards documentation, level 1 checklist, and all raw data.

11.3.2. Level I review will be completed by the analyst.

11.3.3. Level II review will be completed by a senior level laboratory analyst familiar with the technical aspects of ICP-MS and in accordance with the ICP-MS DATA REVIEW checklists. The instrument operator of an analytical run may not perform the Level II review for that run.

12. METHOD PERFORMANCE

Prior to analysis of any analyte using Method 6020, the following requirements must be met.

12.1. Method Detection Limit (MDL) - An MDL must be determined for each analyte/matrix prior to the analysis of any samples. MDL's must be redetermined on an annual basis as detailed in Policy S-Q-003 and further defined in PITT-QA-007.

12.1.1. On occasion, a non-routine analyte is requested by the client. In lieu of a full MDL study, a standard containing the non-routine analyte must be analyzed. The concentration of the standard must correspond to the reporting limit or ½ the reporting limit. This is to verify that the method can satisfactorily quantify the element near the chosen reporting limit. The recovery of the standard must be between 50% and 150% of the expected value. The standard analysis should be kept with the analytical data.

12.1.2. Methodologies for MDL assessment are detailed in SW-846 Chapter 1, method

6020 and in 40 CFR Part 136 Appendix B.

12.2. Initial Demonstration of Capability

12.2.1. For the standard analyte list, the initial demonstration IDC and method detection limit (MDL) studies described in this section must be acceptable before analysis of samples may begin.

12.2.2. For new analytes an MDL study should be performed and calibration curve generated before analyzing any samples.

12.2.3. Control Limits

12.2.4. Control limits are utilized for matrix spikes and laboratory control samples (LCS). These limits must be reviewed at least annually against current data.

QC Type	200.8	6020	ILM05.2
LCS	85 – 115	80 – 120	80 – 120
MS	70 – 130	75 – 125	75 – 125
RPD	± 20	± 20	± 20

12.2.5. All LCS and MS recoveries must be entered into QuantIMS or other database so that accurate historical control charts can be generated. For tests without a separate extraction, matrix spikes will be reported for all dilutions.

12.2.6. Refer to the QC program document (QA-003) for further details regarding control limits.

12.3. Training Qualification

12.3.1. The group/team leader has the responsibility to ensure that this procedure is performed by an associate who has been properly trained in its use and has the required experience.

12.4. Instrumentation Detection Limit (IDL) – IDL for each analyte must be determined for each analyte wavelength used on each instrument. The IDL must be determined quarterly for method 6020 for the standard analytes listed in Appendix A. For method 200.8 IDLs will be determined annually. If the instrument is adjusted in any way that may affect the IDL, the IDL for that instrument must be redetermined.

12.4.1. For 6020 the IDLs shall be determined by performing a blank analysis on 3 non-consecutive days with 7 consecutive measurements per day. The IDL is calculated by summing the standard deviations of the measurements from each day. For 200.8 the IDL is determined by performing 10 replicate blank analysis and mulitplying the resulting standard deviation by 3.

12.4.2. Each measurement must be performed as though it were a separate analytical sample.

12.4.3. Each measurement must be followed by a rinse and/or any other procedure normally performed between the analyses of separate samples.

12.4.4. The IDL measurement must consist of the same number of replicates used for analytical samples with the average result used for reporting.

12.4.5. **DoD samples cannot be analyzed without a valid IDL.**

12.4.6. **For DoD, the established IDL must be less than the MDL (see below) for each analyte.**

12.5. Linear Range Verification (LR) - The linear range is determined semi annually (2x/year) for each element on the standard list. Some regulatory programs, such as AFCEE, may require more frequent determinations.

12.5.1. To determine the linear range, analyze 3 standards at increasing concentration up to 90% of the last concentration where the element was within 10% of true value is considered the upper linear range.

12.5.2. An alternative is to prepare a higher concentration standard and run this in the analytical run. If this standard is within 10% of the expected value this value can be used as the upper linear range. If this option is chosen, then note the action in an anomaly.

13. POLLUTION CONTROL

13.1. It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i.e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage and reagent stability). Employees must abide by the policies in Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention."

14. WASTE MANAGEMENT

14.1. Waste management practices are conducted consistent with all applicable rules and regulations. Excess reagents, samples and method process wastes are disposed of in an accepted manner. Waste description rules and land disposal restrictions are followed. Waste disposal procedures are incorporated by reference to SOP PT-HS-001.

14.2. The following waste streams are produced when this method is carried out.

14.2.1. Acid waste consisting of sample and rinse solution. This waste is collected in waste containers identified as "Acid Waste", Waste #33. It is neutralized to a pH between 6 and 9 and then discharged down a lab sink.

14.2.2. Expired Metals Standards. This waste is collected in waste containers identified as "Acid Waste with Metals", Waste #6.

15. REFERENCES

15.1. Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW846, 3rd Edition, Final Update III, Method 6020, Inductively Coupled Plasma – Mass Spectrometry, Revision 0, September, 1994.

15.2. Thermo Electron X Series Users Manual

15.3. EPA Method 6020 CLP M, Version 8.

15.4. Methods for the Determination of Metals in Environmental Samples, Supplement 1 (EPA/600/R-94/111), Method 200.8, Determination of Trace Elements in Waters by Inductively Coupled Plasma - Mass Spectrometry, Revision 5.4, 1994

15.5. EPA Method 200.8 EMSL Office of Research & Development, Cincinnati, OH (Draft Method, Revision 4.3, August 1990).

15.6. QA-003, TestAmerica Pittsburgh QC Program.

15.7. PT-QA-009, Rounding and Significant Figures.

15.8. PT-QA-025, Implementation of the DoD QSM Version 3.

15.9. PITT-QA-007, Method Detection Limits.

16. METHOD MODIFICATIONS

16.1. Not applicable.

17. ATTACHMENTS

Table 1 – Standard Analyte List and Reporting Limits

Table 2 – Composition of the CAL Standard

Table 3 – Composition of the ICV Standard

Table 4 – Composition of the ICSA Standard

Table 5 – Composition of the ICSAB Standard

Table 6 – Common Molecular Ion Interferences in ICP-MS

Table 7 – Recommended Analytical Isotopes And Additional Masses That May Be Monitored

Table 8 – Recommended Isotopes And Additional Masses That May Be Monitored

Table 9 – Elemental Equations Used To Calculate Results

Table 10 – Internal Standards And Limitations Of Use

Appendix 1 Cleaning Procedure for Glass- and Plastic-ware

Appendix 2 Wash Solution Preparation Instructions

Appendix 3 Daily Instrument Maintenance

Appendix 4 Autotune and Performance Reports

Appendix 5 Resolution Setup

Appendix 6 Instrument Calibrations

Appendix 7 Sample Introduction Plumbing Diagram

Appendix 8 Procedure for Cleaning Sample Introduction Equipment and Cones

18. REVISION HISTORY

18.1. Revision 5, 5/19/08.

18.1.1. Renamed SOP as PT-MT-002.

18.1.2. Changed SOP format to correspond to corporate SOP format.

18.1.3. Corrected several typographical errors and incorrect Section references.

18.1.4. All changes have been highlighted throughout the document.

18.1.5. Updated SOP References

18.1.6. Corrected As and Ni RLs for water and soil.

Tables:

TABLE 1

STANDARD ANALYTE LIST AND REPORTING LIMITS*

Element	Symbol	CAS #	Aqueous RL mg/L	Aqueous QC SPIKE mg/L	Soil/Tissue RL mg/Kg	Soil/Tissue QC SPIKE mg/kg	Wipe RL ug/wipe	Wipe QC SPIKE ug/wipe
Aluminum	Al	7429-90-5	0.03	2.0	3.0	200	1.5	100
Antimony	Sb	7440-36-0	0.002	0.50	0.2	50	0.1	25
Arsenic	As	7440-38-2	0.001	0.04	0.1	4	0.05	100
Barium	Ba	7440-39-3	0.010	2.0	1.0	200	0.5	100
Beryllium	Be	7440-41-7	0.001	0.05	0.1	5	0.05	2.5
Boron	B	7440-42-8	0.005	1.0	0.5	100	0.25	50
Cadmium	Cd	7440-43-9	0.001	0.05	0.1	5	0.05	2.5
Calcium	Ca	7440-70-2	0.10	50	10.0	5000	5.0	2500
Chromium	Cr	7440-47-3	0.002	0.2	0.2	20	0.1	10
Cobalt	Co	7440-48-4	0.0005	0.5	0.05	50	0.025	25
Copper	Cu	7440-50-8	0.002	0.25	0.2	25	0.1	12.5
Iron	Fe	7439-89-6	0.05	1.0	5.0	100	2.5	50
Lead	Pb	7439-92-1	0.001	0.02	0.1	2	0.05	25
Magnesium	Mg	7439-95-4	0.10	50	10.0	5000	5.0	2500
Manganese	Mn	7439-96-5	0.0005	0.5	0.05	50	0.025	25
Molybdenum	Mo	7439-98-7	0.005	1.0	0.5	100	0.25	50
Nickel	Ni	7440-02-0	0.001	0.5	0.1	50	0.05	25
Potassium	K	7440-09-7	0.100	50	10.0	5000	5.0	2500
Selenium	Se	7782-49-2	0.005	0.01	0.5	1	0.25	100
Silver	Ag	7440-22-4	0.001	0.05	0.1	5	0.05	2.5
Sodium	Na	7440-23-5	0.10	50	10.0	5000	5.0	2500
Strontium	Sr	7440-24-6	0.005	1.0	0.5	100	0.25	50
Tin	Sn	7440-31-5	0.005	2.0	0.5	200	0.25	100

TABLE 1								
STANDARD ANALYTE LIST AND REPORTING LIMITS*								
Element	**Symbol**	**CAS #**	**Aqueous RL mg/L**	**Aqueous QC SPIKE mg/L**	**Soil/Tissue RL mg/Kg**	**Soil/Tissue QC SPIKE mg/kg**	**Wipe RL ug/wipe**	**Wipe QC SPIKE ug/wipe**
Titanium	Ti	7440-03-26	0.005	1.0	0.5	100	0.25	50
Thallium	Tl	7440-28-0	0.001	0.05	0.1	5	0.05	100
Vanadium	V	7440-62-2	0.001	0.5	0.1	50	0.05	25
Zinc	Zn	7440-66-6	0.005	0.5	0.5	50	0.25	25

***** *Note: These are the routine reporting limits for most sample types. Lower reporting limits may be achievable for special projects. Difficult sample matrices may cause reporting limits to be raised.*

TABLE 2			
Composition of the CAL Standard			
Element	**Concentration ug/mL**	**Element**	**Concentration ug/mL**
Ag	0.200	Mn	1.0
Al	1.00	Mo	0.200
As	0.200	Na	100
B	0.200	Ni	0.200
Ba	0.200	Pb	0.200
Be	0.200	Sb	0.200
Ca	100	Se	0.200
Cd	0.200	Si	10
Co	0.200	Sn	0.200
Cr	0.200	Sr	0.200
Cu	0.200	Ti	0.200
Fe	50	Tl	0.200
K	100	V	0.200
Mg	100	Zn	0.200

TABLE 3 Composition of the ICV Standard			
Element	Concentration ug/mL	Element	Concentration ug/mL
Ag	0.08	Mn	0.4
Al	0.4	Mo	0.08
As	0.08	Na	40
B	0.08	Ni	0.08
Ba	0.08	Pb	0.08
Be	0.08	Sb	0.08
Ca	40	Se	0.08
Cd	0.08	Si	4.0
Co	0.08	Sn	0.08
Cr	0.08	Sr	0.08
Cu	0.08	Ti	0.08
Fe	20	Tl	0.08
K	40	V	0.08
Mg	40	Zn	0.08

TABLE 4 Composition of the ICSA Standard			
Element	Concentration ug/mL	Element	Concentration ug/mL
Al	100	P	100
Ca	100	S	100
Fe	100	C	200
K	100	Cl^-	1000
Mg	100	Mo	2.0
Na	100	Ti	2.0

TABLE 5
Composition of the ICSAB Standard

Element	Concentration ug/mL	Element	Concentration ug/mL
Ag	0.02	Na	100
Al	100	Ni	0.02
As	0.02	Pb	0.02
B	0.05	Sb	0.02
Ba	0.02	Se	0.05
Be	0.02	Si	0.50
Ca	100	Sn	0.10
Cd	0.02	Sr	0.02
Co	0.02	Ti	2.0
Cr	0.02	Tl	0.02
Cu	0.02	V	0.02
Fe	100	Zn	0.025
K	100	P	100
Mg	100.0	S	100
Mn	0.0225	C	200
Mo	2.00	Cl-	1000

TABLE 6[1]

COMMON MOLECULAR ION INTERFERENCES IN ICP-MS

Molecular	Mass	Element	Molecular	Mass	Element
BACKGROUND MOLECULAR IONS					
NH^+	15		$^{38}ArH^+$	39	
OH^+	17		$^{40}ArH^+$	41	
OH_2^+	18		CO_2^+	44	
C_2^+	24		CO_2H^+	45	Sc
CN^+	26		ArC^+, ArO^+	52	Cr
CO^+	28		ArN^+	54	Cr
N_2^+	28		$ArNH^+$	55	Mn
N_2H^+	29		ArO^+	56	
NO^+	30		$ArOH^+$	57	
NOH^+	31		$^{40}Ar^{36}Ar^+$	76	Se
O_2^+	32		$^{40}Ar^{38}Ar^+$	78	Se
O_2H_+	33		$^{40}Ar_2^+$	80	Se
$^{36}ArH^+$	37				
MATRIX MOLECULAR IONS – Chloride					
$^{35}ClO^+$	51	V	$^{37}ClOH^+$	54	Cr
$^{35}ClOH^+$	52	Cr	$^{35}ClO^+$	51	V
$^{37}ClO^+$	53	Cr	$^{35}ClOH^+$	52	Cr
$Ar^{35}Cl^+$	75	As	$Ar^{37}Cl^+$	77	Se
MATRIX MOLECULAR IONS – Sulfate					
$^{32}SO^+$	48		$^{34}SOH^+$	51	V
$^{32}SOH^+$	49		SO_2^+, S_2^+	64	Zn
$^{34}SO^+$	50	V, Cr			
$Ar^{32}S^+$	72		$Ar^{34}S^+$	74	
MATRIX MOLECULAR IONS – Phosphate					
PO^+	47		PO_2^+	63	Cu
POH^+	48				
ArP^+	71				
MATRIX MOLECULAR IONS – Group I, II Metals					
$ArNa^+$	63	Cu	$ArCa^+$	80	
ArK^+	79				
MATRIX OXIDES[3]					
TiO	62-66	Ni, Cu, Zn	MoO	108-116	Cd
ZrO	106-112	Ag, Cd			

[1] From Method 200.8, Section 13.2.6
[2]Method elements or internal standards affected by the molecular ions.
[3]Oxide interferences will normally be very small and will only impact the method elements when present at relatively high concentrations. Some examples of matrix oxides are listed of which the analyst should be aware. It is recommended that Ti and Zr isotopes be monitored in solid waste samples, which are likely to contain high levels of these elements. Mo is monitored as a method analyte.

TABLE 7 RECOMMENDED ANALYTICAL ISOTOPES AND ADDITIONAL MASSES THAT MAY BE MONITORED [1]			
Isotope	Element of Interest	Isotope	Element of Interest
27	Aluminum [2]	80,**78**,**82**,**76**,**77**,74	Selenium
121,123	Antimony [2]	**107**,**109**	Silver [2]
75	Arsenic [2]	**23**	Sodium [2]
138,**137**,136,**135**,134,132,130	Barium [2]	203, **205**	Thallium [2]
9	Beryllium [2]	**51**,**50**	Vanadium [2]
114,112,**111**,110,113,116,106,**108**	Cadmium [2]	**66**, **68**	Zinc [2]
42,**43**,**44**,46,48	Calcium [2]	83	Krypton
52,**53**,**50**,54	Chromium [2]	72	Germanium
59	Cobalt [2]	139	Lanthanum
63,**65**	Copper [2]	140	Cerium
56,**54**,**57**,58	Iron [2]	129	Xenon
206,207,**208**	Lead [2]	**118**	Tin
24,**25**,**26**	Magnesium [2]	105	Palladium
55	Manganese [2]	47,**49**	Titanium
98,96,92,97,94,95	Molybdenum	125	Tellurium
58,**60**,62,**61**,64	Nickel [2]	69	Gallium
39	Potassium [2]	35,37	Chlorine

[1] *From Method 6020 CLP-M, Table 9*

[2] *Element approved for ICP-MS determination by SW846 Method 6020 CLP-M*

NOTE: Isotopes recommended for analytical determination are **bolded**.

TABLE 8			
RECOMMENDED ISOTOPES AND ADDITIONAL MASSES THAT MAY BE MONITORED			
Rare Earth Elements	**ICPMS Preferred Mass**	**Elemental Equations**	**Additional Masses**
Lanthanum	138.906		
Cerium	139.905		
Praseodymium	140.907		
Neodymium	141.908	-0.125266 * ^{140}Ce	142.910, 144.912
Samarium	151.920	-0.012780 * ^{157}Gd	144.912
Europium	152.929		
Gadolinium	157.924	-0.004016 * ^{163}Dy	156.934
Terbium	158.925		
Dysprosium	163.929	-0.047917 * ^{166}Er	
Holmium	164.930		
Erbium	165.930		
Thulium	168.934		
Ytterbium	173.939	-0.005935 * ^{178}Hf	171.937
Lutetium	174.941		

TABLE 8A
RECOMMENDED ISOTOPES AND ADDITIONAL MASSES THAT MAY BE MONITORED
Rare Earth Elements
Other Elements

TABLE 8A			
RECOMMENDED ISOTOPES AND ADDITIONAL MASSES THAT MAY BE MONITORED			
Rare Earth Elements			
Other Elements			
Boron	11.009		
Calcium	43.956		
Cesium	132.905		
Galium	68.926		
Germanium	71.922		
Gold	196.967		
Hafnium	177.944		176.944
Holmium	164.930		
Iridium	192.963		
Lithium	7.016		
Tungsten	183.951	-0001242* ^{189}Os	
Uranium	238.050		
Yttrium	88.905		
Zirconium	238.050		
Niobium	92.906		
Palladium	104.905		
Phosphorus	30.994		
Platinum	194.965		
Rhenium	186.965	-0.099379 * ^{189}Os	
Rhodium	102.905		
Rubidium	84.912		
Ruthenium	101.904	-0.045678 * ^{105}Pd	
Scandium	44.956		
Strontium	87.906		
Tantalum	180.948		

TABLE 8A			
RECOMMENDED ISOTOPES AND ADDITIONAL MASSES THAT MAY BE MONITORED			
Rare Earth Elements			
Other Elements			
Tellurium	127.905	-0.072348 * ^{129}Xe	
Thorium	232.03		

TABLE 9

ELEMENTAL EQUATIONS USED TO CALCULATE RESULTS

Element	Elemental Equation	Note
Al	(1.000) (^{27}C)	
Sb	(1.000) (^{121}C)	
As	(1.000) (^{75}C) - (3.1278)[^{77}C) - (1.0177)(^{78}C)]	Correction for chloride interference with adjustment for Se77. ArCl 75/77 ratio may be determined from the reagent blank.
Ba	(1.000) (^{137}C)	
Be	(1.000) (^{9}C)	
Cd	(1.000) (^{111}C) - (1.073) [(^{108}C) - (0.712) (^{106}C)]	Correction of MoO interference. An additional isobaric elemental correction should be made if palladium is present.
Cr	(1.000) (^{52}C)	In 0.4% v/v HCl, the background from ClOH will normally be small. However the contribution may be estimated from the reagent blank.
Co	(1.000) (^{59}C)	
Cu	(1.000) (^{63}C)	
Pb	(1.000) (^{206}C) + (1.000) (^{207}C) + (1.000) (^{208}C)	Allowance for isotopic variability of lead isotopes.
Mn	(1.000) (^{55}C)	
Mo	(1.000) (^{98}C) - (0.146) (^{99}C)	Isobaric elemental correction for ruthenium.
Ni	(1.000) (^{60}C)	
Se	(1.000) (^{82}C)	Some argon supplies contain krypton as an impurity. Selenium is corrected for Kr82 by background subtraction.
Ag	(1.000) (^{107}C)	
Tl	(1.000) (^{205}C)	
Th	(1.000) (^{232}C)	
U	(1.000) (^{238}C)	
V	(1.000) (^{51}C) - (3.127) [(^{53}C) - (0.113) (^{52}C)]	Correction of chloride inference with adjustment for Cr53. Cl0 51/53 ratio may be determined from the reagent blank.

TABLE 9

ELEMENTAL EQUATIONS USED TO CALCULATE RESULTS

Zn	(1.000) (^{66}C)	
Internal Standards		
Bi	(1.000) (^{209}C)	
In	(1.000) (^{115}C) -(0.0149) (^{118}C)	Isobaric elemental correction for tin.
Ge	(1.000) (^{72}C)	
Sc	(1.000) (^{45}C)	
Tb	(1.000) (^{159}C)	
Tm	(1.000) (^{169}C)	
Y	(1.000) (^{89}C)	

* Method elements or internal standards affected by the molecular ions. C = Calibration blank subtracted counts at specified mass.

TABLE 10

INTERNAL STANDARDS AND LIMITATIONS OF USE

Internal Standard	Mass	Possible Limitation
Lithium	6	a
Scandium	45	Polyatomic Ion Interference
Germanium	72	
Yttrium	89	a, b
Rhodium	103	
Indium	115	Isobaric Interference by Sn
Terbium	159	
Holmium	165	
Thulium	169	
Lutetium	175	
Bismuth	209	a

a May be present in environmental samples.

b In some instruments Yttrium may form measurable amounts of YO^+ (105 amu) and YOH^+ (106

amu). If this is the case, care should be taken in the use of the cadmium elemental correction equation.

Appendices

Appendix 1

Cleaning Procedure for Glass- and Plastic-ware

All glassware and plastic-ware coming into contact with samples, reagents and standards must be cleaned in the following manner. Plastic pipette tips may be cleaned in the same manner by soaking them in a suitable plastic container.

1) Completely fill the container to be leached with 10% nitric acid solution (6.1.5) and fit the lid.
2) Leave soaking for at least 12 hours.
3) Empty the container of acid and rinse thoroughly with laboratory water (6.1.1). Note that the acid may be collected and re-used until it becomes too contaminated.
4) Allow the vessel to air-dry in a clean area (preferably Class-1000 or better). If no such clean area is available, the container should be allowed to dry in the cleanest possible environment, or may be emptied of residual water as much as is possible and re-capped.
5) Containers should be capped ready for use and stored in the cleanest area available.
6) If pre-cleaned containers are to be stored for long periods (weeks to months) prior to use, it is most effective to store them full of laboratory water (6.1.1). This must be discarded and the containers rinsed thoroughly with laboratory water (6.1.1) and dried before use.

Appendix 2

Wash Solution Preparation Instructions (2% Nitric Acid (v/v))

A large volume of this solution is required for supply to the autosampler rinse station in order to wash the probe between samples. These instructions detail the preparation procedure for 2.5 L of this solution that is normally sufficient for one day of analytical use. The procedure may be scaled up or down as required.

1) Into a 2.5 L container (pre-cleaned as per Appendix 1), add 500±450 mL of laboratory water (6.1.1)
2) Add 50±10 mL of concentrated nitric acid (6.1.3)
3) Make to 2.50±0.25 L with laboratory water (6.1.1)
4) Mix well

Notes:

If preparing larger quantities simply scale-up quantities proportionally.

If analyzing for Ag, add hydrochloric acid at 1% by adding 50±10 mL of concentrated hydrochloric acid (6.1.2) after step 2.

Appendix 3

Daily Instrument Maintenance

1) Wipe all instrument, autosampler and surrounding bench surfaces with a damp wipe – continual cleanliness is important for the minimization of contamination
2) Check Wash Solution volume and remake if necessary (see Appendix 2)
3) Empty Waste Vessel according to laboratory disposal policy
4) Check the condition of all peristaltic pump tubes and replace if required (it is recommended to replace these daily although this may not be necessary with lower sample loads)
5) Check condition of sample introduction system and cones and clean and/or replace as necessary (see Appendix 8)
6) Ensure instrument fume-extraction system is operational

Appendix 4

Autotune and Performance Reports

Description

Autotune is a *PlasmaLab* software tool that allows the X Series to be optimized in a consistent, routine manner, giving reproducible levels of performance and saving the operator time and effort. It works by following a pre-defined sequence, optimizing individual instrument parameters in turn. Default sequences are provided with the software upon installation and a further customized sequence is provided on the CD accompanying this productivity pack.

Performance Reports are a *PlasmaLab* software tool that allows the X Series performance to be checked on a daily basis. The *Performance Report* can be set-up to give information about instrument sensitivity, stability, background, oxide species, doubly charged species, mass-calibration validity and peak resolution. Like *Autotune*, the *Performance Report* is user definable but defaults are provided with the software. Customized *Performance Reports* are provided on the CD accompanying this package.

The philosophy of use of these tools is as follows. After the sample introduction system or the cones have been removed and replaced or upon using the instrument for the first time or following major adjustments, the full *Autotune* sequence should be used to properly optimize the system. This takes about 15 minutes. From this, an *Autotune Update* sequence can be automatically created. This is a shortened version of the optimization sequence and will take about 5 minutes to run. The performance of the X Series is, in general, very stable from day-to-day, meaning that large amounts of optimization are not normally needed on a daily basis. To check whether optimization is needed, a *Performance Report* can be run initially. The results of this tell the operator if the system requires resolution adjustment, re-mass-calibration, or re-optimization. If the required sensitivity, background, stability or oxide performance is not satisfied, an *Autotune* should be run (the faster *Autotune Update* is normally sufficient). The *Performance Report* should then be repeated to ensure that the problem has been resolved.

Installing the EPA Autotune Sequence

To install the custom Autotune sequence, follow the instructions below:

1) Insert the CD in the CD ROM drive of the instrument operating PC. Wait for it to autorun and install the Productivity Pack by following the prompts after clicking on *Install*.
2) Ensure that PlasmaLab version 2.2 (or higher) has been installed
3) In PlasmaLab, go to *Instrument*, *Tune* and click on the down arrow button next to the *Autotune* icon (musical note).

4) Point to *Tools* in the menu and then select *Import Autotune Sequences*
5) Click *Next* in the Autotune Wizard
6) Click on *Browse* and find the path

C:/Program Files/ThermoElemental/PlasmaLab/Data

7) Select *EPA Autotune Sequence* and click on *Open*
8) Click on *Next*
9) Select *EPA – Xi Interface* and click on *Next*
10) Click on *Finish*

Installing the EPA Performance Reports

To install the custom Performance Reports, follow the instructions below:

1) Ensure the Pack is installed from the CD as described above
2) Ensure that PlasmaLab version 2.2 (or higher) has been installed
3) In PlasmaLab, go to *Instrument*, *Tune* and click on the down arrow button next to the *Performance Report* icon (musical note on page).
4) Point to *Tools* in the menu and then select *Import Performance Report*
5) Click *Next* in the Performance Report Wizard
6) Click on *Browse* and find the path for the CD ROM drive

   C:/Program Files/ThermoElemental/PlasmaLab/Data
7) Select *EPA 6020 Report* and click on *Open*
8) Click on *Next*
9) Select *EPA 6020 2.1* and click on *Next*
10) Click on *Finish*

To install the second Performance Report, follow instructions 1) to 10) above, selecting the alternative Performance Report name, i.e. *EPA ILM05_2D Report*.

Running Autotune from the Tune Page

To run an Autotune Sequence, follow the instructions below:

1) In PlasmaLab go to *Instrument*, *Tune* and click on the *Autotune* icon (musical note)

2) Select *Run an Existing Autotune Sequence* and click on *Next*

3) Select the required sequence, e.g. *EPA Xi Interface*, or *EPA Xi Interface – Update* and click on *Next*

4) Ensure that the indicated solution is being aspirated (through both probes if on-line internal standard addition is being used) and allow sufficient time for the solution to be transported into the nebulizer

5) Click on *Finish*

The selected Autotune sequence will now be run. To monitor its progress, observe the processes indicated at the bottom left of the PlasmaLab screen and open the Service Window (double-click on *MS* icon at the bottom right of the screen). A printable *Autotune Report* is generated at the end of the sequence. To continue, this report must be closed. To access this report upon closure, go to *Instrument*, *Configurations*, *Configuration Editor* and point to the appropriate *Instrument Settings* line. Open a pop-up menu by right-clicking and use the *View Tune Report* selection.

Running a Performance Report from the Tune Page

To run a Performance Report, follow the instructions below:

1) In PlasmaLab go to *Instrument*, *Tune* and click on the *Performance Report* icon (musical note on a page)

2) Select *Run an Existing Performance Report* and click on *Next*

3) Select the required sequence, e.g. *EPA ILM05 / 6020*, or *EPA 6020* and click on *Next*

4) Ensure that the indicated solution is being aspirated (through both probes if on-line internal standard addition is being used) and allow sufficient time for the solution to be transported into the nebulizer

5) Click on *Finish*

The selected *Performance Report* will now be run. To monitor its progress, open the Service Window (double-click on *MS* icon at the bottom right of the screen). A printable *Performance Report* is generated at the end of the sequence. To access this report upon closure, go to *Instrument*, *Tune*, and click on the down arrow to the right of the Performance Report icon. Point at *Tools* and then select *View Performance Report Results*. Select the required Performance Report to view and click *OK*.

Running Performance Reports and Autotune in an Experiment

It is also possible to automate the running of these procedures using an instrument setup sample within an experiment. To do this, insert an *Instrument Setup Sample* at the beginning of the Sample List by selecting the first sample and using a right-mouse-click menu to *Insert New Before*. Define the *Sample Type* for this new sample as *Instrument Setup* and click on *Show Advanced*. Click on the *Instrument Performance Tests* tab and setup the Performance Report and Autotune functions following the logic and using the drop-down combo boxes to select the next action. An example would be as follows:

Acquire Performance Report	*EPA ILM05.2 / 6020*
If mass calibration verification fails then	*Abort the Queue*
If the Performance Report fails then	*Autotune using EPA – Xi Interface*
If the Autotune fails then	*Abort the experiment*
If the Autotune passes then	*re-run the Performance Report*
If the Performance Report fails again then	*Abort the Queue*

When Performance Reports and Autotunes are acquired in this way, the results are stored as part of the experiment report. Note that since this method of acquiring the report is done using the autosampler, the solution concentration should be adjusted if on-line internal standard addition is to be used, e.g. if the addition dilutes the samples 1:1, the solution concentration should be doubled to get an accurate measure of sensitivity.

Appendix 5

Resolution Set up

With the instrument in *Operate* mode, aspirate 10-µg/L Tune solution (6.4.1) (through both probes if using on-line internal standard addition). Go to *Instrument*, *Tune* and stop the real time display (RTD) using the square stop icon. Change the display mode from *Time vs ICPS* to *ICPS on the full mass range*. Insert Be as the mass to monitor and change the spacing to 10, the dwell to 1 ms and the channels to 200. Disable all other masses in the grid. Restart the RTD by clicking on the triangular play icon. The software will display the scanned peak for mass 9, Be. To adjust the resolution, go to the *Global* tab and use the slider bar marked *Standard resolution*. This must be set up to give a peak width of less than 0.75 amu at 5% peak height. This is typically reached at a setting of between 100 and 200. If high-resolution mode is to be used, this can be setup by changing the resolution setting on the RTD to *High*. The High Resolution peak width is typically set at about 0.4 amu at 5% peak height, again with values typically between 100 and 200. Note that this method does not use High-resolution mode. Each resolution mode should be checked with several other masses across the mass range, typically 55Mn, 115In, 203Tl and 238U are used. Special attention should be paid to the resolution setup for Mn. This is measured at m/z 55, which is adjacent to both iron and argon oxide at mass 56. These high signals must be properly resolved from the low Mn signal in standard resolution mode. When the correct resolution settings are achieved, save the setting using the disk icon. **Note that a new mass-calibration must always be performed after adjustment of the resolution.**

18.2. Appendix 6

18.3. Instrument Calibrations

There are three instrument calibrations that are fundamental for obtaining good quality data on the X Series. These are:

1) Mass-calibration
2) Detector Plateau and Analogue voltage set routines
3) Detector cross-calibration.

Mass calibration sets the quadrupole scan parameters to give the correct measured mass positions. The detector plateau sets the optimum voltage on the ion or pulse counting section of the discrete dynode detector. The analogue voltage set routine applies an appropriate voltage on the analogue part of the detector to obtain a cross-calibration factor of approximately 20,000 for a mid-mass isotope. The detector calibration, or cross-calibration, calculates the correction factor, for each measured mass, between the two detector modes, pulse counting and analogue. All three calibrations may be performed in a single routine, or may be performed separately.

Mass Calibration

A mass-calibration must be performed whenever the resolution settings are adjusted, as this will affect the apparent mass position. Mass-calibration must be performed when the Performance Report shows that measured peak positions are >0.1 amu from their nominal position. Mass-calibrations are best performed using a solution containing as many elements as possible or with every analyte required for analysis at the very least. The solution should contain Li and U as these are used as low and high mass datum points. An appropriate concentration solution be used (one that gives between **100,000-1,500,000 cps** for each mass to be calibrated is appropriate). To perform a mass calibration, follow the instructions below.

1) Click *Experiment*
2) Select *Create New Experiment*
3) Click *OK*
4) Select the *Default* database
5) Click *Open*
6) Go to *Sample List*
7) Click the *Report* check box in the sample list grid
8) Use the drop-down combo box in the *Type* column to select *Instrument Setup*
9) Click on the *Show Advanced* button

10) Click on the *Instrument Calibrations* tab

11) Check the *Mass-Calibration* box

12) There is an option to *Update current mass-calibration* or form a *New mass-calibration*. Unless a major hardware change has been performed, the *Update current mass-calibration* option should be selected.

13) Click *Queue*

14) Save the experiment with an appropriate name, e.g. *masscal 090902* and click *Save*

15) Click *Append*

16) Click *OK*

Mass-calibration will now be performed.

To view the mass-calibration results, go to *Instrument*, *Calibrations*, *Mass-Calibration*. A mass-calibration for each of the two resolution modes is displayed in the graph of Peak Width and Error (y) versus Mass (x). The current mass-calibration is indicated by the row(s) displayed in green. To display alternative mass-calibrations, click on the appropriate date/time-stamped line in the top grid. The Performance Report function can be used to check mass-calibration accuracy (see Appendix 4).

Detector Plateau and Analogue Voltage Set

These routines can be performed separately, but it is advised to run them simultaneously as described here. The necessary frequency of these calibrations depends upon the amount of signal the detector is exposed to, i.e. how many samples are analyzed, which analytes and what concentrations. For most laboratories running a moderate sample load, this procedure may be run weekly. Up to three masses may be used in this procedure, however here, the use of a single mass is described. A solution that gives a countrate of between **100,000-1,500,000 cps** is appropriate. The default mass used here is indium (m/z 115), so this must be present in the solution for the routine to work. For an X5 instrument, an appropriate concentration would typically be between 10 and 100 µg/L, depending upon the sensitivity of the system. To perform this routine, follow the instructions below.

1) Click *Experiment*

2) Select *Create New Experiment*

3) Click *OK*

4) Select the *Default* database

5) Click *Open*

6) Go to *Sample List*

7) Click in the *Report* check box in the sample list grid

8) Use the drop-down combo box in the *Type* column to select *Instrument Setup*

9) Click on the *Show Advanced* button

10) Click on the *Instrument Calibrations* tab

11) Check *the Set analogue voltage* box

12) Set the *Number of iterations* to *2*

13) Click *Queue*

14) Save the experiment with an appropriate name, e.g. *plateau 090902* and click *Save*

15) Click *Append*

16) Click *OK*

The voltage setup will now be performed. To view the plateau, go to *Instrument*, *Calibrations*, *Detector Plateau*. A graph of signal intensity (y) versus voltage (x) is displayed. The "knee" inflexion on this plot corresponds to the plateau voltage. This is automatically selected and applied to the detector by the software.

Detector Calibration (Cross-Calibration)

This routine must be performed whenever the detector voltages are altered and daily prior to analysis of samples. The solution used must contain all the analytes to be measured as an absolute minimum. The more analytes present, the better. All analytes should ideally be set at a concentration that gives between **500,000 and 1,500,000cps**. To perform the detector calibration, follow the instructions below:

1) Click *Experiment*
2) Select *Create New Experiment*
3) Click *OK*
4) Select the *Default* database
5) Click *Open*
6) Go to *Sample List*
7) Click in the *Report* check box in the sample list grid
8) Use the drop-down combo box in the *Type* column to select *Instrument Setup*
9) Click on the *Show Advanced* button
10) Click on the *Instrument Calibrations* tab
11) Check the *Detector Calibrate* box
12) Click *Queue*
13) Save the experiment with an appropriate name, e.g. *xcal 090902* and click *Save*
14) Click *Append*
15) Click *OK*

The detector calibration will now be performed. To view the cross-calibration grap, go to *Instrument*, *Calibrations*, *Detector Cross-Calibration*. A graph of cross-calibration factor (y) versus mass (x) is displayed. **Use the data table to check that all analytical masses of interest have been used in the cross-calibration**. If not, the cross-calibration factor will be estimated from the equation of the graph. This may result in error.

All Routines in One

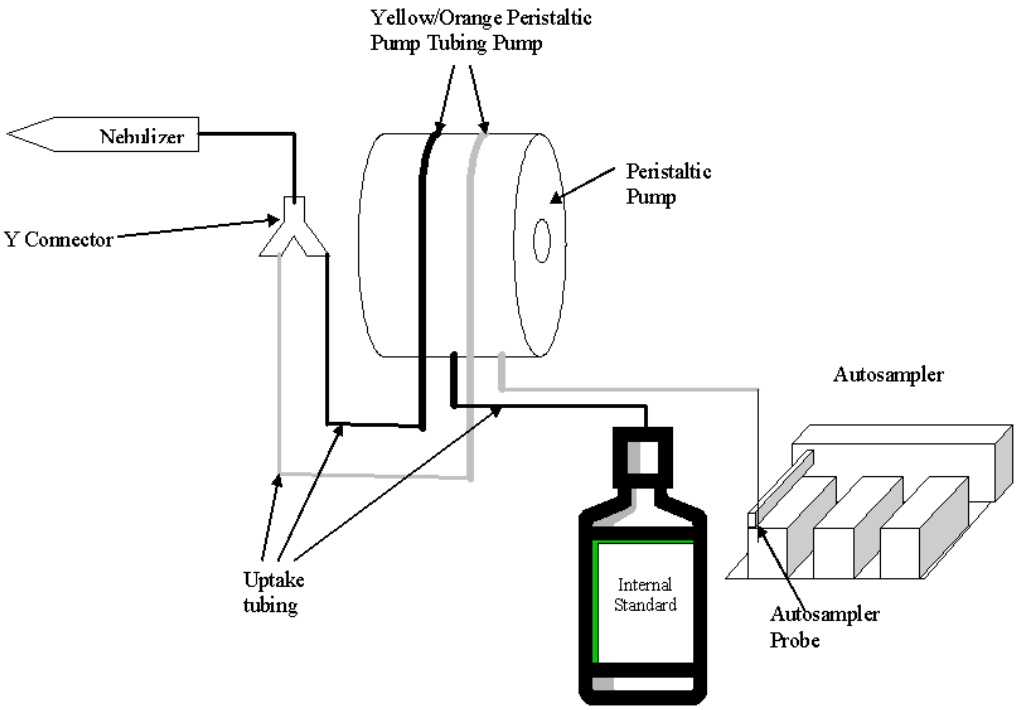
It is possible to run all three of the above routines on a single run if the solution used conforms to all of the criteria spelt out above. To do this, follow the instructions below.

1) Click *Experiment*
2) Select *Create New Experiment*
3) Click *OK*
4) Select the *Default* database
5) Click *Open*
6) Go to *Sample List*
7) Click in the *Report* check box in the sample list grid
8) Use the drop-down combo box in the *Type* column to select *Instrument Setup*
9) Click on the *Show Advanced* button
10) Click on the *Instrument Calibrations* tab
11) Check the *Mass calibration*, *Detector Calibrate* and *Set analogue voltage* boxes
12) Set the *Number of iterations* to *2*
13) Click *Queue*
14) Save the experiment with an appropriate name, e.g. *instr cal 090902* and click *Save*
15) Click *Append*
16) Click *OK*

The instrument calibrations will now be performed. Each parameter can be viewed as described above.

Appendix 7

Sample Introduction Plumbing Diagram



Appendix 8

Procedure for Cleaning Sample Introduction Equipment and Cones

1) Ensure that the instrument is in the *vacuum* or *shutdown* state (i.e. the plasma is OFF and the slide valve is SHUT)
2) Dismantle the sample introduction system as follows:

a) Remove the gas connection from the nebulizer

b) Remove the sample input plug from the nebulizer

c) Remove the metal clip on the spray chamber to elbow joint

d) Remove the drain plug from the spray chamber

e) Slide the spray chamber and nebulizer away from the elbow

f) Carefully slide the nebulizer out of the spray chamber and set both pieces aside in a safe place

g) Open the torch box and the internal Faraday cage

h) Pull the gas connections away from the torch

i) Undo the torch catch

j) Remove the metal clip on the elbow to torch joint

k) Carefully remove the torch from the load coil and set aside in a safe place

l) Remove the elbow by sliding it out of the torch box bulkhead toward spray chamber end

m) Slide the torch box away from the mass spectrometer to reveal the interface

n) Use the flat metal cone tool to undo the locking ring over the sample cone

o) Carefully remove the sample cone and set aside in a safe place

p) Carefully unscrew and remove the skimmer cone from the interface using the cylindrical aluminium tool and set aside in a safe place

3) Clean the cones as follows.

a) Carefully place the cones into a large beaker and fill with sufficient 0.05% nitric acid to cover – CAUTION: Stronger acids will corrode the cone material and reduce lifetime

b) Place the beaker in an ultrasonic bath for about 10 minutes or until surface deposition has been removed

c) Carefully remove the cones from the solution and rinse thoroughly with deionised water

d) Allow the cones to air-dry prior to refitting

4) Clean the sample introduction equipment as follows.

e) Carefully place the glass sample introduction components into a large beaker and fill with sufficient 10% nitric acid to cover all components

f) Place in an ultrasonic bath for between 20 minutes and 1 hour

g) Carefully remove the glass components and rinse thoroughly with deionised water

h) Allow to air-dry prior to refitting

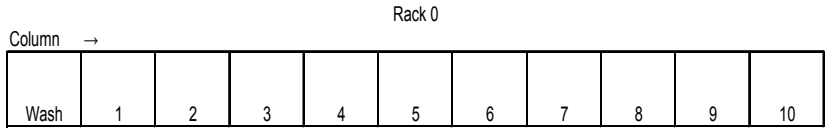
5) Reassemble the components in the reverse order to disassembly

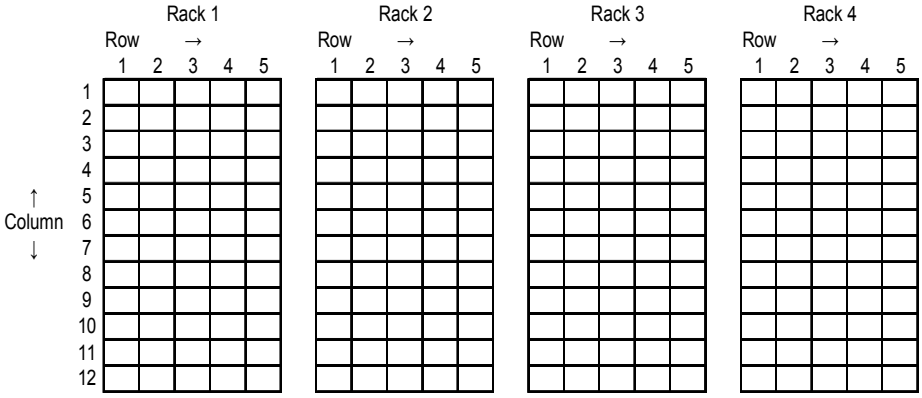
Note: Occasionally, glass sample introduction components crack when the ultrasonic cleaning procedure is used. To avoid this, the components may be soaked in acid, as above, for 12 hours, without ultrasonic treatment.

Thermo Electron cannot take any responsibility for any breakage that occurs during cleaning.

Appendix 9

Autosampler Position Map





NB: This map is only applicable for CETAC ASX-500/510 autosamplers fitted with 60 position racks.

Appendix 10

ILM05.2D Contract Required Quantitation Limits (CRQLs)

Analyte	CRQL (µg/L)
Al	30
Sb	2
As	1
Ba	10
Be	1
Cd	1
Ca	(100)
Cr	2
Co	0.5
Cu	2
Fe	(50)
Pb	1
Mg	(100)
Mn	0.5
Ni	1
K	(100)
Se	5
Ag	1
Na	(100)
Tl	1
V	1
Zn	2

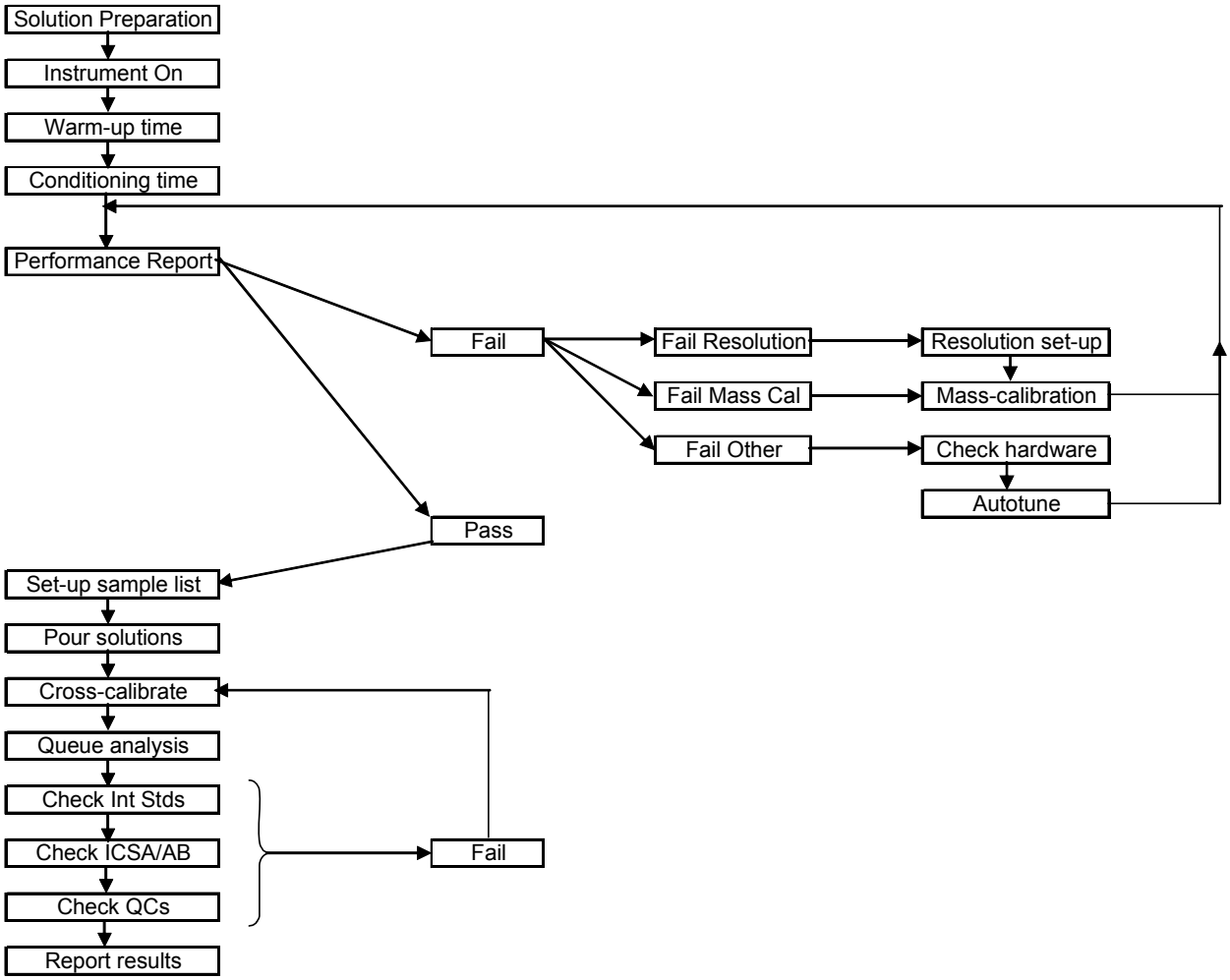
CRQLs given in parentheses are not specified for ICP-MS in EPA document ILM05.2 and are for ICP-AES. This is for information only.

Appendix 11
Spiking Levels

(Concentration in Final Solution Based on Instructions Within this Document)

Analyte	Spike Value (µg/L)
Al	2000
Sb	500
As	40
Ba	2000
Be	50
Cd	50
Cr	200
Co	500
Cu	250
Pb	20
Mn	500
Ni	500
Se	10
Ag	50
Tl	50
V	500
Zn	500

Appendix 12
Work Flow-Chart



Appendix 13
Glossary of Abbreviations

QC Code	QC Name	Purpose	Frequency	Limits
ICV	Initial Calibration Verification	checks the calibration against a second calibration source	After initial calibration	90-110%
ICB	Initial Calibration Blank	initial check of read-back at blank level	After initial calibration	<CRQL (1)
CRI	Contract Required Quantitation Limit Check	checks accuracy at the required limit of quantitation	After each calibration and every 20 samples	50-150% (1)
ICSA	Interference Check Solution A	checks for freedom from interference	After initial calibration	±3CRQL or ±20% of the true value (whichever is the greater) (1)
ICSAB	Interference Check Solution AB	checks that analytes are accurately measured in an interference-producing matrix	After initial calibration	80-120% of true value
CCV	Continuing Calibration Verification	a continuing periodic check on accuracy and drift	After each calibration and every 10 samples	90-110%
CCB	Continuing Calibration Blank	a continuing periodic check on the read-back at blank levels	After each calibration and every 10 samples	<CRQL (1)

QC Code	QC Name	Purpose	Frequency	Limits
PDS	Post Digestion Spike	checks the recovery of analytes spiked into an unknown sample after preparation (digestion)	Once every 20 samples per matrix	75-125%
DUP	Duplicate	checks the reproducibility of results by analyzing an unknown sample in duplicate	Once every 20 samples per matrix	±20% Relative Percentage Difference (RPD)
SER	Serial Dilution	checks for matrix effects by assessing the variation of results for an unknown sample before and after dilution	Once every 20 samples per matrix	±10% of the original undiluted result after dilution correction
LCS	Laboratory Control Sample	checks the accuracy of the entire analytical process	Once every 20 samples per matrix	80-120%

(1) For specific DoD requirements, refer to PT-QA-025.

APPENDIX 34
SOP FOR THE DETERMINATION OF TRACE ELEMENTS IN WATER BY ICP-MS BY EPA 200.8 (BR-ME-006, REV. 2) (TEST AMERICA-BURLINGTON)

Title: DETERMINATION OF TRACE ELEMENTS IN WATER BY ICP-MS EPA Method 200.8

Approval Signatures:

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Quality Assurance Manager

Dan Helfrich
Health & Safety Coordinator

Approval Date: April 20, 2009

Facility Distribution No. Electronic **Distributed To: Facility Intranet**

The controlled copy of this SOP is the PDF copy of the SOP that is posted to the laboratory's SOP Directory. Printed copies of this SOP or electronic copies of this SOP distributed outside the facility are considered uncontrolled.

1.0 Scope and Application

This SOP describes the laboratory procedure for the determination of total recoverable and dissolved elements in potable water samples by Inductively Coupled Mass Plasma- Mass Spectrometry (ICP-MS).

1.1 Analytes, Matrix(s), and Reporting Limits

This procedure may be used for a variety of matrices including: potable and non-potable water.

The list of elements that can be determined from this procedure along with the associated reporting limit (RL) is provided in Section 18.0, Table 1.

2.0 Summary of Method

Sample Preparation:

- Total Recoverable: An aliquot of a well-mixed sample is gently refluxed with nitric and hydrochloric acids then cooled and adjusted to a final volume of 100 mL.

- Dissolved Metals: An aliquot of filtered and acidified sample is taken for direct analysis. Direct analysis (without digestion) of an unfiltered, acidified sample aliquot may also be performed where the turbidity of the sample is < 1 NTU.

Analysis:

The prepared sample is transported by argon gas to a plasma torch. The ions produced are introduced via direct interface into a mass spectrometer and detected by an electron multiplier. The characteristic emission spectra are sorted according to their mass-to-charge ratios and the ion information is processed by the instrument's data handling system, which also recognizes and accounts for interference. Internal standards are used to monitor instrument drift, suppression or enhancement of the instrument response caused by sample matrix.

The SOP is based on the following reference method:

- EPA Method 200.8, Revision 5.4. EMMC Version, USEPA Office of Research and Development.

If this SOP includes modifications to the above referenced test method, these modifications will be listed in Section 16.0 of this SOP.

3.0 Definitions

The definitions for general laboratory terms are provided in Appendix B.

Total Recoverable Metal: The concentration of analyte determined either by "direct analysis" of an unfiltered, acid preserved potable water sample with a turbidity of < 1 NTU or by analysis of a solution extract of an unfiltered aqueous sample following digestion by refluxing with hot dilute mineral acids.

Dissolved Metal: The concentration of metals determined in a potable water that will pass through a 0.45µm filter prior to sample acidification.

4.0 Interferences

Isobaric Elemental Interferences are caused by isotopes of different elements that form singly or doubly charged ions of the same nominal mass-to-charge ratio and cannot be resolved by the mass spectrometer. Correction for this interference is handled by the data system and is accomplished by measuring the signal from another isotope of the interfering element and subtracting the appropriate signal ratio from the isotope of interest.

Abundance Sensitivity is a property that defines the degree to which the wings of a mass peak contribute to adjacent mass. The abundance sensitivity is affected by ion energy and mass filter operating pressure. Wing overlap interferences may result when a small ion peak is being measured adjacent to a large one. The potential for these interferences should be recognized and the spectrometer resolution adjusted to minimize occurrence.

Isobaric Polyatomic Ion Interference is caused by ions consisting of more than one atom, which have the same mass-to-charge ratio as the isotope of interest and cannot be resolved by the mass spectrometer. These interferences should be recognized, and when they cannot be avoided by the selection of alternative isotopes, appropriate corrections should be made to the data. Instrument operating parameters should be set to conditions that will minimize this phenomenon.

Physical interferences such as a change in viscosity, surface tension and dissolved solids are known to affect instrument responses to certain samples. These physical effects can be reduced by dilution, matrix matching, as well as not allowing dissolved solids within the samples to exceed 0.2% (w/v).

Memory interferences result when isotopes of elements in a previous sample contribute to the signals measured in a new sample. An active rinse monitoring cycle is employed by the software and will not allow the analysis of the next sample until levels drop below those of the determined baseline. The analytes chosen for this are B, Al, Ag, and Sb at masses 11, 27, 107, and 123, respectively. The minimum rinse time is set at 120 seconds. Monitoring the three replicate integrations that are used for data acquisition can also help identify memory interference.

Polyatomic Interference: Nitric acid is preferred for ICP-MS in order to minimize polyatomic interferences known in the presence of the chloride ion. Hydrochloric acid is required to maintain stability in solutions containing antimony and silver. Corrections for chloride polyatomic interferences are applied to data regardless of whether hydrochloric acid is used in digestion, as the chloride ion is common in environmental samples.

5.0 Safety

Employees must abide by the policies and procedures in the Corporate Environmental Health and Safety Manual (CW-E-M-001) and this document. This procedure may involve hazardous material, operations and equipment. This SOP does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, gloves, lab coats and closed-toe, nonabsorbent shoes are a minimum.

5.1 Specific Safety Concerns or Requirements

Samples that contain high concentrations of carbonates or organic material or samples that are at elevated pH can react violently when acids are added. Protective clothing such as a lab coat, safety glasses and latex gloves must be worn while performing this procedure.

The ICP plasma emits strong UV light and is harmful to vision. All analysts must avoid looking directly at the plasma.

5.2 Primary Materials Used

Table 2, Section 18.0 lists those materials used in this procedure that have a serious or significant hazard rating along with the exposure limits and primary hazards associated with that material as identified in the MSDS. **NOTE: This list does not include all materials used in the method.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

6.0 Equipment and Supplies

Catalog numbers listed in this SOP are subject to change at the discretion of the vendor. Analysts are cautioned to be sure equipment used meets the specification of this SOP.

6.1 Miscellaneous

- Argon Gas Supply: High purity grade (99.99%), Vermont Air Gas or equivalent.
- Block Digester capable of maintaining temperature of 95°C, Environmental Express or equivalent.
- 125 mL, Polyethylene Digestion Vessel with polyethylene, ribbed watch glasses, Environmental Express or equivalent.
- Borosilicate Solid Watch Glass, Environmental Express or equivalent.
- Adjustable Pipettes: Calibrated daily at volumes bracketing the points of use, Finnpipette or equivalent.
- Filter Paper, Whatman No. 42 or equivalent
- Class A, Volumetric Flasks.
- Filter Paper, Whatman No. 42 or equivalent

6.2 Analytical System

- Inductively Coupled Plasma Mass Spectrometer Analytical System capable of scanning a mass range of 5-250 amu with a minimum resolution capability of 0.9 amu peak width at 5% peak height such as the Thermo Electron X5 ICP-MS or equivalent.

- Cetac ASX-500 autosampler, or equivalent.

- Data acquisition and reporting: Dell Pentium 4 PC, PlasmaLab software system; build version 2.3.0.161, EISC MARRS data reporting software.

7.0 Reagents and Standards

7.1 Reagents

Due to the sensitivity of the ICP/MS, all reagents must be high-purity whenever possible. All acids used for this procedure must be ultra high-purity grade suitable for trace metal analysis.

- Reagent Water

- Nitric Acid, concentrated (HNO_3): JT Baker or equivalent

  Nitric Acid Solution (1:1): Add 10 L of concentrated nitric acid to a 30 L carboy that contains 10 L of reagent water. Assign an expiration date of one year and store this solution at room temperature.

  Nitric Acid Solution (2% v/v): Slowly add 20 mL of concentrated nitric acid to 980 mL of reagent water. Assign an expiration date of one year and store this solution at room temperature.

- Hydrochloric Acid, concentrated (HCl): JT Baker or equivalent

  Hydrochloric Acid (1:1): Add 10 L of concentrated HCl to a 30 L carboy that contains 10 L of reagent water. Assign an expiration date of one year and store this solution at room temperature.

7.2 Standards

Purchase stock standard solutions from commercial vendors and from these, prepare calibration and working standards by diluting a known volume of stock standard in an appropriate acid to the final volume needed to achieve the desired concentration. The recommended formulation for each standard used in this procedure is provided in Appendix A along with the recommended source materials, expiration dates and storage conditions.

8.0 Sample Collection, Preservation, Shipment and Storage

The laboratory does not perform sample collection so these procedures are not included in this SOP. Sampling requirements may be found in the published reference method.

Listed below are minimum sample size, preservation and holding time requirements:

Matrix	Sample Container	Minimum Sample Size	Preservation	Holding Time[1]	Reference
Water	Glass or plastic	500 mL	Preserve with nitric acid to pH<2.	180 days	EPA 200.8

[1]Holding time is determined from date of initiation of collection.

For dissolved metals, immediately after sample collection or as soon as possible thereafter, the samples should be filtered through a 0.45 um then acidified with 1:1 ntiric acid to a pH <2.

Unless otherwise specified by client or regulatory program, after analysis, samples and extracts are retained for a minimum of 30 days after provision of the project report and then disposed of in accordance with applicable regulations.

9.0 Quality Control

9.1 Sample QC

The laboratory prepares the following quality control samples with each batch of samples.

QC Item	Frequency	Acceptance Criteria
Preparation Blank (PB)	1 in 20 or fewer samples	See Table 3
Laboratory Control Sample (LCS)	1 in 20 or fewer samples	See Table 3
Matrix Spike(s) (MS)	Per Batch	See Table 3
Sample Duplicate (SD)	Client Request	See Table 3

9.2 Instrument QC

The following instrument QC is performed:

QC Item	Frequency	Acceptance Criteria
Tune	Daily	See Section 10.0
Initial Calibration (ICAL)	Initially; when ICV or CCV fail	See Section 10.0
Second Source Calibration Verification (ICV)	Once, after each ICAL	See Section 10.0
Instrument Performance Check (CCV)	Daily, every 10 samples, end of sequence	See Section 10.0
Internal Standard	Every standard and sample	See Section 10.0

10.0 Procedure

10.1 Instrument Operating Conditions & Pre-Calibration Routine

Set the instrument operating conditions using the instructions provided by the instrument manufacturer. Use a rinse cycle time of 120 seconds between each acquisition to remove traces of the previous sample (rinse blank).

Allow the instrument to warm-up for at least 30 minutes. Check the pump tubing to ensure the flow to the nebulizer and drain flow is smooth. If the flow is erratic, check the tubing placement on the pump rollers and replace, as necessary.

Perform cross calibration, initial mass calibration and resolution checks in the mass regions of interest using the tune solution. If the mass calibration has shifted more than 0.1 amu from the true value, adjust mass calibration to the correct value. Verify resolution to be less than 0.75 amu at 5% peak height.

Re-determine detector-mass calibration and cross calibration as needed or whenever a major change (i.e. installation of new detector) in instrumentation is made.

Prepare and analyze the tune standard consecutively five times. The recommended components and concentration of the tune solution is given in Appendix A. The percent standard deviation of the absolute signals for all analytes in the tune standard solution must be less than or equal to 5% in order to proceed. If criterion is not met, repeat the tune procedure.

10.2 Initial Calibration (ICAL)

The calibration routine used by the laboratory is consistent with Method B of the reference method where the introduction of internal standard is achieved prior to nebulization using a peristaltic pump and a mixing coil. The internal standard association for each element are provided in Table 1A. Internal standards are associated with elements based on mass to charge ratio and ionization potential. An element may be re-associated to another internal standard (as long as there is not more than a difference of 50 amu between isotopes) in the event of naturally occurring contribution to internal standard response, most notably Y and Li suspected interference, or suspected decrease in ionization ability of the system, e.g. high plasma load. Document any changes to the internal standard association in the analytical records and include an explanation in the narrative notes to the laboratory project manager (PM).

Immediately following the tune standard calibrate the instrument with a calibration blank and three calibration standards. The recommended components and concentration of the calibration standards are given in Appendix A.

Transfer ~40 mL of each calibration standard into individual, labeled autosampler tubes. For the calibration blank use ~ 2% nitric acid solution. Acquire three replicate integrations and use the average of the three integrations for instrument calibration and quantification. The correlation coefficient for the curve for each element must be >0.995.

10.2.1 Second Source Calibration Verification (ICV)

Immediately after each calibration and prior to the analysis of any other QC or field samples, verify the accuracy of the initial calibration by analyzing a second source standard.

Prepare the ICV using the formulation provided in Appendix A. Transfer ~40 mL of the standard into an individual, labeled autosampler tubes. Analyze the standard and acquire the result. The criterion for the ICV is given in Table 3.

10.2.2 Instrument Performance Check (CCV)

After the ICV, re-analyze each of the three calibration standards to verify instrument stability and re-analyze the 2nd level calibration standard after every 10th injection and at the end of the analytical sequence to monitor for drift.

Note: The analysis of the three calibration standards after the ICV may be eliminated when specified on a project basis.

Transfer enough of each calibration standard into the autosampler tubes to ensure sufficient volume during the analytical sequence. After every 10 samples, the autosampler is programmed to return to the CCV solution to inject another aliquot.

The criterion for the calibration verification checks (CCV) is given in Table 3.

10.2.3 Linear Dynamic Range Check (LDR)

Check the linear dynamic range every 3 months by analyzing the high calibration standard. The formulation for the preparation of the calibration standard is provided in Appendix A. Transfer ~40 mL of the prepared standard into a clean and labeled autosampler tube. Analyze the standard as an "unknown" sample.

NOTE: Although the laboratory establishes an LDR and checks the LDR every 3 months, the upper range of calibration is routinely used to determine the need for sample dilution.

10.3 Sample Preparation

10.3.1 Dissolved Metals

If the sample was filtered and preserved with nitric acid in the field, the sample is ready for analysis as received. Transfer 8 mL of sample into an autosampler tube and proceed to Section 10.4.

Note: The pH of the sample is checked upon receipt in sample management. If the pH is not <2, additional preservative is added and the sample is held for 24 hours prior to analysis.

If the sample is to be analyzed for dissolved metals, filter the sample through a 0.45 um membrane filter than acidy the sample to a pH <2 with nitric acid. After preservation the sample must be held for a minimum of 16 hours before digestion.

10.3.2 Total Recoverable Metals

If the sample is drinking water and the turbidity of the sample is < 1 NTU, proceed to Section 10.4.

To check Turbidity:

Allow the Turbidimeter to warm up and the samples to come to room temperature.

Prepare and analyze the method blank by pouring approximately 40 mL of reagent water into a cuvette. Twist the cuvette cap to secure and place the cuvette in the turbidimeter. Record the reading on the bench sheet. Remove the cuvette, empty the contents and wipe the outside of the cuvette with a Kimwipe to remove any residue. Repeat for each field sample. Be sure to agitate the sample prior to transferring the sample aliquot to the cuvette.

For non-potable water or drinking water samples where turbidity is > 1 NTU prepare the samples for digestion as follows:

Note: The pH of the sample is checked upon receipt in sample management. If the pH is not <2, additional preservative is added and the sample is held for 24 hours prior to analysis.

1) Transfer 100 mL of the sample to a polyethylene digestion vessel. Smaller sample volumes may be used, when necessary. Always consult with the department manager prior to reducing the sample volume.
2) Use 100 mL of reagent water for the method blank (MB). To prepare the LFB (LCS), transfer

1 mL of the Intermediate ICV/Aqueous LCS standard to a labeled digestion vessel and dilute the solution to 100 mL with reagent water. To prepare the matrix spike (MS) transfer 100 mL of the parent sample to a polyethylene digestion vessel and add 1 mL of the matrix spike solution to the sample.

3) Add 2 mL of 1:1 nitric acid solution and 1 mL of 1:1 hydrochloric acid solution to each digestion vessel. Place the vessels in the block digestor set to a temperature no higher than 85°C. Record the temperature reading from the calibrated block digestion thermometer on the digestion log.

4) Reduce the volume of the sample aliquot to ~20 mL. The reduction of the sample generally takes about two hours. ***Do not allow the sample to go dry and do not boil the sample.*** When the sample volume has reached ~ 20 mL, cover the digestion vessel with a solid watch glass and allow the digestate to gently reflux for approximately 30 minutes at a temperature of 95°C. ***Avoid vigorous boiling of the sample and do not allow the sample to go dry.***

5) Remove the vessel from the block digestor and allow the sample to cool. Wash down the vessel walls and watch glass with reagent water and adjust the digestate to a final volume of 100 mL with reagent water. Allow any undissolved material to settle overnight. The samples are now ready for analysis.

10.4 Sample Analysis

If samples with <1 NTU are to be run directly, transfer 10 mL of each sample to individual autosampler tubes and add 0.2 mL of concentrated nitric acid to each to yield 2% nitric concentration in each sample.

If samples have been digested, transfer approximately 10 mL of each digestate to individual autosampler tubes.

Place the extra autosampler sipper into the internal standard solution bottle.

Allow the instrument to become thermally stable prior to analysis. Create a new autosampler template on the instrument PC and enter the sample Ids in the order of analysis.

An example analytical sequence that includes initial calibration (ICAL) is provided in the following table:

Example Analytical Sequence

Injection Number	Lab Description
	Tune
1	Calibration Blank
2	Calibration Standard #1
3	Calibration Standard #2
4	Calibration Standard #3
5	ICV
6	CCV (CAL #1)
7	CCV (CAL #2)
8	CCV (CAL #3)
9-18	10 Samples*
19	CCV (CAL #2)
20-29	10 Samples*

30-End	Continue CCV/ Sample Sequence

**The number of samples between each CCV/CCB (10) includes the method blank, laboratory control sample, matrix spike(s) and sample duplicate.*

Place the samples and standards in the position on the autosampler rack that corresponds to their assigned position in the autosampler template. Place the autosampler rack in the autosampler tray and initiate the software macro to begin analysis.

11.0 Calculations / Data Reduction

11.1 Quantitative Identification

The data processing software is configured to acquire three replicate integrations and uses the average of the three integrations for all QC and sample analyses for instrument calibration and quantification. The software also performs correction for internal standardization.

11.2 Calculations

See Appendix C.

11.3 Data Review

11.3.1 Primary Review

Review the results against the criteria given in Table 3 and perform corrective action as needed. If corrective action is not taken document the situation with a nonconformance report (NCR) and provide technical justification for the decision to proceed with analysis in the NCR. If corrective action is not successful, provide explanation as appropriate in the NCR.

If the MB concentration is above 2.2 times MDL or is greater than 1/10 the concentration measured in any sample investigate the source of contamination, eliminate the problem and remake and reanalyze the MB along with associated samples. Otherwise corrective action is not required unless specified on a project basis.

Check the internal standard response. The absolute response of any one internal standard must not deviate more than 30 to 120% of the original response in the calibration blank. If the internal standard is not within this criterion, perform a 1:2 dilution on the associated samples and repeat analysis. If the internal standard still fails at dilution, report the results from the original analysis. Document the situation with a NCR and include a discussion of the internal standard failure in the narrative notes to the PM.

Dilute and reanalyze any samples for which a result exceeds the upper calibration range.

NOTE: The laboratory routinely dilutes samples whose results exceed the upper calibration range but for some project, the LDR may be the desired decision point for dilutions. Either option is considered acceptable.

Transfer the data to the NT server then transfer the data from the network server into the MARRS data processing software program. Forward the digestion log, instrument run logs and the associated raw data to the Inorganic Data Review department for secondary data review and report generation.

11.3.2 Secondary Data Review

Spot-check analytical results using the equations provided in Appendix C.

Verify that the performance criteria for the QC items listed in Table 3 were met. If the results do not fall within the established limits verify the recommended corrective actions were performed. If corrective action was not taken or is unsuccessful, ensure the situation is documented with a nonconformance report (NCR) and ensure data is qualified accordingly. Report the nonconformance in the narrative note program.

11.4 Data Reporting

Unless otherwise specified on a project basis, report data as follows:

- Report target compound concentrations above the reporting limit (RL) as the value found without data qualifier(s). The unadjusted RLs are provided in Table 1.

- Report concentrations less than the MDL to the adjusted RL with a "U" data qualifier. Adjust the RL as needed to account for dilution.

- Report concentrations between the MDL and the RL as the value found qualified with a "J" flag to indicate the data is estimated.

If the sample was analyzed at multiple dilutions, report the result from the appropriate dilution. Provide results for the undiluted or more concentrated analyses when requested.

Review project documents such as the environmental test request (ETR) analytical worksheets, Project Plan (PP), Project Memo or any other document/process used to communicate project requirements to ensure those project requirements were met. If project requirements were not met, immediately notify the project manager (PM) to determine an appropriate course of action.

Generate the data report in the deliverable format specified by the laboratory PM and release the report to report management.

Retain, manage and archive electronic and hardcopy data as specified in laboratory SOP BR-QA-014 *Laboratory Records*.

12.0 Method Performance

12.1 Method Detection Limit Study (MDL)

Perform a method detection limit (MDL) study at initial method set-up following the procedures specified in laboratory SOP BR-QA-005.

12.2 Demonstration of Capabilities (DOC)

Perform a method demonstration of capability at initial set-up and when time there is a significant change in instrumentation or procedure.

Each analyst that performs the analytical procedure must complete an initial demonstration of capability (IDOC) prior to independent analysis of client samples. Each analyst must demonstrate on-going proficiency (ODOC) annually thereafter. DOC procedures are further described in the laboratory's quality system manual (QAM) and in the laboratory SOP for employee training.

12.3 Linear Dynamic Range – Initial Establishment

The upper linear range for each element is established every 3 months by the analysis of the high-level calibration standard (CAL Level 3). The concentration of this standard for each element is given in Appendix A. The high-level calibration check standard is analyzed as part of the sample sequence and is used to verify the accuracy of data up to the high-level concentration. The percent recovery of this standard should be within ±5% of the expected value.

12.4 Training Requirements

Any employee that performs any portion of the procedure described in this SOP must have documentation in their employee training file that they have read this version of this SOP.

Instrument analysts, prior to independent analysis of client samples, must also have documentation of demonstration of initial proficiency (IDOC) and annual on-going proficiency (ODOC) in their employee training files.

13.0 Pollution Control

It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i.e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage and reagent stability). Employees must abide by the policies in Section 13 of the Corporate Safety Manual for "Waste Management and Pollution Prevention."

14.0 Waste Management

Waste management practices are conducted consistent with all applicable rules and regulations. Excess reagents, samples and method process wastes are disposed of in an accepted manner. Waste description rules and land disposal restrictions are followed. Waste disposal procedures are incorporated by reference to laboratory SOP BR-EH-001. Dispose waste to the designated satellite container located in the work area.

The following waste stream is produced when this procedure is performed:

- Acidic Waste - Satellite Container: 5 Gallon Polyethylene Container

15.0 References / Cross-References

- EPA Method 200.8, Determination of Trace Elements in Waters and Wastes by Inductively Coupled Plasma-Mass Spectrometry, Revision 5.4, EMMC Version, 1994. US EPA Office of Research and Development, Cincinnati, Ohio.
- Laboratory SOP BR-QA -019 *Data Review*

- Laboratory SOP BR-QA-011 *Procedures for Employee Training & Demonstration of Proficiency.*
- Laboratory SOP BR-QA-014 *Laboratory Records*
- Laboratory SOP BR-QA-002 *Standard Preparation*
- Laboratory SOP BR-QA-005 *Determination of LOD, LOQ & RL*.
- Laboratory SOP BR-EH-001 *Hazardous Waste*
- Laboratory Quality Assurance Manual (QAM)
- Corporate Environmental Health and Safety Manual (CW-E-M-001)

16.0 Method Modifications

Modification Number	Method Reference	Modification
1	EPA Method 200.8	The method indicates that all three calibration standards are to be run after the initial calibration, after every 10 samples and at the end of the analytical sequence. The lab analyzes all three calibration standards after the initial calibration (unless otherwise specified on a project basis) and then analyzes Calibration Standard #2 after every 10 samples and at the end of the analytical sequence.
2	EPA Method 200.8	The method states that 100 mL of sample is digested and brought to a final volume of 50 mL, then prior to analysis 20 mL of the sample is taken and diluted up to 50 mL. The lab digests 100 mL of sample and brings it to a final volume of 100 mL without the concentration and dilution steps.

17.0 Attachments

- Table 1: Target Analyte List and Reporting Limit
- Table 1A: Internal Standards Association
- Table 2: Primary Materials Used
- Table 3: QC Summary & Recommended Corrective Action
- Appendix A: Terms and Definitions
- Appendix B: Standard Preparation Tables
- Appendix C: Equations

18.0 Revision History

- Added method modification, Section 16.0

Table 1: Routine Target Analyte List & Reporting Limit (RL)

Element		CAS Number	Isotope (amu)	Reporting Limit
				Aqueous (ug/L)
Al	Aluminum	7429-90-5	27	30.0
Sb	Antimony	7440-36-0	123	2.0
As	Arsenic	7440-38-2	75	1.0
Ba	Barium	7440-39-3	135	10.0
Be	Beryllium	7440-41-7	9	1.0
Cd	Cadmium	7440-43-9	111	1.0
Ca	Calcium	7440-70-2	44	500.0
Cr	Chromium	7440-47-3	52	2.0
Co	Cobalt	7440-48-4	59	0.50
Cu	Copper	7440-50-8	65	2.0
Fe	Iron	7439-89-6	56	50.0
Pb	Lead	7439-92-1	208	1.0
Mg	Magnesium	7439-96-5	25	100.0
Mn	Manganese	7439-96-5	55	0.50
Ni	Nickel	7440-02-0	60	1.0
K	Potassium	7440-09-7	39	100.0
Se	Selenium	7782-49-2	82	5.0
Ag	Silver	7440-22-4	107	1.0
Na	Sodium	7440-23-5	23	100.0
Tl	Thallium	7440-28-0	205	1.0
V	Vanadium	7440-62-2	51	2.0
Zn	Zinc	7440-66-6	66	5.0

Table 1A: Internal Standard Associations

Element		Isotope (amu)	Internal Standard Element	Isotope (amu)
Al	Aluminum	27	Scandium	45
Sb	Antimony	123	Indium	115
As	Arsenic	75	Yttrium	89
Ba	Barium	135	Indium	115
Be	Beryllium	9	Lithium	6
Cd	Cadmium	111	Indium	115
Ca	Calcium	44	Scandium	45
Cr	Chromium	52	Scandium	45
Co	Cobalt	59	Scandium	45
Cu	Copper	65	Scandium	45
Fe	Iron	54	Scandium	45
Pb	Lead	208	Bismuth	209
Mg	Magnesium	25	Lithium	6
Mn	Manganese	55	Scandium	45
Ni	Nickel	60	Scandium	45
K	Potassium	39	Lithium	6
Se	Selenium	82	Yttrium	89
Ag	Silver	107	Indium	115
Na	Sodium	23	Lithium	6
Tl	Thallium	205	Bismuth	209
V	Vanadium	51	Scandium	45
Zn	Zinc	66	Scandium	45

Table 2: Primary Materials Used

Material[1]	Hazards	Exposure Limit[2]	Signs and symptoms of exposure
Nitric Acid	Corrosive Oxidizer Poison	2 ppm-TWA 4 ppm-STEL	Nitric acid is extremely hazardous; it is corrosive, reactive, an oxidizer, and a poison. Inhalation of vapors can cause breathing difficulties and lead to pneumonia and pulmonary edema, which may be fatal. Other symptoms may include coughing, choking, and irritation of the nose, throat, and respiratory tract. Can cause redness, pain, and severe skin burns. Concentrated solutions cause deep ulcers and stain skin a yellow or yellow-brown color. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
Hydrochloric Acid	Corrosive Poison	5 ppm-Ceiling	Inhalation of vapors can cause coughing, choking, inflammation of the nose, throat, and upper respiratory tract, and in severe cases, pulmonary edema, circulatory failure, and death. Can cause redness, pain, and severe skin burns. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.

[1] Always add acid to water to prevent violent reactions.
[2] Exposure limit refers to the OSHA regulatory exposure limit.

Table 3: QC Summary, Frequency, Acceptance Criteria and Recommended Corrective Action

QC Check	Acronym	Minimum Frequency	Acceptance Criteria	Corrective Action
Tune Solution		Prior to instrument calibration	See Section 10.2	See Section 10.2
Instrument Calibration	ICAL	Daily prior to sample analysis	$r \geq 0.995$	Correct problem and repeat calibration
ICV	ICV	After each ICAL	±10% of expected value	Correct problem, verify second source standard. If that fails, repeat calibration.
Continuing Calibration Verification	CCV	After the initial calibration blank, every 10 samples and at the end of the analytical sequence	±10% of expected value %RSD between replicate integrations <5%	Correct problem, reanalyze CCV. If that fails, repeat calibration and reanalyze all samples since last successful calibration.
Laboratory Reagent Blank	PB	One per digestion batch of 20 or fewer samples	LRB must not exceed 10% of sample concentration or 2.2X MDL, whichever is greater.	Correct problem, redigest and reanalyze MB and associated samples.
Laboratory Fortified Blank	LCS	One per digestion batch of 20 or fewer samples	%R (85-115)	Correct problem, redigest and reanalyze LCS, MB and associated samples for failed analytes if sufficient sample volume is available.
Matrix Spike	MS	One per every 10 project samples per matrix	%R (70-130)	Examine project DQO's with Project Manager. Evaluate data to determine if outage is related to analytical error or matrix effect. Flag data with appropriate data qualifiers
Internal Standards	IS	Every Sample	IS intensity within 60-125% of intensity of the IS in the initial calibration	Dilute the sample five-fold and reanalyze. Repeat this procedure until the internal standards are within the criteria window.

Appendix A: Terms and Definitions

Acceptance Criteria: specified limits placed on characteristics of an item, process or service defined in requirement documents.

Accuracy: the degree of agreement between an observed value and an accepted reference value. Accuracy includes a combination of random error (precision) and systematic error (bias) components which are due to sampling and analytical operations; a data quality indicator.

Analyte: The specific chemicals or components for which a sample is analyzed. (EPA Risk Assessment Guide for Superfund, OSHA Glossary).

Batch: environmental samples that are prepared and/or analyzed together with the same process, using the same lot(s) of reagents. A preparation/digestion batch is composed of one to 20 environmental samples of similar matrix, meeting the above criteria. An analytical batch is composed of prepared environmental samples (extracts, digestates and concentrates), which are analyzed together as a group.

Calibration: a set of operations that establish, under specified conditions, the relationship between values of quantities indicated by a measuring instrument or measuring system, or values represented by a material measure or a reference material and the corresponding values realized by the standards.

Calibration Curve: the graphical relationship between the known values or a series of calibration standards and their instrument response.

Calibration Standard: A substance or reference used to calibrate an instrument.

Continuing Calibration Verification (CCV): a single or multi-parameter calibration standard used to verify the stability of the method over time. Usually from the same source as the calibration curve.

Corrective Action: the action taken to eliminate the cause of an existing nonconformity, defect or other undesirable occurrence in order to prevent recurrence.

Data Qualifier: a letter designation or symbol appended to an analytical result used to convey information to the data user. (Laboratory)

The qualifiers that are routinely used for this test method are:

U: Compound analyzed for but not detected at a concentration above the reporting limit.
J: Estimated Value
N: Matrix Spike failure
*: Sample Duplicate failure

Demonstration of Capability (DOC): procedure to establish the ability to generate acceptable accuracy and precision.

Dissolved Metals: The concentration of metals determined in a sample after the sample is filtered through a 0.45µm filter (Method 3005).

Holding Time: the maximum time that a sample may be held before preparation and/or analysis as promulgated by regulation or as specified in a test method.

Initial Calibration: Analysis of analytical standards for a series of different specified concentrations used to define the quantitative response, linearity and dynamic range of the instrument to target analytes.

Intermediate Standard: a solution made from one or more stock standards at a concentration between the stock and working standard. Intermediate standards may be certified stock standard solutions purchased from a vendor and are also known as secondary standards.

Instrument Performance Check (IPC): a single or multi-parameter calibration standard used to verify the stability of the method over time. Usually from the same source as the calibration curve.

Laboratory Control Sample (LCS): a blank matrix spiked with a known amount of analyte(s) processed simultaneously with and under the same conditions as samples through all steps of the procedure. Also known as the Laboratory Fortified Blank (LFB).

Matrix Spike (MS): a field sample to which a known amount of target analyte(s) is added.

Matrix Spike Duplicate (MSD): a second replicate matrix spike

Method Blank (MB): a blank matrix processed simultaneously with and under the same conditions as samples through all steps of the procedure. Also known as the preparation blank (PB) or Laboratory Reagent Blank (LRB).

Method Detection Limit (MDL): the minimum amount of a substance that can be measured with a specified degree of confidence that the amount is greater than zero using a specific measurement system. The MDL is a statistical estimation at a specified confidence interval of the concentration at which relative uncertainty is ±100%. The MDL represents a range where qualitative detection occurs. Quantitative results are not produced in this range.

Non-conformance: an indication, judgment, or state of not having met the requirements of the relevant specification, contract or regulation.

Precision: the degree to which a set of observations or measurements of the same property, obtained under similar conditions, conform to themselves.

Preservation: refrigeration and/or reagents added at the time of sample collection to maintain the chemical, physical, and/or biological integrity of the sample.

Quality Control Sample (QC): a sample used to assess the performance of all or a portion of the measurement system.

Reporting Limit (RL): the level to which data is reported for a specific test method and/or sample.

Stock Standard: a solution made with one or more neat standards usually with a high concentration. Also known as a primary standard. Stock standards may be certified solutions purchased from a vendor.

Appendix B: Standard Preparation Tables

The standard formulations contained in this Appendix are recommended and are subject to change. If the concentration of the stock standard is different than those noted in this table, adjust the standard preparation formulation accordingly. Unless otherwise specified, prepare the standard solutions in 2% nitric acid solution using Class A volumetric glassware. The working calibrations standards are assigned an expiration date of 14 days from date of preparation, or the date of expiration of the parent standard, whichever occurs first. Expiration dates for the other multi-component prepared solutions are assigned according to expiration date of the parent standard and prepared as needed or on the expiration date, whichever occurs first. See laboratory SOP BR-QA-002 *Standard Preparation* for further guidance.

Intermediate Tune Standard Solution

Element	Stock Standard Concentration (mg/L)	Volume Used (mL)	Final Volume (mL)	Final Concentration (mg/L)
Li	10000	0.02	200	1.0
Be	1000	0.20		1.0
Mg	10000	0.02		1.0
Al	10000	0.02		1.0
Sc	1000	0.20		1.0
V	1000	0.20		1.0
Co	1000	0.20		1.0
Y	10000	0.02		1.0
In	1000	0.20		1.0
Ba	1000	0.20		1.0
Ce	1000	0.20		1.0
Tb	1000	0.20		1.0
Pb	1000	0.20		1.0
Th	1000	0.20		1.0
U	1000	0.20		1.0
Bi	1000	0.20		1.0

Working Tune Standard Solution

Element	Stock Standard Concentration (mg/L)	Volume Used (mL)	Final Volume (mL)	Final Concentration (ug/L)
Li	1.0	0.5	50	10
Be	1.0			10
Mg	1.0			10
Al	1.0			10
Sc	1.0			10
V	1.0			10
Co	1.0			10
Y	1.0			10
In	1.0			10
Ba	1.0			10
Ce	1.0			10
Tb	1.0			10
Pb	1.0			10
Th	1.0			10
U	1.0			10
Bi	1.0			10

Intermediate Calibration Standard Solution

Element	Stock Standard Concentration (mg/L)	Volume Used (mL)	Final Volume (mL)	Final Concentration (mg/L)
Aluminum	10000	1.5	500	30.0
Antimony	1000	1.0	500	2.0
Arsenic	1000	0.5	500	1.0
Barium	1000	5.0	500	10.0
Beryllium	1000	0.5	500	1.0
Cadmium	1000	0.5	500	1.0
Calcium	10000	25.0	500	500.0
Chromium	1000	1.0	500	2.0
Cobalt	1000	0.25	500	0.5
Copper	1000	1.0	500	2.0
Iron	10000	2.5	500	50.0
Lead	1000	0.5	500	1.0
Magnesium	10000	5.0	500	100.0
Manganese	1000	0.25	500	0.50
Nickel	1000	0.5	500	1.0
Potassium	10000	5.0	500	100.0
Selenium	1000	2.5	500	5.0
Silver	1000	0.5	500	1.0
Sodium	10000	5.0	500	100.0
Thallium	1000	0.5	500	1.0
Vanadium	1000	0.5	500	1.0
Zinc	1000	2.5	500	5.0

Solution: 2% Nitric Acid

Working Calibration Standards (Level 1-3)

Dilute a known volume of the intermediate calibration standard solution in 2% nitric acid solution. The recommended "recipe" and concentration levels are provided in the following table:

Element	Intermediate Calibration Standard (mg/L)	Calibration Level 3			Calibration Level 2 (made from Cal 3)			Calibration Level 1 (made from Cal 3)		
		Volume Used (mL)	Final Volume (mL)	Final Concentration (ug/L)	Volume Used (mL)	Final Volume (mL)	Final Concentration (ug/L)	Volume Used (mL)	Final Volume mL	Final Concentration (ug/L)
Al	30	25	1000	750	100	500	150	20	500	30
Sb	2.0			50			10			2.0
As	1.0			25			5			1.0
Ba	10.0			250			50			10.0
Be	1.0			25			5			1.0
Cd	1.0			25			5			1.0
Ca	100			12500			2500			500
Cr	2.0			50			10			2.0
Co	0.50			12.5			2.5			0.50
Cu	2.0			50			10			2.0
Fe	50.0			1250			250			50.0
Pb	1.0			25			5			1.0
Mg	100			2500			500			100
Mn	0.50			12.5			2.5			0.50
Ni	1.0			25			5			1.0
K	100			2500			500			100
Se	5.0			125			25			5.0
Ag	1.0			25			5			1.0
Na	100			2500			500			100
Tl	1.0			25			5			1.0
V	1.0			25			5			1.0
Zn	5.0			125			25			5.0

Intermediate Quality Control (QCS) Standard

Element	Stock Standard Concentration (mg/L)	Volume Used (mL)	Final Volume (mL)	Final Concentration (mg/L)
Al	10000	7.5	200	375
Sb	1000	5.0		25
As	1000	2.5		12.5
Ba	1000	25		125
Be	1000	2.5		12.5
Cd	1000	2.5		12.5
Ca	10000	25		1250
Cr	1000	5.0		25
Co	1000	1.25		6.25
Cu	1000	5.0		25
Fe	10000	12.5		625
Pb	1000	2.5		12.5
Mg	10000	25		1250
Mn	1000	1.25		6.25
Ni	1000	2.5		12.5
K	10000	25		1250
Se	1000	12.5		62.5
Ag	1000	2.5		12.5
Na	10000	25		1250
Tl	1000	2.5		12.5
V	1000	2.5		12.5
Zn	1000	12.5		62.5

Solution: 2% Nitric Acid

Working QCS / LFB Standard* / LFM Standard Solution*

Dilute a known volume of the intermediate QCS standard solution in 500 mL of 2% nitric acid solution. The recommended "recipe" and concentration level is provided in the following table:

Element	Volume Used mL	Final Volume mL	Final Concentration ug/L
Al	0.5	500	375
Sb			25
As			12.5
Ba			125
Be			12.5
Cd			12.5
Ca			1250
Cr			25
Co			6.25
Cu			25
Fe			625
Pb			12.5
Mg			1250
Mn			6.25
Ni			12.5
K			1250
Se			62.5
Ag			12.5
Na			1250
Tl			12.5
V			12.5
Zn			62.5

Solution: 2% Nitric Acid

*For the LFB (LCSW) digest 100 mL of solution the same as a sample.
*For the LFM (MS) spike sample with 0.1 mL of the intermediate QCS Standard solution.

Intermediate ICP-MS Internal Standard Solution

Element	Mass	Stock Standard Concentration (mg/L)	Volume Used (mL)	Final Volume (mL)	Final Concentration (mg/L)
Y	89	10000	0.25	50	50
In	115	1000	2.5		50
Li	6 & 7	10000	16.7		3333
Sc	45	1000	5.0		100
Tb	159	1000	1.25		25
Bi	209	1000	2.8		56.7

Solution: 2% Nitric Acid

Working ICP-MS Internal Standard Solution

Dilute an appropriate volume of the intermediate internal standard solution in 2000 mL of 2% nitric acid solution. The recommended "recipe" and final concentration is provided in the following table:

Parent Standard	Parent Standard Concentration (mg/L)	Volume Used (mL)	Final Volume (mL)	Final Concentration (mg/L)
Y/ 89	50	Intermediate Internal Standard Solution 2.0	2000mL	0.05
In/115	50			0.05
Li/6&7	3333			3.3
Sc/45	100			0.10
Tb/159	25			0.025
Bi/209	56.7			0.057

Solution: 2% Nitric Acid

Appendix C: Equations

Sample Concentration / Aqueous

$$C_{(\mu g/L)} = \mu g/L_{DIG} * (V_{DIG}/V_{SAMP})$$

Where:
$\mu g/L_{DIG}$ = Sample Result*
V_{DIG} = Digestate volume in Liters
V_{SAMP} = Sample volume in Liters

**adjustment for dilution factor performed by instrument software*

Percent Recovery (%R) LCS and CCVs

$$\%R = \frac{SR}{SA} * 100\%$$

Where:
SR= Sample Result
SA=Concentration of Spike Added

Percent Recovery (%R) MS

$$MSRecovery(\%) = \frac{SSR - SR}{SA} * 100\%$$

Where:
SSR=Matrix Spike Result
SR=Sample Result
SA=Concentration of Spike Added

Relative Percent Difference (%RPD)

$$\%RPD = \frac{|D_1 - D_2|}{\frac{D_1 + D_2}{2}} * 100$$

Where:
D1 = Sample result
D2 = Duplicate Result

APPENDIX 35
SOP FOR THE DETERMINATION OF MERCURY BY EPA METHOD 245.1 (PITT_MT_0005_R7)

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

TestAmerica Pittsburgh

Title: Preparation and Analysis of Mercury in Aqueous Samples by Cold Vapor Atomic Absorption

Method(s): SW-846 7470A and MCAWW 245.1

Approvals (Signature/Date):

1/29/08	1/29/08
William Reinheimer Date	Steve Jackson Date
Technical Manager	Health & Safety Manager / Coordinator
1/29/08	1/31/08
Nasreen DeRubeis Date	Larry Matko Date
Quality Assurance Manager	Laboratory Director

This SOP was previously identified as SOP No. PITT-MT-0005, Rev. 6.

Any reference within this document to Severn Trent Laboratories, Inc. or STL, should be understood to refer to TestAmerica Laboratories, Inc. (formerly known as Severn Trent Laboratories, Inc.)

STL

Implementation Date: 5/7/07

STL PITTSBURGH STANDARD OPERATING PROCEDURE

TITLE: PREPARATION AND ANALYSIS OF MERCURY IN AQUEOUS SAMPLES BY COLD VAPOR ATOMIC ABSORPTION, SW846 7470A AND MCAWW 245.1

(SUPERSEDES: PITT-MT-0005, REVISION 6)

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Approved by: 5.7.07
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Approved by:
Laboratory Director

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1. SCOPE AND APPLICATION

1.1. This procedure describes the preparation and analysis of mercury (Hg, CAS # 7439-97-6) by Cold Vapor Atomic Absorption Spectroscopy (CVAA) using SW-846 Method 7470A and MCAWW Method 245.1. Both the water bath digestion and the autoclave digestion are available at the STL Pittsburgh facility, however the default practice is the autoclave digestion for 7470A. The water bath procedure is always used for 245.1. Both procedures are described in this SOP.

1.2. CVAA analysis provides for the determination of total mercury (organic and inorganic). The combination of the oxidants, potassium permanganate and potassium persulfate, has been found to give 100% recovery with both types of compounds. Detection limits, sensitivity and optimum concentration ranges for mercury analysis will vary with the matrices, instrumentation and volume of sample used.

1.3. Method 7470A is applicable to the preparation and analysis of mercury in ground water, aqueous samples, wastes, wipes, TCLP, EP and other leachates/extracts. Certain solid and sludge type wastes may also be analyzed, however Method 7471A (see C-MT-0007) is usually the method of choice. All matrices require sample preparation prior to analysis.

1.4. Method 245.1 is applicable to the determination of mercury in drinking, surface and saline waters, domestic and industrial wastes. All matrices require sample preparation prior to analysis.

1.5. The STL reporting limit for mercury in aqueous matrices is 0.0002 mg/L.

1.6. For DoD QSM Version 3 requirements, refer to SOP PITT-QA-DoD-0001.

2. SUMMARY OF METHOD

2.1. This SOP describes a technique for the determination of mercury in solution. The procedure is a physical method based on the absorption of radiation at 253.7 nm by mercury vapor. A representative portion of the sample is digested in sulfuric and nitric acids. Organic mercury compounds are oxidized with potassium permanganate and potassium persulfate and the mercury reduced to its elemental state with stannous chloride and aerated from solution in a closed system. The mercury vapor passes through a cell positioned in the light path of an atomic absorption spectrophotometer. Absorbance is measured as a function of mercury concentration. Concentration of the analyte in the sample is determined by comparison of the sample absorbance to the calibration curve (absorbance vs. concentration).

3. DEFINITIONS

3.1. Dissolved Metals: Those elements which pass through a 0.45 um membrane. (Sample is acidified after filtration).

3.2. Suspended Metals: Those elements which are retained by a 0.45 um membrane.

3.3. Total Metals: The concentration determined on an unfiltered sample following digestion.

4. INTERFERENCES

Chemical and physical interferences may be encountered when analyzing samples using this method.

4.1. Potassium permanganate which is used to breakdown organic mercury compounds also eliminates possible interferences from sulfide. Concentrations as high as 20 mg/L of sulfide as sodium sulfide do not interfere with the recovery of inorganic mercury from reagent water.

4.2. Copper has also been reported to interfere; however, copper concentrations as high as 10 mg/L had no effect on the recovery of mercury from spiked samples.

4.3. Chlorides can cause a positive interference. Seawaters, brines and industrial effluents high in chlorides require additional permanganate (as much as 25 mL) because, during the oxidation step, chlorides are converted to free chlorine, which also absorbs radiation at 253.7 nm. Care must be taken to ensure that free chlorine is absent before the mercury is reduced and swept into the cell. This is accomplished by adding excess hydroxylamine reagent (25 mL) and purging the sample head space before stannous chloride is added. Both inorganic and organic mercury spikes have been quantitatively recovered from seawater using this technique.

Note: Sufficient addition of permanganate is apparent when the purple color persists at least 15 minutes. Some samples may require dilution prior to digestion due to extremely high concentrations of chloride.

4.4. Interference from certain volatile organic materials that absorb at this wavelength may also occur. If suspected, a preliminary run without stannous chloride can determine if this type of interference is present. While the possibility of absorption from certain organic substances present in the sample does exist, this problem is not routinely encountered. This is mentioned only to caution the analyst of the possibility. If this condition is found to exist, the mercury concentration in the sample can be determined

by subtracting the result of the sample run without the reducing reagent (stannous chloride) from that obtained with the reducing reagent.

4.5. Samples containing high concentrations of oxidizable organic materials, as evidenced by high COD levels, may not be completely oxidized by this procedure. When this occurs the recovery of mercury will be low. The problem can be eliminated by reducing the volume of original sample used.

4.6. The most common interference is laboratory contamination, which may arise from impure reagents, dirty glassware, improper sample transfers, dirty work areas, etc. Be aware of potential sources of contamination and take appropriate measures to minimize or avoid them.

5. SAFETY

5.1. Employees must abide by the policies and procedures in the Corporate Safety Manual, Radiation Safety Manual and this document.

5.2. Samples that contain high concentrations of carbonates or organic material or samples that are at elevated pH can react violently when acids are added.

5.3. Do not look directly into the beam of the Hg lamp. The UV light that these lamps radiate is harmful to the eyes.

5.4. The following is a list of the materials used in this method, which have a serious or significant hazard rating. NOTE: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table. A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Mercury (1,000 PPM in Reagent)	Oxidizer Corrosive Poison	0.1 Mg/M3 Ceiling (Mercury Compounds)	Extremely toxic. Causes irritation to the respiratory tract. Causes irritation. Symptoms include redness and pain. May cause burns. May cause sensitization. Can be absorbed through the skin with symptoms to parallel ingestion. May affect the central nervous system. Causes irritation and burns to eyes. Symptoms include redness, pain, and blurred vision; may cause serious and permanent eye damage.
Sulfuric Acid	Corrosive Oxidizer Dehydrator Poison	1 Mg/M3-TWA	Inhalation produces damaging effects on the mucous membranes and upper respiratory tract. Symptoms may include irritation of the nose and throat, and labored breathing. Symptoms of redness, pain, and severe burn can occur. Contact can cause blurred vision, redness, pain and severe tissue burns. Can cause blindness.
Nitric Acid	Corrosive Oxidizer Poison	2 ppm-TWA 4 ppm-STEL	Nitric acid is extremely hazardous; it is corrosive, reactive, an oxidizer, and a poison. Inhalation of vapors can cause breathing difficulties and lead to pneumonia and pulmonary edema, which may be fatal. Other symptoms may include coughing, choking, and irritation of the nose, throat, and respiratory tract. Can cause redness, pain, and severe skin burns. Concentrated solutions cause deep ulcers and stain skin a yellow or yellow-brown color. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
Hydrochloric Acid	Corrosive Poison	5 PPM-Ceiling	Inhalation of vapors can cause coughing, choking, inflammation of the nose, throat, and upper respiratory tract, and in severe cases, pulmonary edema, circulatory failure, and death. Can cause redness, pain, and severe skin burns. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.

Potassium Permanganate	Oxidizer	5 Mg/M3 for Mn Compounds	Causes irritation to the respiratory tract. Symptoms may include coughing, shortness of breath. Dry crystals and concentrated solutions are caustic causing redness, pain, severe burns, brown stains in the contact area and possible hardening of outer skin layer. Diluted solutions are only mildly irritating to the skin. Eye contact with crystals (dusts) and concentrated solutions causes severe irritation, redness, and blurred vision and can cause severe damage, possibly permanent.
Stannous Chloride	Irritant	2 Mg/M3 TWA as Tin	Causes irritation to the respiratory tract. Can irritate skin and eyes. Symptoms include coughing and shortness of breath. Contact with skin and/or eyes may cause redness, itching and pain.
Potassium Persulfate	Oxidizer	None	Causes irritation to the respiratory tract. Symptoms may include coughing, shortness of breath. Causes irritation to skin and eyes. Symptoms include redness, itching, and pain. May cause dermatitis, burns, and moderate skin necrosis.
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

5.5. Eye protection that protects against splash, laboratory coat, and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled. Cut resistant gloves must be worn doing any other task that presents a strong possibility of getting cut. Disposable gloves that have been contaminated will be removed and discarded; other gloves will be cleaned immediately.

5.6. Mercury is a highly toxic element that must be handled with care. The analyst must be aware of the handling and clean-up techniques before working with mercury. Since

mercury vapor is toxic, precaution must be taken to avoid its inhalation, ingestion or absorption through skin. All lines should be checked for leakage and the mercury vapor must be vented into a hood or passed through a mercury absorbing media such as:

5.6.1. Equal volumes of 0.1 M $KMnO_4$ and 10% H_2SO_4, or

5.6.2. Iodine, 0.25%, in a 3% KI solution.

5.7. Exposure to chemicals must be maintained **as low as reasonably achievable.** Therefore, unless they are known to be non-hazardous, all samples should be opened, transferred and prepared in a fume hood, or under other means of mechanical ventilation. Solvent and waste containers will be kept closed unless transfers are being made.

5.8. The preparation of standards and reagents will be conducted in a fume hood with the sash closed as far as the operation will permit.

5.9. All work must be stopped in the event of a known or potential compromise to the health and safety of a STL associate. The situation must be reported **immediately** to a laboratory supervisor or EH&S coordinator.

5.10. Cylinders of compressed gas must be handled with caution, in accordance with local regulations. It is recommended that, wherever possible, cylinders be located outside the laboratory and the gas led to the instrument through approved lines.

5.11. The CVAA apparatus must be properly vented to remove potentially harmful fumes generated during sample analysis.

6. EQUIPMENT AND SUPPLIES

6.1. Temperature controlled water bath (capable of maintaining a temperature of 90-95 °C) or autoclave that is able to obtain conditions of 15 lbs., 120 °C for 15 minutes.

6.2. LEEMAN Labs PS200II Mercury Analyzer:

6.2.1. LEEMAN Mercury Lamp P.N. 317-00048.

6.2.2. Peristaltic Pump.

6.2.3. Flow Meter.

6.2.4. Printer.

6.2.5. Dehydrator tube.

6.3. Leeman HYDRA AA Automated Mercury Analysis System.

6.4. Disposable Sealable Sample Containers (Corning).

6.5. Argon gas supply (ultrahigh purity-grade).

6.6. Calibrated automatic pipettes or Class A glass volumetric pipettes.

6.7. Class A volumetric flasks.

6.8. Thermometer (capable of accurate readings at 95 °C).

6.9. Disposable cups or tubes.

7. REAGENTS AND STANDARDS

7.1. Reagent water must be produced by a Millipore DI system or equivalent. Reagent water must be free of the analytes of interest as demonstrated through the analysis of method blanks.

7.2. Stock (1000 ppm) mercury standards (in 10% HNO_3) are purchased as custom STL solutions. All standards must be stored in FEP fluorocarbon or previously unused polyethylene or polypropylene bottles. Stock standard solutions must be replaced prior to the expiration date provided by the manufacturer. If no expiration date is provided, the stock solutions may be used for up to one year and must be replaced sooner if verification from an independent source indicates a problem.

7.3. Intermediate mercury standard (10 ppm): Take 1 mL of the stock mercury standard (7.2) and dilute to 100 mL with reagent water. The intermediate standard must be made monthly and must be prepared in a matrix of 2% HNO_3. This acid (2 mL of concentrated HNO_3) must be added to the flask/bottle before the addition of the stock standard aliquot.

7.4. Working mercury standard (0.1 ppm): Take 1 mL of the intermediate mercury standard (7.3) and dilute to 100 mL with reagent water. The working mercury standard must be made daily and must be prepared in a matrix of 0.15% HNO_3. This acid (150 uL of concentrated HNO_3) must be added to the flask/bottle before the addition of the stock standard aliquot. A second source working standard is prepared at 0.1 ppm for preparation of the ICV.

7.5. The calibration standards listed in Table I must be prepared fresh daily from the working standard (7.4) by transferring 0, 0.2, 0.5, 1.0, 5.0 and 10.0 mL aliquots of the working mercury standard into 100 mL flasks and diluting to volume with reagent water. The 0, .5, 1.0, 5.0 and 10 standards are recommended by Thermo Electron. The 0.2 standard level was selected to include a standard at the RL. See Table 1 (Appendix A) for the preparation of the ICV, CCV and RLV standards.

Note: Alternate approaches to standard preparation may be taken and alternate volumes of standard may be prepared as long as the accuracy and final standard concentrations as detailed in Table I are maintained. For example, automated mercury systems do not require 100 mL of standard and therefore smaller volumes may be generated to reduce waste generation.

7.6. The initial calibration verification standard (ICV) must be made from a different stock solution than that of the calibration standards.

7.7. Refer to Table I (Appendix A) for details regarding the working standard concentrations for calibration, calibration verification and spiking solutions. All standards must be processed through the entire analytical procedure including sample preparation.

7.8. Nitric acid (HNO_3), concentrated, trace metal grade or better.

Note: If a high reagent blank is obtained, it may be necessary to distill the nitric acid.

7.9. Sulfuric acid (H_2SO_4), concentrated, trace metal grade or better.

7.9.1. Sulfuric acid, 0.5 N: Dilute 14.0 mL of concentrated H_2SO_4 to 1 liter with reagent water.

7.10. Stannous chloride solution: Add 200 g of stannous chloride to 2 L of 10% hydrochloric acid.

7.11. Stannous sulfate may be used in place of stannous chloride. This mixture is a suspension and should appear cloudy. This solution should be made daily and should be stirred continuously during use.

7.12. Sodium chloride-hydroxylamine hydrochloride solution: Add 12 g of sodium chloride and 12 g of hydroxylamine hydrochloride to every 100 mL of reagent water.

Note: Hydroxylamine sulfate may be used in place of hydroxylamine hydrochloride.

7.13. Potassium permanganate, 5% solution (w/v): Dissolve 5 g of potassium permanganate for every 100 mL of reagent water.

7.14. Potassium persulfate, 5% solution (w/v): Dissolve 5 g of potassium persulfate for every 100 mL of reagent water.

8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1. Sample holding time for mercury is 28 days from time of collection to the time of analysis. For TCLP leachates, the holding time is 28 days from the time of TCLP extraction to the time of analysis.

8.2. Aqueous samples are preserved with nitric acid to a pH of <2 and may be stored in either plastic or glass. Refrigeration is not required. Preservation must be verified prior to analysis.

9. QUALITY CONTROL

Table II (Appendix A) provides a summary of quality control requirements including type, frequency, acceptance criteria and corrective action.

9.1. Initial Demonstration of Capability

Prior to the analysis of any analyte using 7470A or the 245.1, the following requirements must be met.

9.1.1. Method Detection Limit (MDL) - An MDL must be determined for each analyte/matrix prior to the analysis of any samples. The MDL is determined using seven replicates of reagent water, spiked with all the analytes of interest, that have been carried through the entire analytical procedure. MDLs must be redetermined on an annual basis in accordance with 40 CFR Part 136 Appendix B requirements. The spike level must be between the calculated MDL and 10X the MDL to be valid. The result of the MDL determination must be below the STL reporting limit.

9.1.2. Initial Demonstration Study - This requires the analysis of four QC check samples. The QC check sample is a well characterized laboratory generated

sample used to monitor method performance. The results of the initial demonstration study must be acceptable before analysis of samples may begin.

9.1.2.1. Four aliquots of the check sample (LCS) are prepared and analyzed using the procedures detailed in this SOP and the determinative SOPs.

9.2. Preparation Batch - A group of up to 20 samples that are of the same matrix and are processed together using the same procedures and reagents. The preparation batch must contain a method blank, a LCS and a matrix spike/matrix spike duplicate for 7470A or a matrix spike (one per 10 or fewer samples) for 245.1. In some cases, at client request, it may be appropriate to process a matrix spike and sample duplicate in place of the MS/MSD. If clients specify specific samples for MS/MSD, the batch may contain multiple MS/MSD pairs.

9.3. Sample Count - Laboratory generated QC samples (method blanks, LCS, MS, MSD) are not included in the sample count for determining the size of a preparation batch.

9.4. Method Blank (MB) - One method blank must be processed with each preparation batch. The method blank consists of reagent water containing all reagents specific to the method that is carried through the entire analytical procedure, including preparation and analysis. The method blank is used to identify any system and process interferences or contamination of the analytical system that may lead to the reporting of elevated analyte concentrations or false positive data. The method blank should not contain any analyte of interest at or above the reporting limit, or above 10% of either the measured concentration of that analyte in associated samples or the regulatory limit. See QA-003 for more detail on criteria and corrective actions. In addition, blank contamination should always be evaluated against project specific requirements. **Refer to PITT-QA-DoD-0001 for specific DoD requirements for the method blank.**

- Repreparation and reanalysis of all samples associated with an unacceptable method blank is required when reportable concentrations are determined in the samples (see exception noted above).

- If there is no analyte greater than the RL in the samples associated with an unacceptable method blank, the data may be reported with qualifiers. Such action must be taken in consultation with the client and must be addressed in the project narrative.

- If the above criteria are not met and reanalysis is not possible, then the sample data must be qualified. This anomaly must be addressed in the project narrative and the client must be notified.

9.5. Laboratory Control Sample (LCS) - One aqueous LCS (referred to as a Laboratory Fortified Blank in 245.1) must be processed with each preparation batch. The LCS is used to monitor the accuracy of the analytical process. On-going monitoring of the LCS results provides evidence that the laboratory is performing the method within acceptable accuracy and precision guidelines. The LCS must be carried through the entire analytical procedure. The CCV results can be reported as LCS results since all CCVs (as well as all other standards) are processed through the sample preparation step with the field samples. No more than 20 samples can be associated with one CCV used for the purpose of reporting LCS data.

- If the LCS is outside established control limits the system is out of control and corrective action must occur. Corrective action will result in the batch being re-prepped and re-analyzed. In-house control limits are 80 - 120% for SW-846 method 7470A and 85 – 115% for EPA method 245.1).

- In the instance where the LCS recovery is > 120% (7470A) or > 115% (245.1) and the sample results are < RL, the data may be reported with qualifiers. Such action must be taken in consultation with the client and must be addressed in the case narrative.

- In the event that an MS/MSD analysis is not possible, a Laboratory Control Sample Duplicate (LCSD) must be analyzed. The RPD of the LCS and LCSD must be compared to the matrix spike RPD limits.

- Corrective action will be repreparation and reanalysis of the batch unless the client agrees that other corrective action is acceptable.

9.6. Matrix Spike/Matrix Spike Duplicate (MS/MSD) - One MS/MSD pair must be processed for each preparation batch of up to 20 samples for 7470A or a MS must be processed for every 10 or fewer samples for 245.1. A matrix spike (MS) is a field sample to which known concentrations of target analytes have been added (referred to as a Laboratory Fortified Matrix in 245.1). A matrix spike duplicate (MSD) is a second aliquot of the same sample (spiked identically as the MS) prepared and analyzed along with the sample and matrix spike. Some client specific data quality objectives (DQO's) may require the use of sample duplicates in place of or in addition to MS/MSD's. The MS/MSD results are used to determine the effect of a matrix on the precision and accuracy of the analytical process. Due to the potential variability of the matrix of each sample, these results may have immediate bearing only on the specific sample spiked. Samples identified as field blanks cannot be used for MS/MSD analysis. Spiking levels are provided in Table I (Appendix A).

- If analyte recovery or RPD falls outside the acceptance range, the recovery of that analyte must be in control for the LCS. Until in-house control limits are

established, a control limit of 75 - 125 % (7470A) or 70 – 130% (245.1) recovery and 20% RPD must be applied to the MS/MSD. **Refer to PITT-QA-DoD-0001 for specific DoD requirements for the MS/MSD.** If the LCS recovery is within limits, then the laboratory operation is in control and the results may be accepted. If the recovery of the LCS is outside limits, corrective action must be taken. Corrective action will include repreparation and reanalysis of the batch. MS/MSD results which fall outside the control limits must be addressed in the narrative.

- If the native analyte concentration in the MS/MSD exceeds 4 times the spike level for that analyte, the recovery data are reported as NC (i.e., not calculated). If the reporting software does not have the ability to report NC then the actual recovery must be reported and narrated as follows: "Results outside of limits do not necessarily reflect poor method performance in the matrix due to high analyte concentrations in the sample relative to the spike level."

- If an MS/MSD is not possible due to limited sample volume, then a laboratory control sample duplicate (LCSD) should be analyzed. The RPD of the LCS and LCSD must be compared to the matrix spike RPD limits.

9.7. Initial Calibration Verification (ICV/ICB) - Calibration accuracy is verified by analyzing a second source standard (ICV). The ICV result must fall within 10% (7470A) or 5% (245.1) of the true value for that solution. An ICB is analyzed immediately following the ICV to monitor low level accuracy and system cleanliness. The ICB result must fall within +/- the reporting limit (RL) from zero. **Refer to PITT-QA-DoD-0001 for specific DoD requirements for the ICB.** If either the ICV or ICB fail to meet criteria, the analysis should be terminated, the problem corrected and the instrument recalibrated. If the cause of the ICV or ICB failure was not directly instrument related the corrective action will include repreparation of the associated samples. The ICV is equivalent to the Quality Control Sample (QCS) and the first Initial Performance Check (IPC) specified in 245.1.

9.8. Continuing Calibration Verification (CCV/CCB) - Calibration accuracy is monitored throughout the analytical run through the analysis of a known standard after every 10 samples and at the end of the analytical sequence. The CCV must be a mid-range standard at a concentration other than that of the ICV. The CCV result must fall within 20% (7470A) or 10% (245.1) of the true value for that solution. A CCB is analyzed immediately following each CCV. The CCB result must fall within +/- RL from zero. **Refer to PITT-QA-DoD-0001 for specific DoD requirements for the CCB.** Each CCV and CCB analyzed must reflect the conditions of analysis of all associated samples. Sample results may only be reported when bracketed by valid ICV/CCV and ICB/CCB pairs. If a mid-run CCV or CCB fails, the analysis must be terminated, the problem corrected, the instrument recalibrated, the calibration verified and the affected samples

reanalyzed. If the cause of the CCV or CCB failure was not directly instrument related the corrective action will include repreparation of the associated samples.

9.9. Reporting Limit Verification Standard (RLV) – Calibration accuracy at the laboratory reporting limit is verified after the analysis of the ICB. Until in-house control limits are established, a control limit of 50 – 150% recovery will be applied.

9.10. Method of Standard Addition (MSA) -This technique involves adding known amounts of standard to one or more aliquots of the sample prior to preparation. This technique compensates for a sample interferent that may enhance or depress the analyte signal, thus producing a different slope from that of the calibration standards. It will not correct for additive interferences which cause a baseline shift. Refer to Section 11.2.13 for additional information on when full 4 point MSA is required as well as Appendix C for specific MSA requirements.

10. CALIBRATION AND STANDARDIZATION

10.1. Calibration standards must be processed through the preparation procedure as described in Section 11.1.

10.2. Due to the differences in preparation protocols separate calibration and calibration verification standards must be prepared for aqueous and solid matrices.

10.3. Calibration must be performed daily (every 24 hours) and each time the instrument is set up. The instrument calibration date and time must be included in the raw data.

10.4. Set up the instrument with the operating parameters recommended by the manufacturer. Allow the instrument to become thermally stable before beginning calibration (approximately 30 minutes of warm-up is required). Refer to CVAA instrument manual for detailed setup and operation protocols.

10.5. Calibrate the instrument according to instrument manufacturer's instructions, using a minimum of five standards and a blank. One standard must be at the STL reporting limit. Analyze standards in ascending order beginning with the blank. Refer to Section 7.5 and Table I for additional information on preparing calibration standards and calibration levels.

10.6. The calibration curve must have a correlation coefficient of ≥0.995 or the instrument shall be stopped and recalibrated prior to running samples. Sample results cannot be reported from a curve with an unacceptable correlation coefficient.

10.7. Refer to Section 9.0 and Table II for calibration verification procedures, acceptance criteria and corrective actions. The NELAC requirement for verification of the initial calibration at varied concentrations is met daily since the ICVs, CCVs, and RLVs are all at different concentrations.

11. PROCEDURE

11.1. Sample Preparation:

11.1.1. All calibration and calibration verification standards (ICV, ICB, CCV, CCB, RLV) are processed through the digestion procedure as well as the field samples. *An exception to this is for Method 245.1 samples. The calibration curve samples are* ***not*** *heated.*

11.1.2. Transfer 100 mL of well-mixed sample or standard to a clean sample digestion bottle. Refer to PITT-QA-0024 for subsampling procedures.

Note: Reduced sample volumes can be used as long as a representative sample can be obtained and the reagent levels are adjusted to maintain the same sample to reagent ratio. All samples and standards must be processed similarly.

11.1.3. Add 5 mL of concentrated H_2SO_4 and 2.5 mL of concentrated HNO_3 mixing after each addition.

Note: All spiking (LCS, MS, MSD) should be done after the initial addition of acids (see Appendix A, Table 1).

11.1.4. Add 15 mL of potassium permanganate solution. For samples high in organic materials or chlorides, additional permanganate may be added. Shake and add additional portions of permanganate solution until a purple color persists for at least 15 minutes. If after the addition of up to 25 mL additional permanganate the color does not persist, sample dilution prior to reanalysis may be required.

Note: When performing analyses using automated vs. manual techniques the sample dilution resultant from the addition of more than the original aliquot of permanganate solution must be compensated for by the addition of the same volume of permanganate to all associated samples, standards, *and QC samples (e.g. LCS and blank)* in the run. In instances, where this is not feasible, the addition of excess reagent can be addressed through mathematical correction of the results to account for the resultant dilution effect.

11.1.5. Add 8 mL of potassium persulfate solution and heat for two hours in a water bath at 90 - 95 °C.

NOTE: Alternatively, for analyses using 7470A, samples may be digested using an autoclave for 15 minutes at 120 °C and 15 lbs (default).

11.1.6. Cool samples.

11.2. Sample Analysis:

11.2.1. Refer to the SOP PITT-MT-0028 and the instrument manuals for detailed setup and operation protocols for the LEEMAN PS200II and Hydra AA.

11.2.2. Refer to CVAA instrument manual for detailed setup and operation protocols.

11.2.3. When ready to begin analysis, add 6 mL of sodium chloride-hydroxylamine hydrochloride “clearing solution” to the samples to reduce the excess permanganate (the permanganate has been reduced when no purple color remains). Add this solution in 6 mL increments until the permanganate is completely reduced i.e. colorless.

11.2.4. Automated determination: Follow instructions provided by instrument manufacturer.

11.2.5. Perform a linear regression analysis of the calibration standards by plotting maximum response of the standards vs. concentration of mercury. Determine the mercury concentration in the samples from the linear regression fit of the calibration curve. Calibration using computer or calculation based regression curve fitting techniques on concentration/response data is acceptable.

11.2.6. All measurements must fall within the defined calibration range to be valid. When sample concentrations exceed the upper limit of the calibration curve, the samples will be diluted and reanalyzed (if possible) to bring them within calibration curve. When reported sample concentrations either exceed the upper limit of the curve (i.e. cannot be rerun) or fall below the reporting limit, the data will be qualified as estimated. If the sample results are negative and the absolute value of the negative result is greater than the reporting limit, the sample must be diluted and reanalyzed.

11.2.7. The samples must be allowed to cool to room temperature prior to analysis or a decrease in the response signal can occur.

11.2.8. Baseline correction is acceptable as long as it is performed after every sample or after the CCV and CCB; resloping is acceptable as long as it is immediately preceded and followed by a compliant CCV and CCB.

11.2.9. The following analytical sequence must be used with 7470A and 245.1:

Instrument Calibration
ICV
ICB
RLV
Maximum 10 samples
CCV
CCB
Repeat sequence of 10 samples between CCV/CCB pairs as required to complete run
CCV
CCB

Refer to Quality Control Section 9.0 and Table II (Appendix A) for quality control criteria to apply to Methods 7470A and 245.1.

Note: Samples include the method blank, LCS, MS, MSD, duplicate, field samples and sample dilutions.

11.2.10. The following run sequence is consistent with 7470A, CLP and 245.1 and may be used as an alternate to the sequence in 11.2.11. This run sequence is recommended if multiple method requirements must be accommodated in one analytical run:

Instrument Calibration
ICV
ICB
RLV or CRA*
CCV
CCB
10 samples
CCV
CCB
Repeat sequence of 10 samples between CCV/CCB pairs as required to complete run.
CCV
CCB

Refer to the appropriate CLP SOPs (PITT-MT-0006) for quality control requirements for QC samples.

* Refer to the CLP SOPs for information on the CRA.

11.2.11. For TCLP samples, full four point MSA will be required if all of the following conditions are met:

1) recovery of the analyte in the matrix spike is not at least 50%,

2) the concentration of the analyte does not exceed the regulatory level, and,

3) the concentration of the analyte is within 20% of the regulatory level.

The reporting and matrix spike levels for TCLP analyses are detailed in Table I (Appendix A). Appendix E provides guidance on performing MSA analyses. For TCLP mercury determinations, MSA spikes must be added prior to sample preparation.

11.3. To facilitate the early identification of QC failures and samples requiring rerun it is strongly recommended that sample data be reviewed periodically throughout the run.

11.4. Guidelines are provided in the appendices on procedures to minimize contamination of samples and standards, preventive maintenance and parts maintenance. For instrument troubleshooting, use the auto diagnostics software. If the problem cannot be determined using the software, place a call to service personnel.

11.5. One time procedural variations are allowed only if deemed necessary in the professional judgment of supervision to accommodate variation in sample matrix, radioactivity, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using a Nonconformance Memo and is approved by a Technical Specialist and QA Manager. If contractually required, the client shall be notified. The Nonconformance Memo shall be filed in the project file.

11.6. Any unauthorized deviations from this procedure must also be documented as a nonconformance, with a cause and corrective action described.

12. DATA ANALYSIS AND CALCULATIONS

12.1. ICV percent recoveries are calculated according to the equation:

$$\%R = 100\left(\frac{Found(ICV)}{True(ICV)}\right)$$

12.2. CCV percent recoveries are calculated according to the equation:

$$\%R = 100\left(\frac{Found(CCV)}{True(CCV)}\right)$$

12.3. RLV percent recoveries are calculated using the same equation as the ICV or CCV (replace ICV or CCV with RLV in the above equations).

12.4. Matrix spike recoveries are calculated according to the following equation:

$$\%\ R\ = 100\left(\frac{SSR - SR}{SA}\right)$$

Where:
SSR = Spike Sample Result
SR = Sample Result
SA = Spike Added

12.5. The relative percent difference (RPD) of matrix spike/matrix spike duplicates or sample duplicates are calculated according to the following equations:

$$RPD = 100\left[\frac{|MSD - MS|}{\left(\frac{MSD + MS}{2}\right)}\right]$$

Where:
MS = determined spiked sample concentration
MSD = determined matrix spike duplicate concentration

$$RPD = 100\left[\frac{|DU1 - DU2|}{\left(\frac{DU1 + DU2}{2}\right)}\right]$$

Where:
DU1 = Sample result
DU2 = Sample duplicate result

12.6. The final concentration for an aqueous sample is calculated as follows:

$$mg/L = \text{C x D}$$

Where:
C = Concentration (mg/L) from instrument readout
D = Instrument dilution factor

12.7. The LCS percent recovery is calculated according to the following equation:

$$\%R = 100\left(\frac{Found(LCS)}{True(LCS)}\right)$$

12.8. Appropriate factors must be applied to sample values if dilutions are performed.

12.9. Sample results should be reported with up to three significant figures in accordance with the STL significant figure policy.

13. METHOD PERFORMANCE

13.1. Each laboratory must have initial demonstration of performance data on file for each analyte of interest as described in Section 9.0.

13.2. Method performance is determined by the analysis of method blanks, laboratory control samples, matrix spike and matrix spike duplicate samples. The matrix spike recovery should fall within +/- 25 % (7470A) or +/- 30% (245.1) and the matrix spike duplicates should compare within 20% RPD. **Refer to PITT-QA-DoD-0001 for specific DoD requirements for the MS.** The method blanks must meet the criteria in Section 9.4. **Refer to PITT-QA-DoD-0001 for specific DoD requirements for the method blank.** The laboratory control sample should recover within 20% (7470A) or 15% (245.1) of the true value until in house limits are established.

13.3. Training Qualification:

The group/team leader has the responsibility to ensure that this procedure is performed by an associate who has been properly trained in its use and has the required experience.

14. POLLUTION PREVENTION

14.1. All waste will be disposed of in accordance with Federal, State and Local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this method and the policies in section 13 of the Corporate Safety Manual for "Waste Management and Pollution Prevention."

14.2. This method allows for the proportional reduction of sample and reagent volumes to decrease waste generation.

15. WASTE MANAGEMENT

15.1. The following waste streams are produced when this method is carried out.

15.1.1. Extracted sample containing less than 1 ppb Hg. This waste is collected in waste containers identified as "Acid Waste", Waste #33. It is neutralized to a pH between 6 and 9 and is disposed down a lab sink.

15.1.2. Unused Standards. This waste collected in containers identified as "Mercury Standards Waste", Waste #4.

15.1.3. Extracted sample containing greater than 1 ppb Hg. This waste collected in containers identified as "Mercury Standards Waste", Waste #4.

15.1.4. Mercury Analyzer Waste. Waste discharged from mercury analyzer is collected in containers identified as "Mercury Standards Waste", Waste #4.

16. REFERENCES

16.1. Test Methods for Evaluating Solid Waste , Physical/Chemical Methods, SW-846, 3rd Edition, Final Update II, Revision I, September 1994, Method 7470A (Mercury).

16.2. "Methods for the Chemical Analysis of Water and Wastes", EPA-600/4-79-020, U.S.EPA, 1994, Method 245.1, Revision 3.0.

16.3. U.S.EPA Statement of Work for Inorganics Analysis, ILM04.1.

16.4. QA-003, STL QC Program.

16.5. QA-004, Rounding and Significant Figures.

16.6. PITT-QA-007, Method Detection Limits.

16.7. PITT-QA-DoD-0001, Implementation of the DoD QSM Version 3.

16.8. PITT-QA-0024, Subsampling.

17. MISCELLANEOUS (TABLES, APPENDICES, ETC.)

17.1. Modifications/Interpretations from reference method.

17.1.1. Modifications from both 7470A and 245.1.

17.1.1.1. The 200 series methods and Chapter 1 of SW846 specify the use of reagent water with a purity equivalent to ASTM Type II water. This SOP specifies the use of a Millipore DI system or equivalent to produce reagent water. This SOP requires that reagent water must be free of the analytes of interest as demonstrated through the analysis of method blanks.

17.1.1.2. This SOP allows for the use of reduced sample volumes to decrease waste generation. Reagent levels are adjusted to maintain the same ratios as stated in the source methods. According to a letter from Robert Booth of EPA EMSL-Cinn to David Payne of EPA Region V, "Reduction in sample size and appropriate corresponding reduction in sample volume is not considered a significant change in the methodology."

17.1.1.3. The alternate run sequence presented in Section 11.2.12 is consistent with method requirements.

17.1.2. Modifications from Method 7470A

17.1.2.1. Chapter 1 of SW-846 states that the method blank should not contain any analyte of interest at or above the MDL. This SOP states that the method blank must not contain any analyte of interest at or above the

reporting limit. **Refer to PITT-QA-DoD-0001 for specific DoD requirements for the method blank.**

17.1.2.2. Documentation is on file from EPA's Office of Solid Waste (Oliver Fordham 11/28/95) regarding the acceptance of the autoclave as an equivalent heating device to the water bath. In his letter, Mr. Fordham cited the CLP water protocol 245.1 CLP-M and therefore the operating parameters from that method were adopted for 7470A (15 minutes at 120 °C and 15 lbs.).

17.1.3. Modifications from 245.1

17.1.3.1. Method 245.1, Section 9.3 states concentrations should be reported as follows: Between 1 and 10 ug/L, one decimal; above 10 ug/L, to the nearest whole number. STL reports all Hg results under this SOP to two significant figures.

17.2. Documentation and Record Management

The following documentation comprises a complete CVAA raw data package:

- Raw data (direct instrument printout)
- Run log printout from instrument software where this option is available or manually generated run log. (A bench sheet may be substituted for the run log as long as it contains an accurate representation of the analytical sequence).
- Data review checklist - See Appendix B
- Standards Documentation (source, lot, date).
- Copy of digestion log.
- Non-conformance summary (if applicable).

Figure 1. Aqueous Sample Preparation - Mercury

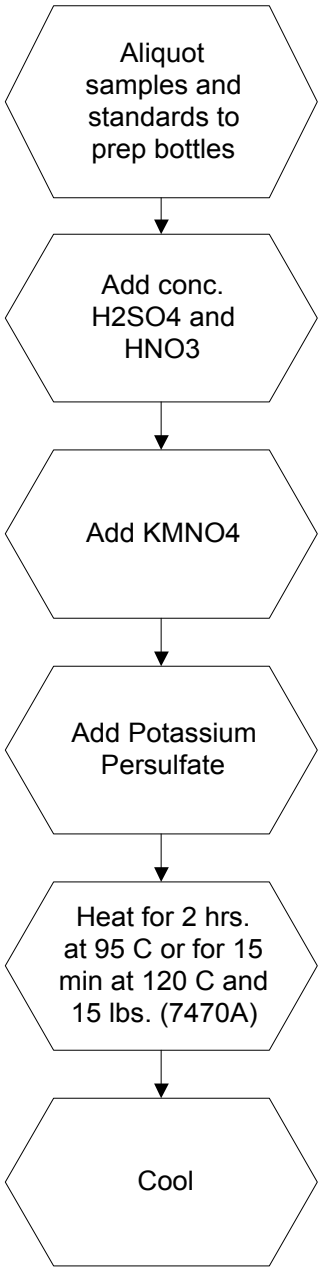
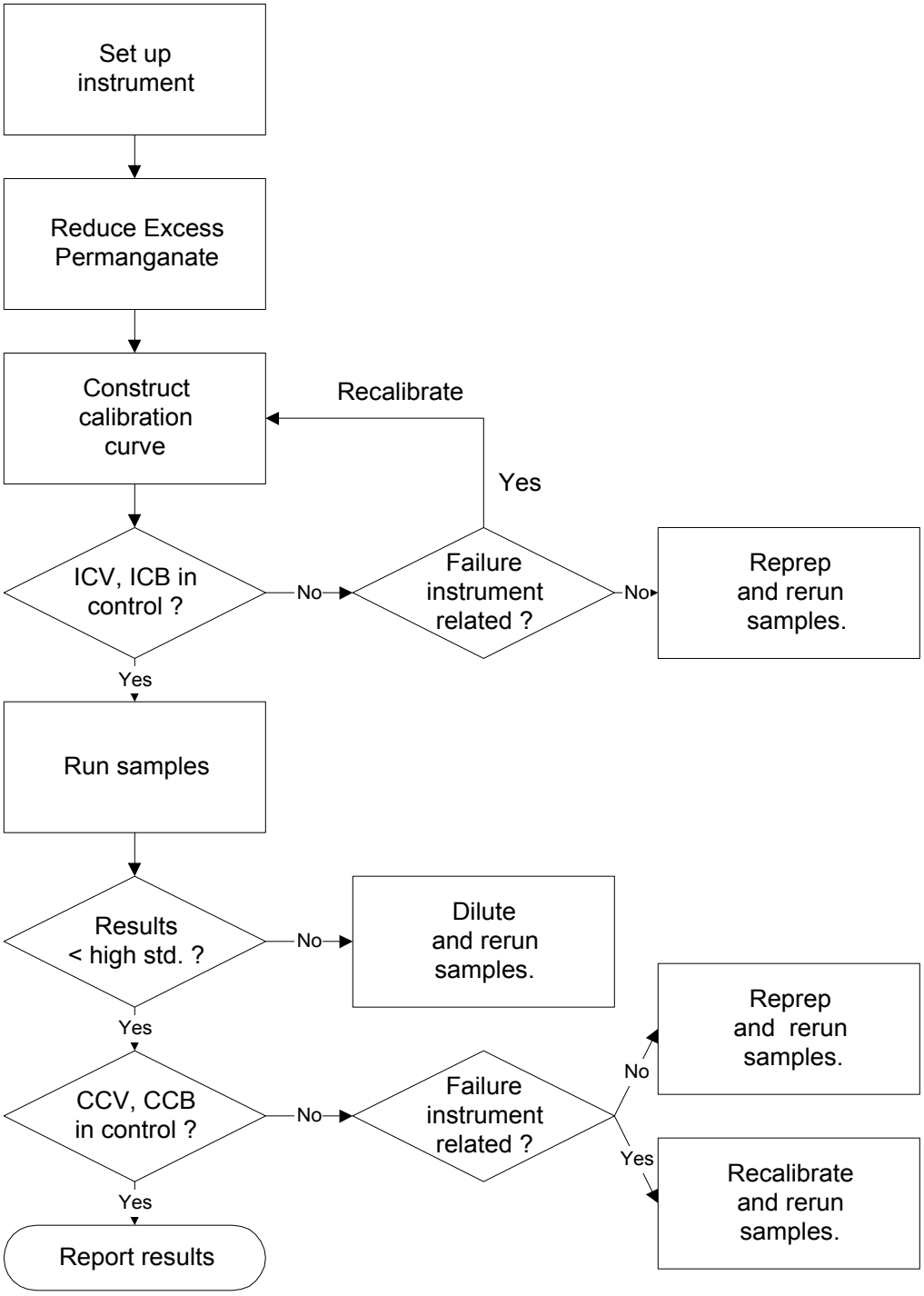


Figure 2. CVAA Mercury Analysis



APPENDIX A

TABLES

TABLE I . MERCURY REPORTING LIMITS, CALIBRATION STANDARD*, QC STANDARD AND SPIKING LEVELS (MG/L)

Method	Reporting Limit	
SW846 7470A	0.0002 mg/L	
SW846 7470A (TCLP)	0.0002 mg/L	
MCAWW 245.1	0.0002 mg/L	
Standard or QC sample	**mLs of 0.1 ppm Working Standard**	**Concentration (mg/L) *** **
Std 0	0	0
Std 1	0.2	0.0002
Std 2	0.5	0.0005
Std 3	1.0	0.001
Std 4	5.0	0.005
Std 5	10.0	0.010
ICV	2.5 **	0.0025
CCV	5.0	0.005
RLV	0.2	0.0002
LCS	2.5	0.0025
Aqueous MS	1.0	0.001
TCLP MS	5.0	0.005

*** SOP specified calibration levels must be used unless prevented by the instrument configuration or client specific requirements.**

**** Prepared from a second source 0.1 ppm working standard.**

***** When brought to a 100 mL final volume.**

TABLE II. Summary Of Quality Control Requirements

QC PARAMETER	FREQUENCY	ACCEPTANCE CRITERIA	CORRECTIVE ACTION
ICV	Beginning of every analytical run.	7470A: 90 - 110 %. 245.1: 95 – 105%	Terminate analysis; Correct the problem; Recalibrate or reprep batch (see Section 9.7).
ICB	Beginning of every analytical run, immediately following the ICV.	The result must be within +/- RL from zero. (1)	Terminate analysis; Correct the problem; Recalibrate or reprep batch (see Section 9.7).
RLV	Beginning of every analytical run, immediately following the ICB.	50 – 150% recovery.	Terminate analysis; Correct the problem; Recalibrate or reprep batch (see Section 9.9).
CCV	Every 10 samples and at the end of the run.	7470A: 80 - 120 %. 245.1: 90 – 110%	Terminate analysis; Correct the problem; Recalibrate and rerun all samples not bracketed by acceptable CCV or reprep batch (see Section 9.8).
CCB	Immediately following each CCV.	The result must be within +/- RL from zero. (1)	Terminate analysis; Correct the problem; Recalibrate and rerun all samples not bracketed by acceptable CCB or reprep batch (see Section 9.8).

TABLE II. Summary of Quality Control Requirements (Continued)

QC PARAMETER	FREQUENCY	ACCEPTANCE CRITERIA	CORRECTIVE ACTION
Method Blank	One per sample preparation batch of up to 20 samples.	The result must be less than or equal to the RL. (1) Sample results greater than 20x the blank concentration are acceptable. Samples for which the contaminant is < RL do not require redigestion (See Section 9.4).	Redigest and reanalyze samples. Note exceptions under criteria section. See Section 9.4 for additional requirements.
Laboratory Control Sample (LCS)	One per sample preparation batch of up to 20 samples.	Aqueous LCS must be within 80 - 120% (7470A) or 85 – 115% (245.1) recovery or in-house control limits.	Terminate analysis; Correct the problem; Redigest and reanalyze all samples associated with the LCS (see Section 9.5).
Matrix Spike	One per sample preparation batch of up to 20 samples (7470A) or one for every 10 or fewer samples (245.1).	75 - 125 % (7470A) or 70 – 130% (245.1) recovery or in-house control limits. (1) If the MS/MSD is out for an analyte, it must be in control in the LCS.	In the absence of client specific requirements, flag the data; no flag required if the sample level is > 4x the spike added. (see Section 9.6) For TCLP see Section 11.2.13
Matrix Spike Duplicate	See Matrix Spike	75 - 125 % (7470A) or 70 – 130% (245.1) recovery or in-house control limits; RPD ≤ 20%. (1) (See MS)	See Corrective Action for Matrix Spike.

(1) For specific DoD requirements, refer to PITT-QA-DoD-0001.

APPENDIX B
STL Hg DATA REVIEW CHECKLIST

STL Pittsburgh Data Review Checklist – Mercury

Run Date: _____ Lots Analyzed: 4. _____ 8. _____ 12. _____

Analyst: _____ 1. _____ 5. _____ 9. _____ 13. _____

Instrument: _____ 2. _____ 6. _____ 10. _____ 14. _____

Methods: _____ 3. _____ 7. _____ 11. _____ 15. _____

Review Item	Yes (✔)	No (✔)	N/A (✔)	2nd Level Review (✔)	Comments
A. Calibration/Instrument Run QC					
1. Instrument calibrated per manufacturer's instructions and at SOP specified levels?					
2. ICV/CCV analyzed at appropriate frequency and within control limits?					
3. ICB/CCB analyzed at appropriate frequency and within +/- RL or +/- CRDL (CLP)?					
4. CRA run? (CLP only)					
B. Sample Results					
1. Were samples with concentrations > the high calibration standard diluted and reanalyzed?					
2. All reported results bracketed by in control QC?					
3. Sample analyses done within holding time?					
C. Preparation/Matrix QC					
1. LCS done per prep batch and within QC limits?					
2. Method blank done per prep batch and < RL or CRDL (CLP)?					
3. MS run at required frequency and within limits?					
4. MSD or DU run at required frequency and RPD within SOP limits?					
D. Other					
1. Are all nonconformances documented appropriately?					
2. Current IDL/MDL data on file?					
3. Calculations and transcriptions checked for error?					
4. All client/project specific requirements met?					
5. Date/Time of analysis verified as correct?					

General Comments:_____

Analyst & Date: _____ Second-Level Review & Date: _____

APPENDIX C

MSA GUIDANCE

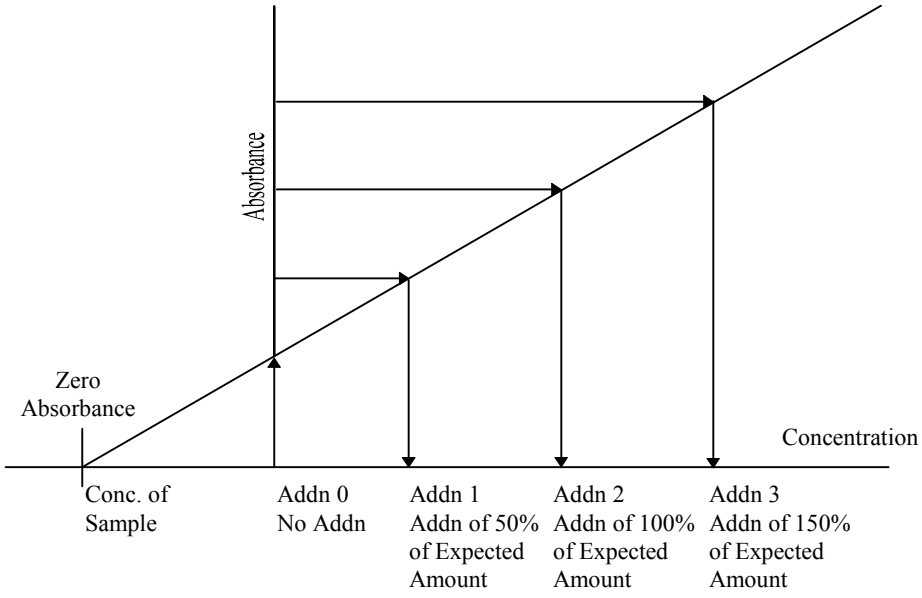
APPENDIX C. MSA GUIDANCE

Method of Standard Addition

Four equal volume aliquots of sample are measured and known amounts of standards are added to three aliquots. The fourth aliquot is the unknown and no standard is added to it. The concentration of standard added to the first aliquot should be 50% of the expected concentration. The concentration of standard added to the second aliquot should be 100% of the expected concentration and the concentration of standard added to the third aliquot should be 150% of the expected concentration. The volume of the unspiked and spiked aliquots should be the same (i.e., the volume of the spike added should be negligible in relation to the volume of sample).

To determine the concentration of analyte in the sample, the absorbance (or response) of each solution is determined and a linear regression performed. On the vertical axis the absorbance (or response) is plotted versus the concentrations of the standards on the horizontal axis using 0 as the concentration of the unspiked aliquot. An example plot is shown in Figure 1. When the resulting line is extrapolated back to zero absorbance, the point of interception of the horizontal axis is the concentration of the unknown. Calculate the correlation coefficient (r) and the x-intercept (where y=0) of the curve. The concentration in the digestate is equal to the negative x-intercept.

Figure 1



- For the method of standard additions to be correctly applied, the following limitations must be taken into consideration.

- The plot of the sample and standards must be linear over the concentration range of concern. For best results, the slope of the curve should be similar to that of a plot of the aqueous standard curve.

- The effect of the interference should not vary as the ratio of the standard added to the sample matrix changes.

APPENDIX D

PARTS MAINTENANCE GUIDE

APPENDIX D. PARTS MAINTENANCE GUIDE

Maintenance Schedule

The software offers a simple to use online Scheduled Maintenance page. To view the page go to Instrument:Scheduled Maintenance (F1 Menu, I, S). A page displaying all items necessary to keep the instrument well maintained is shown (see figure 6.1A).

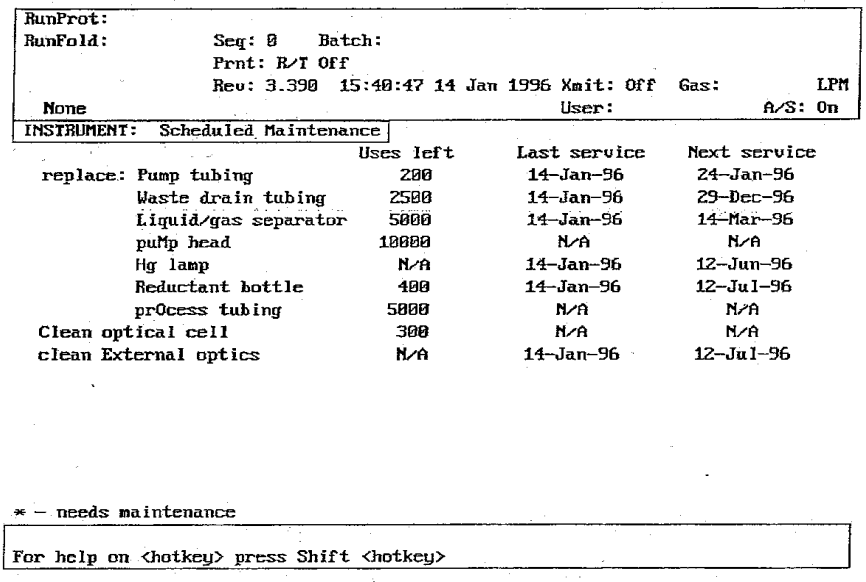


Figure 6.1a. Scheduled maintenance screen

Each scheduled maintenance item has a usage counter, timed usage, or both (N/A indicates that the usage counter or the timed usage is not applicable for that item). If either condition expires for a given item a maintenance message will alert the user at the top of the status box.

Maintenance Procedures

An asterisk(*) will appear next to the item requiring maintenance on the Scheduled Maintenance screen. To clear the message hit <Tab> or replace, clean, or replenish the item using the hot key for the item on the Scheduled Maintenance page. To perform the maintenance on a given item simply type the hot key (e.g. Type <P> for Pump tubing) and follow the directions. Once the directions are followed to completion, the usage counter and timed usage gets updated.

APPENDIX E

CONTAMINATION CONTROL GUIDELINES

APPENDIX E. CONTAMINATION CONTROL GUIDELINES

The following procedures are strongly recommended to prevent contamination:

All work areas used to prepare standards and spikes should be cleaned before and after each use.

All glassware should be washed with detergent and tap water and rinsed with 20% nitric acid followed by deionized water.

Proper laboratory housekeeping is essential in the reduction of contamination in the metals laboratory. All work areas must be kept scrupulously clean.

Powdered or Latex Gloves must not be used in the metals laboratory since the powder contains silica and zinc, as well as other metallic analytes. Only vinyl or nitrile gloves should be used in the metals laboratory.

Glassware should be periodically checked for cracks and etches and discarded if found. Etched glassware can cause cross contamination of any metallic analytes.

Autosampler trays should be covered to reduce the possibility of contamination. Trace levels of elements being analyzed in the samples can be easily contaminated by dust particles in the laboratory.

The following are helpful hints in the identification of the source of contaminants:

Reagents or standards can contain contaminants or be contaminated with the improper use of a pipette.

Improper cleaning of glassware can cause contamination.

Separate glassware if an unusually high sample is analyzed and soak with sulfuric acid prior to routine cleaning.

APPENDIX F

PREVENTIVE MAINTENANCE

APPENDIX F. PREVENTIVE MAINTENANCE

A maintenance log is used to record when maintenance is performed on instruments. When an instrument problem occurs indicate the date, time and instrument number, then identify the problem and corrective action in the maintenance log.

The following procedures are required to ensure that that the instrument is fully operational.

Cold Vapor Atomic Absorption (Leeman PS 200 II and Hydra AA)

Daily	Semi-annually	Annually
Clean lens windows with methanol.	Check Hg lamp intensity.	Change Hg lamp.
Check aperture.		Check liquid/gas separator.
Check argon flow.		
Check tubing and replace, if needed.		
Check drain.		
Replace drying tube.		

APPENDIX 36
SOP FOR THE DETERMINATION OF HEXAVALENT CHROMIUM BY EPA METHOD 7196A (PT_WC_015_R7)

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

Pittsburgh

SOP No. PT-WC-015
Rev.: 12
Effective Date: 11/28/08

Title: Chromium, Hexavalent (Colorimetric)

Method(s): SW846 3060A / 7196A and Standard Methods 20th Edition, Method 3500-Cr B

Approvals (Signature/Date):

Michael P. Wesoloski	
12/08/08	12/05/08
Mike Wesoloski Date	Steve Jackson Date
Technical Specialist	Health & Safety Manager / Coordinator
Nasreen K. DeRubeis	
11/28/08	11/28/08
Nasreen DeRubeis Date	Larry Matko Date
Quality Assurance Manager	Laboratory Director

This SOP was previously identified as SOP No. PT-WC-015, Rev. 11.1.

1. SCOPE AND APPLICATION

1.1. This method is used to determine the concentration of hexavalent chromium (Cr [VI]) in soils by digestion and leachate procedures and in groundwaters.

1.2. For DoD QSM Version 3 requirements, refer to SOP PT-QA- 025.

2. SUMMARY OF METHOD

2.1. Dissolved hexavalent chromium, in the absence of interfering amounts of substances such as molybdenum, vanadium, and mercury, may be determined colorimetrically by reaction with diphenylcarbazide in acid solution. The addition of excess diphenylcarbazide yields the red-violet product and its absorbance is measured photometrically at 540 nm. The reaction is very sensitive, the absorbency index per gram atom of chromium being about 40,000 L $g^{-1}cm^{-1}$ for this procedure.

2.2. The reporting limit for water samples is 0.01 mg/L Cr^{+6}, and for solids it is 0.4 mg/kg Cr^{+6}.

3. DEFINITIONS

3.1. LCS: The Laboratory Control Sample (LCS) is a spiked blank matrix sample used to monitor the accuracy of the analytical process independent of possible interference effects due to sample matrix. The LCS is processed through all method steps with the samples. The LCS is prepared from a source independent of the calibration standard materials. Successful analyte recovery for the LCS assures that the method is in control.

3.1.1. Two secondary source LCSs shall be digested and analyzed per batch of soil samples. Both soluble and insoluble LCSs are analyzed. The soluble LCS contains a soluble form of hexavalent chromium, while the insoluble LCS contains an insoluble form of hexavalent chromium. The insoluble LCS is used to evaluate the dissolution during the digestion process.

3.2. LCSD: The Laboratory Control Sample Duplicate is processed with the LCS when sufficient sample is not available to process a sample duplicate (for solid samples) or an MS/MSD (for aqueous samples). The LCS/LCSD is used to demonstrate batch precision. An LCSD is only required for batch QC, when a sample duplicate (for solid samples) or an MS/MSD (for aqueous samples) is not present. The LCSD is prepared from the same materials as the LCS.

3.3. MB: A method blank is processed using reagent grade water and all chemical reagents and procedures as the associated samples. It is used to monitor laboratory and/or reagent contamination. As a part of the QC batch it accompanies the samples through all the steps of

the analytical procedure. A method blank is run after the initial calibration curve and after each CCV within the analytical sequence.

3.4. PB: The term "preparation blank" is used by the laboratory to distinguish the digestion and analysis method blanks for solid samples. A preparation blank is a control sample that is prepared using the same reagents that were used for the sample analysis. As a part of the QC batch, it accompanies the digested solid samples through all the steps of the analytical procedure. The preparation blank is used to monitor the level of contamination introduced to a batch of samples as a result of processing.

3.5. Calibration blank: A reagent blank, which is prepared using 100 mL of reagent water and diphenylcarbazide reagent. The calibration blank is used for the zero point of the calibration curve.

3.6. CCV: A Continuing Calibration Verification Standard assures that the method calibration is in control. A CCV is run at intervals of up to ten samples within a sequence. The CCV is prepared from the same source material as the calibration curve. The LCS and CCV for liquid samples are prepared and analyzed in the same manner. For solid samples, the CCV is not digested.

3.7. ICV: An Initial Calibration Verification Standard assures that the method calibration is under control before analysis of samples begins. The ICV is prepared from the same source stock standard as the CCV.

3.8. Matrix Spikes:

3.8.1. MS: Matrix Spike is an aliquot of one sample in the QC batch that is spiked with a known amount of the target analyte. As a part of the QC batch, it accompanies the sample through all the steps of the analytical process.

3.8.2. MSD: Matrix Spike Duplicate consists of a replicate portion of the sample, which was designated as the MS. This portion is spiked and processed exactly as the MS.

3.8.3. MS/MSD results (for aqueous samples only) are used to determine the effects of the sample matrix on the precision and accuracy of the analytical process. Due to the potential variability of the matrix of each sample, the MS and the MSD results may not have immediate bearing on any sample except the one spiked.

3.8.4. Both soluble and insoluble pre-digestion matrix spikes must be analyzed at a frequency of one per batch of $\leq$ 20 field samples for soils. As a part of the QC batch, they accompany the samples through all the steps of the analytical process.

3.8.4.1. MSS: Matrix Spike-Soluble is an aliquot of one sample in the QC batch that is spiked with a known amount of a soluble form of hexavalent chromium.

3.8.4.2. MSI: Matrix Spike-Insoluble is an aliquot of one sample in the QC batch that is spiked with a known amount of an insoluble form of hexavalent chromium. It is used to evaluate the dissolution during the digestion process.

3.9. SD: Sample Duplicate is a replicate aliquot of an environmental sample taken from the same sample container, when possible, and processed with the first aliquot of the sample. The sample and sample duplicate result are compared to determine the effect of the sample matrix on the precision of the analytical process.

3.10. Post Digestion Spike: A Post Digestion Spike is an aliquot of a digested sample in the QC batch that is spiked with a known amount of the target analyte. Following the analysis (Colorimetric Determination) a post-digestion spike must be analyzed per batch. It is recommended to perform this analysis on the sample used for the matrix spike.

3.11. QC Batch: QC batch is a set of 20 or fewer environmental samples plus associated laboratory QC samples that are similar in composition and that are processed within the same time period with the same reagents and standard lots. Laboratory QC samples such as LCS, matrix QC samples, and blanks are not included in the sample count for QC batching purposes.

3.12. Reagent Grade Water: Laboratory water, which is produced by a Millipore DI system or equivalent. Reagent grade water must be free of the analyte of interest as demonstrated through the analysis of method blanks.

4. INTERFERENCES

4.1. The chromium reaction with diphenylcarbazide is usually free from interferences. However, certain substances may interfere, if the chromium concentration is relatively low. Hexavalent molybdenum and mercury salts also react to form color with the reagent; however, the red-violet intensities produced are much lower than those for chromium at the specified pH. Concentrations of up to 200 mg/L of molybdenum and mercury can be tolerated. Vanadium interferes strongly, but concentrations up to ten times that of chromium will not cause trouble.

4.2. Iron in concentrations greater than 1 mg/L may produce a yellow color, but the ferric iron color is not strong and difficulty is not normally encountered, if the absorbance is measured photometrically at the appropriate wavelength.

5. SAFETY

5.1. Employees must abide by the policies and procedures in the Corporate Environmental Health and Safety Manual (CW-E-M-001), Radiation Safety Manual and this document. This procedure may involve hazardous material, operations and equipment. This SOP does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, gloves, lab coats and closed-toe, nonabsorbent shoes are a minimum.

5.2. Samples that contain high concentrations of carbonates or organic material or samples that are at elevated pH can react violently when acids are added.

5.3. When adding acid to samples, the sample container lid shall remain open until after the acid has stopped reacting with the sample. This will prevent pressure from building up inside the closed container and causing the acidified sample to splash out of the container.

5.4. The following is a list of the materials used in this method, which have a serious or significant hazard rating. **NOTE: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

5.5. Eye protection that protects against splash, laboratory coat, and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled. Cut resistant

gloves must be worn doing any other task that presents a strong possibility of getting cut. Disposable gloves that have become contaminated will be removed and discarded; other gloves will be cleaned immediately.

5.6. Exposure to chemicals must be maintained as low as reasonably achievable, therefore, unless they are known to be non-hazardous, all samples must be opened, transferred, and prepared in a fume hood or under other means of mechanical ventilation. Solvent and waste containers will be kept closed unless transfers are being made.

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Nitric Acid	Corrosive Oxidizer Poison	2 ppm-TWA 4 ppm-STEL	Nitric acid is extremely hazardous; it is corrosive, reactive, an oxidizer, and a poison. Inhalation of vapors can cause breathing difficulties and lead to pneumonia and pulmonary edema, which may be fatal. Other symptoms may include coughing, choking, and irritation of the nose, throat, and respiratory tract. Can cause redness, pain, and severe skin burns. Concentrated solutions cause deep ulcers and stain skin a yellow or yellow-brown color. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
Potassium Dichromate	Oxidizer Corrosive Carcinogen	0.1 Mg/M3 TWA as CrO3	Extremely destructive to tissues of the mucous membranes and upper respiratory tract. May cause ulceration and perforation of the nasal septum. Symptoms of redness, pain, and severe burn can occur. Dusts and strong solutions may cause severe irritation. Contact can cause blurred vision, redness, pain and severe tissue burns. May cause corneal injury or blindness.
Sodium Hydroxide	Corrosive	2 Mg/M3-Ceiling	Severe irritant. Effects from inhalation of dust or mist vary from mild irritation to serious damage of the upper respiratory tract, depending on severity of exposure. Symptoms may include sneezing, sore throat or runny nose. Contact with skin can cause irritation or severe burns and scarring with greater exposures. Causes irritation of eyes, and with greater exposures it can cause burns that may result in permanent impairment of vision, even blindness.
Sulfuric Acid	Corrosive Oxidizer Dehydrator Poison Carcinogen	1 Mg/M3-TWA	Inhalation produces damaging effects on the mucous membranes and upper respiratory tract. Symptoms may include irritation of the nose and throat, and labored breathing. Symptoms of redness, pain, and severe burn can occur. Contact can cause blurred vision, redness, pain and severe tissue burns. Can cause blindness.
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

5.7. The preparation of standards, reagents, and glassware cleaning procedures that involve solvents such as methylene chloride will be conducted in a fume hood with the sash closed as far as the operations will permit.

5.8. All work must be stopped in the event of a known or potential compromise to the health and safety of a TestAmerica associate. The situation must be reported immediately to a laboratory supervisor or the EH&S coordinator.

6. EQUIPMENT AND SUPPLIES

6.1. Spectrophotometer, for use at 540 nm.

6.2. Volumetric glassware.

6.3. Class “A” Volumetric pipettes or Calibrated Multi-channel pipettes.

6.4. pH meter capable of analyzing pH and Oxidation Reduction Potential (ORP).

6.5. Nalgene 115-mL disposable filter unit with 0.45 micron filter.

6.6. Water bath equipped with shaker (Precision Model 50) used for digestion.

6.7. Nalgene 125-mL small-mouth polypropylene digestion containers.

7. REAGENTS AND STANDARDS

NOTE: The preparation of all standards and reagents must be recorded in the wet chemistry electronic reagent log.

7.1. Note: use manufacturer’s expiration date for determining the maximum shelf life for reagents and standard solutions made from those reagents.

7.2. Nitric Acid: HNO_3, concentrated, analytical reagent grade or spectrograde quality. Store at 20°C to 25°C in the dark. Discard if the solution has yellow tinge; this is indicative of photoreduction of NO_3 to NO_2. **Purchased.**

7.3. Sodium Carbonate: Na_2CO_3, anhydrous, analytical reagent grade. Store at 20°C to 25°C in a tightly sealed container. **Purchased.**

7.4. Sodium Hydroxide: NaOH, analytical reagent grade. Store at 20°C to 25°C in tightly sealed container. **Purchased.**

7.5. Magnesium Chloride: $MgCl_2$ (anhydrous), analytical reagent grade. 392.18 mg $MgCl_2$ is equivalent to 100 mg Mg^{2+}. Store at 20°C to 25°C in a tightly sealed container. ***Purchased or prepared fresh every six months or as needed.***

7.6. Phosphate Buffer:

7.6.1. K_2HPO_4: Analytical reagent grade. **Purchased.**

7.6.2. KH_2PO_4: Analytical reagent grade. **Purchased.**

7.6.3. 0.5M K_2HPO_4/0.5M KH_2PO_4 buffer at pH 7: Dissolve 87.09 g K_2HPO_4 and 68.04 g KH_2PO_4 into 700mL of reagent grade water. Transfer to a 1L volumetric flask and dilute to volume. ***Prepare fresh every six months or as needed.***

7.7. Sulfuric Acid (H_2SO_4), 10 percent (v/v) (1.8M): Add 10 mL of concentrated H_2SO_4 to approximately 70 mL of reagent grade water. Mix well and let cool. Dilute to a final volume of 100 mL with reagent grade water. ***Prepare fresh annually or as needed.***

7.8. Diphenylcarbazide Solution: Dissolve 5.0 g 1,5-diphenylcarbazide in 1000 mL acetone. Store in a brown bottle. Discard when the solution becomes discolored. ***Prepare fresh every six months or as needed.***

7.9. Alkalinity Digestion Solution: Dissolve 40 g of ACS grade NaOH and 60 g of reagent grade sodium carbonate in reagent grade water and dilute to 2 L. Store the solution in a polyethylene bottle at 20-25ºC. ***Prepare fresh monthly or as needed.***

7.10. Acetone: reagent grade. **Purchased.**

7.11. Stock Potassium Dichromate Solution (50 mg/L Cr^{+6}): Dissolve 0.1414 g $K_2Cr_2O_7$ (analytical reagent grade) in reagent grade water and dilute to 1 liter. ***Prepare fresh every six months or as needed.***

7.12. Working Chromium Standard Solution (5 mg/L): Pipette 20 mL of Stock Potassium Dichromate (7.11) into 200 mL volumetric flask. Dilute with reagent grade water. The standard is prepared with a Class A volumetric pipette***. Prepared fresh each day of analysis.***

7.13. Standard Curve: Into seven 50 mL volumetric flasks, pipette, respectively, 0.1, 0.5, 1.0, 2.5, 5.0 and 10.0 mL of the Working Standard Solution (7.12). Dilute to volume with reagent grade water making standards of 0.01, 0.05, 0.10, 0.25, and 0.50 mg/L respectively for water samples. For soil analysis the bench sheet will represent these standards in the equivalent soil concentrations of 0.4, 2.0, 4.0, 10.0, 20.0 and 40.0 mg/kg. The standard curve is prepared using a Class A volumetric pipette and a calibrated pipette. ***Curve is prepared fresh on each day of analysis.***

5mg/L * (1L/1000mL) * 10mL = 0.05mg Cr

0.05mg in 100mL reagent water = 0.5mg/L standard

7.14. LCS/MS (for solid matrix only): Standards for the LCS are prepared from second source materials from the calibration standards. The standard is prepared using a Class A volumetric pipette on the day of analysis.

7.14.1. Soluble LCS and MS: 5 mL of 1000 ppm Cr^{+6} solution from a different lot (purchased commercially from ERA) diluted to 100 mL with reagent water. The final concentration is 50 ppm Cr^{+6}. Spike by adding 1 mL of the 50 ppm Cr^{+6} solution into 50 mL of digestion solution (for the LCS) or 50 mL of sample (for the MS) and carry through the digestion process. A final volume of 100 mL will give a true value of 20 mg/kg.

7.14.2. Insoluble LCS and MS: Add 0.011 g of $PbCrO_4$ (purchased) to 50 mL of digestion solution (for the LCS) or 50 mL of sample (for the MS) and carry through the digestion process. A final volume of 100 mL will give a true value of 708 mg/kg.

7.15. LCS (for liquid matrix only): Stock standard is purchased commercially from ERA. LCS is prepared by adding 0.25 mL of a 50 ppm stock to 50 mL sample. ***Prepare fresh each day of analysis.***

7.16. ICV/CCV (for solid matrix only): Prepared by adding 0.5 mL of the 50 ppm potassium dichromate stock standard (7.11) and diluting to a final volume of 50 mL with reagent grade water. The ICV/CCV may be prepared from the same material as the calibration standards, however the ICV/CCV is not digested. The standard is prepared using a Class A volumetric pipette on the day of analysis.

7.17. ICV/CCV (for liquid matrix only): Prepared by adding 0.25 mL of the 50 ppm potassium dichromate stock standard used to prepare the calibration standards to a 50 mL volumetric flask and diluting to volume. ***Prepare fresh each day of analysis.***

7.18. MS/MSD (for liquid matrix only): 0.25 mL of 50 ppm Cr^{+6} and sample (or an aliquot of liquid sample diluted to 50 mL) is a 0.25 ppm spike. The MS and MSD should be prepared from the same standard material source as the LCS. The MS and MSD are prepared using a Class A volumetric pipette.

7.19. Note: If different stock standards are purchased, the true values of the standards will need to be redetermined and verified.

8. SAMPLE COLLECTION, PRESERVATION, SHIPMENT AND STORAGE

8.1. To retard the chemical activity of Hexavalent Chromium, the samples and extracts should be stored at 4°C until analyzed. Container: Plastic or glass.

8.2. The maximum holding time prior to analysis of the liquid sample is 24 hours from the date of sample collection.

8.3. The holding time for solid samples is 30 days from date of collection to extraction. The extract must be analyzed within 168 hours after the sample is extracted.

9. QUALITY CONTROL

9.1. The QC batch is defined in QA SOP: PT-QA-021: 'The QC batch is a set of up to 20 field samples plus associated laboratory QC samples that are similar in composition (matrix) and that are processed within the same time period using the same reagent and standard lots.'

9.2. An Initial Calibration Verification sample is processed on each day of analysis before the first batch of samples. The ICV is prepared from the same source as the material used for instrument calibration. The ICV recovery must be 90-110 percent of the true value of the standard. The ICV for soil samples is not digested.

9.3. A Laboratory Control Sample (both soluble and insoluble for soil samples) is processed on each day of analysis with every batch of 20 or fewer field samples. The LCS is prepared from a source independent of the material used for instrument calibration. The LCS recovery must be 85 - 115 percent of the true value for water samples. For soil samples the LCS recovery must be 80 - 120 percent. If the LCS fails criteria, the analyst will check calculations and instrument performance and reanalyze the LCS once. If the LCS is still outside control limits, all samples in the QC batch will be reprepared and reanalyzed. If this is not possible due to limited sample quantity, the laboratory project manager will be notified and an analytical narrative provided with the data. If repreparation and reanalysis will be outside of holding time, the client should be notified and approval from the client should be obtained before reanalysis.

9.4. Method Detection Limit (MDL) - An MDL must be determined for each analyte/matrix prior to the analysis of any samples. The MDL is determined using seven replicates of reagent water, spiked with all the analytes of interest that have been carried through the entire analytical procedure. MDLs must be redetermined on an annual basis in accordance with 40 CFR Part 136 Appendix B requirements as detailed in TestAmerica QA Policy: PITT-QA-0007. The spike level must be between the calculated MDL and 10X the MDL to be valid. The result of the MDL determination must be below the TestAmerica reporting limit.

9.5. Method Blanks or Continuing Calibration Blanks (CCBs) are processed and run after every calibration curve and after each CCV within a sequence. Method blanks or CCBs must be free of analyte down to the reporting limit. **Refer to PT-QA- 025 for specific DoD requirements for the method blank.** The method blank immediately precedes the samples associated with it for reporting purposes. All reportable data must be bracketed by acceptable method blanks. Samples associated with the unacceptable blanks will be reanalyzed. If this is not possible due to limited sample quantity, the lab project manager will be notified and the client will be consulted for instructions. Regardless, the analytical narrative will document the event. If reprep and reanalysis is outside of the holding time, approval from the client should be obtained before reanalysis.

9.6. The preparation blank (PB) is only processed with each batch of 20 or fewer solid matrix environmental samples. Analyte concentration in the PB must be less than the reporting limit. **Refer to PT-QA- 025 for specific DoD requirements for the preparation blank.** The PB is used to determine if contamination or any memory effects are occurring. If the PB fails criteria, all samples digested with it will be reprepared and reanalyzed. If this is not possible due to limited sample quantity, the lab project manager will be notified and the client will be consulted for instructions. Regardless, the analytical narrative will document the event. If repreparation and reanalysis is outside holding time, approval from the client must be obtained before reanalysis.

9.7. Continuing Calibration Verifications will be analyzed prior to the analysis of environmental samples and after every 10 or fewer environmental samples. Acceptance limits are ±10 percent of the true value of the standard. The CCV for soil samples is not digested. All reported data must be bracketed by an acceptable calibration curve and a CCV, or by consecutive acceptable CCVs. Samples associated with an unacceptable CCV will be reanalyzed. If this is not possible due to limited sample quantity, the laboratory project manager will be notified and an analytical narrative provided with the data. If repreparation and reanalysis is outside of the holding time, approval from the client must be obtained before reanalysis.

9.8. An MS/MSD pair is processed with each batch of 10 or fewer aqueous environmental samples. A MSS and MSI is processed with each batch of 20 or fewer soil environmental samples. **For aqueous DoD samples, either a sample duplicate or an MSD is required to be analyzed**

for every 10 samples. For soil DoD samples, either a sample duplicate or an MSD is required to be analyzed for every batch of samples. The MS/MSD recoveries must be 85-115 percent of the true value for water samples, and the RPD between the MS and MSD should be ≤ 10 percent. The MSS/MSI recoveries must be within 75-125 percent of the true value for soil samples. If the sample selected for spiking requires dilution because the initial concentration of the sample is excessively high, then the MS/MSD should be run at the same dilution as the unspiked sample. If the resulting spike is over range, this should be documented and narrated in the data report. The MS/MSD should never be run at a dilution greater then the associated sample as this alters the matrix of the sample and thereby makes it invalid.

9.8.1. If the MS and the MSD fails recovery criteria, the analyst will check calculations and instrument performance, in order to evaluate evidence of matrix interference. If the LCS is acceptable and the MS/MSD are comparable and outside of QC limits, then a matrix effect is indicated and narrated accordingly.

9.8.2. If the matrix spike recoveries fall outside these recovery limits for soil samples, the entire batch must be rehomogenized, redigested and reanalyzed. (NOTE: If the spiked sample concentration is greater than 4x the predigestion spike concentration, no redigestion/reanalysis is required unless the samples are from a NJ site in which case the lab project manager should be contacted for further guidance.)

9.8.3. If upon reanalysis, the matrix spike is not within the recovery limits of 75%-125%, but the LCS is within the Criteria specified in Section 9.3, additional laboratory characterization of each sample in the batch for ORP and pH is required to determine if the sample exhibits reducing conditions by plotting the Eh and pH data on the Eh-pH diagram in Figure 1. (Refer to Section 11.1.1 for the procedure to determine the sample's oxidizing/reducing nature.) A value of Eh-pH below the bold diagonal line in Figure 1 indicates a reducing soil for hexavalent chromium and spike recovery is not expected to meet criteria. If the data point falls above this line, the sample is capable of supporting hexavalent chromium. Further characterization for total sulfides, Total Organic Carbon (TOC), Chemical Oxygen Demand (COD), or Biochemical Oxygen Demand (BOD) may be required on a case by case basis at the direction of the Wet Chemistry Manager or Supervisor.

9.8.4. A laboratory control sample duplicate or LCSD is used to demonstrate batch precision when the client has not supplied sufficient sample to prepare an MS/MSD or sample duplicate analysis. In this case the LCSD must be recovered within 85 - 115 percent of the true value and must have an acceptable RPD of ≤ 10 percent with the LCS. For Soils the LCS/LCSD must be recovered within 80 -120 percent recovery and must have an acceptable RPD of ≤ 20. If these criteria are not met, the corrective action noted in Section 9.1 would apply.

9.9. Duplicate - One duplicate laboratory sample must be analyzed for every 10 solid samples. Either a sample duplicate or matrix spike duplicate (MSD) must also be analyzed for every 10 water samples. The sample used for the predigestion spike should be used for this purpose. Duplicate samples must have a Relative Percent Difference (RPD) of $\leq$ 20% (or $\leq$ 30 percent for DoD soil samples), if both the original and the duplicate are $\geq$ four times the laboratory reporting limit. A control limit of ± the laboratory reporting limit is used when either the original or the duplicate sample is < four times the laboratory reporting limit.

9.10. Post Digestion Spike (PDS)- Following the analysis (Colorimetric Determination) a post-digestion spike must be analyzed per batch. The concentration of hexavalent chromium in the PDS should be 30 mg/kg or twice the concentration of hexavalent chromium found in the environmental sample; whichever is greater. The post digestion spike must be performed on a field sample, not on a field blank or preparation blank. It would be helpful to perform this analysis on the sample used for the matrix spike. Recovery limits for the post-digestion spike are 85-115 percent. If the PDS fails to meet recovery limits, a new aliquot of the sample must be re-spiked and re-analyzed. If the PDS recovery limits cannot be met due to sample matrix, this condition must be documented in a non-conformance memo and in the project narrative.

10. PROCEDURE

10.1. Calibration and Standardization

10.1.1. The spectrophotometer is set up according to the manufacturer's specification. Zero or null the instrument using a reagent blank or "calibration blank". Construct a standard curve by plotting the absorbance on the y-axis versus the concentration of each standard solution on the x-axis. An acceptable standard curve for Cr^{+6} is a first order linear regression curve with a correlation coefficient greater than or equal to 0.995.

10.1.1.1. The reagent blank or "calibration blank" is prepared using 50 mL of reagent water and diphenylcarbazide reagent and is processed as described in Section 10.2.3.

10.2. Procedure

10.2.1. Refer to PT-QA-024 for subsampling procedures. Begin at Section 10.2.3 for water samples. Solid samples require an alkaline digestion procedure after which the sample can be treated as a water throughout the remainder of the analysis.

10.2.1.1. For solid samples, a determination of the sample's oxidizing/reducing nature will need to be determined prior to interpretation of the matrix spike recovery results.

10.2.1.1.1. Place 20 g (± 0.5 g) of the sample selected for matrix spike analyses in a beaker or other suitable container.

10.2.1.1.2. Add 20 mL of reagent water and mix for five minutes.

10.2.1.1.3. Allow sample to stand for one hour to allow the solids to settle out.

10.2.1.1.4. Following manufacturer's instructions, calibrate the pH meter and measure the sample pH and Oxidation Reduction Potential (ORP).

10.2.1.1.5. Adjust the ORP measurement based on reference electrode correction factor to yield Eh value.

10.2.1.1.6. Plot the pH and Eh values on Figure 1 in order to determine the sample's oxidizing/reducing nature.

10.2.1.2. Weigh 2.5 g ± 0.10 g of sample into a clean labeled 125 mL bottles. Record the weight up to two decimal places.

10.2.1.3. Add 50 ± 1.0 mL of digestion solution to each sample, 400 mg of $MgCl_2$ and 0.5 mL of 1.0 M phosphate buffer. Place in hot water bath at a temperature of 90 - 95°C and begin shaking at 175 rpm for 5 minutes. Then release pressure by venting caps. After caps are resealed tightly begin heating and shaking for 60 minutes. Start timing after bath has returned to 90 - 95°C and maintain this temperature throughout the 60 minutes. Record temperatures and start and finish time of digestion.

10.2.1.4. Following the heated digestion, gradually cool the solution to room temperature and quantitatively transfer the contents of the bottle to vacuum filtration apparatus with Type I water rinses. Filter the digestion solution through a 0.45 um filter (commercially purchased filter). Transfer the rinsates and the filtrate to a clean, labeled 100 mL plastic cup. (Note: Use a polyethylene bottle if colorimetric analysis is not following immediately.)

10.2.1.5. Proceed to Section 10.2.3.

10.2.1.6. For MSS, solid sample – 1.0 mL of 50 ppm soluble Cr^{+6} spiking solution is spiked into the digestion solution with the sample, then processed through all steps of the method (Section 10.2.1.1). For MSI, solid sample – 0.11 g of $PbCrO_4$ is spiked into the digestion solution with the sample, then processed through all steps of the method (Section 10.2.1.1).

10.2.1.7. For the solid LCS (soluble) – 1.0 mL of 50 ppm soluble Cr^{+6} spiking solution is spiked into the digestion solution then processed through all steps of the method (Section 10.2.1.1). For the solid LCS (insoluble) – 0.011 g of $PbCrO_4$ is spiked into the digestion solution with the sample, then processed through all steps of the method (Section 10.2.1.1).

10.2.2. The solid blank (i.e. PB) is a 50 mL aliquot of digestion solution that is processed through all the steps of the method (Section 10.2.1.1).

10.2.3. **Sample Preparation Procedures** - **All Matrices**: Calibrate the pH meter.

10.2.3.1. For aqueous matrices, adjust the pH of the samples, standards, QC samples, MS, MSD or blanks to 2.0 ± 0.5 with 0.2N H_2SO_4 acid.

10.2.3.2. For digested soil samples, LCS, QC samples, MSS/MSI and blanks, adjust the pH of the digestate to 7.5 ± 0.5 with nitric acid. Record the pH on the digestion log. Dilute to 100 mL final volume. At this point samples can be stored up to 7 days from start date of digestion. The pH is adjusted to 2.0 ± 0.5 using 0.2N H_2SO_4 (see 10.2.4). After this adjustment the sample must be analyzed within 24 hours.

10.2.4. The 100 mL will be split into two 25 mL portions (one portion to measure the sample absorbance and the other to measure the sample blank absorbance) and one 50 mL portion that is reserved for any necessary sample dilutions. To both of the 25 mL portions, add 0.125 mL of sulfuric acid to adjust the pH to 2.0 ± 0.5. If this does not adjust the pH to 2.0 ± 0.5, add additional drops of sulfuric or nitric acid until the pH is within 2.0 ± 0.5. Record the pH on the digestion log. To one of the 25 mL portions, add 0.5 mL of diphenylcarbazide reagent (color reagent is added after acidification), mix, and let stand 10 minutes. This portion is used to measure the sample absorbance. To the other 25 mL portion, add 0.5 mL of acteone, mix, and let stand 10 minutes. This portion is used to measure the sample blank absorbance. The sample is then ready for analysis (Section 10.2.5).

10.2.5. Sample Analysis Procedure: Measure the absorbance (or concentration) of the samples, LCS, standards, QC samples, MS/MSDs, and blanks on a spectrophotometer set at 540 nm. Colored or turbid samples will be filtered using 0.45 micron filter paper. All samples are “blanked out” against themselves by adding acetone to acidified or digested sample in place of the diphenylcarbazide coloring reagent (Section 10.2.4). The absorbance of the sample blank is subtracted from the absorbance of that particular sample prior to calculating its concentration.

10.2.6. Verification for every sample matrix (MS/MSD samples) analyzed: Verification is required to ensure that neither a reducing condition, nor chemical interference is affecting color development. This must be accomplished by analyzing a second aliquot of the pH-adjusted filtrate that has been spiked with Cr^{+6}. To verify the absence of an interference, the spike recovery must be between 85 and 115 percent. If the result of verification indicates a suppressive interference, the sample should be diluted and reanalyzed. If a 1:1 dilution of the sample still indicates an interference, that data must be flagged and an analytical narrative provided with the project data.

10.2.7. Acidic extracts (such as TCLP extracts) that yield recoveries of less than 85 percent should be retested to determine if the low spike recovery is due to the presence of a residual reducing agent. The determination will be performed by making an aliquot of the extract alkaline pH (8.0 to 8.5) using 1 N NaOH and then respiking and analyzing. If a spike recovery of 85 to 115 percent is obtained in the alkaline aliquot, one may conclude that the low recovery was due to a “TCLP” matrix effect and that the method performance has been verified.

10.2.8. Any authorized deviations from this procedure must be documented as a nonconformance, with a cause and corrective action described.

10.2.9. All sample preparation and analysis information will be documented on laboratory bench sheets, computer printouts, standard logbooks, etc. Raw data will be forwarded for reporting and for inclusion in the project files.

11. CALCULATIONS / DATA REDUCTION

11.1. Calculations:

11.1.1. Sample Concentration (where sample concentration is not read directly from the standard curve):

$$\text{mgCr / L} = \frac{\mu\text{g Cr (in 102 mL final volume)}}{\text{A x B}} x100$$

Where:
mg/L Cr as calculated above = C in equations 12.1.2 and 12.1.3
A = mLs original sample, and
B = mLs portion (decimal fraction) of 100 mL digested sample.

11.1.2. Waters, mg/L Cr^{+6} = C x D

Where:
C = (Concentration of sample from Section 12.1.1- sample blank) mg/L.
D = Dilution Factor

11.1.3. Solids, mg/kg Cr^{+6} (dry weight basis) = (C x D x F) ÷ E

Where:
C = (Concentration of sample from Section 12.1.1- sample blank) mg/L
D = Dilution Factor
E = (100 % - percent moisture) ÷ 100 %
F = Volume/Weight Factor - Volume of final extract (mL) divided by weight of sample (g)

11.2. Duplicates (Relative Percent Difference):

$$\text{RPD} = \frac{|X_1 - X_2|}{\left(\frac{X_1 + X_2}{2}\right)} \text{ x 100 \%}$$

X_1 = Original Results
X_2 = Duplicate

11.3. LCS Percent Recovery:

$$\text{LCS \% Recovery} = \left(\frac{\text{Observed Conc. in LCS}}{\text{True LCS Conc.}} \right) \times 100\ \%$$

11.4. MS Adjusted Sample Concentration:

$$\text{Adjusted Sample Conc. (mg / L)} = \text{Original Sample Conc.} \left(\frac{\text{Vol. of Sample Spiked}}{\text{Original Sample Vol.}} \right)$$

11.5. MS Percent Recovery:

$$\text{\% Recovery of MS} = \left(\frac{\text{Observed Conc. in Spiked Sample} - \text{Adjusted Sample Conc.}}{\text{True Spike Conc.}} \right) \times 100\ \%$$

11.6. All analytical data is recorded on the analytical bench sheet.

12. METHOD PERFORMANCE

12.1. The group/team leader has the responsibility to ensure that this procedure is performed by an analyst who has been properly trained in its use and has the required experience. The group/team leader must document the training and PE performance and submit the results to the QA Manager for inclusion in associate training.

12.2. Initial Demonstration and Capability

12.2.1. Prior to analysis of any samples using this SOP, the following requirement must be met:

12.2.2. Initial Demonstration Study: This requires the analysis of four QC check samples. The QC check sample is a well-characterized, laboratory-generated sample used to monitor method performance, which should contain the analyte(s) of interest. The results of the initial demonstration study must be acceptable before analysis of

samples under this SOP may begin. Four aliquots of the check sample (LCS) are prepared and analyzed using the procedures detailed in this SOP. Acceptance criteria for the LCS are given in Section 9.3 and 9.8.

12.3. The method detection limit (MDL) is the lowest concentration that can be detected for a given analytical method and sample matrix with 99% confidence that the analyte is present. The MDL is determined according to the laboratory's MDL procedure SOP PT-QA-007.

13. POLLUTION CONTROL

13.1. It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i.e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage and reagent stability). Employees must abide by the policies in Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention."

14. WASTE MANAGEMENT

14.1. Waste management practices are conducted consistent with all applicable rules and regulations. Excess reagents, samples and method process wastes are disposed of in an accepted manner. Waste description rules and land disposal restrictions are followed. Waste disposal procedures are incorporated by reference to PT-HS-001. The following waste streams are produced when this method is carried out.

14.2. Acidic waste generated by the analysis. This waste is placed in a container identified as "Acid Waste with Metals", Waste #6.

15. REFERENCES

15.1. Alkaline Digestion for Hexavalent Chromium, Method 3060A, SW-846, Test Methods for Evaluating Solid Waste, Third Edition, Revision 1, December 1996.

15.2. Standard Methods for the Examination of Water and Waste Water, 20th Edition, 1998; Method 3500-Cr B and Standard Methods Online.

15.3. Method 7196A, Chromium Hexavalent (Colorimetric), SW-846, Test Methods for Evaluating Solid Waste, 3rd Edition, Revision 1, July 1992.

15.4. PT-QA-025, Implementation of the DoD QSM Version 3.

15.5. PT-QA-024, Subsampling.

15.6. PT-QA-007, Method Detection Limits.

15.7. PT-QA-021, Quality Control Requirements

16. ATTACHMENTS

16.1. Figure 1 – Eh/pH Phase Diagram (Figure 2 of Method 3060A)

16.2. Figure 2 – Example Hexavalent Chromium Log Sheet (Aqueous Samples)

16.3. Figure 3 – Example Hexavalent Chromium Log Sheet (Soil Samples)

16.4. Figure 4 – Method 3060A – Alkaline Digestion For Hexavalent Chromium

17. REVISION HISTORY

17.1. Revision 10, 10/5/07.

17.1.1. Changed laboratory name to TestAmerica.

17.1.2. Changed the format of the SOP to correspond to the new Corporate SOP format.

17.1.3. Added the requirement to do a sample duplicate for every 10 soil samples instead of every 20.

17.2. Revision 11, 05/09/08.

17.2.1. Added a definition for ‘post digestion spike’.

17.2.2. Updated sample volumes in Sections 10.2.4 and 10.2.5 to allow for additional sample to be reserved for dilutions.

17.2.3. Added to Section 10.2.3.2: At this point samples can be stored up to 7 days from start date of digestion. The pH is adjusted to 2.0 ± 0.5 using 0.2N H2SO4 (see 10.2.4). After this adjustment the sample must be analyzed within 24 hours.

17.3. Revision 11.1, 05/16/08

17.3.1. Section 7.13 removed standard concentration 1.0 mg/l.

17.4. Revision 12, 11/28/08

17.4.1. Updated standard concentrations in sections 7.8 and 7.13.

17.4.2. Added latest safety requirements.

17.4.3. Updated references. Updated pollution control and waste management sections.

17.4.4. Added MDL requirements. Moved IDOCs under Method Performance.

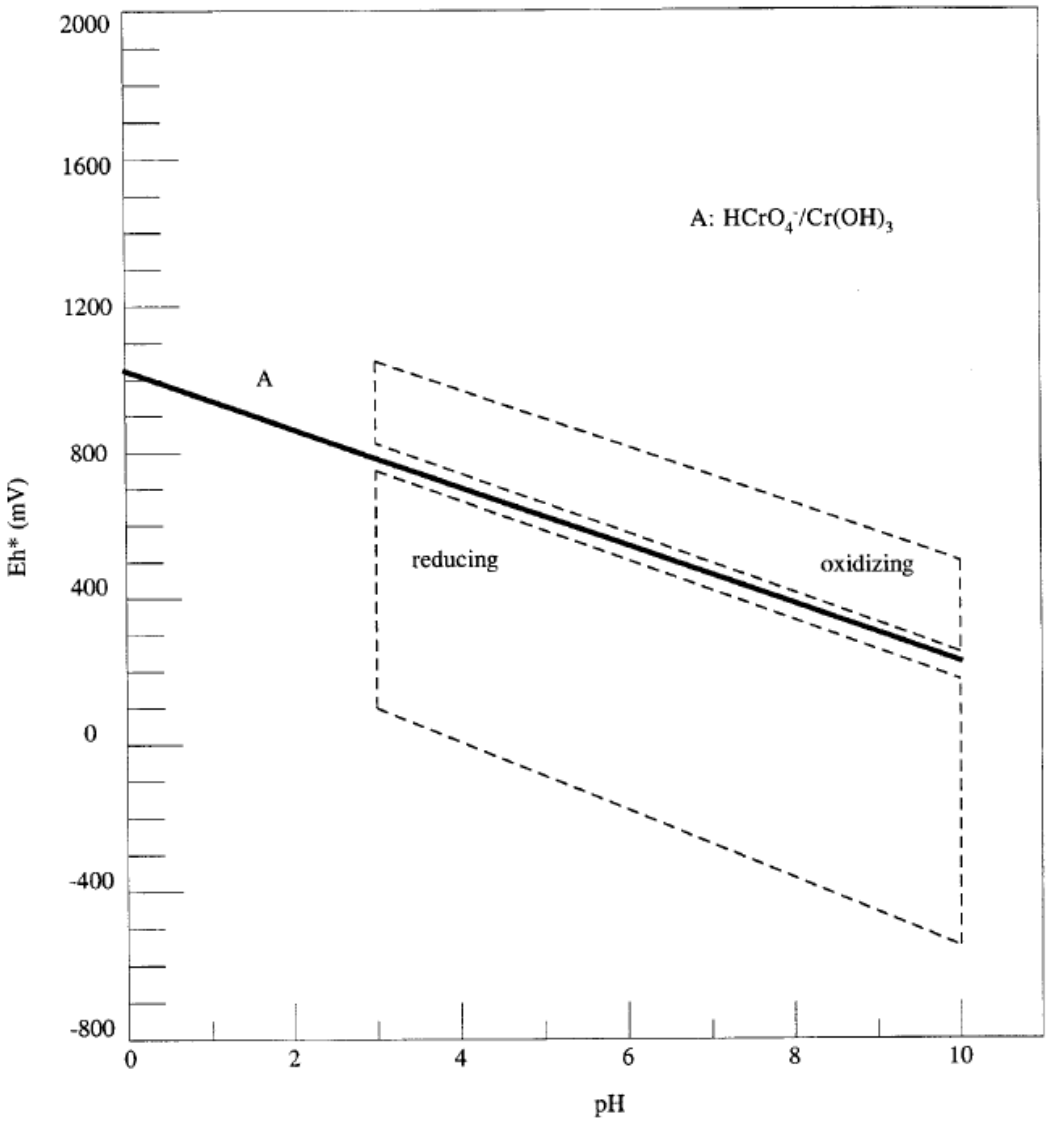
18. METHOD MODIFICATIONS

18.1. Modifications/Interpretations from reference method:

18.1.1. The source method states that the PDS concentration should be 40 mg/kg or twice the sample concentration; whichever is greater. Because the high standard in the calibration curve is at 40 ppm, we have elected to use a PDS concentration of 30 mg/kg.

Figure 1 – Eh/pH Phase Diagram (Figure 2 of Method 3060A)

The dashed lines define Eh-pH boundaries commonly encountered in soils and sediments.



* Note the Eh values plotted on this diagram are corrected for the reference electrode voltage: 244 mV units must be added to the measured value when a separate calomel electrode is used, or 199 mV units must be added if a combination platinum electrode is used.

Figure 2 - Example Hexavalent Chromium Log Sheet (Aqueous Samples)

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Hexavalent Chromium Log Sheet

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Batch	Lot Number	SDG

Water Standards mg/L	Absorbance	Solid Stds* mg/kg
		Blank
0.01		0.40
0.05		2.00
0.10		4.00
0.25		10.00
0.50		20.00
		40.00

*Based on 2.5g to 100mL digestion

Wavelength = 540mm Corr. Coef. = _____

Slope: _____

Intercept: _____

Analyst:			
Date:			
Acetone Lot#:			
Diphenylcarbazide Lot#:			
Digestion Solution ID:			
Phosphate Buffer ID:			
Sulfuric Acid ID:			
Nitric Acid ID:			
Magnesium Chloride ID:			
Start Time:			
Pipet #:			
Thermometer ID:			
Hot Plate Temp (90-95°C):			
Balance ID:			
LCS/CCV ID#:			
True Value:		Range:	
Prep:		Exp:	
Cr6+ 50ppm ID:			
Prep:		Exp:	
True Value for MS/MSD Spike:			

Concentration of Sample in Spike

Orig Smp Conc Vol of Smp in Spike

$$\text{Orig Smp Conc} \times \left(\frac{50}{50}\right) = \text{ND}$$

Orig Samp Vol

Sample ID:

Relative Percent Difference

X1 = Orig Result X2 = Duplicate

$$\left(\frac{X1 - X2}{X1 + X2 / 2}\right) \times 100 =$$

MS Percent Recovery

$$100 \times \left(\frac{\text{Obs Conc of MS} - \text{Conc of Samp in Spike (ND)}}{\text{True Spike Conc (0.00)}}\right) = \#\#\#\#\#\#$$

Sample ID:

MSD Percent Recovery

$$100 \times \left(\frac{\text{Obs Conc of MSD} - \text{Conc of Samp in Spike (ND)}}{\text{True Spike Conc (0.00)}}\right) = \#\text{VALUE!}$$

Sample ID:

Figure 2 - Example Hexavalent Chromium Log Sheet (Aqueous Samples)

Page 2

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Hexavalent Chromium Log Sheet

XXXXXXXXX

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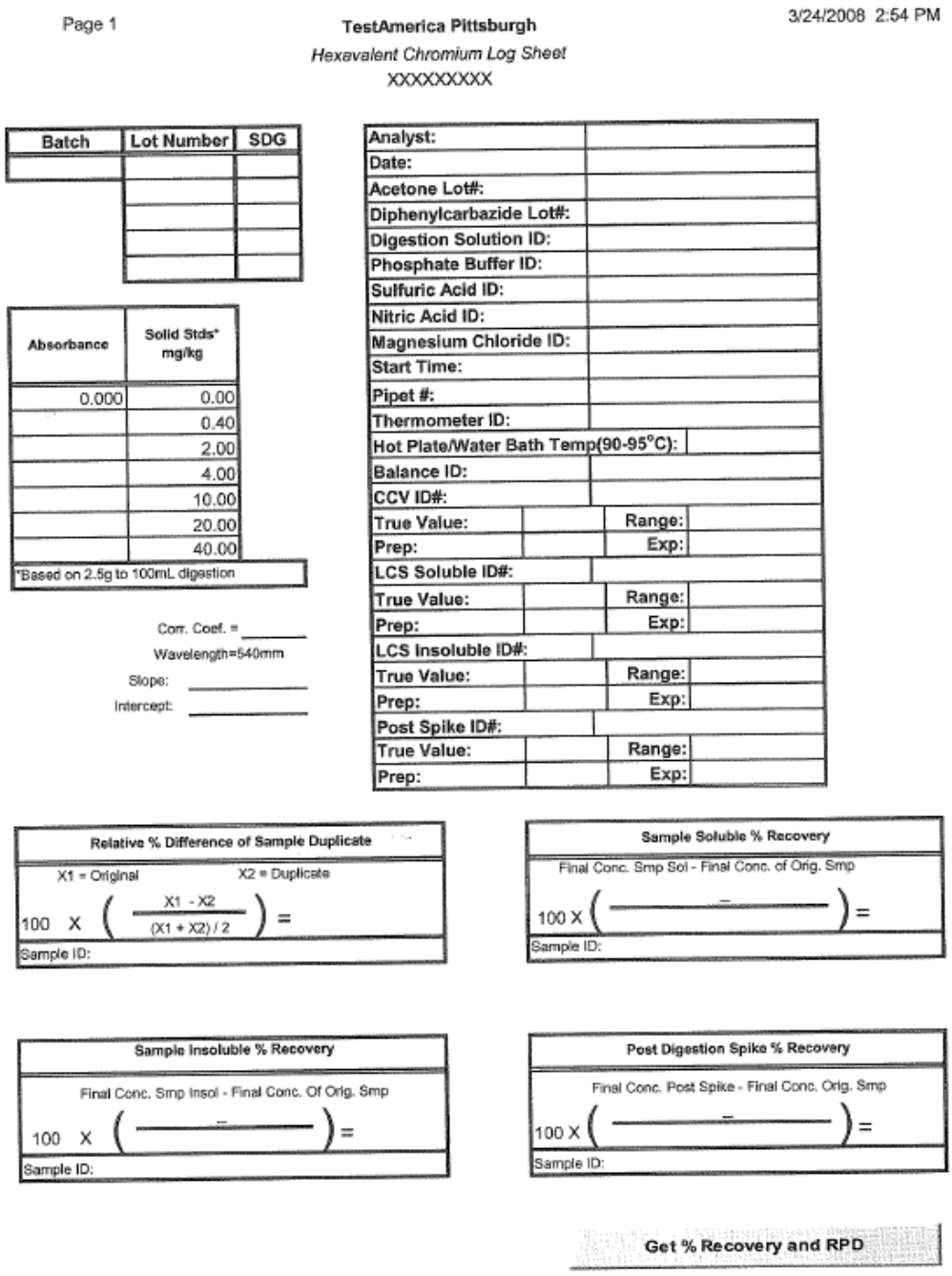
Sample ID	pH*	Time	Absorb	Blank	Absorb	Conc Smp	Dilution Factor	Final Conc (mg/L)	LDL	% Recovery	RPD

*Adjust pH to 2.0 +/- 0.5 for Method SM3500Cr-B (Waters), Methods 7196A (Waters), and 3060A/7196A (Soils)

Analyst: ______________________ Date: ______________________

Reviewed By: ______________________ Date: ______________________

Figure 3 - Example Hexavalent Chromium Log Sheet (Soil Samples)



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TestAmerica Pittsburgh

Hexavalent Chromium Log Sheet

XXXXXXXXX

Batch	Lot Number	SDG

Absorbance	Solid Stds* mg/kg
0.000	0.00
	0.40
	2.00
	4.00
	10.00
	20.00
	40.00

*Based on 2.5g to 100mL digestion

Corr. Coef. = _____

Wavelength=540mm

Slope: _____

Intercept: _____

Analyst:			
Date:			
Acetone Lot#:			
Diphenylcarbazide Lot#:			
Digestion Solution ID:			
Phosphate Buffer ID:			
Sulfuric Acid ID:			
Nitric Acid ID:			
Magnesium Chloride ID:			
Start Time:			
Pipet #:			
Thermometer ID:			
Hot Plate/Water Bath Temp(90-95°C):			
Balance ID:			
CCV ID#:			
True Value:		Range:	
Prep:		Exp:	
LCS Soluble ID#:			
True Value:		Range:	
Prep:		Exp:	
LCS Insoluble ID#:			
True Value:		Range:	
Prep:		Exp:	
Post Spike ID#:			
True Value:		Range:	
Prep:		Exp:	

Relative % Difference of Sample Duplicate

X1 = Original X2 = Duplicate

$100 \times \left(\frac{X1 - X2}{(X1 + X2) / 2} \right) =$

Sample ID:

Sample Soluble % Recovery

Final Conc. Smp Sol - Final Conc. of Orig. Smp

$100 \times \left(\frac{\quad - \quad}{\quad} \right) =$

Sample ID:

Sample Insoluble % Recovery

Final Conc. Smp Insol - Final Conc. Of Orig. Smp

$100 \times \left(\frac{\quad - \quad}{\quad} \right) =$

Sample ID:

Post Digestion Spike % Recovery

Final Conc. Post Spike - Final Conc. Orig. Smp

$100 \times \left(\frac{\quad - \quad}{\quad} \right) =$

Sample ID:

Get % Recovery and RPD

Figure 3 - Example Hexavalent Chromium Log Sheet (Soil Samples)

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Hexavalent Chromium Log Sheet

XXXXXXXXX

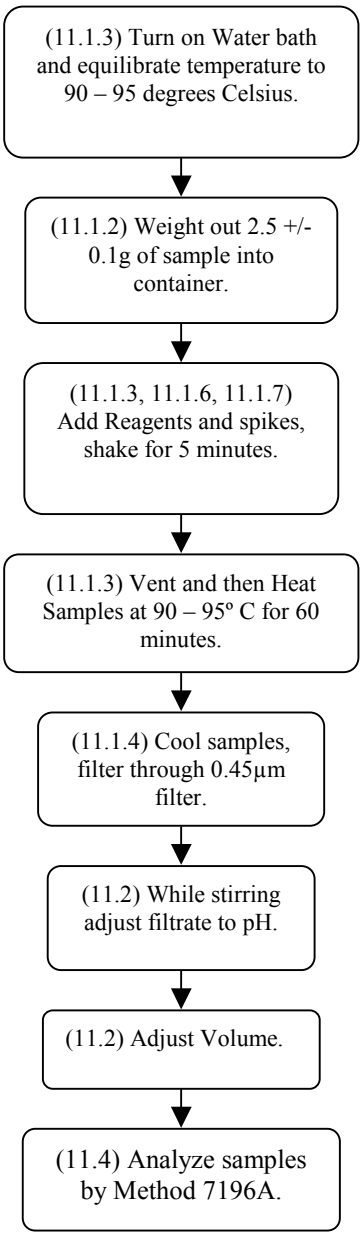
X=Dup SS=Sample Soluble SI=Sample Insoluble PS = Post Spike

Work Order	Suffix	Time	Absorb	Blank	Absorb	Conc Smp	Dilution Factor	Final Conc (mg/L)	LDL	% Rec	RPD	Smp Wght	Adj. Dil

Analyst: ______________________ Date: ______________________

Reviewed By: ______________________ Date: ______________________

Figure 4 - Method 3060A - Alkaline Digestion For Hexavalent Chromium



APPENDIX 37
SOP FOR THE DETERMINATION OF HARDNESS BY STANDARD METHOD 2340B (PT_WC_004_R6) (TEST AMERICA-PITTSBURGH)

Title: Total Hardness (mg/L as CaCO3) and Hardness by Calculation

Methods: Standard Methods 2340B and 2340C

Approvals (Signature/Date):

Michael Wesoloski 10/30/08	Steve Jackson 10/30/08
Michael Wesoloski Date	Steve Jackson Date
Technical Manager	Health & Safety Manager
Nasreen K. DeRubeis 10/28/08	Larry Matko 10/28/08
Nasreen K. DeRubeis Date	Larry Matko Date
Quality Assurance Manager	Laboratory Director

This SOP was previously identified as SOP No. PITT-WC-0004, Rev. 5.

Controlled Source: Intranet

1.0 Scope and Application

1.1 This method is applicable to drinking, surface, and saline waters, domestic and industrial wastes.

1.2 Depending on the indicator used, this method can be used to determine either total hardness or calcium hardness, both expressed in mg/L of $CaCO_3$.

1.3 Hardness by calculation is computed it from the results of separate determinations of calcium and magnesium. This result is typically determined by ICP, methods 200.7 or 200.8. The calculation is outlined in Section 11.6.

2.0 Summary of Method

2.1 Total hardness is defined as the sum of the calcium and magnesium concentrations, both expressed as calcium carbonate in mg/L. Calcium hardness is defined as calcium concentration expressed as calcium carbonate in mg/L.

2.2 For total hardness, calcium and magnesium ions in the sample are sequestered on addition of disodium ethylenediamine tetraacetate (Na_2 EDTA). The end point of the reaction is detected by Eriochrome Black T, which has a red color in the presence of calcium and magnesium and a blue color when the cations are sequestered. For calcium hardness or total calcium, calcium ion is sequestered in the same manner, but the titration end point is detected by means of an indicator, which combines with calcium only.

2.3 The reporting limit for undigested samples is 5 mg/L of $CaCO_3$.

2.4 The reporting limit for digested samples is 10 mg/L of $CaCO_3$. This is presented for information purposes. TestAmerica Pittsburgh recommends that wastewaters be digested, analyzed by ICP and hardness determined by calculation.

3.0 Definitions

3.1 LCS: Laboratory Control Sample is processed through all method steps with the associated samples. The LCS is used to monitor the accuracy of the analytical process independent of possible interference effects due to sample matrix. Successful analyte recovery for the LCS provides assurance that the method is in control.

3.2 LCSD: Laboratory Control Sample Duplicate processed with the LCS when sufficient sample is not available to process a sample duplicate. A LCSD is used to demonstrate

batch precision when the client has not supplied sufficient sample to prepare a duplicate sample analysis. A LCSD is required for each batch if a sample duplicate is not present.

3.3 MB: Method Blank is a control sample that is prepared using reagent water and all other reagents that are used on the associated samples. As part of the QC batch, it accompanies the samples through all steps of the analytical procedure. The method blank is used to monitor laboratory or reagent contamination.

3.4 SD: Sample Duplicate is a replicate aliquot of an environmental sample taken from the same sample container, when possible, and processed with the first aliquot of the sample. The sample and sample duplicate results are compared to determine the effect of the sample matrix on the precision of the analytical process. The sample duplicate should be chosen randomly from each batch. The sample should be representative of the entire batch.

3.5 QC Batch: The QC batch is a set of 20 or fewer environmental samples plus associated laboratory QC samples that are similar in composition and that are processed within the same time period and with the same reagents and standard lots. Laboratory QC samples such as LCS, matrix QC samples, and blanks are not included in the sample count for QC batching purposes.

3.6 Reagent Grade Water: Laboratory water, which is produced by a Millipore DI system or equivalent. Reagent grade water must be free of the analyte of interest as demonstrated through the analysis of method blanks.

4.0 Interferences

4.1 Excessive amounts of heavy metals can interfere. This is usually overcome by complexing the metals with cyanide. Inhibitors are not necessary for most samples.

4.2 For calcium hardness, strontium and barium interfere and alkalinity in excess of 30 mg/L may cause an indistinct end point. Magnesium interference is reduced or eliminated by raising the pH between 12 and 13 in order to precipitate magnesium hydroxide.

5.0 Safety

5.1 Employees must abide by the policies and procedures in the Corporate Environmental Health and Safety Manual (CW-E-M-001), Radiation Safety Manual and this document. This procedure may involve hazardous material, operations and equipment. This SOP does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste

disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, gloves, lab coats and closed-toe, nonabsorbent shoes are a minimum.

5.2 Primary Materials Used

The following is a list of the materials used in this method, which have a serious or significant hazard rating. Note: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table. A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

Material [1]	**Hazards**	**Exposure Limit** [2]	**Signs and symptoms of exposure**
Ammonium Hydroxide	Corrosive Poison	50 ppm-TWA	Vapors and mists cause irritation to the respiratory tract. Causes irritation and burns to the skin and eyes.
Hydrochloric Acid	Corrosive Poison	5 ppm-Ceiling	Inhalation of vapors can cause coughing, choking, inflammation of the nose, throat, and upper respiratory tract, and in severe cases pulmonary edema, circulatory failure, and death. Can cause redness, pain, and severe skin burns. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
[1] Always add acid to water to prevent violent reactions.			
[1] Exposure limit refers to the OSHA regulatory exposure limit.			

5.3 Eye protection that protects against splash, laboratory coat, and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled. Cut resistant gloves must be worn doing any other task that presents a strong possibility of getting cut. Disposable gloves that have become contaminated will be removed and discarded, other gloves will be cleaned immediately.

5.4 Exposure to chemicals must be maintained as low as reasonably achievable, therefore, unless they are known to be non-hazardous, all samples must be opened, transferred, and prepared in a fume hood or under other means of mechanical ventilation. Solvent and waste containers will be kept closed unless transfers are being made.

5.5 All work must be stopped in the event of a known or potential compromise to the health and safety of a TestAmerica's associate. The situation must be reported immediately to a laboratory supervisor or EH&S coordinator.

6.0 Equipment and Supplies

6.1 Class "A" burettes, in an appropriate selection of sizes.

6.2 Standard laboratory glassware.

6.3 Magnetic stir plate and stir bars.

6.4 Hot block.

6.5 Disposable polypropylene digestion cups.

6.6 Polypropylene ribbed watch glasses.

7.0 Reagents and Standards

7.1 Buffer Solution: Dissolve 1.179g disodium EDTA (analytical reagent grade) and 0.780g $MgSO_4 \bullet 7H_2O$ (or 0.644g $MgCl_2 \bullet 6H_2O$) in 50 mL reagent grade water. Add this solution to a 250mL volumetric flask containing 16.9g NH_4Cl and 143mL conc. NH_4OH with mixing and dilute to volume with reagent grade water. Store in a tightly stoppered plastic bottle to prevent loss of NH_3 or absorbance of CO_2. Discard when 1 or 2mL added to sample fails to produce a pH of 10.0 $\pm$ 0.1 at end point of titration. Buffer may also be commercially purchased. Follow manufacturer's expiration date for standard replacement.

7.2 Total Hardness Indicator: Calgamite indicator solution: Commercially purchased, follow manufacturer's expiration guidance. If unavailable it may be prepared as follows: 0.10g of dry powder into a 100 ml volumetric flask and dilute to mark w/ reagent water. Alternatively mix together 0.5g Eriochrome Black T and 100g NaCl. Store in airtight container. Use the least amount of indicator that provides a sharp end point. Follow manufacturer's expiration date for standard replacement.

7.3 Calcium Indicator: Purchased. Follow manufacturer's expiration date for standard replacement.

7.4 Standard EDTA titrant, 0.02N: Place 3.723g Na_2 EDTA ($Na_2H_2C_{10}H_{12}O_8N_2 \bullet 2\ H_2O$) (analytical reagent grade) in a 1L volumetric flask and dilute to volume with reagent grade water. Check with standard calcium solution (7.5) by titration (10.1). Store in plastic containers, as titrant will extract hardness cations from soft glass. Check standardization semiannually. EDTA titrant can be commercially purchased. Follow manufacturer's expiration date for standard replacement.

7.5 Standard calcium solution 0.02 N: This is purchased commercially. If necessary it may be prepared as follows: Place 1.000g anhydrous calcium carbonate (primary standard low in metals) in a 500mL flask. Add slowly 1:1 HCl (7.6) until all $CaCO_3$ has dissolved. Add 200mL of reagent grade water and boil for a few minutes to expel CO_2, then cool. Add a few drops of methyl red indicator (7.7) and adjust to intermediate orange color by adding 3N NH_4OH (7.8) or 1:1 HCl. Transfer to 1L volumetric and dilute to volume with reagent grade water.. Follow manufacturer's expiration date for standard replacement.

7.6 Hydrochloric acid solution, 1:1: Add 10 mL of concentrated HCl to 10mL reagent grade water in a graduated cylinder. Prepare fresh standard every six months or as needed.

7.7 Methyl red indicator: commercially purchased. Follow manufacturer's expiration date for standard replacement.

7.8 Ammonium hydroxide solution, 3 N: Dilute 210 mL of conc. NH_4OH to 1L with reagent grade water. Prepare fresh standard every six months or as needed.

7.9 Ammonium Hydroxide solution 1N: Dilute 70 mL of concentrated NH_4OH to 1 L with reagent grade water. Prepare fresh standard every six months or as needed.

7.10 Concentrated nitric acid (HNO_3).

7.11 LCS: 5mL of the calcium solution (see Section 7.5) diluted to 100mL with reagent grade water. This solution has a theoretical value of 50ppm, total hardness and 20ppm total calcium. The LCS should be prepared fresh on each day of use and must be prepared from a second source standard.

8.0 Sample Collection, Preservation, Shipment and Storage

8.1 Samples are acidified to pH < 2 with HNO_3. Holding time is six months from date of sample collection. Plastic or glass containers can be used.

9.0 Quality Control

9.1 The laboratory control sample is processed with each batch of 20 or fewer environmental samples. The LCS recovery must be ±20 percent of the true value. If the LCS fails criteria, the analyst will check calculations and analytical system performance and reanalyze the LCS once. If the LCS is still outside control limits, all samples in the QC batch will be reprepared and reanalyzed. If this is not possible due to limited sample quantity, the laboratory project manager will be notified and an analytical narrative provided with the data. If repreparation and reanalysis will be outside of holding time, the client should be notified and approval from the client must be obtained before reanalysis.

9.2 Please refer to PT-QA-021 for the selection of any duplicate samples.

9.3 A sample duplicate (SD) is analyzed with every set of ten or fewer samples. Acceptance criteria is calculated as relative percent difference (RPD) between the original and duplicate sample analysis and the acceptable range is ≤20 percent. If the RPD is outside of criteria, the analyst will check calculations and analytical system performance, reanalyze the samples once, evaluate results, and, if appropriate, narrate the problem in the reported data. The duplicate samples are not counted as part of the 20 or fewer environmental samples in the QC batch.

9.4 A laboratory control sample duplicate or LCSD is used to demonstrate batch precision when the client has not supplied sufficient sample to prepare a sample duplicate analysis. In this case the LCSD must pass the LCS criteria of ± 20 % and the precision criteria of ≤ 10 %. If these criteria are not met, the corrective action noted in section 9.1 would apply.

9.5 Method Detection Limit (MDL) - An MDL must be determined for each analyte/matrix prior to the analysis of any samples. The MDL is determined using seven replicates of reagent water, spiked with all the analytes of interest that have been carried through the entire analytical procedure. MDLs must be redetermined on an annual basis in accordance with 40 CFR Part 136 Appendix B requirements as detailed in TestAmerica QA SOP:PT-QA-007, current version. The spike level must be between the calculated MDL and 10X the MDL to be valid. The result of the MDL determination must be below the TestAmerica reporting limit.

9.6 The method blank (MB) is processed with each batch of 20 or fewer environmental samples. All analyte concentrations in the MB must be less than the reporting limit. If the MB fails criteria, the analyst will check the calculations and analytical system performance and reanalyze the MB once. If the MB is still outside of criteria, all samples associated with the unacceptable blank will be reprepared and reanalyzed. If this is not possible due to limited sample quantity, the laboratory project manager will be notified, and an analytical narrative provided with the data. If repreparation and reanalysis is outside of the holding time, the client should be notified and approval from the client must be obtained before reanalysis.

10.0 Procedure

10.1 CALIBRATION AND STANDARDIZATION

Standardization titration procedure: Place 10.0mL standard calcium solution in a flask containing 50mL reagent grade water. Add sufficient buffer to achieve a pH of about 10. Add approximately 1 mL of total hardness (calgamite) indicator. Titrate slowly with stirring until last reddish tinge disappears, adding the last few drops at 3 - 5 second intervals. At the end point, the color is blue. Total titration duration should be 5 minutes from the time of buffer addition.

$$\text{Normality of EDTA} = \frac{0.2\ \text{N}}{\text{mL of EDTA}}$$

Where 0.2 = Normality of Calcium Solution x 10mL of Calcium Solution

10.2 Pretreatment:

For drinking, surface, and saline waters (and dilutions of these), no pretreatment or digestion procedure is necessary. Proceed to Section 10.4 .

For wastewaters and highly polluted waters, the sample must be digested.

10.3 Digestion procedure: Transfer 100 mL of blank, LCS, sample, or sample duplicate to a disposable polypropylene digestion cup and add 3mL of concentrated HNO_3. Cover the beaker with a polypropylene ribbed watch glass. Place the beaker on a hot block and evaporate to near dryness, making certain the sample does not boil. Cool the digestion cup and add another 3 mL of concentrated HNO_3. Cover the digestion cup

and return to the hot block. Increase the temperature of the hot block so that a gentle reflux occurs. Continue heating. If necessary, add more acid until digestion is complete (normally indicated when digestate is light in color or does not change in appearance with continued refluxing). Set digestion cup aside until cool. Add a small amount (about 3-5mLs) of 1:1 HCl and warm the digestion cup to dissolve any precipitate or residue. Wash down the digestion cup walls and watch glass with reagent grade water and filter the sample to remove silicates and other insoluble material. Adjust the volume to 100 mL with reagent grade water in a volumetric container. Results for samples processed in this manner may be analyzed for "Total Hardness, Total Calcium Hardness, or Total Calcium." Digestion may also be performed using a beaker, a ribbed watch glass, and a hot plate if the hot block is unavailable for use.

With each batch of samples, a prep. blank, LCS and associated batch QC must also be digested. The prep blank is reagent grade water consisting of all the reagents used in the sample.

10.4 Titrations :

10.4.1 All samples and reagents must be at room temperature. The color change of the indicator is very sluggish in cool temperatures and the indicator decomposes at high temperatures. For all total hardness digestates, as well as non-digested samples having a high-level total hardness concentration (i.e. > 5 mg/L), proceed to Section 10.4.2. For all non-digested samples with low-level total hardness, proceed to Section 10.5. For all calcium hardness or total calcium samples of all concentration levels both digested and non-digested, proceed to Section 10.6.

10.4.2 Use 25mL or less LCS, sample, or sample duplicate. Neutralize the pH of the aliquot taken with 3N ammonium hydroxide. Then dilute each treated aliquot solution to 50mL with reagent grade water. The 50mL aliquot to be titrated should contain about 25mg or less total hardness as CaCO3.

10.4.2.1 Add sufficient amount of buffer to achieve a pH of about 10, taking care to watch for any precipitation of $CaCO_3$. The pH should not be so high as to precipitate $CaCO_3$, but needs to be high enough for the indicator to change color. Titration must be completed within 5 minutes of the buffer addition. Samples should require <15 mL EDTA titrant, or a sample dilution is necessary. Add a small scoop of total hardness indicator to the prepared aliquot and titrate slowly with EDTA while constantly stirring the sample. The reddish tint of the indicator will change to a blue end point. Record mL titrant and sample volume used on the bench sheet. Proceed to Section 10.5.

10.5 For nondigested low-level total hardness determinations, use 100mLs of the sample or blank. Neutralize the pH of the aliquot taken with 1N ammonium hydroxide.

10.5.1.1 For each nondigested sample or blank use two scoops of total hardness indicator and enough buffer to achieve a pH of about 10, taking care to watch for any precipitation of $CaCO_3$. The pH should not be so high as to precipitate $CaCO_3$, but needs to be high enough for the indicator to change color. Titration must be completed within 5 minutes of buffer addition. Titrate the EDTA titrant slowly while constantly stirring the sample. The reddish tint of the indicator will change to a blue end point. Record mL of titrant and sample volume used on the bench sheet.

10.6 For calcium hardness or total calcium determinations (of all concentration level samples and every digestate for calcium hardness and total calcium), use 50mL (or an aliquot diluted to 50mL) of sample, blank, LCS, or sample duplicate. Adjust the pH to 12 to 13 with 3N ammonium hydroxide solution. The 50mL aliquot to be titrated should contain 5 to 10mg total calcium or about 25mg or less calcium hardness as CaCO3.

NOTE: If the alkalinity is >300mg/L $CaCO_3$ and cannot be reduced by dilution because of low calcium concentration, then the alkalinity must be decreased by acidifying the sample, boiling one minute, and cooling before the 50mL aliquot can be taken.

10.6.1.1 Add approximately 1 ml of calcium indicator and immediately titrate with EDTA while continuously stirring. Record mL of titrant and sample volume used on the benchsheet.

10.7 Any authorized deviations from this procedure must be documented as a nonconformance, with a cause and corrective action described.

11.0 Calculations / Data Reduction

11.1 Hardness (EDTA)

$$\text{mg } CaCO_3 / L = \frac{A \times N \times 50{,}000}{\text{mL sample}}$$

Where:

A = mL EDTA titrant used.

N= normality of EDTA titrant.

11.2 Total calcium:

$$mg/L\ Ca = \frac{A \times N \times 20{,}040}{mL\ of\ sample}$$

Where:

A and N are as defined as in 11.1

11.3 Calcium hardness :

$$mg/L\ CaCO_3 = \frac{A \times N \times 50{,}000}{mL\ of\ sample}$$

Where:

A and N are defined as in 11.1

11.4 Duplicate sample (Relative Percent Difference) :

$$RPD = \frac{|X_1 - X_2|}{\left(\frac{X_1 + X_2}{2}\right)} \times 100\ \%$$

X_1 = Original Result

X_2 = Duplicate Result

11.5 LCS Percent Recovery:

$$\text{LCS \% Recovery} = \left(\frac{\text{Observed Conc. in LCS}}{\text{True LCS Conc.}}\right) \times 100\%$$

11.6 Hardness by Calculation:

11.6.1 Hardness, mg equivalent CaCO3/L = 2.497 [Ca, mg/L] + 4.118 [Mg, mg/L]

12.0 Method Performance

12.1 Method Detection Limit (MDL) - An MDL must be determined for each analyte prior to the analysis of any samples. MDLs are determined yearly. The MDL is determined using seven replicates of reagent water, spiked with all the analytes of interest that have been carried through the entire analytical procedure. MDLs must be redetermined on an annual basis in accordance with 40 CFR Part 136 Appendix B requirements as detailed in TestAmerica QA Policy: PT-QA-007, current version. The spike level must be between the calculated MDL and 10X the MDL to be valid. The result of the MDL determination must be below the TestAmerica reporting limit.

12.2 Initial Demonstration of Capability

Prior to analysis of any samples using this SOP, the following requirements must be met:

Initial Demonstration Study: This requires the analysis of four LCS samples prepared and analyzed using the procedures detailed in this SOP. The LCS samples is a well-characterized, laboratory-generated sample used to monitor method performance, which should contain the analyte(s) of interest. The results of the initial demonstration study must be acceptable before analysis of samples under this SOP may begin. .

Calculations and acceptance criteria for the LCS are given in Sections 11.5 and 9.1.

12.3 Training Requirements

The group/team leader has the responsibility to ensure that this procedure is performed by an analyst who has been properly trained in its use and has the required experience. The group/team leader must document the training and PE performance and submit the results to the QA Manager for inclusion in associate training files.

13.0 Pollution Control

13.1 It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i.e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage and reagent

stability). Employees must abide by the policies in Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention."

13.2 All waste will be disposed of in accordance with Federal, State and Local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this method and the policies in section 13 of the Corporate Safety Manual for "Waste Management and Pollution Prevention."

14.0 Waste Management

14.1 Waste management practices are conducted consistent with all applicable rules and regulations. Excess reagents, samples and method process wastes are disposed of in an accepted manner. Waste description rules and land disposal restrictions are followed. Waste disposal procedures are incorporated by reference to CW-E-M-001. The following waste streams are produced when this method is carried out.

Aqueous waste generated by the analysis. The pH is checked and the neutralized to a pH between 6 and 9.

15.0 References / Cross-References

15.1 Method 130.2, Methods for Chemical Analysis of Water and Wastes, EPA 600/4-79-020; March 1983. This method is withdrawn as per EPA 40 CFR Part 122, 136, et al. Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act; National Primary Drinking Water Regulations; and National Secondary Drinking Water Regulations; Analysis and Sampling Procedures; Final Rule March 12, 2007. Pittsburgh laboratory may use this method a per client request for limited time.

15.2 Method 2340B and C, Standard Methods for the Examination of Water and Wastewater, 20th Ed., 1998.

15.3 PT-QA-021, Pittsburgh QA Program.

15.4 PT-QA-007, SOP for Determination of MDLs.

15.5 Pittsburgh Laboratory Quality Assurance Manual, PT-LQAM, current version.

16.0 Method Modifications:

16.1 NA

17.0 Attachments

17.1 All sample preparation and analysis information will be documented on laboratory bench sheets, computer printouts, standard logbooks, etc. Raw data will be forwarded for reporting and for inclusion in the project files.

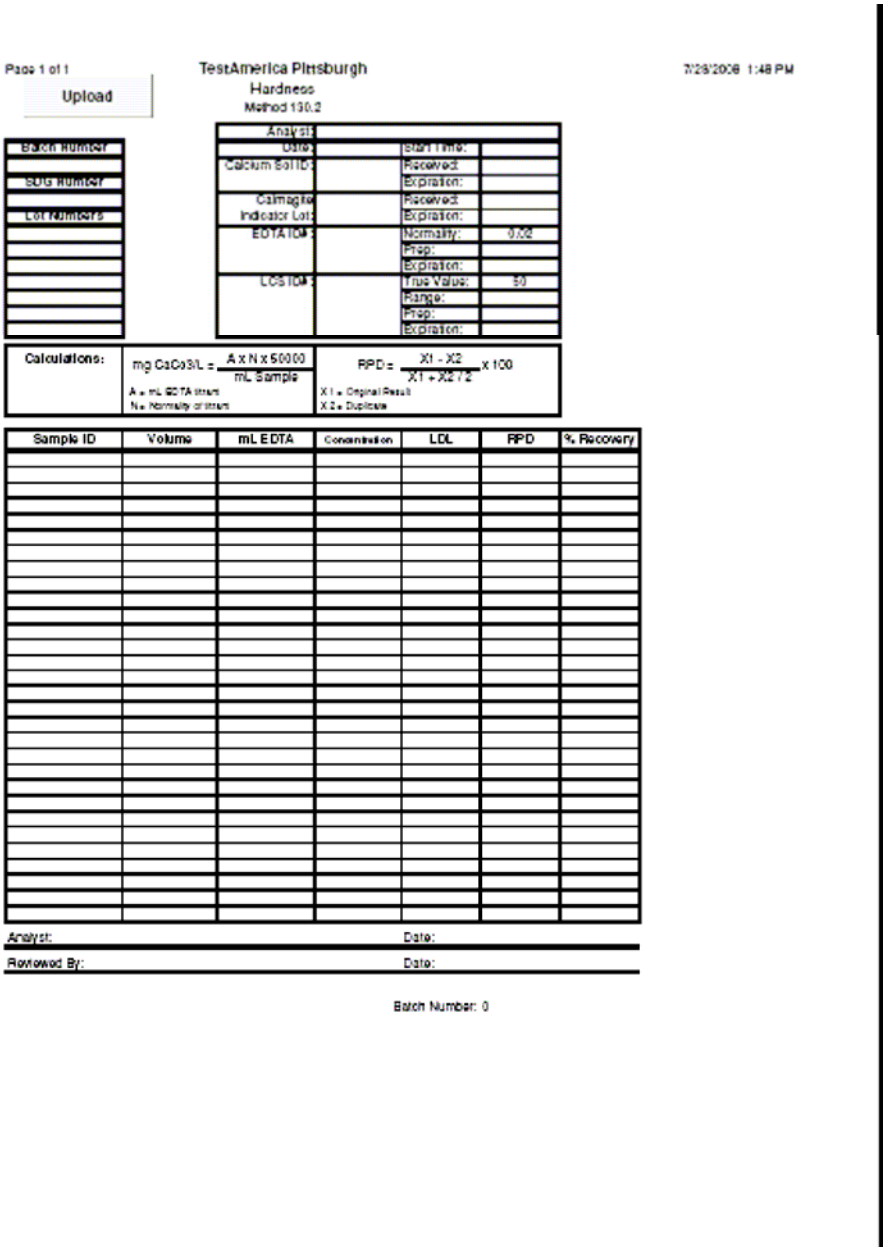
18.0 Revision History

18.1 Revision 6, 10/31/08:

Updated the Headers to the new Corporate format; changed STL to TestAmerica throughout the SOP; removed sections 3.3, 3.4 and 3.5 since there is no MS/MSD for this procedure; added the appropriate Corporate text to the Safety, Pollution Control and Waste Management sections; updated SOP and section references throughout the SOP. Updated section 15, references. Removed reference to method 215.2, this method has been withdrawn as per EPA 40 CFR Part 122, 136, Final Rule March 12, 2007.

Figure 1

Example Hardness Log Sheet



Page 1 of 1

TestAmerica Pittsburgh
Hardness
Method 130.2

7/28/2008 1:48 PM

Upload

Batch Number	Analyst:		
	Date:	Start Time:	
SOG Number	Calcium Soln ID:	Received:	
		Expiration:	
Lot Numbers	Calmagite Indicator Lot:	Received:	
		Expiration:	
	EDTA ID#:	Normality:	0.02
		Prep:	
		Expiration:	
	LCS ID#:	True Value:	50
		Range:	
		Prep:	
		Expiration:	

Calculations:

$$mg\ CaCO_3/L = \frac{A \times N \times 50000}{mL\ Sample}$$

A = mL EDTA titrant
N = Normality of titrant

$$RPD = \frac{X1 - X2}{X1 + X2 / 2} \times 100$$

X1 = Original Result
X2 = Duplicate

Sample ID	Volume	mL EDTA	Concentration	LDL	RPD	% Recovery

Analyst: Date:

Reviewed By: Date:

Batch Number: 0

APPENDIX 38
SOP FOR HARDNESS BY CALCULATION BY SM 2340B (BR-ME-013, REV. 3) (TEST AMERICA-BURLINGTON)

SOP CHANGE-IN-PROGRESS ATTACHMENT (CIPA)

SOP Number	SOP Title	SOP Revision	SOP Effective Date	CIPA Effective Date
BR-ME-013	Hardness by Calculation (SM2340B)	3	11/17/08	04/06/09

Approval Signatures:

William S. Cicero
Laboratory Director

Jessica A. Holzschuh
Department Manager

Kirstin L. McCracken
Quality Assurance Manager

Bryce E. Stearns
Technical Director

Dan Helfrich
Health & Safety Coordinator

Approval Date: April 6, 2009

The following text revision super cedes the existing text in the current SOP. The change is effective on the CIPA Effective Date. The changes will be incorporated into the document with the next revision.

Page 2 of 6:

Summary of Method

Hardness is calculated using the results for calcium and magnesium as determined by laboratory SOPs for test methods EPA 200.7, EPA 200.8, SW-846 6010B or SW-846 6020. Test method EPA 200.7 must be used when the hardness determination is required for regulatory compliance to 40 CFR Part 136.

Title: Hardness by Calculation (Method SM2340B)

Approval Signatures:

William S. Cicero
Laboratory Director

Jessica A. Holzschuh
Department Manager

Kirstin L. McCracken
Quality Assurance Manager

Bryce E. Stearns
Technical Director

Dan Helfrich
Health & Safety Coordinator

Approval Date: November 3, 2008

Facility Distribution No. Electronic **Distributed To: Facility Intranet**

The controlled copy of this SOP is the PDF copy of the SOP that is posted to the laboratory's SOP Directory. Printed copies of this SOP or electronic copies of this SOP distributed outside the facility are considered uncontrolled.

1.0 Scope and Application

This SOP describes the laboratory procedure for the determination of hardness by calculation.

This procedure is applicable to the following matrices: Non-potable water.

2.0 Summary of Method

Hardness is calculated using the results for calcium and magnesium as determined by laboratory SOPs for test methods EPA 200.7 and SW-846 6010B. Test method EPA 200.7 must be used when the hardness determination is required for regulatory compliance under 40 CFR Part 136, otherwise SW-846 6010B may be used.

The analytical result is reported as Hardness, mg equivalent to $CaCO_3$/L.

The reporting limit (RL) is 34 mg/L. Hardness results less than the reporting limit may be reported if substantiated by the instrument detection limit (IDL) or method detection limit (MDL) for calcium and magnesium.

This procedure is based on SM2340B.

3.0 Definitions

A list of terms and definitions are provided in Appendix A.

4.0 Interferences

Not applicable.

5.0 Safety

Employees must abide by the policies and procedures in the Corporate Environmental Health and Safety Manual (CW-E-M-001) and this document. This procedure may involve hazardous material, operations and equipment. This SOP does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, gloves, lab coats and closed-toe, nonabsorbent shoes are a minimum.

5.1 Specific Safety Concerns or Requirements

None.

5.2 Primary Materials Used

Not applicable.

6.0 Equipment and Supplies

Not applicable.

7.0 Reagents and Standards

Not applicable.

8.0 Sample Collection, Preservation, Shipment and Storage

Not applicable.

9.0 Quality Control

Not applicable.

10.0 Procedure

Digest and analyze the samples following appropriate laboratory SOPs.

Using the calcium and magnesium results that were determined from analysis, calculate hardness using the equation given in Section 11.0. Report the calculated result in mg/L.

11.0 Calculations / Data Reduction

Hardness, mg equivalent $CaCO_3$/L = (2.497 × Ca) + (4.118 × Mg).

Where:
Ca = Calcium Result in mg/L
Mg = Magnesium Result in mg/L

11.1 Data Review

11.1.1 Primary Review

Evaluate the calcium and magnesium results following the Data Review section of the applicable SOP.

11.2 Data Reporting

Review project documents such as the environmental test request (ETR) analytical worksheets, Project Plan (PP), Project Memo or any other document/process used to communicate project requirements to ensure those project requirements were met. If project requirements were not met, immediately notify the project manager (PM) to determine an appropriate course of action.

Using the Metals_Hardness_Calc spreadsheet located in the Calculation Spreadsheet folder on server y on btv-future, enter the calcium and magnesium results in mg/L into the respective cells. The spreadsheet will calculate the hardness results in mg/L. The hardness spreadsheet is then imported into the DWS reporting system to generate Form 1's to be included with the metals Form 1's in the final data package.

Generate the data report in the deliverable format specified by the laboratory PM and release the report to report management.

Retain, manage and archive electronic and hardcopy data as specified in laboratory SOP BR-QA-014 Laboratory Records.

12.0 Method Performance

12.1 Method Detection Limit Study (MDL)

A method detection limit (MDL) study is performed for each applicable method from which calcium and magnesium are reported for hardness at initial method set-up following the procedures specified in laboratory SOP BR-QA-005.

12.2 Demonstration of Capabilities (DOC)

Not applicable.

12.3 Training Requirements

Any employee that performs any portion of the procedure described in this SOP must have documentation in their employee training file that they have read this version of this SOP.

13.0 Pollution Control

It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i.e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage and reagent stability). Employees must abide by the policies in Section 13 of the Corporate Safety Manual for "Waste Management and Pollution Prevention."

14.0 Waste Management

Waste management practices are conducted consistent with all applicable rules and regulations. Excess reagents, samples and method process wastes are disposed of in an accepted manner. Waste description rules and land disposal restrictions are followed. Waste disposal procedures are incorporated by reference to BR-EH-001.

Waste Streams generated by this method: None.

15.0 References / Cross-References

- Method 2340B, Standard Methods for the Examination of Water and Wastewater, 18th Edition, Eaton, A.D. Clesceri, L.S. Greenberg; American Water Works Association, Water Pollution Control Federation, American Public Health Association: Washington, D.C., 1992.
- Laboratory SOP BR-QA-005, Procedures for the Determination of Limits of Detection (LOD), Limits of Quantitation (LOQ) and Reporting Limits (RL).
- Laboratory SOP BR-QA-011 Employee Training
- Laboratory SOP BR-LP-011 Hazardous Waste

- Laboratory SOP BR-QA-014 Laboratory Records
- Laboratory SOP BR-QA-006 Procedures & Documentation Requirements for Manual Integration
- Laboratory Quality Assurance Manual (QAM)

16.0 Method Modifications

Not applicable.

17.0 Attachments

Not applicable.

18.0 Revision History

- Title page: Updated to current management team and company template.
- Section 1.2: Removed reference to a CRDL, replaced with RL. Added MDL as level with which to justify lower then RL reporting.
- Section 2.0: Removed reference to ILM05.3 and specified which method must be used when the procedure is performed for regulatory compliance under 40 CFR Part 136.

Appendix A: Terms and Definitions

Analyte: The specific chemicals or components for which a sample is analyzed. (EPA Risk Assessment Guide for Superfund, OSHA Glossary).

Batch: environmental samples that are prepared and/or analyzed together with the same process, using the same lot(s) of reagents. A preparation/digestion batch is composed of one to 20 environmental samples of similar matrix, meeting the above criteria. An analytical batch is composed of prepared environmental samples (extracts, digestates and concentrates), which are analyzed together as a group.

Corrective Action: the action taken to eliminate the cause of an existing nonconformity, defect or other undesirable occurrence in order to prevent recurrence.

Total Hardness: the sum of calcium and magnesium concentrations, both expressed as calcium carbonate in mg/L.

Method Detection Limit (MDL): the minimum amount of a substance that can be measured with a specified degree of confidence that the amount is greater than zero using a specific measurement system. The MDL is a statistical estimation at a specified confidence interval of the concentration at which relative uncertainty is ±100%. The MDL represents a range where qualitative detection occurs. Quantitative results are not produced in this range.

Non-conformance: an indication, judgment, or state of not having met the requirements of the relevant specification, contract or regulation.

Reporting Limit (RL): the level to which data is reported for a specific test method and/or sample.

APPENDIX 39
SOP FOR THE DETERMINATION OF TOTAL SUSPENDED SOLIDS BY STANDARD METHOD 2540D AND SETTLEABLE SOLIDS BY SM 2540F (PT_WC_001_R1)

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

Title: Determination of Solids in Waters and Wastes

Method(s): EPA 160.1, 160.2, 160.3, 160.4 and Standard Methods 2540B, 2540C, 2540D, 2540E, 2540F & 2540G

Approvals (Signature/Date):

Michael P. Wesoloski	
06/5/08	06/5/08
Mike Wesoloski Date	Steve Jackson Date
Technical Specialist	Health & Safety Manager / Coordinator
Nasreen K. DeRubeis	Larry Matko
05/27/08	06/4/08
Nasreen DeRubeis Date	Larry Matko Date
Quality Assurance Manager	Laboratory Director

This SOP was previously identified as SOP No. PITT-WC-0001, Rev. 0.

TABLE OF CONTENTS

1. SCOPE AND APPLICATION

1.1. This SOP is applicable to the determination of total solids, total suspended solids, total dissolved solids, volatile solids, volatile dissolved solids, and volatile suspended solids using gravimetric techniques. This SOP is based on the residue methods contained in *Methods for Chemical Analysis of Waters and Wastes* (MCAWW) and Standard Methods for the Examination of Water and Wastes (SM).

1.2. This SOP is applicable to drinking, surface, and saline waters and domestic and industrial wastes.

1.3. The Total Solids (Residue, Total) protocol is based on MCAWW Method 160.3 and SM 2540B.

1.4. The Total Dissolved Solids (Residue, Filterable) protocol is based on MCAWW Method 160.1 and SM 2540C.

1.5. The Total Suspended Solids (Residue, Non Filterable) protocol is based on MCAWW Method 160.2 and SM 2540D.

1.6. The Volatile Solids protocol is based on MCAWW Method 160.4 and SM 2540G.

1.7. The Volatile Dissolved Solids protocol is based on MCAWW Method 160.4 and SM 2540G.

1.8. The Volatile Suspended Solids protocol is based on MCAWW Method 160.4 and SM 2540E.

1.9. Settleable solids is based on SM 2540F.

1.10. The methods cover a practical range of 10 mg/L to 20,000 mg/L (TSS: 4 mg/L - 20,000 mg/L). As a practical matter, the final residue weight should be limited to about 200 mg.

2. SUMMARY OF METHOD

2.1. Total Solids (TS): A well-mixed aliquot of the sample is quantitatively transferred to a preweighed evaporating dish and evaporated to dryness at 103 -105 °C. The increase in weight over that of the empty dish represents the total solids.

2.2. Total Dissolved Solids (TDS): A well-mixed sample is filtered through a glass fiber filter. The filtrate is quantitatively transferred into a preweighed evaporating dish and is evaporated to dryness and then dried to constant weight at 180 °C. The increase in weight over that of the empty dish represents the total dissolved solids. The filter from this procedure may also be used for TSS/VSS determination.

2.3. Total Suspended Solids (TSS): A well-mixed sample is filtered through a pre-weighed glass fiber filter. The residue on the filter is dried to constant weight at 103 -105 °C. The increase in weight over that of the pre-weighed filter represents the TSS content. The filtrate from this procedure may be used for TDS determination. The filter from this procedure may also be used for VSS analysis.

2.4. Volatile Solids (VS): The residue obtained from the determination of total solids is ignited at 550 °C in a muffle furnace. The loss of weight on ignition is reported as mg/L volatile solids.

2.5. Volatile Dissolved Solids (VDS): The residue obtained from the determination of total dissolved solids is ignited at 550 °C in a muffle furnace. The loss of weight on ignition is reported as mg/L volatile dissolved solids.

2.6. Volatile Suspended Solids (VSS): A well-mixed sample is filtered through a glass fiber filter to separate the suspended material. The filter is dried and weighed, then ignited at 550 °C and reweighed. Volatile suspended solids is determined from the weight loss after ignition. The filter from the analysis of TSS may be used for the determination of VSS.

2.7. Settleable solids (SS): analyzed in surface and saline waters as well as domestic and industrial wastes may be determined and reported on either a volume (mL/L) or a weight (mg/L) basis using Imhoff cone.

3. DEFINITIONS

3.1. Total Solids (TS): The term applied to the residue left in the vessel after evaporation of a sample and its subsequent drying in an oven at 103°C - 105°C. Total solids includes “total suspended solids,” the portion of solids retained by a filter, and “total dissolved solids,” the portion that passes through the filter.

3.2. Total Dissolved Solids (TDS): Those solids capable of passing through a glass fiber filter and dried to constant weight at 180 °C. TDS is also referred to as filterable residue.

3.3. Total Suspended Solids (TSS): Those solids that are retained by a glass fiber filter and dried to constant weight at 103 -105 °C. TSS is also referred to as non-filterable residue.

3.4. Volatile Solids (VS): The portion of total solids that is lost on ignition at 550 °C.

3.5. Volatile Dissolved Solids (VDS): The portion of total dissolved solids that is lost on ignition at 550 °C.

3.6. Volatile Suspended Solids (VSS): The portion of suspended solids that is lost on ignition at 550 °C.

3.7. Settleable Solids (SS): Fill an Imhoff cone to the 1-L mark with a well-mixed sample. Settle for 45 min, gently agitate sample near the sides of the cone with a rod or by spinning, settle 15 min longer, and record volume of settleable solids in the cone as milliliters per liter.

3.8. Aliquot: A representative portion of a sample.

3.9. Reagent Water: Deionized water that is free of the analyte(s) of interest.

4. INTERFERENCES

4.1. Method interferences may be caused by contaminants, reagents, glassware, and other sample processing hardware. All these materials must be routinely demonstrated to be free from interferences under the conditions of analysis by running method blanks.

4.2. Non-homogeneous samples may give erroneous results. Samples should be mixed as thoroughly as possible before removing an aliquot for analysis.

4.3. Non-representative particulates such as leaves, sticks, fish, and lumps of fecal matter should be excluded from the sample if it is determined that their inclusion is not desired in the final result. The presence/removal of these artifacts should be noted on the benchsheet.

4.4. Samples containing large amounts of solids may filter slowly. Prolonged filtration times resulting from filter clogging may produce high TSS results due to increased colloidal materials captured on the clogged filter.

4.5. Oil and grease in the samples will cause unreliable results due to difficulty in drying to constant weight. Floating oil and grease, if present, should be included in the sample and dispersed by a blender device before aliquoting.

4.6. Filtration apparatus, filter material, pre-washing, post-washing, and drying temperatures are specified because these variables have been shown to affect the results.

4.7. The temperature at which the residue is dried has an important bearing on the results because weight losses due to volatilization of organic matter, mechanically occluded water, water of crystallization, and gases from heat-induced chemical decomposition, as well as weight gains due to oxidation, depend on temperature and time of heating.

4.8. Each sample requires close attention to desiccation after drying. Minimize opening the desiccator because moist air enters. Some samples may be stronger desiccants than those used in the desiccator and may take on water.

4.9. Highly mineralized waters containing significant concentrations of calcium, magnesium, chloride, and/or sulfate may be hygroscopic and will require prolonged drying, desiccation and rapid weighing.

4.10. Samples containing high concentrations of bicarbonate may require careful and possibly prolonged drying to ensure that all the bicarbonate is converted to carbonate.

4.11. Too much residue in the drying vessel will crust over, entrapping water that will not be driven off during drying. Total residue should be limited to about 200 mg.

4.12. Some samples may have fine suspended solids that will pass through the glass fiber filter causing high TDS results.

4.13. Aluminum pans should not be used for TS or TDS analyses. Components in some samples may react to form aluminum compounds, causing unreliable results.

4.14. For samples high in dissolved solids, thoroughly wash the filter to ensure removal of dissolved material prior to TSS determination.

4.15. The volatile solids tests are subject to many errors due to the loss of water of crystallization, loss of volatile organic matter prior to combustion, incomplete oxidation of certain complex organics and decomposition of mineral salts during combustion. The results should not be considered an accurate measure of organic carbon in the sample.

5. SAFETY

5.1. Employees must abide by the policies and procedures in the Corporate Safety Manual, Radiation Safety Manual and this document.

5.2. Oily samples or those that contain volatile chemicals may ignite during this procedure. In the case of a fire, the muffle should be turned off and allowed to cool before the sample can be removed and put under a hood.

5.3. Extreme care should be used when using a muffle furnace, as temperatures are extremely high. Gloves designed for dealing with extreme temperatures must be used when handling any samples or glassware that has been in a muffle furnace.

5.4. There are no materials used in this method that have a significant or serious hazard rating. **NOTE: This list does not include all materials used in the method.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

5.5. Eye protection that protects against splash, laboratory coat, and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled. . Cut resistant gloves must be worn doing any other task that presents a strong possibility of getting cut. Disposable gloves that have been contaminated will be removed and discarded; other gloves will be cleaned immediately.

5.6. Exposure to chemicals must be maintained **as low as reasonably achievable**; therefore, unless they are known to be non-hazardous, all samples should be opened, transferred, and prepared in a fume hood, or under other means of mechanical ventilation. Solvent and waste containers will be kept closed unless transfers are being made.

5.7. The preparation of standards and reagents should be conducted in a fume hood with the sash closed as far as the operation will permit.

5.8. All work must be stopped in the event of a known or potential compromise to the health and safety of a TestAmerica associate. The situation must be reported **immediately** to a laboratory supervisor or EH&S coordinator.

5.9. This procedure may involve hazardous material, operations and equipment. This SOP does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, gloves, lab coats and closed-toe, nonabsorbent shoes are a minimum.

6. EQUIPMENT AND SUPPLIES

6.1. Analytical balance capable of weighing to 0.0001 g.

6.2. Vacuum filtration apparatus.

6.3. Vacuum pump equipped with moisture trap.

6.4. Glass fiber filter disks, 47 mm, without organic binder (Gelman Type A/E) or equivalent.

Note: Commercially available pre-weighed filters may be used for TSS and VSS analyses.

6.5. Evaporating dishes, 100 mL, made of either porcelain, Vycor or platinum. These must be thoroughly cleaned, rinsed with deionized water, and baked at 180 ± 2 °C for at least one hour before use. Store in a desiccator.

Note: Glass beakers may also be used for TS or TDS determinations. Glass beakers may not be used for procedures requiring use of a muffle furnace.

6.6. Desiccators providing sufficient space for storage of samples in process separate from filters and evaporating dishes.

6.7. Desiccant containing a color indicator of moisture concentration or an instrumental indicator.

6.8. Drying ovens set at 103 -105 °C and 180 ± 2 °C. Separate ovens should be maintained at appropriate temperatures if possible.

6.9. Muffle furnace (550 °C ± 50 °C).

6.10. Thermometers, NIST traceable.

6.11. Conductivity meter and associated apparatus.

6.12. Graduated cylinders, “to contain,” assorted sizes.

6.13. Volumetric flasks, Class A, assorted sizes.

6.14. Aluminum weighing dishes large enough to hold a 47 mm filter.

6.15. Forceps for handling filters.

6.16. Crucible tongs.

6.17. Zetex gloves or other gloves capable of providing protection at 550 °C.

6.18. Imhoff Cone - used for Settleable Solids

7. REAGENTS AND STANDARDS

7.1. Reagent water must be produced by a Millipore DI system or equivalent (see also Section 10.1.3).

7.2. The LCS standard solution is commercially purchased. The true value varies from lot to lot when received from the manufacturer and the calculation is adjusted accordingly by the laboratory. The standard is received with a certificate of analysis with the true value listed on it and is retained by the laboratory.

7.2.1. If the solution needs to be made by the laboratory the procedure is as follows: LCS solution (500 mg/L TSS and TDS, 1000 mg/L TS): Place 500.0 mg of diatomaceous earth (infusorial earth or celite 545) and 500 mg sodium chloride into a 1000 mL volumetric flask and dilute to volume with deionized water. Mix well. Prepare fresh every three months.

8. SAMPLE COLLECTION, PRESERVATION, SHIPMENT AND STORAGE

8.1. Samples should be collected in either plastic or glass bottles.

8.2. Samples must be stored at 4 °C ± 2 °C to minimize microbiological decomposition of solids. Bring samples to room temperature before analysis.

8.3. To achieve the reporting limits listed in Section 12, the recommended minimum volumes are as follows: TestAmerica Pittsburgh recommends 250 ml volume be used if available. If less than minimum volumes are used because of limited sample or solids loading this should be indicated in the project narrative.

Parameter	Volume (mL)
TS	100
TDS	100
TSS	100
VS	100
VDS	100
VSS	250
SS	1000

8.4. Holding times for solids determinations are as follows:

Parameter	Holding Time (days)
TS	7
TDS	7
TSS	7

VS	7
VDS	7
VSS	7
SS	48 Hours

9. QUALITY CONTROL

The TestAmerica QC Program document (QA-003) provides further details of the QC and corrective action guidelines presented in this SOP. Refer to this document if additional guidance is required.

Table 1 provides a summary of quality control requirements including type, frequency, acceptance criteria, and corrective action.

9.1. Initial Demonstration of Capability

Prior to analysis of any samples using this SOP, the following requirements must be met:

9.1.1. Initial Demonstration Study: This requires the analysis of four QC check samples. The QC check sample is a well-characterized, laboratory-generated sample used to monitor method performance, which should contain the analyte(s) of interest. The results of the initial demonstration study must be acceptable before analysis of samples under this SOP may begin.

9.1.1.1. Four aliquots of the check sample (LCS) are prepared and analyzed using the procedures detailed in this SOP.

9.1.1.2. Calculations and acceptance criteria for the LCS are given in Section 9.4.

9.2. Batch Definition: Batch definitions are provided in the Policy #: QA-003: 'The QC batch is a set of up to 20 field samples plus associated laboratory QC samples that are similar in composition (matrix) and that are processed within the same time period using the same reagent and standard lots.'

9.3. Method Blank (MB): One method blank must be processed with each batch of 20 or less samples. The method blank consists of reagent water that is carried through the entire analytical procedure, including filtration as applicable. The method blank is used to identify any system and process interferences or contamination of the analytical system that may lead to the reporting of elevated analyte concentrations or false positive data.

9.3.1. A reagent water blank is prepared and analyzed with each batch of samples. The volume of reagent water used should be the same as the minimum sample volume used for the test (Section 8.3).

9.3.2. Corrective Action for Blanks

9.3.2.1. If the analyte level in the method blank is $\geq$ the RL for the analyte of interest in the sample, all associated samples with reportable levels of analyte are reprepared and reanalyzed. If this is not possible due to limited sample quantity or other considerations, the corresponding sample data **must be addressed in the project narrative**. Refer to QA-003 for further details of corrective actions.

9.3.2.2. High blank results indicate contamination. Make sure the glassware and filtering apparatus is clean.

9.3.2.3. Low blanks typically indicate that the balance was not operating correctly or the filter/weighing dish was not completely dry when the initial weights were measured.

9.3.2.4. If there is no analyte greater than the RL in the samples associated with an unacceptable method blank, the data may reported with qualifiers. **Such action must be taken in consultation with the client and must be addressed in the project narrative.**

9.4. Laboratory Control Sample (LCS): One LCS must be processed with each batch of 20 or fewer samples. The LCS must be carried through the entire analytical procedure. The LCS is used to monitor the accuracy of the analytical process. On-going monitoring of the LCS results provides evidence that the laboratory is performing the method within acceptable accuracy and precision guidelines. No LCS is available for volatile residue procedures.

9.4.1. An LCS is prepared and analyzed with each analytical batch of samples. Refer to Section 7.2 for instructions on how to prepare the LCS solution. The LCS should be the same volume as the method blank.

9.4.2. Corrective Action for LCS

9.4.2.1. A control limit of 80 -120% recovery must be applied until in-house control limits are established. If the result is outside established control limits, the system is out of control and corrective action must occur.

9.4.2.2. Corrective action will include repreparation and reanalysis of the batch unless the client agrees that another corrective action is acceptable. If this is not possible due to limited sample quantity or other considerations, the corresponding sample data **must be addressed in the project narrative**.

9.4.2.3. Poor LCS results are usually the result of contamination or poor mixing.

9.5. Duplicate (D): A duplicate sample analysis is required with every batch of 20 samples or less. Sample results should agree within 20% if both the sample and sample duplicate results are > 5x RL.

9.5.1. Corrective Action for Duplicates

9.5.1.1. The failure of the sample duplicates to meet precision criteria must be addressed in the project narrative.

10. PROCEDURE

10.1. Calibration and Standardization

10.1.1. Since this method is based on gravimetric techniques, there is no calibration in the usual sense. Proper balance operation will be verified daily or prior to sample analysis by following the lab-specific balance calibration SOP. Analytical balance calibration must be performed daily (every 24 hours).

10.1.2. Oven temperature must be checked daily and recorded either on the benchsheet or in an oven temperature logbook.

10.1.3. Conductivity of the water must be monitored and recorded in the Conductivity Logbook daily. The maximum permissible conductivity is 1.0 umhos/cm (at 25 °C). If the conductivity reading on the water system exceeds this level, do not use the water for these procedures and notify the supervisor immediately.

10.2. Procedure

10.2.1. One-time procedural variations are allowed only if deemed necessary in the professional judgment of supervision to accommodate variation in sample matrix, radioactivity, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using a Nonconformance Memo and must be approved by a Technical Specialist and QA Manager. If contractually required, the client shall be notified. The Nonconformance Memo shall be filed in the project file.

10.2.2. Any unauthorized deviations from this procedure must also be documented as a nonconformance with a cause and corrective action described.

10.2.3. All samples are to be checked out of sample control with the chain of custody documentation filled out completely.

10.2.4. Proper sample identification is extremely important in any analytical procedure. Labeling of evaporating dishes and filters holders must be done in a manner to ensure connection with the proper sample.

10.2.5. If possible, analyze all the samples of a project at the same time to minimize the QC required and streamline the flow of the project through the lab and reporting group.

10.2.6. Non-representative particulates such as leaves, sticks, fish, and lumps of fecal matter should be excluded from the sample if it is determined that their inclusion is not desired in the final result. The presence/removal of these artifacts should be noted on the benchsheet.

10.2.7. If samples are visibly oily, this should be noted on the benchsheet.

10.2.8. If there is limited sample volume or high solids content, smaller amounts of sample may need to be processed than detailed in the following sections. This occurrence must be noted on the benchsheet and reporting limits must be adjusted appropriately.

10.2.9. Proceed to the appropriate section for the desired method as follows:

Total Solids	10.2.10
Total Dissolved Solids	10.2.11
Total Suspended Solids	10.2.12
Volatile Solids	10.2.13
Volatile Dissolved Solids	10.2.14
Volatile Suspended Solids	10.2.15
Settleable Solids	10.2.16

10.2.10. **Total Solids**

10.2.10.1. Preparation of Evaporating Dish:

10.2.10.1.1. If only total solids are to be measured, heat clean dish to 103 -105 °C for one hour. If volatile solids are to be measured in addition to total solids, ignite the clean evaporating dish at 550 °C for one hour in a muffle furnace.

10.2.10.1.2. Remove the dish from the muffle furnace using tongs and heat resistant gloves.

10.2.10.1.3. Cool and store dish in desiccator until dish reaches room temperature or until needed.

10.2.10.1.4. Weigh immediately before use to the nearest 0.1 mg. Record the weight on the benchsheet.

10.2.10.2. Sample Analysis:

10.2.10.2.1. Transfer a measured aliquot of well-mixed sample to the pre-weighed, labeled dish. Record the volume of sample (to the nearest mL) on the benchsheet.

10.2.10.2.1.1. Choose an aliquot of sample sufficient to contain a residue of at least 25 mg but less than 200 mg. To obtain a weighable residue, successive aliquots of sample may be added to the same dish after evaporation. The following screening technique may be utilized to assist in estimating sample loading. If sample results indicate >2000 mg/L sample should be re-analyzed at a lesser volume.

10.2.10.2.1.2. If the sample is known to contain > 2000 mg/L dissolved solids, it should be diluted. Prescreening may be performed using a conductivity meter to determine the required sample volume or dilution. For this purpose, the following formula should be used to approximate the required sample volume:

(2000 x 100) / Conductivity = mL sample to use

Note: To avoid “oddball” reporting limits, round the determined sample volume to one of the following volume increments: 5, 10, 20, 25, 50, or 100 mL.

10.2.10.2.1.3. For the LCS, measure 50 mL of the LCS Solution (Section 7.2) and pour into the dish.

10.2.10.2.1.4. For the MB, measure 100 mL of reagent water and pour into the dish.

10.2.10.2.2. Evaporate the sample to dryness on a steam bath or in a drying oven. If evaporation is performed in a drying oven, the temperature should be lowered as necessary to prevent boiling and splattering of the sample.

10.2.10.2.3. Dry the evaporated sample for at least one hour at 103 -105 °C.

10.2.10.2.4. Record the date, time, and oven temperature on the benchsheet when the samples are initially placed in the oven and again when they are removed from the oven.

10.2.10.2.5. Using tongs, remove the weighing dish from the oven and place in a desiccator and cool to room temperature.

10.2.10.2.6. Weigh the dish to the nearest 0.1 mg. Record the weight on the benchsheet.

10.2.10.2.7. Return the samples to the oven for another hour, cool in a desiccator, and reweigh. Repeat the drying, cooling, desiccating, and weighing cycle until a constant weight is obtained or weight loss is less than 0.5 mg. If more than three cycles are required, prepare a Nonconformance Memo.

Note: When weighing dried sample, be alert to change in weight due to air exposure and/or sample degradation.

10.2.10.2.8. If volatile solids are to be determined, treat the residue according to Section 10.2.13.

10.2.10.2.9. Calculate results according to the equation provided in Section 11.1. Use the lowest final weight achieved for calculating TS.

10.2.11. **Total Dissolved Solids**

10.2.11.1. Preparation of Glass Fiber Filter Disc: Refer to Section 18.2.

10.2.11.2. Preparation of Evaporating Dishes:

10.2.11.2.1. If only total dissolved solids are to be measured, heat clean dish to 180 ± 2 °C for one hour. If volatile dissolved solids are to be measured in addition to TDS, ignite the clean evaporating dish at 550 ± 50 °C for one hour in a muffle furnace.

10.2.11.2.2. Heat resistant gloves and tongs must be used when removing items from the muffle furnace.

10.2.11.2.3. Store and cool dish in desiccator until dish reaches room temperature or until needed.

Note: Always transfer the dish with gloves or tongs to prevent added weight due to oil from fingerprints.

10.2.11.2.4. Weigh immediately before use to the nearest 0.1 mg. Record the weight of the dish on the benchsheet.

10.2.11.3. Sample Analysis

10.2.11.3.1. Thoroughly rinse the entire filtration apparatus with reagent water before filtering each sample.

10.2.11.3.2. Assemble the filtering apparatus, place a glass fiber filter in the apparatus, pre-wet the filter using reagent water, and begin suction.

Note: If the sample also requires TSS, preweigh the prepared filter and refer to Section 10.2.12 for additional guidance.

10.2.11.3.3. Shake the sample vigorously and rapidly transfer 100 mL or greater volume (or a smaller portion which will yield between 10 and 200 mg dried residue) to the funnel by means of a graduated cylinder. If total dissolved solids content is low, a larger volume may be filtered. If more than 10 minutes are required to complete filtration, decrease sample size. If results are > 2000 mg/L sample should be re-analyzed at a lesser volume.

Note: Multiple filters may be used if performing only TDS analysis.

10.2.11.3.3.1. The conductance of each sample may be used to determine the appropriate sample volume to process.

Note: TDS is typically 55 - 90% of the conductance result. The exact relationship depends on the compounds present in the samples and may not hold for very high concentrations or samples containing non-ionic species or samples with conductance greater than 10,000 umho/cm or less than 50 umho/cm.

10.2.11.3.3.1.1. If the sample has a conductance less than 3,000 umhos/cm, 100 mL should be used.

10.2.11.3.3.1.2. If the conductance is 3,000 to 10,000 umhos/cm, use 20 mL of sample.

10.2.11.3.3.1.3. If the conductance is extremely high (> 10,000 umhos/cm) smaller volumes may be used.

10.2.11.3.3.2. Record the volume of sample used (to the nearest mL) on the benchsheet.

10.2.11.3.3.3. For the method blank, process 100 mL of reagent water as the sample.

10.2.11.3.3.4. For the LCS, process 100 mL of the LCS Solution. Refer to Section 7.2 for instructions on how to prepare the LCS.

10.2.11.3.4. Filter the sample through the glass fiber filter.

10.2.11.3.5. Rinse the graduated cylinder, funnel walls, and filter with three successive 10 mL portions of reagent water and allow for complete drainage between washings. Continue to apply vacuum for about three minutes after filtration is complete to remove as much water as possible.

10.2.11.3.6. Transfer the filtrate (including the washings) to a pre-weighed evaporating dish. Rinse the receiving flask with 10 - 25 mL of reagent water and transfer washings into the dish to ensure complete transfer of the sample.

10.2.11.3.7. Evaporate the samples to dryness on a steam bath or in an oven set slightly below boiling. If filtrate volume exceeds dish capacity, add successive portions to the same dish after evaporation.

10.2.11.3.8. Dry the evaporated sample in an oven for at least one hour at 180 ± 2 °C.

10.2.11.3.9. Record the date, time on the benchsheet when the samples are initially placed in the oven and again when they are removed from the oven.

10.2.11.3.10. Using tongs, remove the weighing dish from the oven and place in a desiccator and cool to room temperature.

10.2.11.3.11. Weigh the dish to the nearest 0.1 mg. Record the combined weight of the dried residue and the dish on the benchsheet.

10.2.11.3.12. Return the samples to the oven for another hour, cool in a desiccator, and reweigh. Repeat the drying, cooling, desiccating and weighing cycle until a

constant weight is obtained or weight loss is less than 0.5 mg. If more than three cycles are required, prepare a Nonconformance Memo.

10.2.11.3.13. Calculate results according to the equation in Section 11.2. Use the lowest final weight achieved for calculating TDS.

10.2.12. **Total Suspended Solids**

10.2.12.1. Preparation of Glass Fiber Filter Disc:

Note: As an alternative to the steps outlined in Sections 10.2.12.1.1 through 10.2.12.1.7, prepared and pre-weighed filters may be purchased for use under this method. The certificate of analysis is retained for the filters. The filter lot number will be documented on the bench sheet.

10.2.12.1.1. Place the glass fiber filter discs, one at a time, on the membrane filter apparatus or insert into bottom of a suitable Gooch crucible with wrinkled surface up.

10.2.12.1.2. While vacuum is applied, wash the disc with three successive 20 mL volumes of distilled water.

10.2.12.1.3. Remove all traces of water by continuing to apply vacuum after water has passed through and discard washings.

10.2.12.1.4. Remove filter from membrane filter apparatus and place in a labeled, aluminum weighing dish (or remove both the crucible and filter if a Gooch crucible is used), and dry in an oven at 103 -105 °C for one hour.

Note: If volatile suspended solids (VSS) are to be determined as well as total suspended solids, the filter must be heated at 550 ^{o}C for one hour, instead of 103 -105 ^{o}C.

10.2.12.1.5. Using tongs, remove the weighing dish from the oven and place in a desiccator and cool to room temperature.

10.2.12.1.6. Weigh the cooled filter using an analytical balance to the nearest 0.1 mg. Handle the filters or crucible/filter only with forceps. Record the weight and the dish identification number on the benchsheet.

10.2.12.1.7. Repeat the drying, cooling, and weighing cycle until a constant weight is obtained or weight loss is less than 0.5 mg.

10.2.12.2. Selection of Sample Volume

10.2.12.2.1. For a 47 mm diameter filter, filter 100 mL of sample.

10.2.12.2.2. If during filtration of this initial volume, the filtration rate drops rapidly or if filtration time exceeds 5 - 10 minutes, a smaller volume of sample should be processed.

Note: If the sample appears high in TSS, start with a sample volume < 100 mL.

10.2.12.3. Sample Analysis:

10.2.12.3.1. Assemble the filtering apparatus, place the pre-weighed glass fiber filter in the apparatus, pre-wet the filter using reagent water and begin suction.

Note: Handle the filters or crucible/filter only with forceps.

10.2.12.3.2. Shake the sample vigorously and quantitatively transfer 100 mL (or an appropriate aliquot- 250 ml recommended to improve accuracy of method if available.) of the sample to the filter using a graduated cylinder or pipette. A smaller amount should be filtered if the sample is high in TSS or is otherwise slow to filter. Filter 25 mL at a time until filtration slows. Record the volume of sample filtered (to the nearest mL) on the benchsheet.

Note: If Total Dissolved Solids (TDS) is also required, the filtrate may be used. Refer to Section 10.2.11 for additional guidance.

10.2.12.3.3. Remove all traces of water by continuing to apply vacuum after the sample has passed through.

10.2.12.3.4. With suction on, rinse the graduated cylinder, filter, suspended solids residue, and filter funnel wall with three 10 mL portions of reagent water allowing complete drainage between washings.

10.2.12.3.5. Remove all traces of water by continuing to apply vacuum for about three minutes after the sample has passed through.

10.2.12.3.6. Carefully remove the filter from the filter support and transfer to an aluminum weighing dish. Alternatively, remove the crucible and filter from the crucible adapter.

10.2.12.3.7. Dry the filter at least one hour at 103 -105 °C.

10.2.12.3.8. Record the date, time, on the benchsheet when the samples are initially placed in the oven and again when they are removed from the oven.

10.2.12.3.9. Using tongs, remove the weighing dish from the oven and place in a desiccator and cool to room temperature.

10.2.12.3.10. Cool the samples in a desiccator, weigh (to the nearest 0.1 mg), and record the weight on the benchsheet.

10.2.12.3.11. Return the samples to the oven for another hour, cool in a desiccator, and reweigh. Repeat the drying, cooling, desiccating, and weighing cycle until a constant weight is obtained or weight loss is less than 0.5 mg. If more than three cycles are required, prepare a Nonconformance Memo.

10.2.12.3.12. If volatile suspended solids are to be determined, treat the residue according to Section 10.2.15.

10.2.12.3.13. Calculate the results using the formula given in Section 11.3. Use the lowest final weight achieved for calculating TSS.

10.2.13. **Volatile Solids**

10.2.13.1. Heat muffle furnace up to temperature (550 ± 50 °C).

10.2.13.2. Place evaporating dish containing residue generated by Total Solids protocol (Section 10.2.10) in muffle furnace to ignite the residue.

10.2.13.3. Record the date, time, on the benchsheet when the samples are initially placed in the oven and again when they are removed from the oven.

10.2.13.4. Typically, 15 - 20 minutes ignition is required for 200 mg of residue. However, more than one sample and/or heavier residues may necessitate longer ignition times.

10.2.13.5. Let dish cool partially in air until most of the heat has dissipated before transferring to a desiccator for final cooling.

10.2.13.6. Using tongs and heat resistant gloves, remove the weighing dish from the muffle furnace and place in a desiccator and cool to room temperature.

10.2.13.7. Weigh dish as soon as it has cooled to room temperature.

10.2.13.8. Return the samples to the oven for another hour, cool in a desiccator and reweigh. Repeat the drying, cooling, desiccating, and weighing cycle until a constant weight is obtained or weight loss is less than 0.5 mg. If more than three cycles are required, prepare a Nonconformance Memo.

10.2.13.9. Calculate the results using the formula given in Section 12.4. Use the lowest final weight achieved for calculating VS.

10.2.14. **Volatile Dissolved Solids**

10.2.14.1. Heat muffle furnace up to temperature (550 ± 50 °C).

10.2.14.2. Place evaporating dish containing residue generated by Total Dissolved Solids protocol (Section 10.2.3) in muffle furnace to ignite the residue.

10.2.14.3. Record the date, time, and oven temperature on the benchsheet when the samples are initially placed in the oven and again when they are removed from the oven.

10.2.14.4. Typically, 15 - 20 minutes ignition is required for 200 mg of residue. However, more than one sample and/or heavier residues may necessitate longer ignition times.

10.2.14.5. Let dish cool partially in air until most of the heat has dissipated before transferring to a desiccator for final cooling.

10.2.14.6. Using tongs and heat resistant gloves, remove the weighing dish from the muffle furnace and place in a desiccator and cool to room temperature.

10.2.14.7. Weigh dish as soon as it has cooled to room temperature.

10.2.14.8. Return the samples to the oven for another hour, cool in a desiccator and reweigh. Repeat the drying, cooling, desiccating and weighing cycle until a constant weight is obtained or weight loss is less than 0.5 mg. If more than three cycles are required, prepare a Nonconformance Memo.

10.2.14.9. Calculate the results using the formula given in Section 11.5. Use the lowest final weight achieved for calculating VDS.

10.2.15. **Volatile Suspended Solids**

10.2.15.1. Heat muffle furnace up to temperature (550 ± 50 °C).

10.2.15.2. Place glass fiber filter disc containing residue generated by Total Suspended Solids protocol (Section 10.2.12) in muffle furnace to ignite the residue.

10.2.15.3. Record the date, time, on the benchsheet when the samples are initially placed in the oven and again when they are removed from the oven.

10.2.15.4. Typically, 15 - 20 minutes ignition is required for 200 mg of residue. However, more than one sample and/or heavier residues may necessitate longer ignition times.

10.2.15.5. Let filter cool partially in air until most of the heat has dissipated before transferring to a desiccator for final cooling.

10.2.15.6. Using tongs and heat resistant gloves, remove the weighing dish from the muffle furnace and place in a desiccator and cool to room temperature.

10.2.15.7. Weigh filter as soon as it has cooled to room temperature.

10.2.15.8. Return the samples to the oven for another hour, cool in a desiccator, and reweigh. Repeat the drying, cooling, desiccating, and weighing cycle until a constant weight is obtained or weight loss is less than 0.5 mg. If more than three cycles are required, prepare a Nonconformance Memo.

10.2.15.9. Calculate the results using the formula given in Section 11.6. Use the lowest final weight achieved for calculating VSS.

10.2.16. **Settleable Solids**

10.2.16.1. Volumetric: Fill an Imhoff cone to the 1-L mark with a well-mixed sample. Settle for 45 min, gently agitate sample near the sides of the cone with a rod or by spinning, settle 15 min longer, and record volume of settleable solids in the cone as milliliters per liter. If the settled matter contains pockets of liquid between large settled particles, estimate volume of these and subtract from volume of settled solids. The practical lower limit of measurement depends on sample composition and generally is in the range of 0.1 to 1.0 mL/L. Where a separation of settleable and floating materials occurs; do not estimate the floating material as settleable matter.

10.2.16.2. Where biological or chemical floc is present, the gravimetric method is preferred. Gravimetric: 1) Determine total suspended solids as in Section 10.2.12. 2) Pour a well-mixed sample into a glass vessel of not less than 9 cm diameter using not less than 1 L and sufficient sample to give a depth of 20 cm. Alternatively use a glass vessel of greater diameter and a larger volume of sample. Let stand quiescent for 1 h and, without disturbing the settled or floating material, siphon 250 mL from center of container at a point halfway between the surface of the settled material and the liquid surface. Determine total suspended solids (milligrams per liter) of this supernatant liquor (Section 10.2.12). These are the nonsettleable solids.

10.3. Documentation and Record Management

The following documentation comprises a complete raw data package:

- Raw data (direct instrument printout signed by analyst) if available from balance.
- Relevant sample analysis benchsheets which contain the following minimum information:
  - Analysis date, analyst name, SOP reference
  - Standard concentration
  - Oven temperature, date, and time that samples were placed in/out of oven
  - Lab ID, weighing dish ID, initial and final weights
- Data review checklist
- Standards documentation (including expiration date, source, and lot number).
- Nonconformance summary (if applicable).

11. CALCULATIONS / DATA REDUCTION

11.1. Calculate **Total Solids** as follows:

$$\text{Total Solids, mg / L} = \frac{(A - B) \times 1000}{C}$$

Where: A = weight of dried residue + dish (mg)
B = weight of dish (mg)
C = volume of sample (mL)

11.2. Calculate **Total Dissolved Solids** as follows:

$$\text{Total Dissolved Solids, mg / L} = \frac{(A - B) \times 1000}{C}$$

Where: A = weight of dried residue + dish (mg)
B = weight of dish (mg)
C = volume of sample (mL)

11.3. Calculate **Total Suspended Solids** as follows:

$$\text{Total Suspended Solids, mg/L} = \frac{(A - B) \times 1000}{C}$$

Where: A = weight of filter + residue (mg)
B = weight of filter (mg)
C = volume of sample filtered (mL)

11.4. Calculate **Volatile Solids** as follows:

$$\text{Volatile Solids, mg/L} = \frac{(A - B) \times 1000}{C}$$

Where: A = weight of residue + dish before ignition (mg)
B = weight of residue + dish after ignition (mg)
C = volume of sample (mL)

11.5. Calculate **Volatile Dissolved Solids** as follows:

$$\text{Volatile Dissolved Solids, mg/L} = \frac{(A - B) \times 1000}{C}$$

Where: A = weight of residue + dish before ignition (mg)
B = weight of residue + dish after ignition (mg)
C = volume of sample (mL)

11.6. Calculate **Volatile Suspended Solids** as follows:

$$\text{Volatile Suspended Solids, mg/L} = \frac{(A - B) \times 1000}{C}$$

Where: A = weight of residue + filter before ignition (mg)
B = weight of residue + filter after ignition (mg)
C = volume of sample (mL)

11.7. Calculate the mg **Settleable Solids**/L = mg total suspended solids/L_- mg nonsettleable solids/L

11.8. The relative percent difference (RPD) of duplicates are calculated according to the following equation:

$$RPD = 100\left[\frac{|DU1 - DU2|}{\left(\frac{DU1 + DU2}{2}\right)}\right]$$

Where: DU1 = Sample result
DU2 = Sample duplicate result

11.9. LCS Percent Recovery

11.10. If multiple weighing cycles are required, the lowest final sample weight is used for calculating solids content.

11.11. If smaller or larger sample volumes are processed than are specified in the method, the reporting limit must be adjusted accordingly.

11.12. Sample results should be reported according to the following significant figure rules:

Significant Figures	Sample Result
2	< 10
3	≥ 10

12. METHOD PERFORMANCE

12.1. The reporting limit is 10 mg/L for TS, TDS, VS, VDS, and VSS.

12.2. The reporting limit is 4 mg/L for TSS.

12.3. The initial demonstration study as detailed in Section 9.1.2 must be acceptable before the analysis of field samples under this SOP may begin.

12.4. The group/team leader has the responsibility to ensure that this procedure is performed by an analyst who has been properly trained in its use and has the required experience.

13. POLLUTION CONTROL

13.1. All waste will be disposed of in accordance with Federal, State and Local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this method and the policies in Section 13 of the Corporate Safety Manual for "Waste Management and Pollution Prevention."

13.2. This method does not contain any specific modifications that serve to minimize or prevent pollution

14. WASTE MANAGEMENT

14.1. The following waste streams are produced when this method is carried out.

14.1.1. Unpreserved waste samples. This waste is disposed down a lab sink.

14.1.2. Aluminum weighing tins, contaminated filter and filter residue generated by the analysis. This waste is disposed trashcans and disposed with the building trash.

15. REFERENCES

15.1. Methods for the Chemical Analysis of Water and Wastes, EPA-600/4-79-020, March 1979: Methods 160.1, 160.2, 160.3 and 160.4.

15.2. Standard Methods for the Examination of Water and Waste Water, 20th Edition, 1998 or Standard Methods Online; Methods: 2540 Solids B, C, D, E, F and G.

15.3. QA Policy QA-003, TestAmerica QC Program.

15.4. SOP PT-QA-009, Rounding and Significant Figures.

15.5. TestAmerica Pittsburgh Laboratory Quality Assurance Manual, PT-LQAM, current version.

16. ATTACHMENTS

16.1. Figure 1. Total Solids (TS)

16.2. Figure 2. Total Dissolved Solids (TDS)

16.3. Figure 3. Total Suspended Solids (TSS)

16.4. Figure 4. Volatile Solids (VS)

16.5. Figure 5. Volatile Dissolved Solids

16.6. Figure 6. Volatile Suspended Solids (VSS)

16.7. Table 1. Summary of Quality Control Requirements for Solids Determinations

17. REVISION HISTORY

17.1. Revision 0, Added:

17.1.1. Section 10.2.16 Settleable Solids procedure added.

17.2. Revision 1, 05/30/08

17.2.1. Changed laboratory name to TestAmerica.

17.2.2. Updated SOP to reflect new corporate SOP format.

17.2.3. Removed references for method 160.5, using method 2540F now.

17.2.4. Added to Safety section: This procedure may involve hazardous material, operations and equipment. This SOP does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, gloves, lab coats and closed-toe, nonabsorbent shoes are a minimum.

17.2.5. Added Section 7.2: The LCS standard solution is commercially purchased. The true value varies from lot to lot when received from the manufacturer and the calculation is adjusted accordingly by the laboratory. The standard is received with a certificate of analysis with the true value listed on it and is retained by the laboratory.

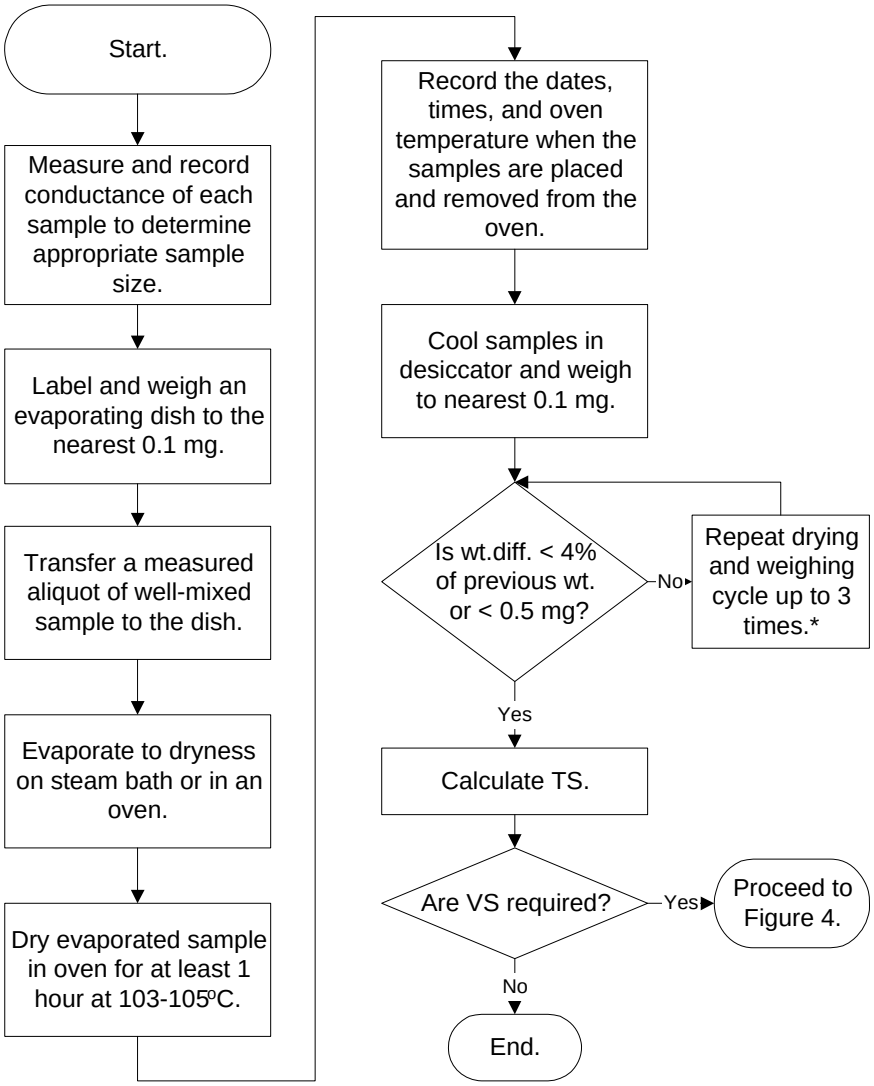
17.2.5.1. Modified section 7.2.1: If the solution needs to be made by the laboratory the procedure is as follows: LCS solution (500 mg/L TSS and TDS, 1000 mg/L TS): Place 500.0 mg of diatomaceous earth (infusorial earth or celite 545) and 500 mg sodium chloride into a 1000 mL volumetric flask and dilute to volume with deionized water. Mix well. Prepare fresh every three months.

18. METHOD MODIFICATIONS

18.1. Samples are not taken through the drying, cooling, and weighing cycle more than three times. If the sample fails to reach constant weight within three cycles, this is documented in a Nonconformance Memo and the lowest final weight is used for the calculation.

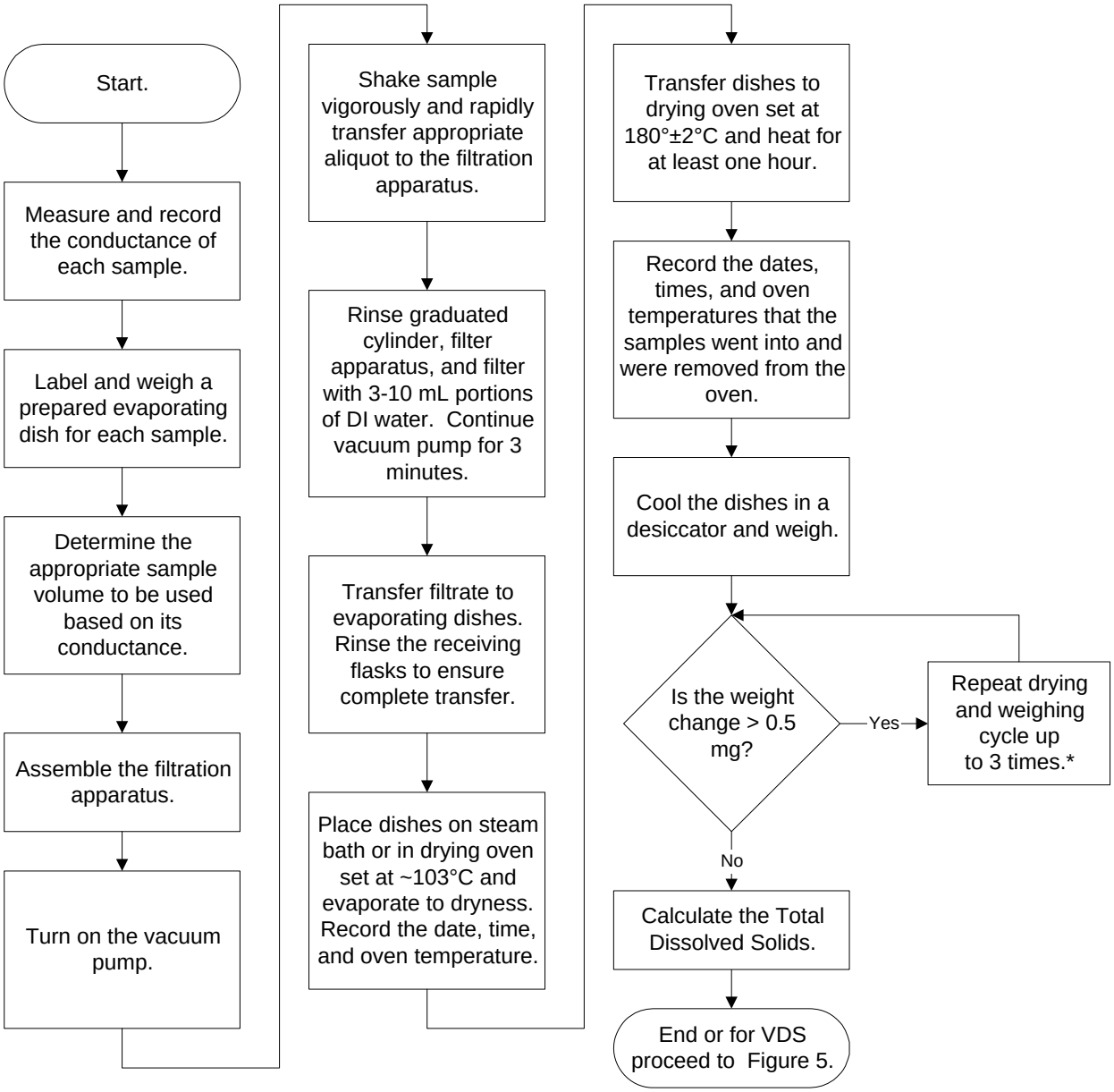
18.2. The filter cleaning procedure outlined in Method 160.1 is not applied. This SOP requires the use of method blanks to document system cleanliness.

Figure 1. Total Solids (TS)



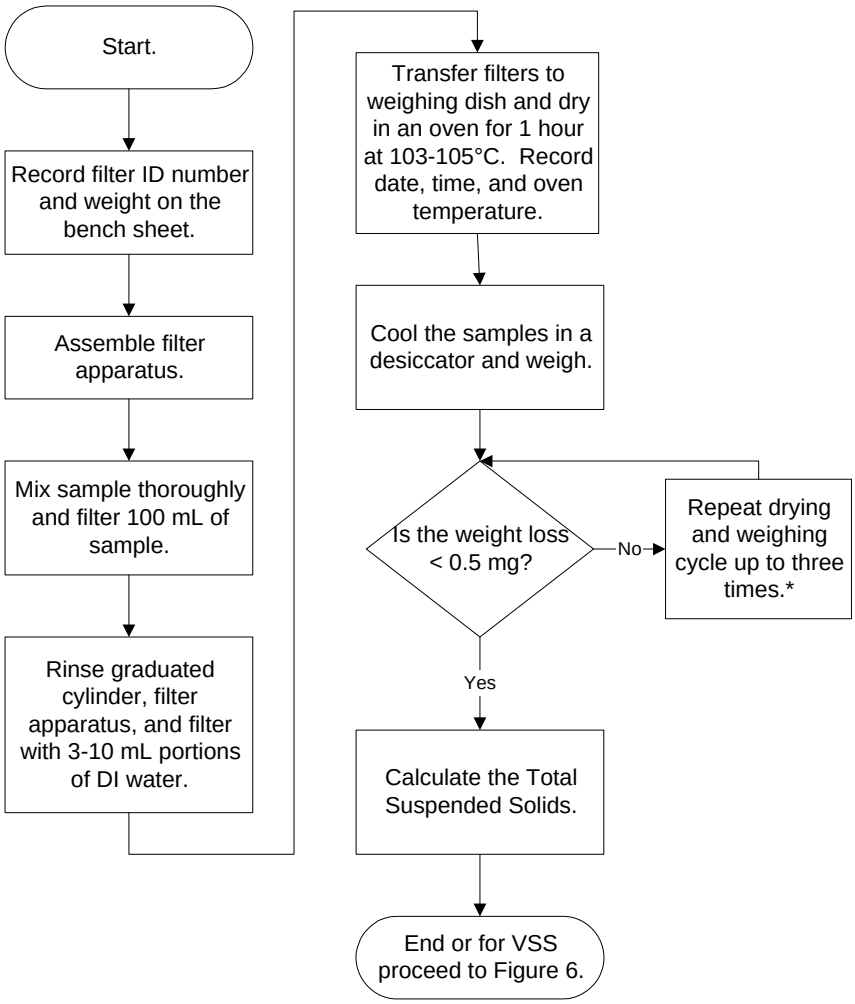
***** See Section 18.1

Figure 2. Total Dissolved Solids (TDS)



*See Section 18.1

Figure 3. Total Suspended Solids (TSS)



***** See Section 18.1

Figure 4. Volatile Solids (VS)

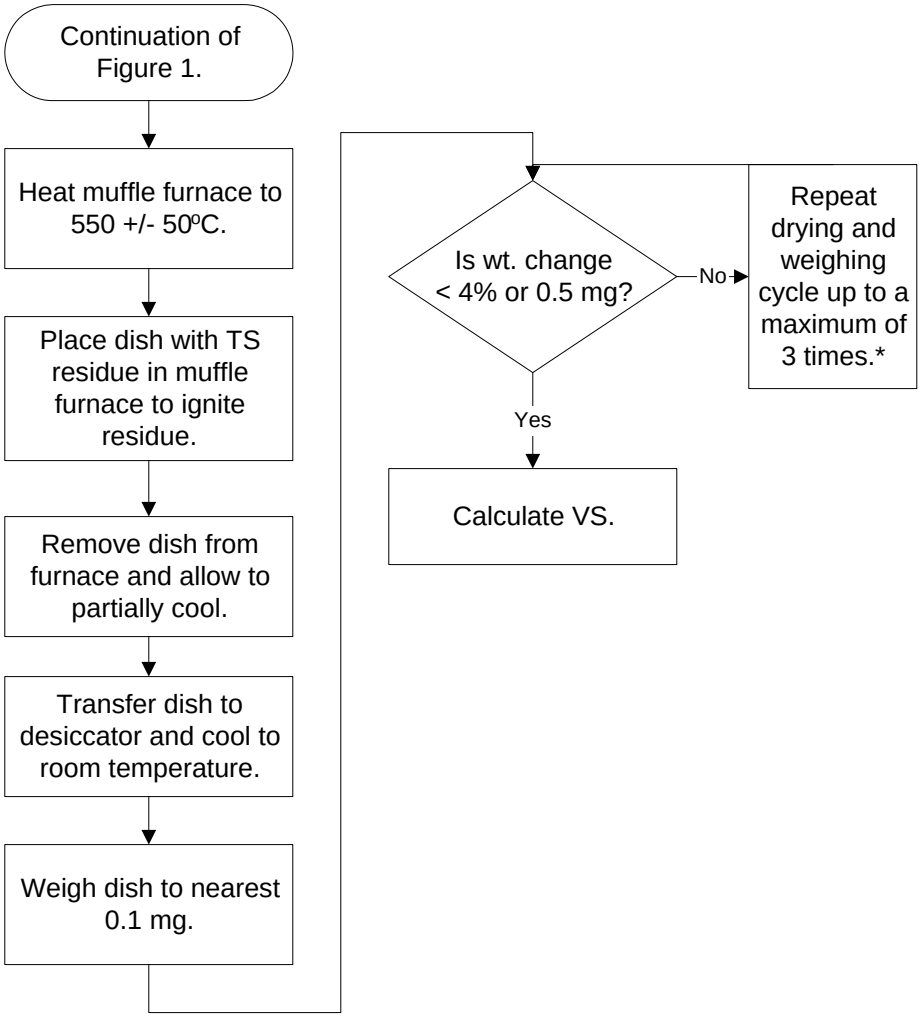
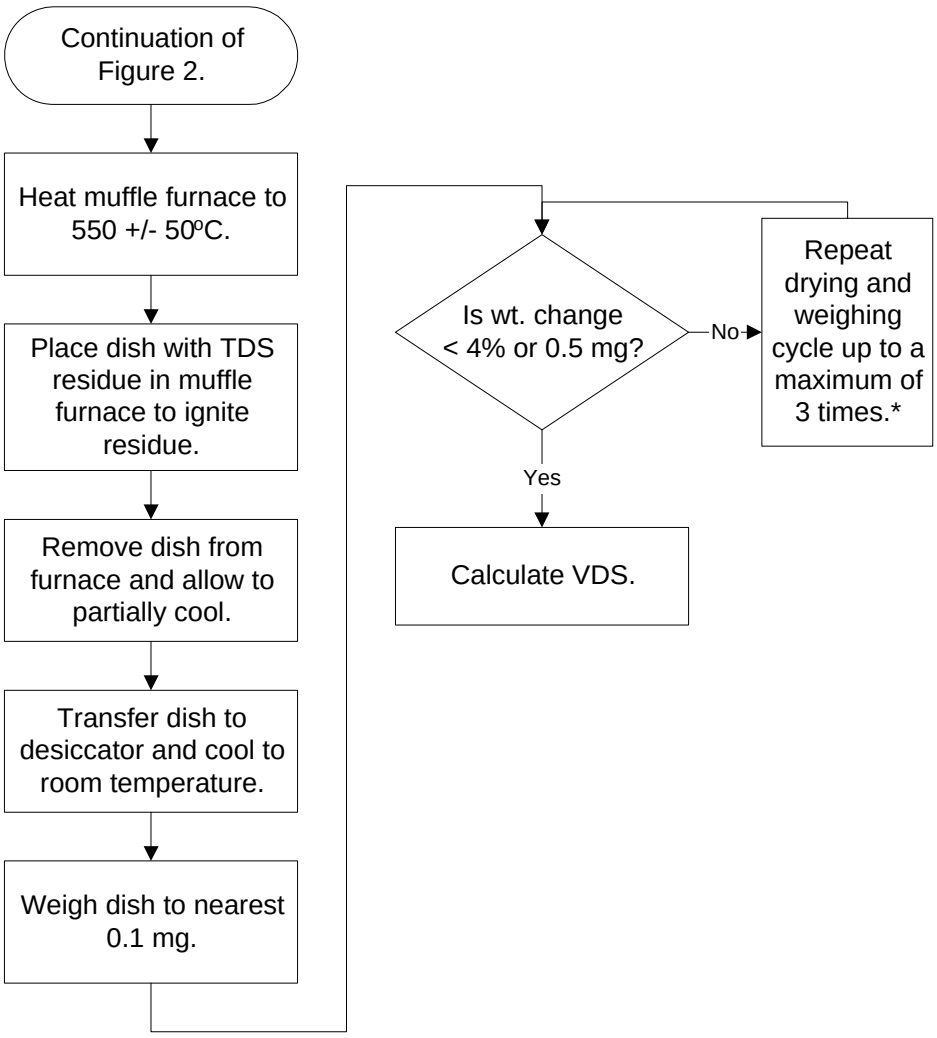
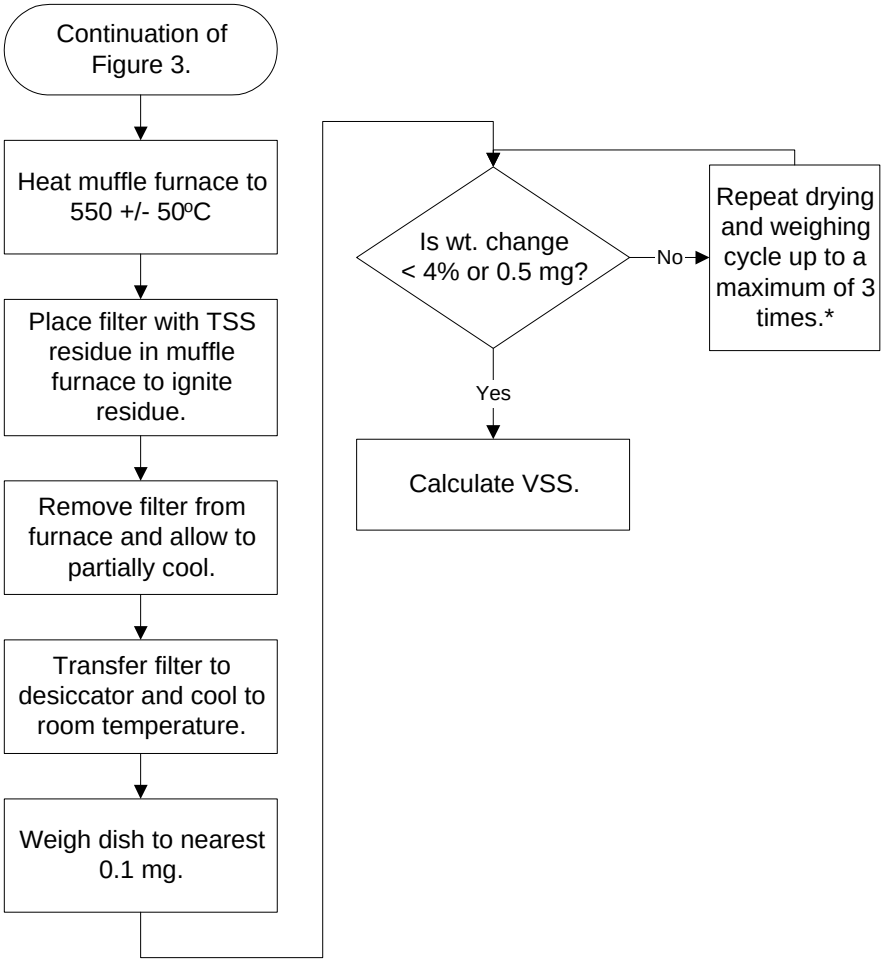


Figure 5. Volatile Dissolved Solids



*See Section 18.1

Figure 6. Volatile Suspended Solids (VSS)



*See Section 18.1

Table 1. Summary of Quality Control Requirements for Solids Determinations

QC Samples	Frequency	Acceptance Criteria	Corrective Action
Method Blank (MB)	1 per batch of up to 20 samples	< ± RL	Reanalyze all samples associated with unacceptable MB
Laboratory Control Sample (LCS)	1 per batch of up to 20 samples	80 - 120 % until in-house limits established	Reanalyze all samples associated with unacceptable LCS
Duplicate Sample (D)	1 per batch of up to 20 samples	≤ 20% RPD when results > 5x RL	Narrate the results

APPENDIX 40
SOP FOR THE DETERMINATION OF TOC BY STANDARD METHOD 5310B (PT_WC_017)

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

Title: Total Organic Carbon (TOC) and Total Inorganic Carbon (TIC)

Method(s): USEPA Methods 415.1, Standard Methods 20th Ed. 5310B and SW-846 Method 9060

Approvals (Signature/Date):

Michael Wesoloski 10/8/07 Michael Wesoloski Date Technical Manager	Larry Matko 9/20/07 Larry Matko Date Acting Health & Safety Manager
Nasreen K. DeRubeis 9/20/07 Nasreen K. DeRubeis Date Quality Assurance Manager	Larry Matko 9/20/07 Larry Matko Date Laboratory Director

This SOP was previously identified as SOP No. PITT-WC-0017, Rev. 4

1. SCOPE AND APPLICATION

1.1 The purpose of this SOP is to provide a procedure for the determination of Total Organic Carbon (TOC) or Total Inorganic Carbon (TIC) in waters and similar matrices. This SOP is based on SW-846 Method 9060, Standard Methods 20th Ed. 5310B and EPA Method 415.1.

1.2 The working linear range is instrument dependent at 1mg/L to 50mg/L with a reporting limit of 1mg/L.

2. SUMMARY OF METHOD

2.1 Organic carbon is converted to carbon dioxide (CO_2) using chemical oxidation. The CO_2 is then measured by an infrared detector.

3. DEFINITIONS

3.1 LCS: Laboratory Control Sample is processed through all method steps with the associated samples. The LCS is used to monitor the accuracy of the analytical process independent of possible interference effects due to sample matrix. Successful analyte recovery for the LCS provides assurance that the method is in control.

3.2 LCSD: Laboratory Control Sample Duplicate processed with the LCS when sufficient sample is not available to process a sample duplicate. A LCSD is used to demonstrate batch precision when the client has not supplied sufficient sample to prepare a duplicate sample analysis. A LCSD is required for each batch if a sample duplicate is not present.

3.3 MB: Method Blank is a control sample that is prepared using reagent water and all other reagents that are used on the associated samples. As part of the QC batch, it accompanies the samples through all steps of the analytical procedure. The method blank is used to monitor laboratory or reagent contamination.

3.4 MS: Matrix Spike is an aliquot of one sample in the QC batch that is spiked with a known amount of the target analyte. As a part of the QC batch, it accompanies the sample through all the steps of the analytical process.

3.5 MSD: Matrix Spike Duplicate consists of a replicate portion of the sample, which was designated as the MS. This portion is spiked and processed exactly as the MS.

3.6 MS/MSD results are used to determine the effects of the sample matrix on the precision and accuracy of the analytical process. Due to the potential variability of the matrix of each sample, the MS and the MSD results may not have immediate bearing on any sample except the one spiked.

3.7 SD: Sample Duplicate is a replicate aliquot of an environmental sample taken from the same sample container, when possible, and processed with the first aliquot of the sample. The sample and sample duplicate results are compared to determine the effect of the sample matrix on the precision of the analytical process.

3.8 QC Batch: The QC batch is a set of 20 or fewer environmental samples plus associated laboratory QC samples that are similar in composition and that are processed within the same time period and with the same reagents and standard lots. Laboratory QC samples such as LCS, matrix QC samples, and blanks are not included in the sample count for QC batching purposes.

3.9 Reagent Grade Water: Laboratory water, which is produced by a Millipore DI system or equivalent. Reagent grade water must be free of the analyte of interest as demonstrated through the analysis of method blanks.

3.10 Refer to the glossary in the Pittsburgh Laboratory Quality Manual (LQM) for other common laboratory terms.

4. INTERFERENCES

4.1 Contaminants in solvents, reagents, glassware, and other processing apparatus that lead to discrete artifacts may cause method interferences. All of these materials must be routinely demonstrated to be free from interferences under conditions of the analysis by running laboratory method blanks as described in the Quality Control section. Specific selection of reagents may be required to avoid introduction of contaminants.

4.2 Carbonate and bicarbonate interfere but are eliminated by the acidification and purging step of the instrument.

5. SAFETY

5.1 Employees must abide by the policies and procedures in the Corporate Safety Manual, Radiation Safety Manual and this document.

5.2 The auto sampler has a probe that is sharp; use caution not to stick yourself.

5.3 The furnace is very hot and can cause severe burns if touched.

5.4 The Sodium Persulfate is a strong oxidizer. Avoid contact with combustible materials, organic materials, strong reducing agents, and excess heat.

5.5 The following is a list of the materials used in this method, which have a serious or significant hazard rating. **NOTE: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Sulfuric Acid	Corrosive Oxidizer Dehydra-dator	1 mg/m^3	This material will cause burns if comes into contact with the skin or eyes. Inhalation of vapors will cause irritation of the nasal and respiratory system.
Phosphoric Acid	Corrosive	1 Mg/M3 TWA	Inhalation is not an expected hazard unless misted or heated to high temperatures. May cause redness, pain, and severe skin burns. May cause redness, pain, blurred vision, eye burns, and permanent eye damage.
Sodium Persulfate	Oxidizer Corrosive	0.1 Mg/M3-TWA as Persulfates	Causes irritation to the respiratory tract. Symptoms may include sore throat, shortness of breath, inflammation of nasal passages, coughing, and wheezing. Causes severe irritation or burns to the skin and eyes. Symptoms include redness, itching, pain and burns. May cause allergic skin reactions. Can cause eye damage.
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

5.6 Eye protection that protects against splash, laboratory coat, and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled. Cut resistant gloves must be worn doing any other task that presents a strong possibility of getting cut. Disposable gloves that have become contaminated will be removed and discarded; other gloves will be cleaned immediately.

5.7 Exposure to chemicals must be maintained **as low as reasonably achievable**, therefore, unless they are known to be non-hazardous, all samples must be opened, transferred, and prepared in a fume hood or under other means of mechanical ventilation. Solvent and waste containers will be kept closed unless transfers are being made.

5.8 The preparation of standards and reagents will be conducted in a fume hood with the sash closed as far as the operation will permit.

5.9 All work must be stopped in the event of a known or potential compromise to the health and safety of a TestAmerica associate. The situation must be reported immediately to a laboratory supervisor or EH&S coordinator.

6. EQUIPMENT AND SUPPLIES

6.1 OI Corporation Model 1010 TOC Analyzer with 1051 vial multisampler and 1030 TOC Analyzer with 1088 vial multisampler.

6.2 Nitrogen gas and regulator.

6.3 Volumetric flasks: Various sizes.

6.4 Volumetric pipettes: Various sizes.

6.5 Vials: 40mL glass.

6.6 Graduated cylinders: Various sizes.

6.7 pH strips.

6.8 Top loading balance: capable of weighing to ± 0.01g.

7. REAGENTS AND STANDARDS

7.1 Sodium Persulfate: Reagent Grade.

7.2 Sodium Persulfate Solution: Add 100g sodium persulfate ($Na_2S_2O_8$) to a 1L volumetric flask and dilute to volume with reagent water.

7.3 Phosphoric Acid, concentrated: Reagent Grade.

7.4 Phosphoric Acid Solution: Carefully add 59mL concentrated phosphoric acid (H_2PO_4) to 900mL of reagent water in a 1L volumetric flask. Dilute to volume with reagent water.

7.5 Sulfuric Acid, concentrated: Reagent Grade.

7.6 TOC Stock Standard 1000ppm: This is purchased commercially. If necessary it may be prepared as follows: Dilute 1.06g KHP (potassium acid phthalate) to volume in a 500mL volumetric flask. KHP is oven dried overnight at 180°C and stored in a dessicator for at least an hour before use.

7.7 TOC Calibration Standards: Prepare the following standards from the primary stock standard (7.6).

Concentration (mg/L)	Volume (mL)	Stock Concentration (mg/L)	Final Volume (mL)
100[(1)]	10	1000	100
50	5	1000	100
25	2.5	1000	100
10	1	1000	100
1	0.1	1000	100

[(1)] This standard used with the 1030 TOC Analyzer only.

7.8 TOC Verification Standard (CCV): Prepare a 25mg/L verification standard by adding 5.0mL of the stock standard (7.6) to a 200mL volumetric flask and diluting to volume. Prepare every day of analysis.

7.9 TOC MS/MSD: Add 200µL of the 1000 mg/L stock standard to 20 mL of sample for a final concentration of 10 mg/L.

7.10 TIC stock standard (1000 mg/L): This is purchased commercially. If necessary it may be prepared as follows: Prepare by adding 3.5g Na_2HCO_3 (sodium bicarbonate) to a 1L flask. Dilute to volume with reagent water. Keep tightly stoppered. Do not acidify. Alternatively, use any other inorganic carbonate compound of adequate purity, stability, and water solubility. TIC Calibration Standards: Prepare in the same manner as the TOC calibration standards (7.7) using the TIC stock standard (7.9). Prepare standards daily as needed.

7.11 TIC Verification Standard (LCS, MS/MSD, and CCV): Prepare in the same manner as the TOC verification standard (7.8) using the TIC stock standard (7.9). Prepare every day of analysis.

7.12 Laboratory Control Sample: 20 ppm; transfer 4 ml of 1000 ppm solution to a 200 ml volumetric flask, dilute to volume with reagent grade water. This should be prepared from a second source than the calibration standards.

7.13 Alternative (NELAC) CCV – This is a calibration verification standard prepared at a different level than the CCV sample analyzed throughout the analytical run. It is analyzed as part of initial calibration verification.

8. SAMPLE COLLECTION, PRESERVATION, SHIPMENT AND STORAGE

8.1 Samples are preserved to a pH < 2 with sulfuric acid (H_2SO_4) or hydrochloric acid (HCl) and stored in plastic or glass containers at 4°C ±2°C.

8.2 Holding Time: 28 days from sample collection to analysis.

9. QUALITY CONTROL

9.1 See Document QA-003 QC Policy for additional detail.

9.2 A batch is a group of no greater than 20 samples, excluding QC samples (LCS, MS, MSD, and Method Blanks) that are processed similarly with respect to the

procedure. All samples within the batch must be treated with the same lots of reagents and the same processes.

9.3 The laboratory control sample is processed with each batch of 20 or fewer environmental samples. The LCS recovery must be ± 20 percent of the true value. If the LCS fails criteria, the analyst will check calculations and analytical system performance and reanalyze the LCS once. If the LCS is still outside control limits, all samples in the QC batch will be reprepared and reanalyzed. If this is not possible due to limited sample quantity, the laboratory project manager will be notified and an analytical narrative provided with the data. If repreparation and reanalysis will be outside of holding time, the client should be notified and approval from the client must be obtained before reanalysis.

9.4 One MS/MSD pair must be processed for every 10 samples analyzed. Samples identified as field blanks cannot be used for MS/MSD analysis. Recovery of the MS/MSD samples should be ± 25% and the RPD ± 20%.

9.5 One sample per matrix and per QC batch must be spiked with inorganic carbon to determine the efficiency of the inorganic carbon removal process. To perform this check, split a sample into two portions and spike one portion with the inorganic carbon spike. Analyze both samples and calculate and record the percent recovery using the formula in Section 11.2. There should not be any inorganic carbon recovered in the spiked portion of the sample. If inorganic carbon is recovered, adjust sample container, sample volume, pH, purge gas flow rate and/or purge time to obtain complete removal of inorganic carbon. Enter the results for the inorganic spike in the LIMs system; however, do not report this result.

9.6 A duplicate sample must be analyzed for every 10 samples analyzed. The RPD must by < 20% for samples with results > 5X the Reporting limit and +/- the Reporting limit for those samples having results < 5X the RL.

9.7 Method Detection Limit (MDL) - An MDL must be determined for each analyte/matrix prior to the analysis of any samples. The MDL is determined using seven replicates of reagent water, spiked with all the analytes of interest that have been carried through the entire analytical procedure. MDLs must be redetermined on an annual basis in accordance with 40 CFR Part 136 Appendix B requirements as detailed in TestAmerica SOP PITT-QA-0007. The spike level must be between the calculated MDL and 10X the MDL to be valid. The result of the MDL determination must be below the TestAmerica reporting limit.

9.8 The method blank (MB) is processed with each batch of 20 or fewer environmental samples. All analyte concentrations in the MB must be less than the reporting limit. If the MB fails criteria, the analyst will check the calculations and analytical system performance and reanalyze the MB once. If the MB is still outside of criteria, all samples associated with the unacceptable blank will be reprepared and reanalyzed. If this is not possible due to limited sample quantity, the laboratory project manager will be notified, and an analytical narrative provided with the project data. If repreparation and reanalysis will be outside of the holding time, the client should be notified and approval from the client should be obtained before reanalysis.

9.9 Initial Demonstration of Capability

Prior to analysis of any samples using this SOP, the following requirements must be met:

Initial Demonstration Study: This requires the analysis of four QC check samples. The QC check sample is a well-characterized, laboratory-generated sample used to monitor method performance, which should contain the analyte(s) of interest. The results of the initial demonstration study must be acceptable before analysis of samples under this SOP may begin. Four aliquots of the check sample (LCS) are prepared and analyzed using the procedures detailed in this SOP. Acceptance criteria for the LCS are given in Section 9.3.

10. PROCEDURE

10.1 Calibration

10.1.1 Initial setup.

Constant Settings	
STD Mass	6.76ug C
Sample Volume	2.0mL
Acid Volume	2 x 100uL
Oxidant Volume	10 x 100uL

10.1.2 Adjust the nitrogen to 50 psi using the flow valve on the tank. The gauge should always be set at 50 psi when the instrument is not in use.

10.1.3 If the main valve reads < 200 psi, the tank should be changed. **Do not** allow the tank to go empty.

10.1.4 Remove the reagent bottles and fill with appropriate reagents (phosphoric acid solution and sodium persulfate). Do not fill bottles completely full; leave a small amount of air space. Loosely reconnect caps (and tubing), and replace the bottles into the instrument.

10.1.5 Blank and calibrate the instrument when CCVs and/or CCBs fail to meet acceptance criteria or when other problems are encountered.

10.1.5.1 Choose “sequences” from the “databases” menu option, open up the calibration template.

10.1.5.2 Confirm all information. If blanking is required, it is best if done at this step. Enter the desired number of blanks (no less than five) in the “reagent blanks before” field.

10.1.5.3 Analyze an ICV (NELAC CCV) /ICB.

10.1.5.4 Save the file using the current date as the filename.

10.1.5.5 Update data file information: Choose the setup menu option, go into win TOC output, change the log fill name and prefix counter.

10.1.5.6 Evaluate the data. The correlation coefficient of the original curve must be ≥ 0.995 or recalibration is required.

10.1.6 Continuing Calibration: The run is checked at the beginning, after every ten environmental samples, and at the end of the run of the same species (TOC or TIC) using a midrange CCV made from a secondary source (Section 7.2.4 or 7.2.7) to verify continued linearity. A CCV cannot vary from the original curve by more than ± 10% or recalibration is required.

10.1.7 System cleanliness is checked every ten environmental samples and at the end of the run using a Continuing Calibration Blank (CCB). A CCB cannot contain the analyte of interest above the reporting limit, or recalibration is required.

10.1.8 Analytical Documentation: Record all analytical information in the analytical logbook/logsheet, including the analytical data from standards, blanks, LCSs, MS/MSDs, and any corrective actions or modifications to the method.

10.1.9 All standards that are not prepared daily are logged into laboratory standard database. All standards are assigned a unique number for identification. The supervisor or designee reviews logbooks.

10.1.10 Documentation, such as all associated instrument printouts (final runs, screens, reruns, QC samples, etc.) and daily calibration data corresponding to all final runs, is available for each data file.

10.1.11 Sample results and associated QC are entered into the Laboratory Information Management System (LIMS) after final technical review.

10.2 **Sample Preparation:** Check the pH of the sample. If the pH > 2, add concentrated H_2SO_4 dropwise to the sample (in the TOC vial) until the pH is < 2. This is performed at the time of sample receipt.

10.3 The TOC samples, which come from the field in containers ready for analysis, are sparged by the instrument prior to TOC analysis to remove inorganic carbons that may be present. Samples requiring both TOC & TIC are received as two separate samples that are analyzed separately.

10.4 The instrument has analytical modes for TIC, TOC & TC analysis. Analysis after sparging is calculated by the instrument as TOC. Unsparged analysis is calculated as TC. The difference between the two results is calculated as TIC. All calculations are performed by the instrument software program based on analytical curves.

10.5 All sample preparation and analysis information will be documented on laboratory bench sheets, computer printouts, standard logbooks, etc. Raw data will be forwarded for reporting and for inclusion in the project files.

10.6 See the manufacturer's instructions for an instrument troubleshooting guide and maintenance requirements.

11. CALCULATIONS / DATA REDUCTION

11.1 Total Organic Carbon, mg/L = Instrument Value x Dilution

Where replicate measurements are performed:

TOC, mg/L = average of the 4 instrument values* x dilution

* The four values will be considered to have an acceptable level of consistency, if each of the values lies within ± 35% of the mean. If analysis of any replicate exceeds the 35%, reanalysis will be performed and the findings narrated.

11.2 MS/MSD % Recovery = ((observed spike-sample conc.)/true spike)x100

11.3 Duplicate Sample (Relative Percent Difference):

$$RPD = \frac{|X_1 - X_2|}{\left(\frac{X_1 + X_2}{2}\right)} \text{ x } 100\%$$

X_1 = Original Result.
X_2 = Duplicate.

11.4 LCS Percent Recovery:

$$\text{LCS \% Recovery} = \left(\frac{\text{Observed Conc. in LCS}}{\text{True LCS Conc.}}\right) \text{ x } 100\%$$

11.5 Calculation of TIC

TIC = TC – TOC

Where:

TIC = Total Inorganic Carbon

TC = Total Carbon

TOC = Total Organic Carbon

Note: the calculation for TC, TOC and TIC is a function of the instrument's analytical software.

11.6 If quadruplicate analysis is requested by the client each analytical result is reported individually, average results may be reported in the narrative by request

12. METHOD PERFORMANCE

12.1 The group/team leader has the responsibility to ensure that this procedure is performed by an analyst who has been properly trained. The group/team leader must document the training and PE performance and submit the results to the QA Manager for inclusion in associate training files.

13. POLLUTION CONTROL

13.1 All waste will be disposed of in accordance with Federal, State and Local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this method and the policies in section 13 of the Corporate Safety Manual for "Waste Management and Pollution Prevention."

14. WASTE MANAGEMENT

14.1 The following waste streams are produced when this method is carried out.

14.1.1 Acidic waste from the auto-analyzer. (This waste is collected in a waste container identified as "Acid Waste", Waste #33. This waste is neutralized to a final pH between 6 and 9 and discharged down into a lab sink.

15. REFERENCES

15.1 SW846, Test Methods for Evaluating Solid Waste, Third Edition, Total Organic Carbon, Method 9060.

15.2 EPA 600, Methods for Chemical Analysis of Water and Wastes, Organic Carbon, Method 415.1.

15.3 Standard Methods for the Examination of Water and Wastewater, 20th Ed., 1998, Method 5310B.

15.4 TestAmerica Pittsburgh LQM, current version.

16. ATTACHMENTS

16.1 Not Applicable.

17. REVISION HISTORY

17.1 Revision 5, 8/3/07.

17.1.1 Changed laboratory name to TestAmerica.

17.1.2 Changed the format of the SOP to correspond to the new Corporate SOP format.

17.1.3 Added references to Standard Methods 20th Edition, method 5310B.

17.1.4 Added procedures for determining the efficiency of inorganic carbon removal.

17.1.5 Added new instrumentation.

18. METHOD MODIFICATIONS

18.1 If samples require dilution or smaller volumes than specified in this method, the RL will be elevated.

18.2 SW-846 Method 9060 indicates that four replicate measurements be performed on each sample. However, some projects may not require replicate measurements, in which case single measurements are performed. Determination of the number of measurements to be performed on a sample is made by the Project Manager and the Client. The LIMS system permits the Project Manager to differentiate between single and multiple measurements, and communicates the project requirements to the analyst. If four replicates are requested and there is insufficient sample to run four, the corrective action will include writing a non-conformance memo and contacting the Project Manager who in turn will contact the client as to how to proceed. This non-conformance will also be narrated on the report sent to the client.

APPENDIX 41
OIL AND GREASE EPA METHOD 1664 (PT_WC_028)

Title: Hexane Extractable Material (HEM; Oil and Grease) and Silica Gel Treated Hexane Extractable Material (SGT-HEM; TPH) Method 1664A

Methods: Method 1664A

Approvals (Signature/Date):

Michael P. Wesoloski 11/17/08	[signature] 11/17/08
Michael Wesoloski Date	Steve Jackson Date
Technical Manager	Health & Safety Manager / Coordinator
Nasreen K. DeRubeis 11/10/08	[signature] 11/17/08
Nasreen DeRubeis Date	Albert F. Vicinie for Larry Matko Date
Quality Assurance Manager	General Manager / Laboratory Director

This SOP was previously identified as SOP No. PITT-WC-0062, Rev.5

1.0 Scope and Application

1.1 This method quantifies the n-hexane extractable material (HEM; Oil and Grease) and n-hexane extractable material that is not adsorbed by silica gel (SGT-HEM or TPH;non-polar material) in surface and saline waters and aqueous wastes. Generally, the extractables consist of non-volatile hydrocarbons, vegetable oils, animal fats, waxes, soaps, greases, and similar materials.

1.2 This method is for use in the Environmental Protection Agency's (EPA's) survey and monitoring programs under the Clean Water Act; the Resource Conservation and Recovery Act; the Comprehensive Environmental Response, Compensation, and Liability Act; and other EPA regulatory programs. "Oil and grease" is a conventional pollutant under the Clean Water Act and codified at 40 CFR 401.16. The term "n-hexane extractable material" reflects that this method can used to determine materials other than oils and greases. Similarly, the term "silica gel treated n-hexane extractable material" reflects that this method can be used to determine material that is not adsorbed by silica gel (non-polar material).

1.3 If only SGT-HEM is required, the HEM determination can be skipped only if the HEM concentration is known. If the HEM concentration is not known, then the HEM determination must be performed prior to the SGT-HEM determination.

1.4 This method is applicable to surface waters, sewages, and aqueous wastes containing approximately 5 mg/L to approximately 1000 mg/L using a 1L sample. The reporting limit for both HEM and SGT-HEM is 5 mg/L in water and 165 mg/kg in waste.

2.0 Summary of Method

2.1 Using a solid phase extraction manifold, a 1.0 L aqueous sample (acidified to pH <2) is filtered through an extraction disk. The extractable materials are rinsed from this disk with n-hexane, collected into a 40 ml VOA vial. The extract is filtered through a phase separation filter paper into a pre-weighed pan, for evaporation on the Speedvap 9001. This step concentrates the HEM portion of the sample. The pans are allowed to cool in a desiccator, and then re-weighed to determine the HEM concentration. In order to determine the SGT-HEM (TPH), the sample is then reconstituted with hexane and treated with silica gel. The silica gel treated extract is filtered into a pre-weighed pan, for evaporation on the Speedvap 9001. This step concentrates the SGT-HEM portion of the sample. The pans are allowed to cool in a desiccator, and then re-weighed to determine the SGT-HEM concentration.

3.0 Definitions

3.1 N-hexane extractable material (HEM): Material that is extracted from a sample and determined by this method (oil and grease). Examples of this material include relatively

non-volatile hydrocarbons, vegetable oils, animal fats, waxes, soaps, greases, and other materials with similar characteristics.

3.2 Silica gel treated n-hexane extractable material (SGT-HEM): Material that is extracted from a sample and determined by this method that are not adsorbed by silica gel (TPH).

3.3 See TestAmerica Pittsburgh Laboratory's Quality Assurance Manual (PT-LQAM) for glossary of common terms.

4.0 Interferences

4.1 This method is not designed to quantify substances, which volatilize at temperatures below approximately 85^{O}C. Petroleum products, ranging from gasoline to #2 fuel oils, may be partially lost during the extraction process. Certain crude or heavy oils contain portions of material not soluble in n-hexane, often resulting in low recoveries.

4.2 All glassware and other apparatus in contact with the sample must be thoroughly washed and solvent rinsed to eliminate contamination from artifacts. In addition, reagent grade or better solvents must be used to ensure that the glassware, etc… is free of artifacts.

4.3 For samples consisting of complex matrices (such as particulates or detergents) that may interfere with the extraction process, a smaller sample size may be used.

4.4 Care must be taken to avoid contamination of the final extract with sodium sulfate, silica gel and /or water. This can be avoided by filtering the HEM or SGT-HEM very slowly. Should contamination occur, apparent by visible amounts of crystalline material in the residue, the residue must be re-suspended in n-hexane. The re-suspended material can be filtered with additional solvent washings of the flask through Whatman® phase separator filter paper. The method then resumes with the evaporation process.

4.5 Samples must be brought to room temperature prior to analysis in order to reduce the amount of solid material adhering to the walls of the collection containers. Erroneous low results may be obtained from samples analyzed at refrigeration temperatures.

5.0 Safety

5.1 Employees must abide by the policies and procedures in the Corporate Environmental Health and Safety Manual (CW-E-M-001), Radiation Safety Manual and this document. This procedure may involve hazardous material, operations and equipment. This SOP does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, gloves, lab coats and closed-toe, nonabsorbent shoes are a minimum.

5.2 The following is a list of the materials used in this method, which have a serious or significant hazard rating. **NOTE: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Acetone	Flammable	1000 ppm-TWA	Inhalation of vapors irritates the respiratory tract. May cause coughing, dizziness, dullness, and headache.
Hexane	Flammable Irritant	500 ppm-TWA	Inhalation of vapors irritates the respiratory tract. Overexposure may cause lightheadedness, nausea, headache, and blurred vision. Vapors may cause irritation to the skin and eyes.
Hydrochloric Acid	Corrosive Poison	5 ppm-Ceiling	Inhalation of vapors can cause coughing, choking, inflammation of the nose, throat, and upper respiratory tract, and in severe cases, pulmonary edema, circulatory failure, and death. Can cause redness, pain, and severe skin burns. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
Methanol	Flammable Poison Irritant	200 ppm-TWA	A slight irritant to the mucous membranes. Toxic effects exerted upon nervous system, particularly the optic nerve. Symptoms of overexposure may include headache, drowsiness and dizziness. Methyl alcohol is a defatting agent and may cause skin to become dry and cracked. Skin absorption can occur; symptoms may parallel inhalation exposure. Irritant to the eyes.
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

5.3 Eye protection that protects against splash, Laboratory coat, and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled. . Cut resistant gloves must be worn doing any other task that presents a strong possibility of getting cut. Disposable gloves that have been contaminated will be removed and discarded; other gloves will be cleaned immediately.

5.4 Exposure to chemicals must be maintained **as low as reasonably achievable,** therefore, unless they are known to be non-hazardous, all samples must be opened, transferred and

prepared in a fume hood, or under other means of mechanical ventilation. Solvent and waste containers will be kept closed unless transfers are being made.

5.5 The preparation of standards and reagents will be conducted in a fume hood with the sash closed as far as the operations will permit, or under other adequate ventilation.

5.6 All work must be stopped in the event of a known or potential compromise to the health and safety of an TestAmerica Pittsburgh Associate. The situation must be reported **immediately** to a supervisor or the EH&S coordinator.

6.0 Equipment and Supplies

6.1 Analytical balance capable of weighing to 0.1 mg.

6.2 Vacuum source and tubing to connect apparatus.

6.3 Waste receptacle and tubing to connect manifold.

6.4 JT Bakerbond Speedisk Extraction Station Oil and Grease apparatus equipped for each unit with the following:

6.4.1 1.0 L reservoir funnel

6.4.2 Rinsing flask (one per manifold set-up)

6.4.3 JT Baker 50mm Disk

6.5 Horizon SpeedVap 9000II.

6.6 Desiccator.

6.7 70 & 150 ml Disposable Evaporation Pans.

6.8 Glass, class A, graduated cylinders, 1 L and 100 mL.

6.9 pH indicator strips.

6.10 40 mL VOA vials or other suitable glass container used as Collection flasks.

6.11 Phase separation filter paper.

6.12 Glass filter funnels.

7.0 Reagents and Standards

7.1 Reagent water- Super Q water.

7.2 Hydrochloric acid or sulfuric acid (ACS). Mix equal volumes of concentrated HCl and reagent water or 1 part H_2SO_4 and 5 parts reagent water to produce an approximately 6N solution.

7.3 Acetone, Reagent grade, residue less than 1.0 mg/L.

7.4 n-Hexane, 85% minimum purity, 99.0% minimum saturated C6 isomers, residue less than 1.0 mg/L.

7.5 Methanol, pesticide grade or better.

7.6 Sodium Sulfate: Granular, anhydrous.

7.7 Silica Gel: Chromatographic, 100-200 mesh.

7.8 Laboratory control standard (LCS). Purchased Speedisk Oil and Grease standards kit of 2 mg/mL stearic acid and 2 mg/mL hexadecane in acetone. Spike 10.0 mL of the solution into a 1 L aliquot of acidified reagent water (Super Q water acidified with 5 mL of 1:1 HCl). The resulting concentrations in the LCS are 40 mg/L HEM and 20 mg/L SGT-HEM (stearic acid is removed by the silica gel treatment.

7.9 Hexadecane/stearic acid matrix spike solution – Each vial from the Speedisk Oil and Grease standards kit contains 51 mL of 2 mg/mL stearic acid and 2 mg/mL n-Hexadecane in ultra resi-analyzed acetone. Spike 10.0 mL of the solution into a 1 L aliquot of sample. Samples must be spiked prior to transfer to the reservoir funnel. The resulting concentrations in the matrix spike are 40 mg/L HEM and 20 mg/L SGT-HEM based on a 1 L sample.

7.9.1 The spiking solution may be prepared by weighing 200 ± 2 mg hexadecane and 200 ± 2 mg stearic acid into a 100 mL volumetric flask. Dilute to volume with acetone. Store in the dark at room temperature. To minimize evaporation of acetone, wrap the stopper and neck area of the flask with parafilm. Sonicate and warm to provide adequate dissolution of the solution. Prior to use, verify that the solution level is at the 100mL mark. In the event that some acetone has evaporated, bring the solution to volume again with acetone.

7.9.2 Note: Stearic acid tends to stick to everything. It is very important that all surfaces, that the extract comes in contact with, are rinsed with hexane to ensure complete recovery.

8.0 Sample Collection, Preservation, Shipment and Storage

8.1 All samples should be collected in 1L glass bottles and stored at 4°C ± 2°C.

8.2 Sample bottles are pre-preserved using 5 mL of 1:1 HCl or 5 mL of 1:1 H_2SO_4 for a 1 L sample. This should bring the pH to <2.

8.3 Analysis must begin within 28 days after sample collection.

9.0 Quality Control

9.1 The TestAmerica-Pittsburgh QC Program document (PT-QA-021) provides further details of the QC and corrective action guidelines presented in this SOP. Refer to this document for additional guidance.

9.2 A Method Blank, LCS, Matrix Spike (MS) and Matrix Spike Duplicate (MSD) are to be analyzed per batch of 20 or less samples analyzed together.

9.3 The Method Blank (MB) must contain less than 5.0 mg/L of HEM and/or SGT-HEM.

9.3.1 Samples associated with method blanks, which fail the acceptance criteria, must be prepared and analyzed again with an acceptable blank. If there is insufficient sample to reanalyze, or the reanalysis will be outside of holding time, a Non-Conformance Memo (NCM) must be prepared. Reanalysis outside of holding time must be approved by the client as directed by the project manager.

9.4 The acceptable LCS recoveries are 78% - 114% for HEM; and 64% - 132% for SGT-HEM.

9.4.1 Samples associated with a LCS, which fails the acceptance criteria, must be prepared and analyzed again with an acceptable LCS. If there is insufficient sample to reanalyze, or the reanalysis will be outside, a Non-Conformance Memo (NCM) must be prepared. Reanalysis outside of holding time must be approved by the client as directed by the project manager.

9.5 The acceptable MS and MSD recoveries are 78% - 114% for HEM; and 64% - 132% for SGT-HEM. The acceptable relative percent difference (RPD) between the MS and MSD results are 18% for HEM; and 34% for SGT-HEM.

9.5.1 If the MS and/or MSD recoveries or RPD are outside of acceptance limits, the LCS results should be evaluated. If the LCS recovery is acceptable, the method is considered in-control and the results are reported with appropriate qualifications. If the LCS recoveries are also outside of acceptance limits, the method is out-of-control and the appropriate corrective actions noted in Section 9.5.1 must be initiated.

9.5.2 If insufficient sample is available to prepare a MS and/or MSD, than a duplicate LCS will be analyzed with the batch. The RPD between the two LCSs must meet the RPD criteria noted in Section 9.6.

9.6 One time procedural variations are allowed only if deemed necessary in the professional judgment of supervision to accommodate variation in sample matrix, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using a Nonconformance Memo and approved by a Technical Specialist and QA Manager. If contractually required, the client shall be notified. The Nonconformance Memo shall be filed in the project file.

10.0 Procedure

10.1 Calibrate the analytical balance at 2 mg and 1000 mg using class "S" weights before and after each batch of samples.

10.1.1 Calibration shall be within ± 10% (i.e. ± 0.2 mg) at 2 mg and ± 0.5% (i.e. ± 5 mg) at 1000 mg. If values are not within these limits, recalibrate the balance.

10.2 Verify that the pH of the sample is less than 2 using the following procedure:

10.2.1 Dip a disposable pipette into the well-mixed sample.

10.2.2 Withdraw the pipette and allow a drop of sample to fall on or touch the pH paper.

10.2.3 If the sample is at neutral or greater pH, add 5-6 mL of 6N HCl or H_2SO_4 solution or other appropriate amount to adjust the pH of the 1 L sample to less than 2. Document if acid needed to be added.

10.2.4 Use a new disposable pipette for each sample.

10.3 Connect the JT Bakerbond speedisk extraction station Oil & Grease manifold to a vacuum source as per manufacturer's instructions. Prewash the funnels, and body with n-hexane. Assemble the reservoir funnel for each apparatus.

10.4 Weigh Disposable Evaporation Pans using an analytical balance, record the weights, and put pans aside to be used later.

10.5 Disk conditioning

10.5.1 Assemble a Speedisk Extraction Station and mount a collection chamber on each active port. Mount disk and wash with approximately 10 mL of hexane. With the vacuum on, pull through a small amount of hexane. Turn off the vacuum and soak the disk for 2 minutes. Pull the remaining solvent through the disk and allow it to dry. Repeat the above wash procedure two more times.

10.5.2 Add approximately 10 mL of methanol to the disk, pull through a small amount and then allow the disk to soak for 2 minutes. Pull most of the methanol through, but not all (enough methanol should remain to keep the disk wet). (For a uniform flow and reproducible recovery, keep the disk wet from this point until the end of the sample addition).

10.6 Mark the meniscus on the 1 liter sample bottle. Spike the MS and MSD aliquots with Matrix Spike solution (Refer to Section 7.9). Mix well.

10.7 Add the water sample under full vacuum. Drain as much water from the sample bottle as possible (Do not let the disk go dry between additions of sample).

10.7.1 The method blank consists of 1 L of acidified reagent water.

10.7.2 The LCS is prepared as stated in Section 7.8.

10.7.3 The MS and MSD are prepared by spiking the designated sample aliquots directly in the sample bottles (see Section 7.9).

10.8 Filtration should progress at a steady rate and finish between 10 and 15 minutes. Air-dry the disk for 15-20 minutes at full vacuum.

10.9 Remove the disk from the extraction station and insert a suitable collection flask (40mL VOA vial) into the collection chamber.

10.10 Rinse the empty sample bottle or container holding the method blank and LCS with approximately 10 mL of hexane. Transfer the hexane to the disk, making sure to rinse the sides of the disk.

10.11 Pull through half of the hexane by slowly releasing the vacuum. Soak the disk for 2 minutes and then pull the remaining hexane through the disk.

10.12 Repeat steps 10.10 and 10.11 for a total of three times.

10.13 The initial sample volume is determined by filling the sample bottle with reagent water up to the meniscus and measuring that volume in a graduated cylinder. Record the volume to the nearest 10 mL.

10.14 If only SGT-HEM is required, and the HEM concentration is known, proceed to section 10.16. Otherwise, HEM must be determined.

10.15 HEM Determination

10.15.1 Place a phase separation filter paper into a filter funnel. Add approximately 5-10 grams of sodium sulfate on top of the filter paper. Rinse with hexane and dispose of the rinsate.

10.15.2 Filter the extract through the sodium sulfate and phase separator filter paper into a pre-weighed 70 mL evaporation pan. Rinse the collection flask, sodium sulfate and filter paper twice with approximately 5 mL portions of hexane.

10.15.3 Place pans into the Speedvap and evaporate to dryness. The Speedvap is set to 50 ° C.

10.15.4 Place the pans in a desiccator for one hour.

10.15.5 Weigh the pans on an analytical balance and record the weights to the nearest 0.1 mg.

10.15.6 Determine the HEM concentration using the equation in section 11.2.

10.16 SGT-HEM Determination

10.16.1 If the HEM concentration was known and thus not determined (i.e., extract from section 10.14), then the extract must be dried using sodium sulfate before the silica gel treatment (refer to Sections 10.15.1 - 10.15.2). Filter into a suitable glass container and bring up to approximately 75 mL in hexane.

10.16.2 If the HEM determination was performed, the residue in the evaporation pan from Section 10.15.5 is re-dissolved in hexane in a suitable glass container with approximately 75 mL of hexane.

10.16.3 If the HEM was determined and the HEM is less than the SGT-HEM reporting limit, the analyst may report SGT-HEM as less than the reporting limit and stop at this point. SGT-HEM should always be less than or equal to HEM.

10.16.4 Add 3.0 g of silica gel for every 100 mg of HEM in the extract up to a maximum of 30 grams of silica gel (maximum of 1000 mg of HEM).

10.16.5 The HEM in the extract should be rounded up to the next 100 mg. For example, if the HEM is 735 mg, the amount of silica gel added should be based on 800 mg or 24 grams of silica gel (3 g. x 8).

10.16.6 If the HEM concentration is greater than 1000 mg, the extract must be brought to a known final volume in hexane in a Class A volumetric flask. From this, a fraction of the extract, that contains less than 1000 mg of HEM, is pipetted into another container using a Class A volumetric pipette, brought up to approximately 75 mL with hexane, and silica gel treated. For example, if the sample had 5000 mg of HEM and the extract was taken to a 100 mL final volume, than a 10.0 mL aliquot of that extract (1/10th), which would have 500 mg of HEM, is pipetted into the other flask and diluted to approximately 75 mL in hexane. This extract would than be treated with 15 grams of silica gel (5 x 3 grams). A dilution factor of 10 would be included in the final sample calculation.

10.16.7 Add a stir bar to the flask and stir for 15 minutes.

10.16.8 Filter with phase separator paper into a previously weighed 150 mL evaporation pan. Rinse the flask, silica gel and filter paper with several small amounts of hexane to complete the transfer.

10.16.9 Place pans into the Speedvap and evaporate to dryness. The Speedvap is set to 50 ° C.

10.16.10 Place the pans in a desiccator for one hour.

10.16.11 Weigh the pans on an analytical balance and record the weights to the nearest 0.1 mg.

10.16.12 Determine the SGT-HEM concentration using the equation in section 11.2.

11.0 Calculations / Data Reduction

11.1 **ICV / CCV, LCS % Recovery** = observed concentration / known concentration x 100

11.2 **HEM or SGT-HEM (mg/L)** = $\frac{[A - B] \times 1{,}000{,}000 \times DF}{\text{mL of sample}}$

Where:
A = final pan weight in grams.
B = initial pan weight in grams.
DF = Dilution factor (= 1 if no dilution performed

11.3 LCS Recovery:

$$\%\ \text{Recovery} = \frac{Concentration\ (or\ amount)\ found}{Concentration\ (or\ amount)\ spiked} \times 100$$

Note: the spike concentration for SGT-HEM is half of the HEM concentration due to the removal of stearic acid during the silica gel treatment.

11.4 MS/MSD Recovery and RPD:

$$\%\ Spike\ Recovery\ (\%R) = \frac{SSR - SR}{SA}\ x\ 100$$

where:
SSR=Spiked Sample Result
SR=Sample Result
SA=Spike Added

11.5 Relative Percent Difference (RPD) between the MS and MSD:

$$RPD = \frac{|Conc.\ 1 - Conc.\ 2|}{(Conc.\ 1 + Conc.\ 2)/2} \times 100$$

Where: Conc. 1 and Conc. 2 are the concentrations (mg/L HEM or SGT-HEM) in the MS and MSD samples, respectively.

Note: the spike concentration for SGT-HEM is half of the HEM concentration due to the removal of stearic acid during the silica gel treatment.

12.0 Method Performance

12.1 Method Detection Limit Study (MDL)

12.1.1 The method detection limit (MDL) is the lowest concentration that can be detected for a given analytical method and sample matrix with 99% confidence that the analyte is present. The MDL is determined according to the laboratory's MDL procedure in SOP PT-QA-007. MDLs reflect a calculated (statistical) value determined under ideal laboratory conditions in a clean matrix. The MDL study frequency and MDL verification requirements are outlined in SOP PT-QA-007.

12.2 Demonstration of Capabilities(DOC)

12.2.1 This requires the analysis of four LCS samples. The LCS sample is a well-characterized, laboratory-generated sample used to monitor method performance, which should contain the analyte(s) of interest. The results of the initial demonstration study must be acceptable before analysis of samples under this SOP may begin. Four aliquots of the LCS are prepared and analyzed using the procedures detailed in this SOP

12.3 Training Requirements

12.3.1 The group/team leader has the responsibility to ensure that an analyst who has been properly trained in its use and has the required experience performs this procedure. The training documentation will be forwarded to QA for inclusion in the training files. DOCs will be documented for each analyst in the training file.

13.0 Pollution Control

13.1 It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i.e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage and reagent stability). Employees must abide by the policies in Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention."

14.0 Waste Management

14.1 Waste management practices are conducted consistent with all applicable rules and regulations. Excess reagents, samples and method process wastes are disposed of in an accepted manner. Waste description rules and land disposal restrictions are followed. Waste disposal procedures are incorporated by reference to PT-HS-001. The following waste streams are produced when this method is carried out.

14.2 The following waste streams are produced when this method is carried out.

14.3 Solvent or oily waste. This waste is collected in a waste container identified as "Mixed Flammable Solvent Waste", Waste #3.

14.4 Contaminated filter Paper with Sodium Sulfate, Speed Disc, and aluminum pan. This waste is collected in containers identified as "Lab Trash", Waste #12.

15.0 References / Cross-References

15.1 Method 1664, Revision A: N-Hexane Extractable Material (HEM; Oil and Grease) and Silica Gel Treated N-Hexane Extractable Material (SGT-HEM; Non-polar Material) by Extraction and Gravimetry, EPA-821-R-98-002, February 1999.

15.2 EPA 2000. Analytical Method Guidance for EPA Method 1664A Implementation and Use (40 CFR part 136), EPA/821-R-00-003, January 2000.

15.3 Bakerbond application note. Extraction of Oil & Grease from water, EPA Method 1664.

15.4 PT-QA-021, Pittsburgh Quality Control Program.

16.0 Method Modifications

16.1 **NA**

17.0 Attachments

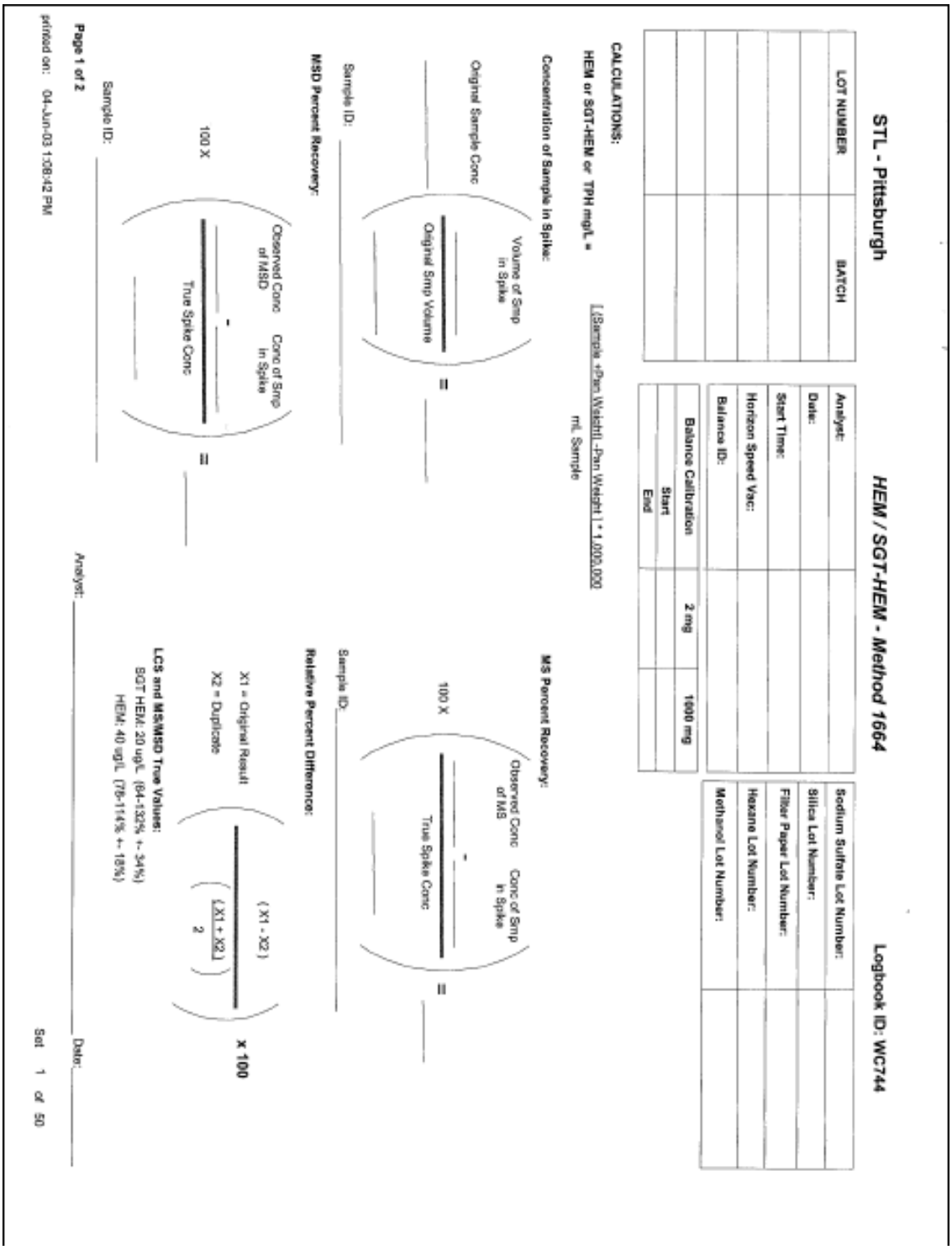
17.1 Records Management/Documentation: Data is recorded on an example HEM and SGT-HEM data sheet (Figure 1).

18.0 Revision History

18.1 Revision 6, 11/12/08:

18.1.1 Updated to new TA SOP format. Updated sections: Safety, Method Performance, Pollution Control, Waste Management and update cross references. All Changes are highlighted.

FIGURE 1 – Example HEM and SGT-HEM Log



STL - Pittsburgh

HEM / SGT-HEM - Method 1664

Logbook ID: WC744

LOT NUMBER	BATCH

Analyst:	
Date:	
Start Time:	
Horizon Speed Vac:	
Balance ID:	

Balance Calibration	2 mg	1000 mg
Start		
End		

Sodium Sulfate Lot Number:	
Silica Lot Number:	
Filter Paper Lot Number:	
Hexane Lot Number:	
Methanol Lot Number:	

CALCULATIONS:

HEM or SGT-HEM or TPH mg/L = [(Sample +Pan Weight) -Pan Weight] * 1,000,000 / mL Sample

Concentration of Sample in Spike:

Original Sample Conc = (Volume of Smp in Spike / Original Smp Volume) =

Sample ID:

MSD Percent Recovery:

100 X (Observed Conc of MSD - Conc of Smp in Spike) / True Spike Conc =

Sample ID:

MS Percent Recovery:

100 X (Observed Conc of MS - Conc of Smp in Spike) / True Spike Conc =

Sample ID:

Relative Percent Difference:

X1 = Original Result

X2 = Duplicate

$$\frac{(X1 - X2)}{\left(\frac{X1 + X2}{2}\right)} \times 100$$

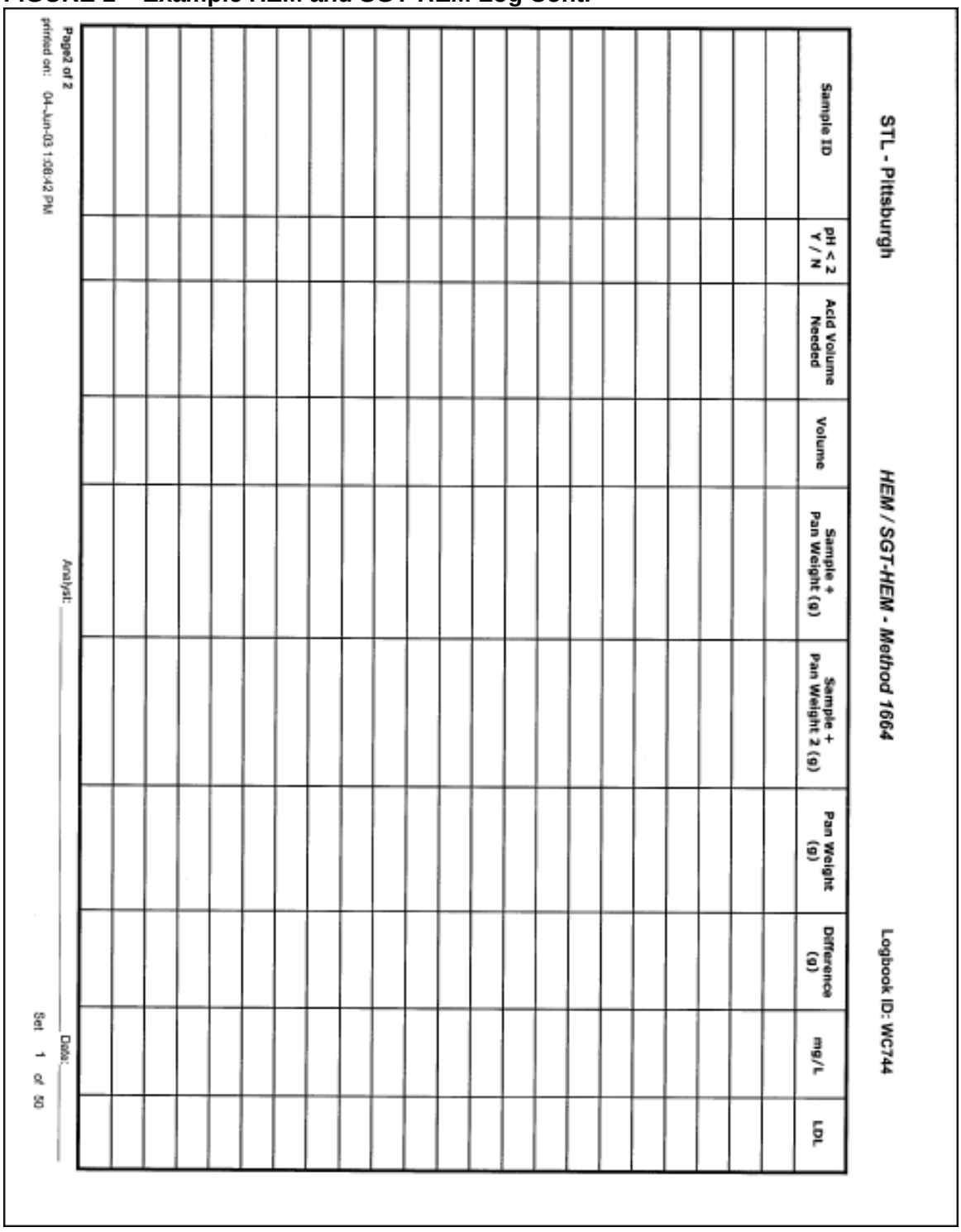
LCS and MS/MSD True Values:

SGT HEM: 20 ug/L (64-132% +- 34%)

HEM: 40 ug/L (78-114% +- 18%)

Analyst: _____ Date: _____

FIGURE 1 – Example HEM and SGT-HEM Log Cont.



APPENDIX 42
SOP FOR THE ANALYSIS OF AROCLOR PCBS BY SW-846 608 (PITT_MT_0005_R7)

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

TestAmerica Pittsburgh

Title: Analysis of Organochlorine Pesticides and PCBs

Method(s): EPA Method 608

Approvals (Signature/Date):

1/30/08	1/29/08
John Oravec Date	Steve Jackson Date
Technical Manager	Health & Safety Manager / Coordinator
1/29/08	1/31/08
Nasreen DeRubeis Date	Larry Matko Date
Quality Assurance Manager	Laboratory Director

This SOP was previously identified as SOP No. PITT-GC-0032, Rev. 0.

Any reference within this document to Severn Trent Laboratories, Inc. or STL, should be understood to refer to TestAmerica Laboratories, Inc. (formerly known as Severn Trent Laboratories, Inc.)

OPERATION-SPECIFIC STANDARD OPERATING PROCEDURE

TITLE: ANALYSIS OF ORGANOCHLORINE PESTICIDES AND PCBs BY METHOD 608 (SUPERSEDES: REVISION 0)

Prepared by: Walter E. Miller 6/2/03

Reviewed by: [signature] 6/3/03
Technical Specialist

Approved by: [signature] 6/3/03
Quality Assurance Manager

Approved by: [signature] for Greg McDonough 6/3/03
Environmental, Health and Safety Coordinator

Approved by: [signature] 6/3/03
Laboratory Director

TABLE OF CONTENTS

List of Tables

1. SCOPE AND APPLICATION

1.1. This SOP describes procedures to be used when 40 CFR 136 Appendix A, Method 608 is applied to the analysis of organochlorine pesticides and PCBs by GC/ECD. The PCBs are identified and quantitated as Aroclors. This SOP is applicable to extracts derived from any aqueous matrices which are prepared according to the appropriate STL sample extraction SOP (C-OP-0001).

1.2. Table 1 identifies compounds for which this method has been applied, along with expected Reporting Limits (RLs). Matrix interferences may result in higher RLs than those listed.

2. SUMMARY OF METHOD

2.1. This SOP presents conditions for the analysis of prepared extracts for organochlorine pesticides and PCBs. The extracts are analyzed by GC/ECD using a dual column injection and external standard calibration techniques.

3. DEFINITIONS

3.1. Extraction Batch: An extraction batch consists of a group of samples of the same matrix that is as a unit extracted, concentrated, etc., using the same reagents. An extraction batch cannot exceed 20 samples, not including method blanks, spikes, and other QC samples.

3.2. Method Blank: A method blank is a laboratory initiated sample consisting of blank water which is carried through all of the steps of an analysis. This sample serves to monitor the introduction of artifacts into the process.

3.3. Matrix Spike (MS): A matrix spike is a sample aliquot that has been spiked with known quantities of target analytes before being subjected to the entire analytical procedure. The recovery of the analytes is determined after the analysis of both the sample and its' spiked aliquot.

3.4. Aliquot: An aliquot is a representative portion of a sample.

3.5. Surrogate: A surrogate is a compound having similar chemical/physical properties as some or all of the compounds of interest and is added to all samples, including QC samples, prior to sample preparation. The percent recovery of the surrogate is expected to give an indication of the extraction efficiency for the sample. The surrogate should be a compound not expected to be found in the sample.

3.6. Laboratory Control Sample (LCS) (QC Check Sample in reference method): The LCS is the same as a method blank, spiked with the surrogate solution and the matrix spike solution, extracted and analyzed following the same procedure as used for the samples. A LCS must be performed once for each matrix spike analysis.

3.7. Reagent grade: This is the deionized distilled water system used in the laboratory. This water is equivalent to ASTM Type II water.

4. INTERFERENCES

4.1. Any compound that can give a measurable response on the electron capture detector is a potential interference.

4.1.1. Phthalate esters, which are common plasticizers, can pose a major problem in the determinations. Interferences from phthalates are minimized by avoiding contact with any plastic materials.

4.1.2. Sulfur is a strong interferant.

4.2. Interferences co-extracted from samples will vary considerably from source to source. The presence of interferences may raise quantitation limits for individual samples. Specific cleanups may be performed on the sample extracts, including florisil cleanup, sulfur cleanup, and acid cleanup (PCBs only). These cleanup procedures are included in SOP # C-OP-0001.

5. SAFETY

5.1. Procedures shall be carried out in a manner that protects the health and safety of all STL associates. The following requirements must be met:

5.2. Eye protection that satisfies ANSI Z87.1 (as per the Chemical Hygiene Plan), laboratory coat, and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled. Disposable gloves that have become contaminated will be removed and discarded, other gloves will be cleaned immediately.

5.3. The health and safety hazards of many of the chemicals used in this procedure have not been fully defined. Additional health and safety information can be obtained from the MSDS files maintained in the laboratory. The following specific hazards are known:

5.3.1. Chemicals that have been classified as **carcinogens**, or **potential carcinogens**, under OSHA include: methylene chloride, PCBs, etc.

5.3.2. Chemicals known to be **flammable** are: methanol, etc.

5.3.3. The following materials are known to be **corrosive**: sulfuric acid, hydrochloric acid, nitric acid, sodium hydroxide, etc.

5.3.4. Hearing protection is required when ultrasound digestion is carried out.

5.4. Exposure to chemicals must be maintained as low as reasonably achievable, therefore, unless they are known to be non-hazardous, all samples must be opened, transferred, and prepared in a fume hood or under other means of mechanical ventilation. Solvent and waste contains will be kept closed unless transfers are being made.

5.5. The preparation of standards, reagents, and glassware cleaning procedures that involve solvents such as methylene chloride will be conducted in a fume hood with the sash closed as far as the operations will permit.

5.6. All work must be stopped in the event of a known or potential compromise to the health and safety of a STL associate. The situation must be reported immediately to a laboratory supervisor.

5.7. All ^{63}Ni sources shall be leak tested every six months, or in accordance with the manufacturer's general radioactive material license.

5.8. All ^{63}Ni sources shall be inventoried every six months. If a detector is missing, the Director, EH&S shall be immediately notified and a letter sent to the NRC or local state agency.

6. EQUIPMENT AND SUPPLIES

6.1. GC, equipped with all necessary gases, syringes, ^{63}Ni electron capture detectors, etc. Suggested operating conditions and columns are included in Table 2.

6.1.1. Data System capable of collecting, sorting and plotting the data.

6.2. Microsyringes, various sizes, for standards preparation, sample injection, and extract dilution.

7. REAGENTS AND STANDARDS

7.1. Hexane: pesticide grade or equivalent

7.2. Standards

7.2.1. All standards are purchased as stock solutions, but may be optionally prepared from singles or neat. Secondary dilution standards (prepared from the stock) must be prepared every six months or sooner, if standards have degraded or concentrated. Refer to Table 3 for concentrations of working calibration standards. Refer to Tables 10 and 11 for preparation of the calibration standards.

7.2.2. A proprietary software database program is utilized for providing and managing all necessary detail regarding standards associated with this method. An example copy of a print out available from this database is provided in Figure 1.

8. SAMPLE PRESERVATION AND STORAGE

8.1. Extracts must be protected from light and refrigerated at 4° $\pm$ 2° C.

8.2. Analysis of all extracts must be performed within 40 days of the start of sample extraction.

9. QUALITY CONTROL

9.1. The STL-Pittsburgh QC Program document (QA-003) provides further details of the QC and corrective action guidelines presented in this SOP. Refer to this document if additional guidance is required

9.2. A method blank must be extracted with each extraction batch and must be analyzed on each instrument on which associated samples are analyzed. The method blank must yield concentrations of target analytes less than the RLs in Table 1, and the surrogate recoveries must be within laboratory established limits; or else all associated samples must be reextracted. The project manager must be contacted prior to reextraction. A reextraction outside holding time must be approved. If reextraction is not possible, sample results should be evaluated for usability and appropriate comments made in the case narrative. In addition, a Nonconformance Memo must be completed.

9.2.1. Corrective Action:

9.2.1.1. If a method blank does not meet the technical acceptance criteria, the Laboratory must consider the analytical system to be out of control. It is the Laboratory's responsibility to ensure that method interferences caused by contaminants in solvents, reagents, glassware, and other sample storage and processing hardware that lead to discrete artifacts and/or elevated baselines in gas chromatograms be eliminated. If contamination is a problem, the source of the contamination must be investigated and appropriate corrective measures MUST be taken and documented before further sample analysis proceeds.

9.2.1.2. All samples processed with a method blank that is out of control (i.e., contaminated) will require reextraction and reanalysis. Reextraction outside holding time must be approved.

9.3. A matrix spike (MS) must be analyzed every 10 samples. Client specifications or sample volume availability may override this frequency of analysis. The recoveries must be evaluated against the limits given in Table 9.

9.3.1. Corrective Action

9.3.1.1. If any MS recovery is outside of QC limits, the recovery for the impacted analyte(s) is to be evaluated in the LCS. If the LCS recovery is acceptable, than a matrix effect is assumed and no further corrective action is required. If both the MS and LCS recoveries are outside of QC limits, the Laboratory must consider the analytical system to be out of control and the samples should be reextracted. The project manager must be contacted prior to reextraction. A reextraction outside holding time must be approved. If reextraction is not possible, sample results should be evaluated for usability and appropriate comments made in the case narrative. In addition, a Nonconformance Memo must be completed.

9.4. Surrogate recoveries must be reported for each sample and QC sample. For this procedure, the surrogates are Tetrachloro-m-xylene (TCMX) and Decachlorobiphenyl (DCB). The recoveries must be evaluated against laboratory established limits. Corrective action, which may include reextraction, is only required if both surrogate recoveries are outside of laboratory QC limits.

9.4.1. A reextraction outside holding time must be approved. If reextraction is not possible, sample results should be evaluated for usability and appropriate comments made in the case narrative. In addition, a Nonconformance Memo must be completed.

9.4.2. For each sample and QC sample, the retention times of both surrogates must be within the appropriate retention time window. Any analyses that do not meet this requirement must be reanalyzed until this criteria is met.

9.5. Laboratory Control Sample (LCS)

9.5.1. A LCS is one liter of Reagent grade water, spiked with the surrogate and matrix spike solutions, and treated like all other water samples. LCSs must be performed once for each matrix spike analysis (i.e., one for every 10 samples).

9.5.2. In order to be acceptable, a LCS must meet the recovery limits listed in Table 9.

9.5.3. All samples associated with an unacceptable LCS must be reextracted and reanalyzed. A reextraction outside holding time must be approved. If reextraction is not possible, sample results should be evaluated for usability and appropriate comments made in the case narrative. In addition, a Nonconformance Memo must be completed.

10. CALIBRATION AND STANDARDIZATION

External calibration will be used. Prepare standards containing each analyte of interest at a minimum of three concentration levels (typically five levels). The low-level standard must be less than or equal to the RLs in Table 1. The other standards define the working range of the detector. Recommended calibration levels are given in Table 3.

10.1. A new calibration curve must be generated after major changes to the system or when the continuing calibration criteria cannot be met. Major changes include new columns and any changes in instrument operation parameters, including gas flow, detector temperatures, oven temperatures, etc.

10.2. With the exception of Section 10.3 below, it is NOT acceptable to remove points from a calibration curve for the purpose of meeting criteria, unless the points are the highest or lowest on the curve AND the reporting limit and/or linear range is adjusted accordingly. In any event, at least 3 points must be included in the calibration curve.

10.3. A level may be removed from the calibration if the reason can be clearly documented, for example a broken vial or no purge run. A minimum of three levels must remain in the calibration. The documentation must be retained with the initial calibration. Alternatively, if the analyst believes that a point on the curve is inaccurate, the point may be reanalyzed and the reanalysis used for the calibration.

All initial calibration points must be analyzed without any changes to instrument conditions.

10.3.1. The single peak analytes are separated into two mixes (Mix A and Mix B). The surrogate calibration curve is calculated from the Mix A. Surrogates in the other calibration standards are used only as retention time markers.

10.3.2. The PCBs are analyzed separately from the pesticides. The surrogate curve is calculated from the Aroclor 1016/1260 Mix. Surrogates in the other calibration standards are used only as retention time markers.

10.3.3. For multi-component pesticides and PCBs:

Single point calibration is used for multicomponent pesticides (typically toxaphene and technical chlordane), and for all PCBs except Aroclors 1016 and 1260 (a multi-point curve is analyzed for those Aroclors).

10.3.4. For multicomponent analytes, the mid level standard must be analyzed as part of the initial calibration (except Aroclors 1016 and 1260 as noted above). This single point calibration is used to qualitatively identify these multicomponent analytes. If one of these multicomponent analytes is detected in a sample, the sample must be reanalyzed following an acceptable multi-point initial calibration (minimum of 3 points) of that multicomponent analyte.

10.4. External standard calibration: Quantitation by the external standard method assumes a proportional relation ship between the calibration run and the analyte in the sample. To use this approach, introduce each calibration standard into the GC using the technique that will be used for samples. The ratio of the peak height or area response to the mass or concentration injected may be used to prepare a calibration curve.

Equation 1

$$\text{CalibrationFactor(CF)} = \frac{\text{Area or Height of Peak}}{\text{Mass Injected (ng)}}$$

Some data systems may use the inverse of this formula. This is acceptable so long as the same formula is used for standards and samples. Use of peak area or height must be consistent. It is not permitted to switch between using peak area and height for quantitation within an analytical sequence.

10.5. Calibration curve fits: Average calibration/response factors, linear regression, or quadratic curves may be used to fit the data.

10.5.1. Average calibration/response factor: The average response factor may be used to quantitate a compound if the percent relative standard deviation (%RSD) of the response factors from all standard levels in the initial calibration is <10 percent. The equation for average response factor is:

Equation 2

$$\text{Average response factor} = \frac{\sum RF_1 \text{ - } n}{n}$$

Where:

n = Number of calibration levels

$\sum RF_1$ - n = Sum of response factors for each calibration level.

10.5.2. Linear regression: The linear fit uses the following functions:

10.5.2.1. External standard:

Equation 3

$$y = ax + b$$

or

$$x = \frac{(y - b)}{a}$$

Where: y = Instrument response
x = Concentration
a = Slope
b = Intercept

10.5.3. Quadratic curve: The quadratic curve uses the following functions:

10.5.3.1. External standard.

Equation 4:

$$y = ax + cx^2 + b$$

Where c is the curvature

10.6. Evaluation of calibration curves

10.6.1. The percent relative standard deviation (%RSD) from the calibration curve is used to evaluate the initial calibration. This provides a measure of how much error is associated with using the calibration curve for quantitation.

10.6.2. The percent relative standard deviation (%RSD) is calculated as follows:

Equation 5

$$\%RSD = \frac{SD}{RRF_A} x100$$

Where:
%RSD=Percent Relative Standard Deviation
SD=Standard Deviation (n-1) of the response factors or calibration factors in curve
RRF_A=Average response factor or calibration factor of all points in curve

10.6.3. The following requirements must be met for any calibration to be used:

- Response must increase with increasing concentration.
- If a curve is used, the intercept of the curve at zero response must be less than the reporting limit for the analyte.
- Relative standard deviation of the calibration points from the curve used must be <10 percent.
- If a curve is used, the Correlation Coefficient (linear regression) or the Coefficient of Determination (quadratic) must be greater than 0.990.

10.6.4. Weighting of data points: In a linear or quadratic calibration fit, the points at the lower end of the calibration curve have less weight in determining the curve generated than points at the high concentration end of the curve. However, in environmental analysis, accuracy at the low end of the curve is very important. For this reason it is preferable to increase the weighting of the lower concentration points. $1/Concentration^2$ weighting (often called $1/X^2$ weighting) will improve accuracy at the low end of the curve and should be used if the data system has this capability.

10.7. Column Degradation Evaluation

The column evaluation mix must be injected before each initial or daily calibration (see Table 4 for standard concentrations). The degradation of DDT and endrin must be calculated (see equations 13 and 14) and each shown to be less than 15%

before calibration can proceed. This is only necessary if the target compound list includes DDT, Endrin, or any of their degradation products.

If the breakdown of DDT and/or endrin exceeds the limits given above, corrective action must be taken. This action may include:

- Replacement of the injection port liner or the glass wool.
- Cutting off a portion of the injection end of a capillary column.
- Replacing the GC column.

10.8. Calibration Verification:

10.8.1. Initial Calibration Verification (ICV): The working calibration curve or average response factor must be verified with second source standards of all single peak pesticides and all PCB Aroclors. The ICV must be analyzed prior to the analysis of any samples.

10.8.2. Continuing Calibration Verification (CCV): The working calibration curve or average response factor must be verified by the analysis of a mid-point continuing calibration standard at the beginning, after every 20 samples, and at the end of the analysis sequence (QC and instrument blanks included).

10.8.2.1. At least once each day that this method is performed, a CCV will be analyzed at a concentration other than the mid-level concentration to meet the NELAC requirement for verifying the calibration at varied concentrations.

10.8.3. Daily Calibration Verification: At least every 24 hours a daily calibration must be analyzed. The requirements of the daily calibration are the same as the CCV with the addition that retention times are updated.

10.8.4. Any analyte that is reportable as found must have a percent difference of $\leq$15 percent in the continuing calibration standards analyzed before and after the sample, on the column used for quantitation. For dual column analysis, the column used for quantitation will be the column with the lower result unless one of the column analyses had a percent difference >15%. In this situation, the column with the acceptable percent difference will be the quantitation column.

10.8.4.1. Reportable as found is defined as any analyte that would be reported as anything other than a nondetect (ND).

10.8.5. It is not necessary to run a continuing calibration standard at the beginning of the sequence if the first 20 samples are analyzed immediately after the completion of an acceptable initial calibration and ICV.

10.8.6. The last sample in the sequence must be followed by an ending calibration. The ending calibration serves the analyst in judging the validity of the sequence.

10.8.7. Percent Difference Calculation:

Equation 6 (Average calibration factors)

$$\%\ Difference = \frac{RRF_A - RF}{RRF_A} x\ 100$$

Where:

RF = Calibration factor from the analysis of the verification standard

RRF_A = Average calibration factor from the initial calibration

Equation 7 (Linear or Quadratic Curves)

$$\%Difference = \frac{\text{Expected Value} - \text{Calculated Value}}{\text{Expected Value}} \text{ x } 100\%$$

10.8.8. Corrective Actions for Continuing Calibration: If the percent difference for any analyte is >15 percent, corrective action must be taken. This may include clipping the column, changing the injection port liner or other minor instrument adjustments, followed by reanalyzing the standard. If the response for any analyte still varies by more than 15 percent, a new calibration curve must be prepared.

10.8.9. Corrective Action for Samples: Any samples injected after the standard exceeding the continuing calibration criteria must be reinjected.

11. PROCEDURE

11.1. Extraction

Extraction procedures are referenced in SOP C-OP-0001.

11.2. Cleanup

Cleanup procedures are referenced in SOP C-OP-0001.

11.3. Chromatography

Suggested chromatographic conditions are presented in Table 2.

11.4. Sample Introduction

Analytes are introduced by direct injection of the extract. Samples, standards, and QC must be introduced using the same procedure.

11.5. Analytical Sequence

An analytical sequence starts with an initial calibration or a daily calibration. Refer to Table 8 for an example of an analytical sequence.

11.6. Retention Time Windows

11.6.1. A Fixed retention time window of ± .05 minutes will be used for all analytes. Alternatively, if it is determined through calculation that wider limits are necessary, the limits will be developed as follows: Make an injection of all analytes of interest each day over a three day period. Calculate the standard deviation of the three retention times for each analyte (relative retention times may also be used). For multiresponse analytes (e.g., Aroclors) use the retention time of major peaks. Plus or minus three times the standard deviation of the retention times of each analyte defines the retention time window.

11.6.2. The center of the retention time window is the retention time from the last of the three standards. The centers of the windows are updated with the mid point of the initial calibration and each daily calibration. The widths of the windows will remain the same until new windows are generated following the installation of a new column. Where calculated limits are being used, if the retention time window as calculated above is less than +/- 0.05 minutes, use +/- 0.05 minutes as the retention time window. This allows for slight variations in retention times caused by sample matrix.

11.6.3. Where calculated limits are being used, the laboratory must calculate new retention time windows each time a new column is installed. The new windows must be generated within one week of the installation of the new column. Until these standards have been run on the new column, the retention time windows from the old column may be used, updated with the retention times from the new initial calibration.

11.6.4. Corrective Action for Retention Times

The retention times of all compounds in each continuing calibration must be within the retention time windows established by the daily calibration. If this condition is not met, all samples analyzed after the last compliant standard must be reanalyzed unless the following conditions are met for any compound that elutes outside the retention time window:

- The retention time of that compound in the standard must be within a retention time range equal to twice the original window and,
- No peak that would be reportable may be present on the sample chromatogram within an elution time range equal to three times the original retention time window.

11.7. Procedural Variations

Procedural variations are allowed only if deemed necessary in the professional judgment of the supervisor to accommodate variation in sample matrix, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using a Nonconformance Memo and approved by a supervisor and QA/QC manager. If contractually required, the client shall be notified. The Nonconformance Memo shall be filed in the project file. The nonconformance is also addressed in the case narrative. Any unauthorized deviations from this procedure must also be documented as a nonconformance, with a cause and corrective action described.

12. DATA ANALYSIS AND CALCULATIONS

12.1. Qualitative Identification:

12.1.1. Tentative identification occurs when a peak is found within the retention time window for an analyte, at a concentration above the reporting limit, or above the MDL if estimated results ("J" qualified) are required. Normally confirmation is required on a second column, but if the sample matrix is well enough defined, single column analysis may be adequate. Identification is confirmed if a peak is also present in the retention time window for that analyte on the confirmatory column, at a concentration greater than the reporting limit (or MDL if estimated results are required). For confirmed results, the lower of the two column results is reported unless one of the column analyses is bracketed by an unacceptable calibration verification standard for the compound being confirmed. In that situation, the result for the column analysis that is bracketed with acceptable standards is reported.

12.1.2. Multiresponse Analytes: For multiresponse analytes, the analyst should use the retention time windows, but should rely primarily on pattern recognition. The pattern of peaks will normally serve as confirmation.

12.1.3. The experience of the analyst should weigh heavily in the interpretation of the chromatogram. For example, sample matrix or laboratory temperature fluctuation may result in variation of retention times.

12.2. Calibration Range: If concentrations of any analytes exceed the working range as defined by the calibration standard, then the sample must be diluted and reanalyzed. Dilutions should target the most concentrated analyte in the upper half (over 50 percent of the high-level standard) of the calibration range. It may be necessary to dilute samples due to matrix.

12.3. Dilutions: Samples may be screened to determine the appropriate dilution for the initial run. If the initial diluted run has no hits or hits below 20 percent of the calibration range and the matrix allows for analysis at a lesser dilution, then the sample must be reanalyzed at a dilution targeted to bring the largest hit above 50 percent of the calibration range.

12.3.1. Guidance for Dilutions Due to Matrix: If the sample is initially run at a dilution and the baseline rise is less than half the height of the peaks in the mid-level calibration standard, then the sample should be reanalyzed at a more concentrated dilution.

12.3.2. Reporting Dilutions: The most concentrated dilution with no target compounds above the calibration range will be reported. Other dilutions will only be reported at client request.

12.4. Interferences: If peak detection is prevented by interferences, further cleanup should be attempted. If no further cleanup is reasonable, then elevation of reporting levels and/or lack of positive identification must be addressed in the case narrative.

12.5. Calculations: Capabilities of individual data systems may required the use of different formulas than those presented here. When this is the case, the calculations used must be shown to be equivalent and must be documented in the appendix attached to this document.

12.5.1. Sample Results

Equation 8 (using average Calibration Factor)

$$\text{Concentration } (mg / L) = \frac{(A_x \times V_t \cdot D_f)}{(CF \times V_i \times V_x)}$$

Where:
A_x = Response for the analyte in the sample.
V_i = Volume of extract injected, µL.
D_f = Dilution factor.

V_t = Volume of total extract, µL
V_s = Volume of sample extracted, mL
CF = Average Calibration factor, area or height/ng

If linear regression or quadratic curves are used, the above equation is used with the following exceptions:

A_x = Concentration in the extract from the curve, ng.
CF = Does not apply (can be assumed to be 1).

12.5.2. LCS Recovery

Concentrations of each compound in the LCS are calculated using the same equations as for the target compounds. The response factor from the initial calibration is used. LCS recoveries are calculated using the following equation:

Equation 9

$$\% \text{ Recovery} = \frac{Concentration\ (or\ amount)\ found}{Concentration\ (or\ amount)\ spiked} \times 100$$

12.5.3. MS/MSD Recovery and RPD

Concentrations of each compound in the MS and MSD are calculated using the same equations as for the target compounds. The response factor from the initial calibration is used. The MS and MSD recoveries and the RPD between the MS and MSD are calculated using the following equations:

Equation 10

$$\%\ Spike\ Recovery\ (\%R) = \frac{SSR - SR}{SA}\ x\ 100$$

Where:

SSR=Spiked Sample Result
SR=Sample Result
SA=Spike Added

Equation 11

$$RPD = \frac{\left|Conc.\ 1 - Conc.\ 2\right|}{\left(Conc.\ 1 + Conc.\ 2\right)/2} \times 100$$

Where:

Conc. 1=MS Concentration
Conc. 2=MSD Concentration

12.6. Surrogate Recovery: Concentrations of surrogate compounds are calculated using the same equations as for the target compounds. The response factor from the initial calibration is used. Surrogate recovery is calculated using the following equations:

Equation 12

$$\%\text{Recovery} = \frac{\text{Concentration (or amount) found}}{\text{Concentration (or amount) spiked}} \times 100$$

12.7. Calculation of Column Degradation/% Breakdown (%B)

Equation 13

$$DDT\ \%B = \frac{A_{DDD} + A_{DDE}}{A_{DDD} + A_{DDE} + A_{DDT}} \times 100$$

where:
A_{DDD}, A_{DDE}, and A_{DDT} = the response of the peaks for 4,4'-DDD, 4,4'-DDE, and 4,4'-DDT in the column degradation evaluation mix.

Equation 14

$$Endrin\ \%B = \frac{A_{EK} + A_{EA}}{A_{EK} + A_{EA} + A_{E}} \times 100$$

where:
A_{EK}, A_{EA}, and A_{E} = the response of endrin ketone, endrin aldehyde, and endrin in the column degradation evaluation mix.

13. METHOD PERFORMANCE

13.1. Method Detection Limit: Each laboratory must generate a valid method detection limit for each analyte of interest. The MDL must be below the reporting limit for each analyte. The procedure for determination of the method detection limit is given in 40 CFR Part 136, Appendix B, and further defined in QA Policy No. QA-005.

13.2. Initial Demonstration: Each laboratory must make a one-time initial demonstration of capability for each individual method. This requires analysis of LCSs (QC Check Samples) containing all of the standard analytes for method. For this method, it will be necessary to use more than one QC check mix to cover all analytes of interest.

13.2.1. Four aliquots of the QC check sample are analyzed using the same procedures used to analyze samples, including sample preparation.

13.2.2. Calculate the average recovery and relative standard deviation of the recoveries for each analyte of interest. Compare these results with the acceptance criteria given in Table 9.

13.2.3. If any analyte does not meet the acceptance criteria, the test must be repeated. Only those analytes that did not meet criteria in the first test need to be evaluated. Repeated failure for any analyte indicates the need for the laboratory to evaluate the analytical procedure and take corrective action.

13.3. Training Qualification: The group/team leader has the responsibility to ensure that this procedure is performed by an analyst who has been properly trained in its use and has the required experience.

14. POLLUTION PREVENTION

14.1. This method does not contain any specific modifications that serve to minimize or prevent pollution.

15. WASTE MANAGEMENT

15.1. Waste generated in the procedure will be segregated, and disposed according to the facility hazardous waste procedures. The Environmental Health and Safety Coordinator should be contacted if additional information is required.

16. REFERENCES

16.1. 40 CFR Part 136, Appendix A, United States Environmental Protection Agency. 1984, Methods 608.

17. MISCELLANEOUS (TABLES, APPENDICES, ETC.)

17.1. All sample preparation and analysis information will documented on laboratory bench sheets, computer printouts, standard log books, etc. All the documents associated with an analysis will be forwarded for reporting and for inclusion in the project files.

TABLE 1
STANDARD ANALYTE LIST AND REPORTING LIMITS

COMPOUND	CAS #	REPORTING LIMIT, µg/L WATER
Aldrin	309-00-2	0.01
alpha-BHC	319-84-6	0.01
beta-BHC	319-85-7	0.01
delta-BHC	319-86-8	0.01
gamma-BHC (Lindane)	58-89-9	0.01
alpha-Chlordane	5103-71-9	0.01
Gamma-Chlordane	5103-74-2	0.01
4,4'-DDD	72-54-8	0.01
4,4'-DDE	72-55-9	0.01
4,4'-DDT	50-29-3	0.01
Dieldrin	60-57-1	0.01
Endosulfan I	959-98-8	0.01
Endosulfan II	33213-65-9	0.01
Endosulfan sulfate	1031-07-8	0.01
Endrin	72-20-8	0.01
Endrin aldehyde	7421-93-4	0.01
Endrin ketone	53494-70-5	0.01
Heptachlor	76-44-8	0.01
Heptachlor epoxide	1024-57-3	0.01
Methoxychlor	72-43-5	0.02
Toxaphene	8001-35-2	0.4
Aroclor-1016	12674-11-2	0.2
Aroclor-1221	11104-28-2	0.2
Aroclor-1232	11141-16-5	0.2
Aroclor-1242	53469-21-9	0.2
Aroclor-1248	12672-29-6	0.2
Aroclor-1254	11097-69-1	0.2
Aroclor-1260	11096-82-5	0.2
Technical Chlordane	57-74-9	0.1

The following concentration factors are assumed in calculating the reporting limits:

	EXTRACTION VOL.	FINAL VOL.
Aqueous	1000 mL	2.0 mL

TABLE 2
SUGGESTED INSTRUMENT CONDITIONS

Organochlorine Pesticides	
Parameter	**Recommended Conditions**
Injection port temp	220°C
Detector temp	325°C
Temperature program	120°C for 1 min, 8.5°C/min to 285°C, , 6 min hold
Column 1	DB-1701, 30m X 0.53 mm id, 1.0µm
Column 2	DB-608, 30m X 0.53 mm id, 0.8µm
Injection	2µL
Carrier gas	Helium or Hydrogen
Make up gas	Nitrogen
Y splitter	Restek or J&W or Supelco glass tee

PCBs	
Parameter	**Recommended Conditions**
Injection port temp	220°C
Detector temp	325°C
Temperature program	70°C for 0.5min, 30°C/min to 190°C, 2.5°C/min to 225, 18°C/min to 280°C, 3 min hold
Column 1	DB-1701 or Rtx 1701 30m x 0.53 mm id, 1.0µm
Column 2	DB-608, 30m X 0.53 mm id, 0.8µm
Injection	1-2µL
Carrier gas	Helium or Hydrogen
Make up gas	Nitrogen
Y splitter	Restek or J&W or Supelco glass tee

TABLE 3
CALIBRATION LEVELS
(ng/mL)

	LEVEL 1	LEVEL 2	LEVEL 3	LEVEL 4	LEVEL 5	LEVEL 6[2]
Individual Mix AB[1]						
Aldrin	5	10	25	50	100	200
g-BHC (Lindane)	5	10	25	50	100	200
Heptachlor	5	10	50	50	100	200
Methoxychlor	10	10	50	100	200	400
Dieldrin	5	10	25	50	100	200
Endosulfan I	5	10	25	50	100	200
Endosulfan II	5	10	25	50	100	200
4,4'-DDT	5	10	25	50	100	200
Endrin Aldehyde	5	10	25	50	100	200
Endrin Ketone	5	10	25	50	100	200
b-BHC	5	10	25	50	100	200
d-BHC	5	10	25	50	100	200
a-BHC	5	10	25	50	100	200
4,4'-DDD	5	10	25	50	100	200
4-4'-DDE	5	10	25	50	100	200
Endosulfan Sulfate	5	10	25	50	100	200
Endrin	5	10	25	50	100	200
a-Chlordane	5	10	25	50	100	200
g-Chlordane	5	10	25	50	100	200
Multicomponent Standards						
Chlordane (Technical)[3]			250			
Toxaphene[3]			1000			
Aroclor 1016/1260	50	200	500	100	2000	4000
Aroclor 1242[3]			500			
Aroclor 1221 + 1254[3]			500			
Aroclor 1232[3]			500			
Aroclor 1248[3]			500			
Surrogates are included with all the calibration mixes at the following levels:						
Tetrachloro-m-xylene	2.5	10	25	50	100	200
Decachlorobiphenyl	2.5	10	25	50	100	200

[1]Standards are split into an A and B mix.
[2]Level 6 is optional and should only be used if the linearity can be maintained on the instrument to this level.
[3] A multipoint calibration (minimal of 3 levels) is required if qualitatively identified in a sample.

TABLE 4
COLUMN DEGRADATION EVALUATION MIX
ng/mL

COMPONENT	CONCENTRATION
4,4'-DDT	25
Endrin	25
Tetrachloro-m-xylene (Surrogate)	20
Decachlorobiphenyl (Surrogate)	20

TABLE 5
FULL ANALYTE PESTICIDE MATRIX SPIKE
µg/L

COMPONENT	CONCENTRATION
Alpha-BHC	0.05
Gamma-BHC	0.05
Beta-BHC	0.05
Delta-BHC	0.05
Heptachlor	0.05
Aldrin	0.05
Heptachlor Epoxide	0.05
Endosulfan I	0.05
Gamma-Chlordane	0.05
Alpha-Chlordane	0.05
Endosulfan II	0.05
Dieldrin	0.05
4,4'-DDE	0.05
Endrin	0.05
4,4'-DDD	0.05
4-4'-DDT	0.05
Endosulfan Sulfate	0.05
Endrin Aldehyd	0.05
Endrin Ketone	0.05
Methoxychlor	0.05

TABLE 6
PCB MATRIX SPIKE
µg/L

COMPONENT	CONCENTRATION
Aroclor 1016	2.0
Aroclor 1260	2.0

TABLE 7
SURROGATE SPIKE
µg/L

COMPONENT	CONCENTRATION
Tetrachloro-m-xylene	0.04
Decachlorobiphenyl	0.04

TABLE 8
SUGGESTED ANALYTICAL SEQUENCE

Organochlorine Pesticides

With Initial Calibration:

Solvent blank (optional)
Breakdown Mix
Individual mix A — All levels
Individual mix B — All levels
Technical Chlordane — Level 3[1]
Toxaphene — Level 3[1]
ICV (all single component analytes)
Solvent blank
Up to 20 samples
Solvent blank (optional)
Individual mix A and B — Mid level (Continuing calibration)
Up to 20 samples
Solvent blank (optional)
Individual mix A and B — Mid level (Continuing calibration)
Etc.

With Daily Calibration:

Solvent blank (optional)
Breakdown mix
Individual mix A and B — Mid level (Continuing calibration)
Technical Chlordane — Level 3[1]
Toxaphene — Level 3[1]
Up to 20 samples
Solvent blank (optional)
Individual mix A and B — Mid level (Continuing calibration)
Etc.

PCBs

With Initial Calibration:

Solvent blank (optional)
Aroclor 1221/1254 — Level 3
Aroclor 1232 — Level 3
Aroclor 1242 — Level 3
Aroclor 1248 — Level 3
Aroclor 1016/1260 — Level 1
Aroclor 1016/1260 — Level 2
Aroclor 1016/1260 — Level 3

TABLE 8 (cont.)

Aroclor 1016/1260 Level 4
Aroclor 1016/1260 Level 5
Aroclor 1016/1260 Level 6 (optional)
ICVs (second source standard of all Aroclors)

Solvent blank (optional)
Up to 10 samples
Solvent blank (optional)
Aroclor 1016/1260 Level 3
Etc.

With Daily Calibration:

Solvent blank (optional)
Aroclor 1221/1254 Level 3
Aroclor 1232 Level 3
Aroclor 1242 Level 3
Aroclor 1248 Level 3
Aroclor 1016/1260 Level 3
Up to 10 samples
Solvent blank (optional)
Aroclor 1016/1260 Level 3
Etc.

Table 9

Performance Limits
Initial Demonstration of Capability (IDC), LCS, and MS Acceptance Limits

Compound	IDC, LCS, and MS recovery limits	IDC RSD limits *
Aldrin	42-122	20
alpha-BHC	37-134	20
beta-BHC	17-147	26
delta-BHC	19-140	23
gamma-BHC	32-127	20
Chlordane	45-119	20
4,4'-DDD	31-141	23
4,4'-DDE	30-145	22
4,4'-DDT	25-160	27
Dieldrin	36-146	23
Endosulfan I	45-153	22
Endosulfan II	1-202	44
Endosulfan Sulfate	26-144	24
Endrin	30-147	24
Heptachlor	34-111	20
Heptachlor Epoxide	37-142	20
Toxaphene	41-126	20
Aroclor 1016	50-114	20
Aroclor 1260	8-127	20

* If a MS/MSD pair is analyzed, these are the RPD limits between the MS and MSD.

Table 10
Preparation of Pesticide Calibration Standards

Calibration Level	Mix A Intermediate (uL)	Mix B Intermediate (uL)	Toxaphene Stock (uL)	Chlordane Stock (uL)
Level 1	20	20		
Level 2	40	40		
Level 3	500	500	400	100
Level 4	200	200		
Level 5	400	400		
Level 6	800	800		

The single peak pesticide stock standards are purchased as certified standards in two separate solutions in 50%hexane/50% toluene. The A Mix stock includes alpha-BHC, Dieldrin, Endosulfan I, Endrin, gamma-BHC, Heptachlor, 4,4'-DDD, 4,4'-DDT, Decachlorobiphenyl (surrogate) and Tetrachloro-m-xylene (surrogate) at 100 ug/mL; and Methoxychlor at 200 ug/mL. The B Mix stock includes Aldrin, alpha-Chlordane, beta-BHC, delta-BHC, Endosulfan II, Endosulfan sulfate, Endrin aldehyde, Endrin ketone, gamma-Chlordane, Heptachlor epoxide, and 4,4'-DDE at 100 ug/mL. An intermediate A and B standard is prepared by diluting 1.0 mL of each of the appropriate stock mix to 10.0 mL in hexane. The intermediate A mix concentrations are 10 ug/mL for all compounds except methoxychlor which is 20 ug/mL. All compounds in the intermediate B mix are at 10 ug/mL. The working standards are prepared by diluting the volume noted in Table 10 to a 40.0 mL final volume in hexane except for the Level 3 standard, which is taken to a 200 mL final volume in hexane.

Toxaphene and Technical Chlordane stock standards are purchased certified solutions at 100 ug/mL. The mid level (Level 3) Toxaphene calibration standard is prepared by diluting 0.40 mL of the stock standard mix to 40 mL in hexane. The mid level (Level 3) Technical Chlordane calibration standard is prepared by diluting 0.10 mL of the stock standard mix to 40 mL in hexane.

Table 11					
Preparation of PCB Calibration Standards					
Calibration Level	**1016/1260 Intermediate (uL)**	**1221 + 1254 Stock (uL)**	**1232 Stock (uL)**	**1242 Stock (uL)**	**1248 Stock (uL)**
Level 1	20				
Level 2	80				
Level 3	1000	250	250	250	250
Level 4	400				
Level 5	800				
Level 6	1600				

The surrogate stock is purchased (Decachlorobiphenyl and Tetrachloro-m-xylene) at 200 ug/mL.

The Aroclor 1016 and 1260 stock standards are purchased as certified standards in isooctane at 1000 ug/mL. The other five Aroclor stock standards are purchased at 200 ug/mL.

For Aroclors 1016 and 1260, an intermediate standard is prepared by diluting 1.0 mL of each of the stock standards and 0.25 mL of the surrogate stock standard to 10.0 mL in hexane. The intermediate Aroclor 1016/1260 standard concentrations are 100 ug/mL for each Aroclor and 5 ug/mL for each surrogate.

The Aroclor 1016/1260 calibration standards are prepared by diluting the volumes noted in Table 11 to a 40.0 mL final volume in hexane except for the Level 3 standard, which is taken to a 200 mL final volume in hexane.

The mid level (Level 3) calibration standards for each of the other five Aroclors (1221, 1232, 1242, 1248, 1254) are prepared by diluting 0.25 mL of the appropriate stock standard to a final volume of 100 mL in hexane. Aroclors 1221 and 1254 are combined into one standard and Aroclors 1232, 1242, and 1248 are prepared individually.

Figure 1

STL Pittsburgh

Standards Preparation Logbook Summary

May-30-2003

Logbook: \\Qpitpa01\StdsLog\GC.std

Date Prep/Opened	Std ID	Mix Name	Component	Parent ID	Parent Concentration	Aliquot	Final Volume	Final Concentration	Solvent	Analyst	Exp. Date(1)	Exp. Date(2)
05/21/2003	GC0418-03	Custom 8081 "A" Mix	4,4'-DDD		100.00 ug/ml			100.00 ug/ml	Hex/Toluene 50:50	cppinger	02/28/2004	02/28/2004
05/21/2003	GC0418-03	Custom 8081 "A" Mix	4,4'-DDT		100.00 ug/ml			100.00 ug/ml	Hex/Toluene 50:50	cppinger	02/28/2004	02/28/2004
05/21/2003	GC0418-03	Custom 8081 "A" Mix	Alpha-BHC		100.00 ug/ml			100.00 ug/ml	Hex/Toluene 50:50	cppinger	02/28/2004	02/28/2004
05/21/2003	GC0418-03	Custom 8081 "A" Mix	DCB		100.00 ug/ml			100.00 ug/ml	Hex/Toluene 50:50	cppinger	02/28/2004	02/28/2004
05/21/2003	GC0418-03	Custom 8081 "A" Mix	Dieldrin		100.00 ug/ml			100.00 ug/ml	Hex/Toluene 50:50	cppinger	02/28/2004	02/28/2004
05/21/2003	GC0418-03	Custom 8081 "A" Mix	Endosulfan I		100.00 ug/ml			100.00 ug/ml	Hex/Toluene 50:50	cppinger	02/28/2004	02/28/2004
05/21/2003	GC0418-03	Custom 8081 "A" Mix	Endrin		100.00 ug/ml			100.00 ug/ml	Hex/Toluene 50:50	cppinger	02/28/2004	02/28/2004
05/21/2003	GC0418-03	Custom 8081 "A" Mix	Gamma-BHC		100.00 ug/ml			100.00 ug/ml	Hex/Toluene 50:50	cppinger	02/28/2004	02/28/2004
05/21/2003	GC0418-03	Custom 8081 "A" Mix	Heptachlor		100.00 ug/ml			100.00 ug/ml	Hex/Toluene 50:50	cppinger	02/28/2004	02/28/2004
05/21/2003	GC0418-03	Custom 8081 "A" Mix	Methoxychlor		200.00 ug/ml			200.00 ug/ml	Hex/Toluene 50:50	cppinger	02/28/2004	02/28/2004
05/21/2003	GC0420-03	Custom 8081 "A" Mix	TCX		100.00 ug/ml			100.00 ug/ml	Hex/Toluene 50:50	cppinger	02/28/2004	02/28/2004
05/21/2003	GC0420-03	8081 STK A STD	4,4'-DDD	GC0418-03	100.00 ug/ml	1.0000 ml	10.000 ml	10.000 ug/ml	Hexane	cppinger	02/28/2004	
05/21/2003	GC0420-03	8081 STK A STD	4,4'-DDT	GC0418-03	100.00 ug/ml	1.0000 ml	10.000 ml	10.000 ug/ml	Hexane	cppinger	02/28/2004	
05/21/2003	GC0420-03	8081 STK A STD	Alpha-BHC	GC0418-03	100.00 ug/ml	1.0000 ml	10.000 ml	10.000 ug/ml	Hexane	cppinger	02/28/2004	
05/21/2003	GC0420-03	8081 STK A STD	DCB	GC0418-03	100.00 ug/ml	1.0000 ml	10.000 ml	10.000 ug/ml	Hexane	cppinger	02/28/2004	
05/21/2003	GC0420-03	8081 STK A STD	Dieldrin	GC0418-03	100.00 ug/ml	1.0000 ml	10.000 ml	10.000 ug/ml	Hexane	cppinger	02/28/2004	
05/21/2003	GC0420-03	8081 STK A STD	Endosulfan I	GC0418-03	100.00 ug/ml	1.0000 ml	10.000 ml	10.000 ug/ml	Hexane	cppinger	02/28/2004	
05/21/2003	GC0420-03	8081 STK A STD	Endrin	GC0418-03	100.00 ug/ml	1.0000 ml	10.000 ml	10.000 ug/ml	Hexane	cppinger	02/28/2004	
05/21/2003	GC0420-03	8081 STK A STD	Gamma-BHC	GC0418-03	100.00 ug/ml	1.0000 ml	10.000 ml	10.000 ug/ml	Hexane	cppinger	02/28/2004	
05/21/2003	GC0420-03	8081 STK A STD	Heptachlor	GC0418-03	100.00 ug/ml	1.0000 ml	10.000 ml	10.000 ug/ml	Hexane	cppinger	02/28/2004	
05/21/2003	GC0420-03	8081 STK A STD	Methoxychlor	GC0418-03	200.00 ug/ml	1.0000 ml	10.000 ml	20.000 ug/ml	Hexane	cppinger	02/28/2004	
05/21/2003	GC0420-03	8081 STK A STD	TCX	GC0418-03	100.00 ug/ml	1.0000 ml	10.000 ml	10.000 ug/ml	Hexane	cppinger	02/28/2004	
05/21/2003	GC0421-03	LOW 8081 A STD	4,4'-DDD	GC0420-03	10.000 ug/ml	0.0200 ml	40.000 ml	0.0050 ug/ml	Hexane	cppinger	11/21/2003	
05/21/2003	GC0421-03	LOW 8081 A STD	4,4'-DDT	GC0420-03	10.000 ug/ml	0.0200 ml	40.000 ml	0.0050 ug/ml	Hexane	cppinger	11/21/2003	
05/21/2003	GC0421-03	LOW 8081 A STD	Alpha-BHC	GC0420-03	10.000 ug/ml	0.0200 ml	40.000 ml	0.0050 ug/ml	Hexane	cppinger	11/21/2003	
05/21/2003	GC0421-03	LOW 8081 A STD	DCB	GC0420-03	10.000 ug/ml	0.0200 ml	40.000 ml	0.0050 ug/ml	Hexane	cppinger	11/21/2003	
05/21/2003	GC0421-03	LOW 8081 A STD	Dieldrin	GC0420-03	10.000 ug/ml	0.0200 ml	40.000 ml	0.0050 ug/ml	Hexane	cppinger	11/21/2003	
05/21/2003	GC0421-03	LOW 8081 A STD	Endosulfan I	GC0420-03	10.000 ug/ml	0.0200 ml	40.000 ml	0.0050 ug/ml	Hexane	cppinger	11/21/2003	
05/21/2003	GC0421-03	LOW 8081 A STD	Endrin	GC0420-03	10.000 ug/ml	0.0200 ml	40.000 ml	0.0050 ug/ml	Hexane	cppinger	11/21/2003	
05/21/2003	GC0421-03	LOW 8081 A STD	Gamma-BHC	GC0420-03	10.000 ug/ml	0.0200 ml	40.000 ml	0.0050 ug/ml	Hexane	cppinger	11/21/2003	
05/21/2003	GC0421-03	LOW 8081 A STD	Heptachlor	GC0420-03	10.000 ug/ml	0.0200 ml	40.000 ml	0.0050 ug/ml	Hexane	cppinger	11/21/2003	
05/21/2003	GC0421-03	LOW 8081 A STD	Methoxychlor	GC0420-03	20.000 ug/ml	0.0200 ml	40.000 ml	0.0100 ug/ml	Hexane	cppinger	11/21/2003	
05/21/2003	GC0421-03	LOW 8081 A STD	TCX	GC0420-03	10.000 ug/ml	0.0200 ml	40.000 ml	0.0050 ug/ml	Hexane	cppinger	11/21/2003	

Reviewed By: _____

Page 1 of 1

APPENDIX 43
SOP FOR THE EXTRACTION AND CLEANUP OF ORGANIC COMPOUNDS FROM WATER AND SOLIDS (PT-OP-001)

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

Title: Extraction and Cleanup of Organic Compounds from Waters and Solids

Method(s): SW846 3500 Series, 3600 Series, 8151A and EPA 600 Series Methods

Approvals (Signature/Date):

Brian A. Pino	Steve Jackson
10/17/07	10/16/07
Brain Pino, Technical Manager, Date	Steve Jackson, Health & Safety Manager / Coordinator, Date
Nasreen K. DeRubeis	Larry Matko
10/16/07	10/16/07
Nasreen DeRubeis, Quality Assurance Manager, Date	Larry Matko, Laboratory Director, Date

This SOP was previously identified as SOP No. PITT-OP-0001, Rev. 9.

1 SCOPE AND APPLICATION

This SOP describes procedures for preparation (extraction and cleanup) of semivolatile organic analytes in aqueous, TCLP leachate, soil, sediment, tissue and wipe matrices for analysis by Gas Chromatography (GC), Gas Chromatography / Mass Spectrometry (GC/MS), and High Performance Liquid Chromatography (HPLC). The procedures are based on SW-846 and 600 series methodology and are applicable for measurements made to comply with the Resource Conservation and Recovery Act (RCRA) and for wastewater testing.

1.1 Extraction procedures for the following determinative methods are covered:

8081A, 8082, 8141A, 8151A, 8270C (including SIM), 8310, 608, 610, and 625

1.1.1 For methods 608 and 610, which are only applicable to aqueous matrices, only the separatory funnel extraction procedure applies.

1.1.2 For sediment samples being analyzed in support of Dredged Material Management programs, method modifications are often necessary, to compensate for the high moisture content, to meet project goals. This may include increased sample weight or decreased final extract volumes. Typically these volume modifications are up to a factor of 2.

1.2 The extraction procedures here may be appropriate for other determinative methods when appropriate spiking mixtures are used.

1.3 For DoD requirements, refer to DoD SOP, PITT-QA-DoD-0001, Implementation of the DoD QSM Versions 3, January 2006.

2 SUMMARY OF METHOD

2.1 Separatory Funnel Extraction

A measured volume of sample, typically 1 liter, is adjusted, if necessary, to a specified pH and serially extracted with methylene chloride using a separatory funnel.

2.2 Continuous Liquid/Liquid Extraction

A measured volume of sample, typically 1 liter, is placed into a continuous liquid/liquid extractor, adjusted, if necessary, to a specific pH and extracted with methylene chloride for 18-24 hours.

2.3 Sonication Extraction

Low level: A measured weight of sample, typically 30 g, is mixed with anhydrous sodium sulfate to form a free flowing powder. This is solvent extracted three times using an ultrasonic horn. High level: A 2 g sample is mixed with anhydrous sodium sulfate. This is solvent extracted once with a microtip ultrasonic horn.

2.4 Soxhlet Extraction

A measured weight of sample, typically 30 g, is mixed with anhydrous sodium sulfate to form a free flowing powder. This is extracted with refluxing solvent.

2.5 Accelerated Soxhlet (Soxtherm®) Extraction

A measured weight of sample, typically 15 g, or one whole wipe sample is mixed with anhydrous sodium sulfate and magnesium sulfate to form a free flowing powder. This is extracted with an accelerated soxhlet unit.

2.6 Cleanup and Concentration

Procedures are presented for removing interferents from sample extracts, and for drying and concentration of the extract to final volume for analysis.

2.7 Phenoxy Acid Herbicide extractions

Procedures for the extraction and cleanup of phenoxy acid herbicides are presented in Appendix A.

3 DEFINITIONS

Definitions of terms used in this SOP may be found in the glossary of the Quality Management Plan (QMP).

4 INTERFERENCES

4.1 Method interferences may be caused by contaminants in solvents, reagents, glassware, and other processing apparatus. All these materials must be routinely demonstrated to be free from interferences under conditions of the analysis by running laboratory method blanks as described in the Quality Control section. Specific selection of reagents may be required to avoid introduction of contaminants.

4.2 Visual interferences or anomalies (such as foaming, emulsions, odor, etc.) must be documented.

5 SAFETY

5.1 Employees must abide by the policies and procedures in the Corporate Safety Manual, Radiation Safety Manual and this document.

5.2 Samples containing or suspected to contain cyanide or sulfide concentrations at or greater than 250 ppm or 500 ppm, respectively, shall be processed in a fume hood.

5.3 The use of separatory funnels to extract aqueous samples with Methylene Chloride creates excessive pressure very rapidly. Initial venting should be done immediately after the sample container has been sealed and inverted. Vent the funnel into the hood away from people and other samples. This is

considered a high-risk activity, and a face shield must be worn over safety glasses or goggles when it is performed.

5.4 Nitrile gloves should be used when performing this extraction. Latex and vinyl gloves provide no significant protection against the organic solvents used in this SOP, and should not be used.

5.5 During Kuderna-Danish (KD) concentration, do not allow the extract to boil to dryness. The solvent vapors remaining in the KD apparatus may superheat and create an explosion or fire hazard. The KD apparatus and glass separatory funnels have ground glass joints, which can become stuck. Technicians must use Kevlar or other cut/puncture resistant gloves when separating stuck joints.

5.6 Ultrasonic disrupters can produce high intensity noise and must be used in an area with adequate noise protection.

5.7 Care must be used when separating soxhlet bodies. Protective gloves must be used when separating stuck glass joints.

5.8 Sulfuric acid cleanup must not be performed on any matrix that may have water present as a violent reaction between the acid and water may result in acid exploding out of the vessel.

5.9 Mercury is a highly toxic compound that must be handled with care. Spilled mercury requires that special clean-up tools and procedures be used. Mercury is a corrosive material that will readily react with aluminum foil. Do not use aluminum foil or any aluminum products when working with mercury.

5.10 The following is a list of the materials used in this method, which have a serious or significant hazard rating. NOTE: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table. A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

Material	Hazards	Exposure Limit[i]	Signs and symptoms of exposure
Acetone	Flammable	1000 ppm-TWA	Inhalation of vapors irritates the respiratory tract. May cause coughing, dizziness, dullness, and headache.
Hexane	Flammable Irritant	500 ppm-TWA	Inhalation of vapors irritates the respiratory tract. Overexposure may cause lightheadedness, nausea, headache, and blurred vision. Vapors may cause irritation to the skin and eyes.
Ethyl Ether	Flammable Irritant Peroxide Former	400 ppm-TWA	General anesthesia by inhalation can occur. Continued exposure may lead to respiratory failure or death. Early symptoms include irritation of nose and throat, vomiting, and irregular respiration, followed by dizziness, drowsiness, and unconsciousness. May cause irritation, redness and pain to the eyes. Irritating to the skin and mucous membranes by drying effect. Can cause dermatitis on prolonged exposure. May be absorbed through skin. **May form explosive peroxides on long standing or after exposure to air or light. This material must be disposed of with six months.**
Florisil	**Irritant**	**TLV 10mg/m3 PEL 5mg/m3**	**May cause irritation if inhaled or adsorbed through the skin.**
Mercury	Poison	0.1 Mg/M3 Ceiling (Mercury Compounds)	Extremely toxic. Causes irritation to the respiratory tract. Causes irritation. Symptoms include redness and pain. May cause burns. May cause sensitization. Can be absorbed through the skin with symptoms to parallel ingestion. **May affect the central nervous system.** Causes irritation and burns to eyes. Symptoms include redness, pain, and blurred vision; may cause serious and permanent eye damage.
Methylene Chloride	Carcinogen Irritant	25 ppm-TWA 125 ppm-STEL	Causes irritation to respiratory tract. Has a strong narcotic effect with symptoms of mental confusion, light-headedness, fatigue, nausea, vomiting and headache. Causes irritation, redness and pain to the skin and eyes. Prolonged contact can cause burns. Liquid degreases the skin. May be absorbed through skin.
Sodium Hydroxide	Corrosive Poison	2 ppm, 5 mg/m^3	This material will cause burns if comes into contact with the skin or eyes. Inhalation of Sodium Hydroxide dust will cause irritation of the nasal and respiratory system.
Sulfuric Acid[ii]	Corrosive Oxidizer Dehydrator	1 mg/m^3	This material will cause burns if comes into contact with the skin or eyes. Inhalation of vapors will cause irritation of the nasal and respiratory system.

[i] Exposure limit refers to the OSHA regulatory exposure limit.
[ii] Always add acid to water to prevent violent reactions.

5.11 Eye protection that satisfies protects against splash, laboratory coat and appropriate gloves must be worn while samples, standards, solvents and reagents are being handled. Cut resistant gloves must be worn doing any other task that presents a strong possibility of getting cut. Disposable gloves that have become contaminated will be removed and discarded; other gloves will be cleaned immediately.

5.12 The preparation of standards and reagents and glassware cleaning procedures that involve solvents such as methylene chloride will be conducted in a fume hood with the sash closed as far as the operations will permit. Use of methylene chloride for glassware cleaning should be avoided as far as possible.

5.13 All work must be stopped in the event of a known or potential compromise to the health and safety of a TestAmerica associate. The situation must be reported **immediately** to a laboratory supervisor or EH&S coordinator.

6 EQUIPMENT AND SUPPLIES

6.1 Glassware should be cleaned with soap and water, rinsed with water and dried in an oven at 400°C for at least 2 hours. Alternatively the glassware can be solvent rinsed with acetone or methanol followed by methylene chloride after the water rinse.

6.2 Equipment and supplies for extraction procedures

EQUIPMENT AND SUPPLIES	Sep .fun.	CLLE	Soni	Sox	Accel Sox.	Conc
Separatory Funnel: 2 L	√					
Separatory Funnel Rack	√					
Balance: >1400 g capacity, accurate ±1 g	√	√				
pH indicator paper, wide-range: covers extraction pH	√	√				
Graduated cylinder: 1 liter. (other sizes may be used)	√	√				
Erlenmeyer Flask or Fleaker: 125 & 300 mL (other sizes optional)	√		√			
Solvent Dispenser Pump or 100 mL Graduated Cylinder	√		√			
Continuous Liquid/Liquid Extractor		√				
Round or flat Bottom: 250, 500 mL or 1 L		√				
Boiling Chips: Contaminant free, approximately 10/40 mesh (Teflon® PTFE, carbide or equivalent).		√		√	√	√
Cooling Condensers		√		√	√	
Heating Mantle: Rheostat controlled		√		√	√	
Auto-timer for heating mantle		√		√	√	
Beakers: 250 & 400 mL, graduated			√	√	√	
Balance: >100 g capacity, accurate ±0.1 g			√	√	√	
Soxhlet Extractor				√		

EQUIPMENT AND SUPPLIES	Sep .fun.	CLLE	Soni	Sox	Accel Sox.	Conc
Soxtherm® Extractor Gerhardt Model S 306A					√	
Glass Thimbles					√	
Sonicator (at least 300 watts)			√			
Sonicator horn, 3/4 inch			√			
Kuderna-Danish (K-D) Apparatus: 500 mL						√
Concentrator Tube: 10 mL, attached to K-D with clips						√
Snyder Column: Three-ball macro						√
Water Bath: Heated, with concentric ring cover, capable of temperature control (± 5°C) up to 95°C. The bath must be used in a hood or with a solvent recovery system.						√
Vials: Glass, 2 mL, 4 mL, and 10 mL capacity with Teflon®-lined screw-cap						√
Nitrogen Blowdown Apparatus						√
Nitrogen: reagent grade.						√
Culture tubes: 10 mL, 16 mmx100 mm						√
Syringe: 1 mL	√	√	√	√	√	
Phase Separation Paper	√	√	√	√	√	
Glass Wool	√	√	√	√	√	
Glass Funnel: 75 X 75 mm	√	√	√	√	√	√
Disposable Pipettes	√	√	√	√	√	√
Aluminum foil	√	√	√	√	√	√
Paper Towels	√	√	√	√	√	√
Horizon Dry Vaps						√
Dry disk separation membranes						√

6.3 Equipment and Supplies for Cleanup Procedures

EQUIPMENT AND SUPPLIES	GPC	Florisil	Sulfur	Acid
Gel permeation chromatography system (GPC Autoprep Model 1002A or 1002B Analytical Biochemical Laboratories, Inc. or Zymark Benchmate or equivalent).	√			
Bio Beads: (S-X3) -200-400 mesh, 70 gm (Bio-Rad Laboratories, Richmond, CA, Catalog 152-2750 or equivalent).	√			
Chromatographic column: 700 mm x 25 mm ID glass column. Flow is upward.	√			
Ultraviolet detector: Fixed wavelength (254 nm) and a semi-prep flow-through cell.	√			
Strip chart recorder, recording integrator, or laboratory data system.	√			
Syringe: 10 mL with Luerlok fitting.	√			
Syringe filter assembly, with disposable 5 um filter discs, Millipore No. LSWP 01300 or equivalent.	√			
Chromatographic column: 250 mm long x 10 mm ID; with Pyrex glass wool at the bottom and a Teflon stopcock (for silica gel cleanup).	√			

EQUIPMENT AND SUPPLIES	GPC	Florisil	Sulfur	Acid
Vacuum system for eluting multiple cleanup cartridges. Vac Elute Manifold - Analytichem International, J.T. Baker, or Supelco (or equivalent). The manifold design must ensure that there is no contact between plastics containing phthalates and sample extracts.		√		
Vacuum trap made from a 500 mL sidearm flask fitted with a one-hole stopper and glass tubing.		√		
Vacuum pressure gauge.		√		
Rack for holding 10 mL volumetric flasks in the manifold.		√		
Mechanical shaker or mixer: Vortex Genie or equivalent.			√	√
Separatory Funnels with Ground-Glass Stoppers: 250 mL				
Erlenmeyer Flasks: 125 mL				
Disposable Pipettes		√	√	√
Culture tubes: 10 mL, 16 mmx100 mm	√	√	√	√

7 REAGENTS AND STANDARDS

7.1 Reagents for Extraction Procedures

All reagents must be ACS reagent grade or better unless otherwise specified.

REAGENTS	Sep fun.	CLLE	Soni	Sox	Accel. Sox.	Conc
Sodium hydroxide (NaOH), Pellets: Reagent Grade	√	√				
Sodium hydroxide solution, 10 N: Dissolve 40 g of NaOH in reagent water and dilute to 100 mL.	√	√				
Sulfuric acid (H_2SO_4), Concentrated: Reagent Grade	√	√				
Sulfuric acid (1:1): Carefully add 500 mL of H_2SO_4 to 500 mL of reagent water. Mix well.	√	√				
Organic free reagent water.	√	√				
Sodium sulfate (Na_2SO_4), Granular, Anhydrous: Purify by heating at 400°C a minimum of two hours.	√	√			√	
Magnesium Sulfate, Anhydrous powder				√	√	
Extraction/Exchange Solvents: Methylene chloride, hexane, acetonitrile, acetone, pesticide quality or equivalent	√	√	√	√	√	√
Acetone: Used for cleaning	√	√	√	√	√	√
50:50 Sodium Sulfate/Magnesium Sulfate			√	√	√	

7.2 Reagents for Cleanup Procedures

REAGENTS	GPC	Florisil	Sulfur	Acid
Florisil: 500 mg or 1 g cartridges with stainless steel or Teflon frits (catalog 694-313, Analytichem, 24201 Frampton Ave., Harbor City, CA, or equivalent.)		√		
Mercury: triple distilled			√	
Tetrabutylammonium hydrogen sulfate			√	
Sodium sulfite			√	
Tetrabutylammonium (TBA) sulfite reagent: Prepare reagent by dissolving 3.39 g of Tetrabutylammonium hydrogen sulfate in 100 mL organic-free reagent water. Extract this solution 3 times with 20 mL portions of hexane. Discard the hexane extracts. Add 25 g sodium sulfite to the water solution.			√	
2-Propanol			√	
Nitric acid: 1N			√	
Copper powder: remove oxides (if powder is dark) by treating with 1N nitric acid, rinse with organic-free reagent water to remove all traces of acid, rinse with acetone, and dry under a stream of nitrogen.			√	
Sulfuric acid, Concentrated				√
Sodium hydroxide, Pellets Sodium hydroxide, 10N: Dissolve 40 g of NaOH in 100 mL of reagent water Sulfuric acid (H_2SO_4), Concentrated: Reagent Grade Sulfuric acid (1:1): Carefully add 500 mL of H_2SO_4 to 500 mL of reagent water. Mix well.				

7.3 Standards

7.3.1 Stock Standards

Stock standards are purchased as certified solutions or prepared from neat. Semivolatile stock standards are stored at $\leq 6^{\circ}C$. All stock standards must be protected from light. Stock standard solutions must be replaced after one year (from the time of preparation, if prepared in house, or from the time the ampule is opened if purchased.) Standards must be allowed to come to room temperature before use.

7.3.2 Surrogate Spiking Standards

Prepare or purchase surrogate spiking standards at the concentrations listed in Table 5. Surrogate spiking standards are prepared as dilutions of the stock standards. Surrogate spiking solutions must be refrigerated and protected from light. The standards must be replaced at least every six months or sooner if there is reason to believe that the standard has degraded or concentrated.

7.3.3 Matrix Spiking and Laboratory Control Spiking Standards.

The same spiking solution is used for the matrix spike and the Laboratory Control Sample. Prepare MS/LCS spiking standards at the concentrations listed in Table 6. Spiking standards are purchased or prepared as dilutions of the stock standards. Spiking solutions must be refrigerated and protected from light. The standards must be replaced at least every six months or sooner if there is reason to believe that the standard has degraded or concentrated.

7.3.4 GPC calibration solution - prepare or purchase a solution in methylene chloride that contains the following analytes in the concentrations listed below:

Analyte	mg/mL
Corn Oil	25.0
Bis (2-ethylhexyl) phthalate	1.0
Methoxychlor	0.2
Perylene	0.02
Sulfur	0.08

NOTE: Sulfur is not very soluble in methylene chloride; however, it is soluble in warm corn oil. Therefore, one approach is to weigh out the corn oil, warm it, and transfer the weighed amount of sulfur into the warm corn oil. Mix it and then transfer into a volumetric flask with methylene chloride, along with the other calibration compounds. This standard has a lifetime of 6 months.

8 SAMPLE COLLECTION PRESERVATION, SHIPMENT AND STORAGE

8.1 Samples are not chemically preserved.

8.2 Samples are stored at 4°C ± 2°C in glass containers with Teflon®-lined caps except for tissue samples, which are stored frozen.

8.3 Holding Times

8.3.1 Extraction is initiated within 7 days of the sampling date for aqueous samples, 14 days for solid and waste samples, and 1 year for tissue samples.

8.3.2 For TCLP leachates, extraction is initiated within 7 days from when the leaching procedure is completed.

8.3.3 Analysis of the extracts is completed within 40 days of extraction.

9 QUALITY CONTROL

9.1 Quality Control Batch

The batch is a set of up to 20 samples that are of the same matrix and are processed together using the same procedures and reagents. The batch must contain a method blank, an LCS and a matrix spike / matrix spike duplicate. (In some cases, at client request, it may be appropriate

to process a matrix spike and sample duplicate in place of the MS/MSD). If clients specify specific samples for MS/MSD, the batch may contain multiple MS/MSD. For methods 608 and 610, a matrix spike is specified for every 10 samples. This will be done if the project/program requires a 10% matrix spike frequency and if sufficient sample volume is provided. See policy QA-003 for further definition of the batch.

9.2 Definition of matrix

The possible matrix types are aqueous, soil, sediment, tissue, waste, wipe and TCLP leachate.

9.3 Insufficient Sample

If insufficient sample is available to process a MS/MSD, then a second LCS must be processed. The LCS pair is then evaluated according to the MS/MSD criteria. Use of a LCS pair in place of a MS/MSD must be documented. Because subsamples cannot be taken from a wipe sample for MS/MSD analyses, wipe samples should be processed with a LCS/LCSD.

9.4 Sample count

Laboratory generated QC samples (method blanks, LCS, MS/MSD) are not included in the sample count. Field samples are included.

9.5 Method Blank

A method blank consisting of all reagents added to the samples must be prepared and analyzed with each batch of samples. Surrogates are spiked into the method blank at the same level as the samples. The method blank is used to identify any background interference or contamination of the analytical system, which may lead to the reporting of elevated concentration levels or false positive data.

9.5.1 Aqueous Method Blanks use 1000 mL of reagent water spiked with the surrogates. The method blank goes through the entire analytical procedure, including any cleanup steps.

9.5.2 Solid method blanks use the same weight of sodium sulfate (acidified sodium sulfate for herbicides) as the extracted weights of the associated samples, spiked with the surrogates. The method blank goes through the entire analytical procedure, including any cleanup steps.

9.5.3 Method blanks for wipes consist of clean, unused gauze pads (that are the same as those used for the associated wipe samples) that are spiked with the surrogates and carried through the entire analytical procedure, including any cleanup steps.

9.5.4 TCLP method blanks use 200 mL of leachate fluid for GC/MS Semivolatiles and 100 mL for organochlorine pesticides, spiked with the surrogates. The leachate may optionally be diluted to 1000 mL with reagent water. The

method blank goes through the entire analytical procedure, including any cleanup steps.

9.6 Laboratory Control Sample (LCS)

Laboratory Control Samples are well characterized, laboratory-generated samples used to monitor the laboratory's day-to-day performance of routine analytical methods. The LCS, spiked with a group of target compounds representative of the method analytes, is used to monitor the accuracy of the analytical process, independent of matrix effects. On-going monitoring of the LCS results provides evidence that the laboratory is performing the method within accepted QC guidelines for accuracy and precision. The LCS goes through the entire analytical procedure, including any cleanup steps.

9.6.1 The LCS is made up in the same way as the method blank (See sections 9.5.1 - 9.5.3) but spiked with the LCS standard and the surrogates.

9.6.2 For the 600 series methods (608, 610, and 625), the LCS is equivalent to the QC Check Sample specified in the reference methods. For methods 608 and 610, a LCS is required for every 10 samples extracted.

9.7 Surrogates

9.7.1 Surrogates are organic compounds which are similar to the target analyte(s) in chemical composition and behavior in the analytical process, but which are not normally found in environmental samples.

9.7.2 Each applicable sample, blank, LCS and MS/MSD is spiked with surrogate standards. Surrogate spike recoveries must be evaluated by determining whether the concentration (measured as percent recovery) falls within the required recovery limits.

9.8 Matrix Spike/Matrix Spike Duplicate (MS/MSD)

A matrix spike is an environmental sample to which known concentrations of target analytes have been added. A matrix spike duplicate is a second spiked aliquot of the same sample, which is prepared and analyzed along with the sample and matrix spike.

9.9 Initial Demonstration of Capability

The initial demonstration of capability and method detection limit studies described in section 13 must be acceptable before analysis of samples may begin.

9.10 Quality Assurance Summaries

Certain clients may require specific project or program QC, which may supersede these method requirements. Quality Assurance Summaries (QAS) should be developed to address these requirements.

9.11 TestAmerica QC Program

Further details of QC and corrective action guidelines are presented in the TestAmerica QC Program document (QA-003). Refer to this document if in doubt regarding corrective actions.

10 PROCEDURE

Procedures for separatory funnel liquid/liquid extraction (10.2), continuous liquid/liquid extraction (10.3), sonication extraction (10.4), soxhlet extraction (10.5), accelerated soxhlet extraction (10.6), waste dilution (10.7), extract concentration (10.8), and extract cleanup (10.9) are presented in this section.

10.1 Procedural Variations

Procedural variations are allowed only if deemed necessary in the professional judgment of the supervisor to accommodate variation in sample matrix, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using a Nonconformance memo and approved by a supervisor and QA/QC manager. If contractually required, the client will be notified. The Nonconformance memo will be filed in the project file.

Any deviations from this procedure identified after the work has been completed must be documented as a nonconformance, with a cause and corrective action described. A Nonconformance memo shall be used for this documentation.

10.2 Separatory Funnel Liquid/Liquid Extraction of Water Samples.

Refer to Figure 1 – Separatory Funnel Extraction flowchart.

10.2.1 Remove surrogate and matrix spiking solutions from refrigerator and allow to warm to room temperature.

10.2.2 Measure the initial sample pH with wide-range pH paper and record on the extraction benchsheet. If sample is a leachate (e.g. TCLP), compare the current pH against leachate log, Note on the benchsheet, if there is any discrepancy.

10.2.3 The normal sample volume is approximately 1 liter. Other sample volumes may be used to obtain specific reporting limits, and reduced sample volumes, diluted to 1 liter with reagent water, may be used for very dirty samples.

10.2.4 Mark the meniscus on the 1 liter sample bottle. Spike the sample in the bottle with surrogate solution. Also spike the MS and MSD aliquots with Matrix Spike solution (Refer to Tables 3 and 4 for spike volumes). Mix well.

Note: If the sample bottle is completely full, it may be difficult to add the spike solutions to the bottle. In this case, transfer the sample to the separatory funnel and then add the spike.

10.2.5 Sample pH is adjusted, as indicated in Table 1 for the initial extraction. Use the minimum amount of 1:1 H_2SO_4 or 10 N NaOH necessary. Recheck the sample with pH paper by dipping a disposable pipette into the sample and wetting the pH paper. Record adjusted pH, spiking volumes and standard numbers on the benchsheet. Return spiking solutions to the refrigerator as soon as possible.

10.2.6 Transfer the entire sample to the separatory funnel. Rinse the sample bottle with 60 mL of methylene chloride and transfer to the separatory funnel.

> Warning: Dichloromethane creates excessive pressure very rapidly! Therefore, initial venting should be done immediately after the sample container has been sealed and inverted. Vent into hood away from analysts and other samples.

10.2.7 The sample volume is determined by filling the sample bottle with reagent water up to the meniscus and measuring that volume in a graduated cylinder. Record the volume to the nearest 10 mLs.

10.2.7.1 If the entire sample bottle will not be used (i.e., for smaller sample aliquots such as TCLP), mix the sample in the bottle and measure out the desired volume in a graduated cylinder. Spike the surrogate, and MS solution, where appropriate, and adjust initial sample pH in the cylinder. Transfer the aliquot to the separatory funnel.

10.2.7.2 Rinse the cylinder with 60 mL of methylene chloride and transfer to the separatory funnel.

10.2.8 Prepare a method blank and LCS for each batch as specified in section 9 of this SOP. Use 1 L of reagent water for method blanks and LCS. The LCS is spiked with the surrogate and matrix spike solutions, the method blank only with the surrogates (see Tables 3 and 4 for spike volumes).

10.2.9 Use 100 mL of leachate for TCLP pesticides, and 200 mL of leachate for TCLP semivolatiles, measured in a graduated cylinder. The leachate may be made up to 1 L in volume with reagent water.

10.2.10 For a TCLP method blank, measure 100 mL (pesticides) or 200 mL (semivolatiles) of the buffer solution used in the leaching procedure and transfer to the separatory funnel. Add 60 mL of methylene chloride to the separatory funnel. The TCLP leachate may be diluted to approximately 1 liter before extraction, if desired.

10.2.11 Seal and shake or rotate the separatory funnel vigorously for 2 minutes with periodic venting to release excess pressure.

> Warning: Dichloromethane creates excessive pressure very rapidly! Therefore, initial venting should be done immediately after the separatory funnel has been sealed and inverted. Vent into hood away from analysts and other samples.

10.2.12 Allow the organic layer to separate from the water phase until complete visible separation has been achieved (approximately 10 minutes). If the emulsion interface between layers is more than one-third the size of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. The optimum technique depends upon the sample and may include stirring, filtration of the emulsion through glass wool, centrifugation, or other physical methods. If the emulsion cannot be broken (recovery of <80% of the methylene chloride*), transfer the sample, solvent, and emulsion into the extraction chamber of a continuous liquid-liquid extractor (CLLE) and proceed as described in continuous liquid-liquid extraction (Section 10.3). If this is done, the sample must be extracted as part of a valid CLLE batch.

*Note: 15 - 20 mL of methylene chloride is expected to dissolve in 1 L of water. Thus, solvent recovery could be as low as 35 mL from the first shake and still be acceptable. Subsequent shakes should recover at least 50 mL of solvent.

10.2.13 Fill a funnel with 10-20 g of anhydrous sodium sulfate. The funnel can be plugged with glass wool or filter paper may be used to hold the sodium sulfate. Drain the solvent extract from the separatory funnel through the prepared filtration funnel into a clean glass container. The extract may be drained directly into the KD flask. Close the stopcock just before the water level begins draining out of the separatory funnel. If the sodium sulfate becomes saturated with water add more to the funnel or replace the existing sodium sulfate with fresh drying agent.

10.2.14 Repeat the extraction process two more times using fresh 60 mL portions of solvent, combining the three solvent extracts in the collection container.

10.2.15 If extraction at a secondary pH is required, adjust the pH of the sample in the separatory funnel to the pH indicated in Table 1 with a minimum amount of 10 N NaOH or 1:1 H_2SO_4. Measure with pH paper and record the adjusted pH on the benchsheet. Serially extract with three 60 mL portions of methylene chloride, as outlined in Steps *10.2.10 to 10.2.12.* Collect these three extracts in the same container used for the initial pH fraction.

Note: Alternatively, the acid and base fractions may be kept separate. This may be required for method 625. Separate analysis of the acid and base fractions may also be required for method 625. Individual client requirements must be checked before starting the extraction.

10.2.16 Rinse the extract residue from the sodium sulfate by pouring 20-30 mL of clean methylene chloride through the funnel and into the collection container.

10.2.17 Dispose of solvent and water remaining in the separatory funnel into the appropriate waste container.

10.2.18 Cover with aluminum foil if the extract is not concentrated immediately. Refer to Section 10.8 for concentration and Section 10.9 for cleanup.

10.3 Continuous Liquid/Liquid Extraction from Water Samples:

Refer to Figure 2 – Continuous Liquid/Liquid Extraction flowchart.

10.3.1 Remove surrogate and matrix spiking solutions from refrigerator and allow to warm to room temperature.

10.3.2 Assemble the apparatus. Add 200-300 mL of methylene chloride to the extractor body. Add 3 to 5 boiling chips to the round-bottom distilling flask.

10.3.3 Measure the initial sample pH with wide-range pH paper and record on the extraction benchsheet. If sample is a leachate (e.g. TCLP), compare the current pH against the leachate log. Note on the benchsheet if there is any discrepancy.

10.3.4 Mark the meniscus on the 1 liter sample bottle. Spike the sample in the bottle with surrogate solution. Also spike the MS and MSD aliquots with Matrix Spike solution (see Tables 3 and 4 for spike volumes). Mix well.

Note: If the sample bottle is completely full, it may be difficult to add the spike solutions to the bottle. In this case, transfer the sample to the extractor and then add the spike.

10.3.5 Sample pH is adjusted, as indicated in Table 1 for the initial extraction. Use the minimum amount of 1:1 H_2SO_4 or 10 N NaOH necessary. Recheck the sample with pH paper by dipping a disposable pipette into the sample and wetting the pH paper. Record adjusted pH, spiking volumes and standard numbers on the benchsheet. Return spiking solutions to the refrigerator as soon as possible.

10.3.6 Transfer the entire sample to the liquid-liquid extractor. Rinse the sample bottle with 60 mL of methylene chloride and transfer to the liquid-liquid extractor.

Warning: Dichloromethane creates excessive pressure very rapidly! Therefore, initial venting should be done immediately after the sample container has been sealed and inverted. Vent into hood away from analysts and other samples.

10.3.7 The sample volume is determined by filling the sample bottle with reagent water up to the meniscus and measuring that volume in a graduated cylinder. Record the volume to the nearest 10 mLs.

10.3.7.1 If the entire sample bottle will not be used (i.e., for smaller sample aliquots such as TCLP), mix the sample in the bottle and measure out the desired volume in a graduated cylinder. Spike the surrogate, and MS solution, where appropriate, and adjust initial sample pH in the cylinder. Transfer the aliquot to the liquid-liquid extractor.

10.3.7.2 Rinse the cylinder with 60 mL of methylene chloride and transfer to the liquid-liquid extractor.

10.3.8 Prepare a method blank and LCS for each batch as specified in section 9 of this SOP. Use 1 L of reagent water for method blanks and LCS. The method blank is spiked with the surrogates, the LCS and matrix spikes with the surrogates and matrix spiking solutions. Note that different spiking solutions are used for methods 625, 8270 and TCLP (see Tables 3 and 4 for spike volumes).

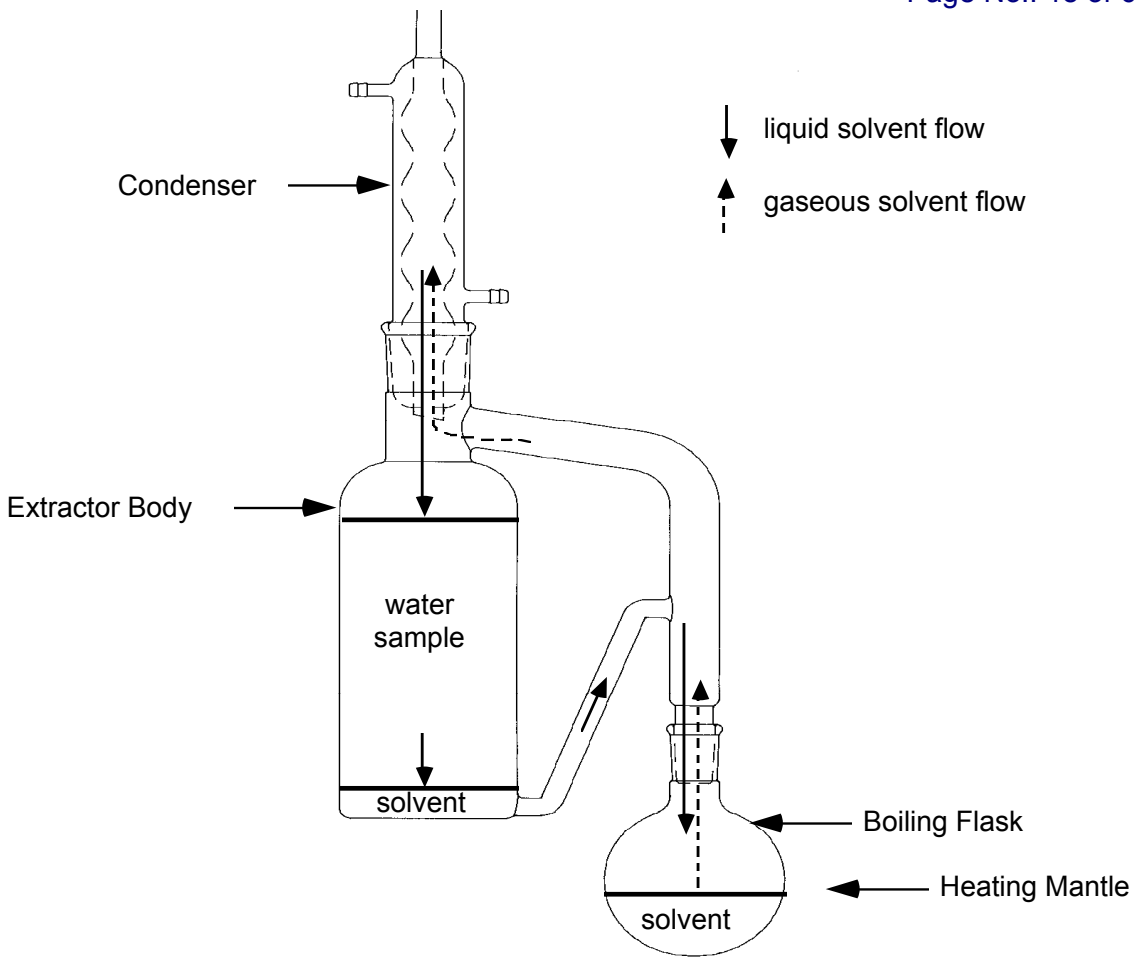
10.3.9 Use 100 mL of leachate for TCLP pesticides, and 200 mL of leachate for TCLP semivolatiles, measured in a graduated cylinder. The leachate may be made up to 1 L in volume with reagent water.

10.3.10 For a TCLP method blank, measure 100 mL (pesticides) or 200 mL (semivolatiles) of the buffer solution used in the leaching procedure and transfer to the separatory funnel. Dilute to about 1 liter with reagent water.

10.3.11 Add reagent water to the extractor body until approximately 125 mL of methylene chloride is pushed over into the round-bottomed flask to ensure proper operation and solvent cycling. Attach cold condenser (about 10^{o}C). Turn on heating mantle. Inspect joints for leaks once solvent has begun cycling. Extract for 18-24 hours. (24 hours required for Method 625)

10.3.12 If extraction at a secondary pH is required, (see Table 1) turn off the heating mantle and allow the extractor to cool. Detach the condenser and adjust the pH of the sample in the extractor body to the pH indicated in Table 1 with a minimum amount of 10 N NaOH or 1:1 H_2SO_4. Measure with pH paper and record the adjusted pH on the benchsheet. If desired, the acid and base fractions may be kept separate by replacing the boiling flask with a clean flask and fresh solvent. Reattach the condenser and turn on heating mantle. Extract for 18-24 hours (24 hours for Method 625).

Note: Alternatively, the acid and base fractions may be kept separate. This may be required for method 625. Separate analysis of the acid and base fractions may also be required for method 625. Individual client requirements must be checked before starting the extraction.



10.3.13 Turn off the heating mantle and allow the extractor to cool.

10.3.14 Place a funnel containing 10-20 g of anhydrous sodium sulfate on the Kuderna-Danish (K-D) apparatus or other glass container. The funnel can be plugged with glass wool enabling it to hold the granular anhydrous sodium sulfate or phase separation filter paper may be used.

10.3.15 Dry the extract in the round bottom flask by filtering it through the sodium sulfate filled funnel. Note that it is not necessary or advisable to attempt to add the solvent remaining in the continuous extractor body to the extract.

10.3.16 Collect the dried extract in a K-D or other glass container. Rinse the flask that contained the solvent extract with 20-30 mL of methylene chloride and add it to the funnel to complete the quantitative transfer. Dispose of solvent and water remaining in the extractor in the appropriate waste container.

Note: Some types of CLLE apparatus have built in drying columns. If this type of apparatus is used then a drying step subsequent to the extraction may not be necessary.

10.3.17 Cover with aluminum foil if the extract is not concentrated immediately. Refer to Section 10.8 for concentration and Section 10.9 for cleanup.

10.4 Sonication

Refer to Figure 3 – Sonication Extraction flowchart.

10.4.1 Most samples will be extracted following the low-level sonication procedure. However, if high concentrations are suspected, the high-level sonication extraction procedure may be used. Both procedures are described below.

10.4.2 Decant and discard any water layer on a sediment/soil sample. Note: For sediment samples associated with most Dredged Material Management projects, the water layer is considered part of the whole sediment and should not be decanted, but re-mixed into the sample. Check project requirements before decanting any water layer. Homogenize the sample by mixing thoroughly. Tissue samples should be homogenized prior to extraction. Discard any foreign objects such as sticks, leaves and rocks, unless extraction of this material is required by the client. If the sample consists primarily of foreign materials consult with the client (via the Project Manager). Document if a water layer was discarded. See Tables 7 and 8 for Initial Extraction weight Adjustment for sediment samples.

10.4.3 Remove surrogate and matrix spiking solutions from refrigerator and allow to warm to room temperature.

10.4.4 Low Level Procedure

10.4.5 Weigh 30 g of sample ± 1.0 g into a 250 or 400 mL beaker. Record the weight to the nearest 0.1 g in the appropriate column on the benchsheet. Use 30 g of 50:50 sodium sulfate/magnesium sulfate for the method blank and the LCS.

10.4.6 Mix weighed sample with a spatula adding enough 50:50 sodium sulfate/magnesium sulfate (approximately 30 g) to be free flowing. (If the sample is not free flowing extraction efficiency may be reduced)

10.4.7 Prepare a method blank, LCS and MS/MSD for each batch as specified in Section 9 of this SOP.

10.4.8 Add surrogate spiking solution to each sample, method blank, Laboratory Control Sample (LCS), and matrix spikes. Add the appropriate matrix spiking solution to each Matrix Spike/Matrix Spike Duplicate (MS/MSD) and LCS. Refer to Tables 3 and 4 for spike volumes. Record spiking volumes and standard numbers on the benchsheet. Return spiking solutions promptly to refrigerator.

Note: The same volume of surrogate and matrix spiking solution is used if GPC is indicated since the final volume would be reduced to compensate for loss of extract during the GPC procedure.

10.4.9 Immediately add a minimum of 100 mL of solvent to the beaker.

Solvents:

All Tests 1:1 Methylene Chloride / Acetone

Note: Steps 10.4.5 - 10.4.9 should be performed rapidly to avoid loss of the more volatile extractables.

10.4.10 Place the bottom surface of the 3/4" horn approximately ½ inch below the surface of the solvent, but above the sediment layer.

10.4.11 Sonicate for 3 minutes, making sure the entire sample is agitated. If the W-380 or W-385 sonicator is used the output should be set at 10 with mode switch on pulse, and percent-duty cycle knob set at 50%.

10.4.12 Loosely plug the stem of a 75 mm x 75 mm glass funnel with glass wool and/or line the funnel with filter paper. Add 10-20 g of anhydrous sodium sulfate to the funnel cup.

10.4.13 Place the prepared funnel on a collection apparatus (beaker or K-D Apparatus.

10.4.14 Decant and filter extracts through the prepared funnel into a clean beaker or K-D Apparatus.

10.4.15 Repeat the extraction two more times with additional 100 mL minimum portions of solvent each time. Decant off extraction solvent after each sonication. On the final sonication pour the entire sample (sediment and solvent) into the funnel and rinse with an additional 10 mL-20 mL of the methylene chloride/acetone.

Note: Alternatively, the three extracts may be collected together and then filtered through the sodium sulfate.

10.4.16 Cover with aluminum foil if the extract is not concentrated immediately. Refer to Section 10.8 for concentration and Section 10.9 for cleanup.

10.4.17 High Level Procedure

10.4.18 Weigh 2 g of sample into a 20 mL vial. Record the weight to the nearest 0.1 g in the appropriate column on the benchsheet. Use 2 g of sodium sulfate for the method blank and the LCS.

10.4.19 Add 2 grams of sodium sulfate to each sample and mix well.

10.4.20 Add 1 mL of surrogate to all samples including QC samples. Add 1 mL of the matrix spike solution to the LCS, MS and MSD. Depending on the test, surrogate and matrix spike solutions at higher concentrations may need to be prepared. If necessary, the preparation of these solutions will be documented in the standards database.

10.4.21 Add 8.0 mL of extraction solvent (7.0 mL to the LCS, MS, MSD) so that the final volume is 10.0 mL. The extraction solvent is as follows:

10.4.21.1 For organochlorine pesticides, organophosphorus pesticides, and PCBs (Aroclors and congeners), the solvent is hexane.

10.4.21.2 For PAHs by HPLC, the solvent is acetonitrile.

10.4.21.3 For GC/MS semivolatiles, the solvent is methylene chloride.

10.4.22 Place the bottom surface of a 1/8" tapered microtip attached to a 1/2" horn approximately ½ inch below the surface of the solvent, but above the solid layer.

10.4.23 Sonicate each sample for 2 minutes. If the W-380 or W-385 sonicator is used, the output should be set at 10 with mode switch on pulse, and the percent-duty cycle knob set at 100% full power.

10.4.24 Loosely pack a disposable Pasteur pipette with 2 to 3 cm of glass wool. Filter the extract through the glass wool into a suitable container.

10.4.24.1 If the samples do not require cleanups or additional concentration, than the extract is ready for analysis

10.4.24.2 If cleanups (10.9) or additional concentration (10.8) are required, collected a standard volume (i.e., 5.0 mL, which represents ½ of the extract). Either account for the "loss" of half of the extract in the final sample calculations, or concentrate the extract to ½ of the standard final volume to compensate for the loss.

10.4.25 Sonicator Tuning.

10.4.25.1 Tune the sonicator according to manufacturer's instructions. The sonicator must be tuned at least every time a new horn is installed.

10.5 Soxhlet

Refer to Figure 4 – Soxhlet Extraction flowchart.

10.5.1 Decant and discard any water layer on a sediment/soil sample. Note: For sediment samples associated with most Dredged Material Management projects, the water layer is considered part of the whole sediment and should not be decanted, but re-mixed into the sample. Check project requirements before decanting any water layer. Homogenize the sample by mixing thoroughly. Tissue samples should be homogenized prior to extraction. Discard any foreign objects such as sticks, leaves and rocks, unless extraction of this material is required by the client. If the sample consists primarily of foreign materials consult with the client. Document on benchsheet if a water layer was discarded.

10.5.2 Remove surrogate and matrix spiking solutions from refrigerator and allow to warm to room temperature.

10.5.3 Weigh 30 g of sample ± 1.0 g into a beaker, recording the weight to the nearest 0.1 g on the benchsheet. Use 30 g of 50:50 sodium sulfate/magnesium sulfate for the method blank and LCS. Add 30 g of 50:50 sodium sulfate/magnesium sulfate and mix well. The mixture should have a free flowing texture. If not, add more sodium sulfate. Add the sample/sodium sulfate mixture to a soxhlet thimble, but do not pack the thimble tightly. The

extraction thimble must drain freely for the duration of the extraction period. A glass wool plug above and below the sample in the soxhlet extractor is an acceptable alternative for the thimble.

10.5.3.1 Sample weights less than 30 g but over 5 g may be used if the appropriate reporting limits can be met.

10.5.4 Prepare a method blank, LCS and MS/MSD for each batch as specified in Section 9 of this SOP, using sodium sulfate as the matrix. The weight of 50:50 sodium sulfate/magnesium sulfate used should be approximately the weight of soil used in each sample.

10.5.5 Add the surrogate spiking solution to each sample, method blank, Laboratory Control Sample (LCS), and matrix spikes. Add the appropriate matrix spiking solution to each Matrix Spike/Matrix Spike Duplicate (MS/MSD) and LCS. Refer to Tables 3 and 4 for details of the spiking solutions. Record spiking volumes and standard numbers on the benchsheet. Return spiking solutions promptly to refrigerator.

Note: The same volume of surrogates and matrix spiking compounds is used if GPC is indicated since the final volume would be reduced to compensate for loss of extract during the GPC procedure.

10.5.6 Place approximately 250 mL of solvent into a 500 mL flat bottom flask containing one or two clean boiling chips. Attach a cold condenser (about 10°C) to the top of the extractor. Attach the flask to the extractor and extract the sample for 16-24 hours at 4-6 cycles per hour. Check the system for leaks at the ground glass joints after it has warmed up.

Solvents:

All Tests 1:1 Methylene Chloride / Acetone

10.5.7 Allow the extract to cool after the extraction is complete, and then disassemble by gently twisting the soxhlet from the flask. Dry the extract in the flask by filtering it through a sodium sulfate filled funnel.

10.5.8 Collect the dried extract in a K-D or other glass container. Rinse the flask that contained the solvent extract with 20-30 mL of methylene chloride and add it to the funnel to complete the quantitative transfer.

10.5.9 Cover with aluminum foil if the extract is not concentrated immediately. Refer to Section 10.8 for concentration and Section 10.9 for cleanup.

10.6 Accelerated Soxhlet (Soxtherm®)

Refer to Figure 5 – Accelerated Soxhlet Extraction (Soxtherm) flowchart.

10.6.1 Decant and discard any water layer on a sediment/soil sample. Note: For sediment samples associated with most Dredged Material Management projects, the water layer is considered part of the whole sediment and should not be decanted, but re-mixed into the sample. Check project requirements

before decanting any water layer. Homogenize the sample by mixing thoroughly. Tissue samples should be homogenized prior to extraction. Discard any foreign objects such as sticks, leaves and rocks, unless extraction of this material is required by the client. If the sample consists primarily of foreign materials consult with the client. Document on benchsheet if a water layer was discarded. For wipe samples, the entire contents of the original sample container will be extracted (i.e., no subsample will be taken) following the procedure for solid samples.

10.6.2 Remove surrogate and matrix spiking solutions from the refrigerator and allow to return to room temperature.

10.6.3 Weigh 15 g of sample ± 0.5 g into a beaker, recording the weight to the nearest 0.1 g on the benchsheet. Use 15 g of 50:50 sodium sulfate/magnesium sulfate for the method blank and LCS. Add 15 g of anhydrous 50:50 sodium sulfate/magnesium sulfate and mix well. The mixture should have a free flowing texture. If not, add more sodium sulfate. Add the sample/50:50 sodium sulfate/magnesium sulfate mixture to a soxhlet thimble, but do not pack the thimble tightly. The extraction thimble must drain freely for the duration of the extraction period. A glass wool plug above and below the sample in the thimble is required.

10.6.3.1 Sample weights less than 15 g but over 5 g may be used if the appropriate reporting limits can be met.

10.6.4 Prepare a method blank, LCS and MS/MSD for each batch as specified in Section 9 of this SOP, using sodium sulfate as the matrix. Use a new, clean gauze pad as the blank matrix for wipe samples and follow the procedure for extraction of solid samples. The weight of 50:50 sodium sulfate/magnesium sulfate used should be approximately the weight of soil used in each sample.

10.6.5 Add the surrogate spiking solution to each sample, method blank, Laboratory Control Sample (LCS), and matrix spikes. Add the appropriate matrix spiking solution to each Matrix Spike/Matrix Spike Duplicate (MS/MSD) and LCS. Refer to Tables 3 and 4 for details of the spiking solutions. Record spiking volumes and standard numbers on the benchsheet. Return spiking solutions promptly to refrigerator.

> **Note:** The same volume of surrogates and matrix spiking compounds is used if GPC is indicated since the final volume would be reduced to compensate for loss of extract during the GPC procedure.

10.6.6 Place thimble in beaker containing clean boiling chips and add approximately 140 mL of solvent (see below). Place beakers into positions on the accelerated soxhlet unit. Run the appropriate program for the extraction solvent. Periodically, check the system for leaks at the joints.

10.6.6.1 For organochlorine pesticides, organophosphorus pesticides, and PCBs (Aroclors and congeners), the extraction solvent is 1:1 hexane/acetone except

if GPC cleanup is being done. If GPC cleanup is being done, the extraction solvent is 1:1 methylene chloride/acetone.

10.6.6.2 For all other parameters, the extraction solvent is 1:1 methylene chloride/acetone.

10.6.7 Upon completion of the program, remove the beaker from the accelerated soxhlet unit and dispose of the extracted sample.

10.6.8 Collect the extract in a K-D or other glass container. Rinse the flask that contained the solvent extract with 5-10 mL of methylene chloride and add it to the funnel to complete the quantitative transfer.

10.6.9 Cover with aluminum foil if the extract is not concentrated immediately. Refer to Section 10.8 for concentration and Section 10.9 for cleanup.

10.7 Waste Dilution

10.7.1 This method is used for materials that are soluble in an organic solvent.

10.7.2 Remove surrogate and matrix spiking solutions from refrigerator and allow to warm to room temperature.

10.7.3 Transfer 10 mL of the solvent to be used for dilution into a Teflon capped vial. Mark the meniscus on the vial, and then discard the solvent.

10.7.4 Tare the vial, and then transfer approximately 1g of sample to the vial. Record the weight to the nearest 0.1 g.

10.7.5 Add 1 mL of surrogate solution to each sample. Add 1 mL of matrix spike solution to the MS, MSD and LCS. Depending on the test, surrogate and matrix spike solutions at higher concentrations may need to be prepared. If necessary, the preparation of these solutions will be documented in the standards database.

10.7.6 Dilute to 10 mL with the appropriate solvent (hexane for organochlorine pesticides, organophosphorus pesticides, and PCBs (Aroclors and congeners); acetonitrile for PAHs by HPLC; methylene chloride for GC/MS semivolatiles).

10.7.7 Add 2 g + 0.1 g sodium sulfate to the sample. Cap and shake for 2 minutes.

10.7.8 Add 4-5 g sodium sulfate to a small funnel. The funnel can be plugged with glass wool or phase separation filter paper may be used to hold the sodium sulfate.

10.7.9 Pour the sample through the funnel, collecting as much as possible in a clean vial. Do NOT rinse the funnel with additional solvent, and do NOT concentrate the sample. The final volume is defined as 10 mL.

10.7.10 Label the sample, which is now ready for cleanup or analysis.

10.8 Concentration

According to the type of sample and any cleanup procedures needed, different final solvents and volumes will be required. Refer to Table 2 for the appropriate final volumes and concentrations.

Refer to Figure 6 – Concentration and Cleanup flowchart.

10.8.1 Kuderna-Danish (KD) Method:

10.8.1.1 Assemble a Kuderna-Danish concentrator by attaching a 10 mL concentrator tube to the 500 mL KD flask. For procedures where the final volume is 10 mL, a 250 mL Erlenmyer flask may be used as an alternative to the KD flask.

10.8.1.2 Add one or two clean boiling chips and the dried extract to be concentrated to the KD flask and attach a three ball Snyder Column. Add approximately 1 mL of clean methylene chloride to the top of the Snyder column (this is important to ensure that the balls are not stuck and that the column will work properly).

10.8.1.3 Place the KD apparatus on a water bath (80-90^{o}C) so that the tip of the concentrator tube is submerged. The water level should not reach the joint between the concentrator and the KD flask. At the proper rate of distillation, the balls will actively chatter but the chambers should not flood.

10.8.1.4 Concentrate to 5-15 mL. If the determinative method requires a solvent exchange add the appropriate exchange solvent (see Table 2) to the top of the Snyder Column, and then continue the water bath concentration back down to 1-4 mL. Refer to Table 2 for details on final volumes. The Snyder column may be insulated if necessary to maintain the correct rate of distillation.

Note: Add an additional boiling chip with the addition of exchange solvent.

An alternative technique for solvent exchange is to replace the macro Snyder column and KD flask with a micro Snyder column, concentrate to approximately 1 mL, add 10 mL of exchange solvent, and concentrate back down to 1 mL. The extract must be cool before the macro Snyder assembly is removed.

Note: It is very important not to concentrate to dryness as analytes will be lost.

10.8.1.5 Remove the KD apparatus from the water bath and allow to cool for a minimum of 10 minutes. If the level of the extract is above the level of the concentrator tube joint, continue to distill the solvent as necessary. Again, allow the KD flask to cool for a minimum of 10 minutes.

10.8.1.6 If the final volume is 5 or 10 mL the extract may be made up to volume in the graduated KD tube or transferred to a 12 mL vial previously marked at the appropriate volume level. Document the final volume. Otherwise proceed to section 10.8.2

10.8.2 Nitrogen Evaporation to Final Concentration

10.8.2.1 Transfer the entire extract to a calibrated evaporation tube. Rinse the concentrator tube with 1-2 mL of the appropriate solvent and transfer the solvent rinsate to the evaporation tube.

10.8.2.2 Place the tube in a warm water bath that is at approximately 35°C and evaporate the solvent using a gentle stream of nitrogen. The nitrogen flow will form a slight depression on the surface of the solvent, but should not create splattering of the extract.

10.8.2.3 During the course of the evaporation rinse the sides of the evaporation tube twice with approximately 1 mL of clean solvent. The first rinse should be about half way through the process, with the second rinse when the solvent volume gets close to 1 mL. Concentrate the solvent accurately to the calibrated volume line and transfer the extract to the appropriate storage vial.

Note: It is very important not to concentrate to dryness as analytes will be lost.

10.8.2.4 An alternative technique is to follow the previous steps concentrating the solvent to slightly below the required final volume and then drawing the extract into a syringe. Rinse the evaporation tube with a small amount of solvent and draw additional solvent into the syringe to make up the accurate final volume.

Note: The final concentration and volume measurement steps are critical. Use care when concentrating and make certain that the final volume measurement is accurate.

10.9 Cleanup Techniques

Refer to Figure 6 – Concentration and Cleanup flowchart.

The following techniques may be used to remove interfering peaks, and /or to remove materials that may cause column deterioration and/ or loss of detector sensitivity.

Gel Permeation Chromatography (Section 10.9.1) is a generally applicable technique, which can be used to prepare extracts for Semivolatiles (8270), PAHs (8310), Organochlorine pesticides (8081A), PCBs (8082), and Organophosphorus Pesticides (8141A) analysis. It is capable of separating high molecular weight material from the sample analytes, and so is particularly useful if tissue or vegetable matter is part of the sample, and for many soil samples.

Florisil column cleanup (Section 10.9.2) is particularly useful for cleanup of Organochlorine pesticides (8081A/608) and PCB (8082/608) analyses, and should normally be applied to these samples unless the matrix is clean. It separates compounds with a different polarity from the target analytes.

Gel Permeation Chromatography and Florisil column cleanup may both be applied to samples. In this case the GPC should be performed first.

Sulfur cleanup (Section 10.9.3) is generally applied to samples for analysis by methods 8081A, 8082, and 608 since the Electron Capture Detector responds strongly to sulfur. It is performed after GPC and Florisil cleanup, if performed.

Sulfuric acid cleanup (Section 10.9.4) is applied to samples requiring analysis for PCBs (Aroclors and congeners) only. Most organic matter is destroyed by the sulfuric acid.

WARNING: Sulfuric acid cleanup must not be performed on any matrix that may have water present as a violent reaction between the acid and water may result in acid exploding out of the vessel.

10.9.1 Gel Permeation Chromatography (GPC)

Note: GPC systems include the GPC Autoprep Model 1002A or 1002B Analytical Biochemical Laboratories, Inc., or equivalent.

10.9.1.1 GPC Column Preparation

10.9.1.1.1 Weigh out 70 g of Bio Beads (SX-3) into a 400-mL beaker.

10.9.1.1.2 Add approximately 300 mL of methylene chloride and stir gently.

10.9.1.1.3 Cover with aluminum foil and allow the beads to swell for a minimum of two hours. Maintain enough solvent to sufficiently cover the beads at all times.

10.9.1.1.4 Position and tighten the outlet bed support (top) plunger assembly in the tube by inserting the plunger and turning it clockwise until snug. Install the plunger near the column end but no closer than 5 cm (measured from the gel packing to the collar).

10.9.1.1.5 Turn the column upside down from its normal position with the open end up. Place the tubing from the top plunger assembly into a waste beaker below the column.

10.9.1.1.6 Swirl the bead/solvent slurry to get a homogeneous mixture and pour the mixture into the open end of the column. Transfer as much as possible, with one continuous pour, trying to minimize bubble formation. Pour enough to fill the column. Wait for the excess solvent to drain out before pouring in the rest. Add additional methylene chloride to transfer the remaining beads and to rinse the beaker and the sides of the column. If the top of the gel begins to look dry, add more methylene chloride to rewet the beads.

10.9.1.1.7 Wipe any remaining beads and solvent from the inner walls of the column with a laboratory tissue. Loosen the seal slightly on the other plunger assembly (long plunger) and insert it into the column. Make the seal just tight enough so that any beads on the glass surface will be pushed forward, but loose enough so that the plunger can be pushed forward.

CAUTION: Do not tighten the seal if beads are between the seal and the glass surface because this can damage the seal and cause leakage.

10.9.1.1.8 Push the plunger until it meets the gel, and then compress the column bed about 4 cm.

10.9.1.1.9 Connect the column inlet to the solvent reservoir and place the column outlet tube in a waste container. Pump methylene chloride through the column at a rate of 5 mL/min. for one hour.

10.9.1.1.10 After washing the column for at least one hour, connect the column outlet tube to the inlet side of the UV detector. Connect the system outlet to the outlet side of the UV detector. Placing a restrictor (made from a piece of capillary tubing of 1/16"OD x 10/1000"ID x 2") in the outlet tube from the UV detector will prevent bubble formation, which causes a noisy UV baseline. The restrictor will not affect the flow rate. After pumping methylene chloride through the column for an additional 1-2 hours, adjust the inlet bed support plunger until approximately 6-10 psi back-pressure is achieved. Push the plunger in to increase pressure or slowly pull outward to reduce pressure.

10.9.1.1.11 When the GPC column is not to be used for several days, connect the column inlet and outlet lines to prevent column drying and/or channeling. If channeling occurs, the gel must be removed from the column, re-swelled, and re-poured as described above. If drying occurs, pump methylene chloride through the column until the observed column pressure is constant and the column appears wet. Always recalibrate after column drying has occurred to verify that retention volumes have not changed.

10.9.1.2 Initial Calibration of the GPC Column

10.9.1.2.1 Before use, the GPC must be calibrated based on monitoring the elution of standards with a UV detector connected to the GPC column.

10.9.1.2.2 Pump solvent through the GPC column for 2 hours. Verify that the flow rate is 4.5-5.5 mL/min. Corrective action must be taken if the flow rate is outside this range. Record the column pressure (should be 6-10 psi) and room temperature (22°C is ideal).

Note: Changes in pressure, solvent flow rate, and temperature conditions can affect analyte retention times and must be monitored. If the flow rate and/or column pressure do not fall within the above ranges, a new column should be prepared.

10.9.1.2.3 Inject the calibration solution and retain a UV trace that meets the following requirements (See resolution calculation in section 10.9.1.7):

- Peaks must be observed and should be symmetrical for all compounds in the calibration solution.
- Corn oil and phthalate peaks must exhibit >85% resolution.
- Phthalate and methoxychlor peaks must exhibit >85% resolution.

- Methoxychlor and perylene peaks must exhibit >85% resolution.
- Perylene and sulfur peaks must not be saturated and must exhibit >90% baseline resolution.

10.9.1.2.4 A UV trace that does not meet the criteria in paragraph 10.9.1.2.3 indicates the need for system maintenance and/or the need for a new column.

10.9.1.2.5 Determine appropriate collect and dump cycles.

10.9.1.2.6 The calibrated GPC program for organochlorine pesticides/PCB Aroclors should dump >85% of the phthalate and should collect >95% of the methoxychlor and perylene. Use a wash time of 10 minutes.

10.9.1.2.7 For GC/MS semivolatile and PAHs by HPLC extracts, initiate a column eluate collection just before the elution of bis (2-ethylhexyl) phthalate and after the elution of the corn oil. Stop eluate collection shortly after the elution of perylene. Stop collection before sulfur elutes. Use a wash time of 10 minutes after the elution of sulfur.

10.9.1.2.7.1 For PCB Congeners and Organophosphorus pesticides, this collection window should be appropriate but needs to be verified with spike solutions containing all analytes of interest.

10.9.1.2.8 Reinject the calibration solution after appropriate dump and collect cycles have been set.

10.9.1.2.9 Measure and record the volume of collected GPC eluate in a graduated cylinder.

10.9.1.2.10 The retention times for both bis(2-ethylhexyl) phthalate and perylene must not vary more than +/- 5% between calibrations.

10.9.1.3 GPC calibration check

Check the calibration of the GPC immediately after the initial calibration and at least every 7 days thereafter, while the column is in use.

10.9.1.3.1 Inject the calibration solution, and obtain a UV trace. If the retention times of bis(2-ethylhexyl)phthalate or perylene have changed by more than ± 5% use this run as the start of a new initial calibration. Otherwise, proceed with the recovery check. Excessive retention time shifts may be caused by poor laboratory temperature control or system leaks, an unstabilized column, or high laboratory temperature causing outgassing of methylene chloride. Pump methylene chloride through the system and check the retention times each day until stabilized.

10.9.1.4 GPC Recovery Check for Organoclorine Pesticides/ PCB Aroclors

10.9.1.4.1 The recovery from the GPC must be verified immediately after the initial calibration and at least every 7 days, when the instrument is in use. Two recovery check solutions are used. The first mixture is prepared by diluting 1.0 mL of the organochlorine pesticide matrix spiking solution (Table 6) to 10

mL in methylene chloride. The second mixture is prepared by diluting 1 mL of the PCB Aroclor matrix spiking solution (Table 6) to 10 mL with methylene chloride.

10.9.1.4.2 Load the pesticide matrix spike mixture, the PCB mixture, and a methylene chloride blank onto the GPC using the GC dump and collect values.

Note: If the analysis is for PCB Aroclors only, then the pesticide recovery check is not necessary.

10.9.1.4.3 After collecting the GPC calibration check fraction, concentrate, solvent exchanging to hexane. Adjust the final volume to 5.0 mL, and analyze by GC/EC. Refer to concentration, section 10.8.

10.9.1.4.4 The methylene chloride blank may not exceed more than one half the reporting limit of any analyte. And if the recovery of each of the single component analytes is 80-110% and if the Aroclor pattern is the same as previously run standards, then the analyst may use the column. If the above criteria are not met, there may be a need for system maintenance.

10.9.1.5 GPC Recovery Check for All other Semivolatiles

10.9.1.5.1 The recovery from the GPC must be verified immediately after the initial calibration and at least every 7 days, when the instrument is in use. Dilute 1.0 mL of the GC/MS semivolatiles matrix spiking solution (Table 6) to 10 mL in methylene chloride for GC/MS Semivolatiles and PAHs by HPLC. For PCB Congeners and Organophosphorus pesticides, a solution containing all analytes of interest should be prepared in 10 mL of methylene chloride.

10.9.1.5.2 Load the spike mixture and a methylene chloride blank onto the GPC using the semivolatiles dump and collect values.

10.9.1.5.3 After collecting the GPC recovery check fraction, concentrate to 0.5 mL, and analyze by GC/MS for the GC/MS Semivolatiles and PAHs by HPLC. Analyze by GC/ECD for the PCB Congeners and GC/FPD for the Organophosphorus pesticides. Refer to the concentration section 10.8.

10.9.1.5.4 Recovery of the spiked analytes should be at least 60%. The blank should not contain any analytes at or above the reporting limit. If these conditions are met the column may be used for sample analysis. Otherwise correct the contamination problem, or extend the collect time to improve recovery of target analytes.

10.9.1.6 Sample Extract Cleanup

10.9.1.6.1 Reduce the sample extract volume to 1-2 mL, then adjust to 10 mL with methylene chloride prior to cleanup. This reduces the amount of acetone in the extract. Refer to section 10.8.

10.9.1.6.2 Start the pump and let the flow stabilize for 2 hours. The solvent flow rate should be 4.5-5.5 mL/min. The ideal laboratory temperature to prevent

outgassing of the methylene chloride is 22°C. The normal backpressure is 6-10 psi.

10.9.1.6.3 In order to prevent overloading of the GPC column, highly viscous sample extracts must be diluted prior to cleanup. Any sample extract with a viscosity greater than that of a 1:1 glycerol:water solution (by visual comparison) must be diluted and loaded into several loops.

10.9.1.6.4 Samples being loaded onto the GPC should be filtered with a 5 micron (or less) filter disk. Attach a filter to a 10 mL Luerlok syringe and filter the 10 mL sample extract into the sample tube.

10.9.1.6.5 Load the filtered samples into the proper sample tubes and place on the GPC.

Note: For the GPC Autoprep Model 1002A, wash the loading port with methylene chloride after loading each sample loop in order to minimize cross contamination. This step is automated on the GPC Autoprep 1002B.

10.9.1.6.6 Set the collect, dump, and wash times determined by the calibration procedure.

10.9.1.6.7 Switch to the run mode and start the automated sequence. Process each sample using the collect and dump cycle times established by the calibration procedure.

10.9.1.6.8 Collect each sample in a suitable glass container. Monitor sample volumes collected.

10.9.1.6.9 Any samples that were loaded into 2 or more positions must be recombined.

10.9.1.6.10 Concentrate semivolatile sample extracts to 0.5 mL in methylene chloride. Refer to the concentration section 10.8.

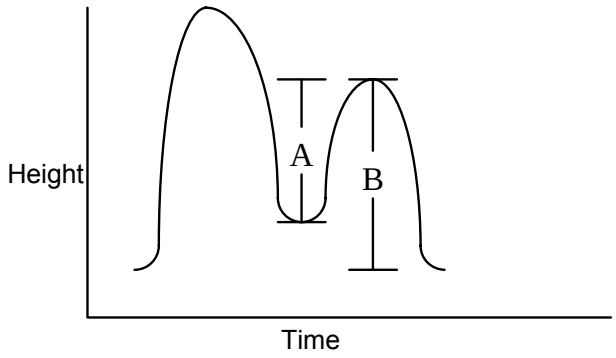
10.9.1.6.11 Solvent exchange pesticide/PCB sample extracts into hexane and concentrate to 5.0 mL. Refer to the concentration section 10.8.

10.9.1.7 Calculations

10.9.1.7.1 Resolution

To calculate the resolution between two peaks on a chromatograph, divide the depth of the valley between the peaks by the peak height of the smaller peak being resolved and multiply by 100.

Resolution Calculation



$$\% \text{ Resolution } = \frac{A}{B} \times 100$$

Where: A = depth of valley to height of smaller peak
B = peak height of smaller peak

10.9.1.7.2 Dump Time

Mark on the chromatograph the point where collection is to begin. Measure the distance from the injection point. Divide the distance by the chart speed. Alternatively the collect and dump times may be measured by means of an integrator or data system.

$$\text{Dump time (min)} = \frac{\text{Distance (cm) from injection to collection start}}{\text{Chart speed (cm / min)}}$$

10.9.1.7.3 Collection Time

$$\text{Collection time (min)} = \frac{\text{Distance (cm) between collection start and stop}}{\text{Chart speed (cm / min)}}$$

10.9.2 Florisil Cartridge Cleanup

Florisil cleanup is generally used for organochlorine pesticides, although it may be applied to other analytes. Sections 10.9.2.1 through 10.9.2.8 outline the procedure for organochlorine pesticides, while section 10.9.2.9 outlines modifications required for other analytes.

Note 1: Systems for eluting multiple cleanup cartridges include the Supelco, Inc. Solid Phase Extraction (SPE) assembly, or equivalent.

10.9.2.1 Before Florisil cleanup sample volume must be reduced to 10 mL (5 mL if GPC cleanup was used) and the solvent must be hexane. Refer to Section 10.8 for details of concentration.

10.9.2.2 Attach a vacuum manifold to a vacuum pump or water aspirator with a trap installed between the manifold and the vacuum. Adjust the vacuum in the manifold to 5-10 psi.

10.9.2.3 Place one Florisil cartridge into the vacuum manifold for each sample extract. Prior to cleanup of samples, pre-elute each cartridge with 5 mL of hexane/acetone (9:1). Adjust the vacuum applied to each cartridge so that the flow through each cartridge is approximately 2 mL/min. Do not allow the cartridges to go dry.

10.9.2.4 Just before the cartridges go dry, release the vacuum to the manifold and remove the manifold top.

10.9.2.5 Place a rack of clean labeled 12 mL concentrator tubes into the manifold and replace the manifold top. Make sure that the solvent line from each cartridge is placed inside the appropriate tube.

10.9.2.6 After the clean tubes are in place, vacuum to the manifold is restored and 2.0 mL of the extract is added to the appropriate Florisil cartridge.

10.9.2.7 The organochlorine pesticides/aroclors in the extract concentrates are then eluted through the column with 8 mL of hexane/acetone (90:10) and are collected into the 10 mL culture tube or concentrator tube held in the rack inside the vacuum manifold.

10.9.2.8 Transfer the extract to a graduated concentrator tube and concentrate the extract to 2 mL. Refer to the concentration Section (10.8)

Note 1: A cartridge performance standard must be run with each lot of Florisil cartridges.

Note 2: Florisil cartridge performance check--every lot number of Florisil must be tested before use. Add 0.5 ug/mL of 2,4,5-trichlorophenol solution and 0.5 mL of Organochlorine Pesticide Calibration Standard Mix A (midpoint concentration) to 4 mL hexane. Reduce volume to 0.5 mL. Add the concentrate to a pre-washed Florisil cartridge and elute with 9 mL hexane/acetone [(90:10)(v/v)]. Rinse cartridge with 1.0 mL hexane two additional times. Concentrate eluate to 1.0 mL final volume and transfer to vial. Analyze the solution by GC/EC. The test sample must show 80 to 120% recovery of all pesticide analytes with <5% trichlorophenol recovery, and no peaks interfering with target compounds can be detected. This standard has a lifetime of six months. Alternatively, this standard may be purchased as a stock solution.

10.9.2.9 Modifications for other analyte classes

10.9.2.9.1 PCBs

Pre-elute the cartridge with 4 mL hexane. Add 2 mL of the sample extract and elute with 3 mL hexane. The eluant will contain the PCBs together with any heptachlor, aldrin, 4,4'DDE and part of any 4,4'DDT. Any BHC isomers, heptachlor epoxide, chlordane, endosulfan I and II, endrin aldehyde and endrin sulfate and methoxychlor will be retained on the column and can be eluted in a separate fraction with 8 mL 90:10 hexane:acetone if required.

10.9.2.9.2 PAHs by GC/MS SIM (Tissue matrices only)

The extract is concentrated to approximately 2 mL. The florisil cartridge is rinsed with approximately 5 mL of methylene chloride. Discard the rinse. While collecting in a clean concentrator tube, pre-elute the cartridge with 5 mL methylene chloride and add the ~2 mL of the sample extract to the top of the cartridge. Quantitatively transfer the sample by rinsing the original vial 2-3 times with methylene chloride and add to the top of the cartridge. Once the sample extract and rinses have gravity filtered through the cartridge, add 5 mL of methylene chloride to rinse the cartridge. After the last rinse is collected, the extract is ready to be concentrated to the appropriate final volume (see Table 2).

10.9.3 Sulfur Removal

10.9.3.1 Sulfur can be removed by one of two methods: copper or tetrabutylammonium sulfite (TBA) according to laboratory preference. The TBA procedure is the laboratory default procedure. If the sulfur concentration is such that crystallization occurs in the concentrated extract, centrifuge the extract to settle the crystals, and carefully draw off the sample extract with a disposable pipette, leaving the excess sulfur in the centrifuge tube. Transfer the extract to a clean concentrator tube before proceeding with further sulfur cleanup.

10.9.3.2 Sulfur Removal with Copper

10.9.3.2.1 Transfer 1.0 mL of sample extract into a centrifuge or concentrator tube.

10.9.3.2.2 Add approximately 2 g of cleaned copper powder (see 7.2 for copper cleaning procedure) to the sample extract tube.

10.9.3.2.3 Mix for one minute on a mechanical shaker.

10.9.3.2.4 If the copper changes color, sulfur was present. Repeat the sulfur removal procedure until the copper remains shiny.

10.9.3.2.5 Transfer the supernate to a clean vial.

10.9.3.3 Sulfur Removal with Tetrabutylammonium (TBA) Sulfite Reagent

10.9.3.3.1 Transfer 1.0 mL of sample extract into a culture tube.

10.9.3.3.2 Add 1.0 mL TBA sulfite reagent and 2 mL 2-propanol to the sample extract. Cap and shake for 1 minute. If clear crystals (precipitated sodium sulfite) form, sufficient sodium sulfite is present.

10.9.3.3.3 If a precipitate does not form, add sodium sulfite in approximately 0.1 g portions until a solid residue remains after repeated shaking.

10.9.3.3.4 Add 5 mL organic free reagent water and shake for 1 minute. Allow sample to stand for 5-10 minutes. (Centrifuge if necessary to separate the layers). Transfer the sample extract (top layer) to a vial. The final volume is defined as 1.0 mL in section 10.9.3.3.1.

10.9.4 Sulfuric Acid Cleanup

10.9.4.1 Add approximately 2-5 mL of concentrated sulfuric acid to 2 mL of sample extract in a Teflon capped vial.

Caution: There must be no water present in the extract or the reaction may shatter the sample container.

10.9.4.2 Shake or vortex for about thirty seconds and allow to settle. (Centrifuge if necessary)

10.9.4.3 Remove the sample extract (top layer) from the acid using a Pasteur pipette and transfer to a clean vial. ***CAUTION:*** It is not necessary to remove all the extract since the final volume is already determined. Transfer of small amounts of sulfuric acid along with the extract will result in extremely rapid degradation of the chromatographic column.

10.9.4.4 If the sulfuric acid layer becomes highly colored after shaking with the sample extract, transfer the hexane extract to a clean vial and repeat the cleanup procedure until color is no longer being removed by the acid, or a maximum of 5 acid cleanups.

10.9.4.5 Properly dispose of the acid waste.

11 CALCULATIONS / DATA REDUCTION

Not applicable.

12 METHOD PERFORMANCE

12.1 Method detection limit

Each laboratory must generate a valid method detection limit for each analyte of interest. The procedure for the determination of the method detection limit is given in TestAmerica Pittsburgh SOP PITT-QA-0007.

12.2 Initial demonstration

Each laboratory must make an initial demonstration of capability for each individual method. This requires analysis of four QC Check samples. The QC check sample is a well-characterized laboratory generated sample used to monitor method performance, which should contain all the

analytes of interest. The spiking level should be equivalent to a mid-level calibration. (For certain tests more than one set of QC check samples may be necessary in order to demonstrate capability for the full analyte list.)

12.2.1 Four aliquots of the QC check sample are analyzed using the same procedures used to analyze samples, including sample preparation.

12.2.2 Calculations and acceptance criteria for the QC check samples are given in the determinative SOPs.

12.3 Training Qualification

The group/team leader has the responsibility to ensure that this procedure is performed by an analyst who has been properly trained in its use and has the required experience.

13 POLLUTION CONTROL

13.1 All waste will be disposed of in accordance with Federal, State and Local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this method and the policies in Section 13 of the Corporate Safety Manual for “Waste Management and Pollution Prevention.”

13.2 Within the constraints of following the methodology in this SOP, use of organic solvents should be minimized.

14 WASTE MANAGEMENT

14.1 The following waste streams are produced when this method is carried out.

14.1.1 Methylene Chloride extraction waste. This waste is collected in waste containers identified as “Methylene Chloride Waste”, Waste #2.

14.1.2 Extracted water samples. This waste is collected in a waste container identified as “Extraction Water”, Waste #35. The bottom organic layer is drained into a container identified as “Methylene Chloride Waste”, Waste #2. The remaining aqueous layer is neutralized to a pH between 6 and 9 and discharged down lab sink/ drain.

14.1.3 Used sodium sulfate and glass wool or filter paper contaminated with methylene chloride from the extract drying step. This waste is collected in a container identified as “Lab Trash Waste”, Waste #12.

14.1.4 Assorted flammable solvent waste from various rinses. This waste is collected in waste containers identified as “Mixed Flammable Solvent Waste”, Waste 3.

14.1.5 Methylene chloride waste from various rinses. This waste is collected in waste containers identified as “Methylene Chloride Waste”, Waste #2.

14.1.6 Miscellaneous disposable glassware contaminated with acids, caustics, solvents and sample residue. This waste is collected in a container identified as “Lab Trash Waste”, Waste #12.

15 REFERENCES

15.1 Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW846, 3rd Edition, Final Update III (December 1996). Sections 3500B, 3510C, 3520C, 3540C, 3541 3550B, 3580A 3600C, 3620B, 3640A, 3660B, and 3665A.

15.2 40 CFR Part 136, Appendix A, United States Environmental Protection Agency. 1984, Methods 608, 610, and 625.

15.2.1 PITT-QA-DoD-0001, Implementation of the DoD QSM Versions 3, January 2006.

16 ATTACHMENTS

16.1 Table 1 – Liquid/Liquid Extraction Conditions

16.2 Table 2 – Initial Volumes/Weights, Exchange Solvents and Final Volumes

16.3 Table 3 – Surrogate Spiking Solutions

16.4 Table 4 – Matrix Spike and LCS Solutions

16.5 Table 5 – Surrogate Spike Components

16.6 Table 6 – Matrix Spike Components

16.7 Table 7 – Initial Extraction Weight Adjustments for Sediment Samples (based on % Solids), Method 8270

16.8 Table 8 – Initial Extraction Weight Adjustments for Sediment Samples (based on % Solids), Methods 8081A, 8082 and 8141

16.9 Figure 1 – Separatory Funnel Extraction

16.10 Figure 2 – Continuous Liquid/Liquid Extraction

16.11 Figure 3 – Sonication Extraction

16.12 Figure 4 – Soxhlet Extraction

16.13 Figure 5 – Accelerated Soxhlet Extraction (Soxtherm)

16.14 Figure 6 – Concentration and Cleanup

16.15 Appendix A – Herbicides by Method 8151A

17 REVISION HISTORY

17.1 Revision 9, 02/01/07

17.1.1 Added wipe matrix.

17.1.2 Added procedures for low-level determinations.

17.1.3 Changed the laboratory name to TestAmerica.

17.1.4 A number of clarifications have been made.

17.2 Revision 10, 09/24/07

17.2.1 Changed the SOP format to the new corporate SOP format.

17.2.2 Added the requirement (in Appendix A) to document the derivitization of the stock standard for herbicides by Method 8151 in the extraction log and subsequently forward it to the GC Department.

17.2.3 Added the requirement (in Sections 10.2, 10.3 and 10.7) to allow the surrogate and spiking solutions to warm to room temperature prior to adding them to the samples.

17.2.4 Made revisions to Table 8 – Initial Extraction Weight Adjustments for Sediment Samples (based on % Solids), Methods 8081A, 8082 and 8141.

17.2.5 Removed the final filtering/drying step in Section 10.6.7.

18 METHOD MODIFICATIONS

18.1 Some surrogate spiking concentrations are modified from those recommended in SW-846, in order to make the concentrations more consistent with the calibration levels in the determinative methods.

18.2 Spiking levels for method 608 have been reduced by a factor of ten to bring the levels within the normal calibration range of the instrument.

Table 1
Liquid /Liquid Extraction Conditions

Determinative Method	Initial Ext. pH[1]	Secondary Ext. pH[1]
BNA (8270[2]) including SIM	1-2	11-12
BNA (625)	11-12	1-2
Pesticides (8081A & 608)	5-9	None
PCB Aroclors (8082 & 608)	5-9	None
PCB Congeners (8082)	5-9	None
OP Pesticides (8141A)	as received	None
Phenols (8041)	1-2	None
PAHs (8310 & 610)	as received	None

[1] If the laboratory has validated acid only 8270C extraction (including SIM) for the target compound list required, then the base extraction step may be omitted. The required validation consists of a 4 replicate initial demonstration of capability and a method detection limit study. (See Section 13).

[2] If the laboratory has validated acid only 8270C extraction (including SIM) for the target compound list required then the base extraction step may be omitted. The required validation consists of a 4 replicate initial demonstration of capability and a method detection limit study. (See section 13).

Table 2

Initial Volumes/Weights, Exchange Solvents, and Final Volumes[3]

Type	Initial Water Vol. (mL)	Initial Solid Wt (g)[4]	Initial Tissue Wt (g)	Exchange Solvent for Analysis	Final Volume for Analysis (mL)
Semivolatiles (8270C including SIM & 625)	1000	30 (15) NA for 625	25 NA for 625	N/A	1.0, 0.5 (low-level analyses)
Pesticides (8081A)	1000	15	6	Hexane	40.0 (waters), 20 (solids), 8.0 (tissue), 1.0 (low-level analyses)
PCB Aroclors (8082)	1000	15	6	Hexane	40.0 (waters), 20.0 (solids), 8.0 (tissue), 1.0 (low-level analyses)
Pesticide and PCB Aroclors (608)	1000	NA	NA	Hexane	8.0ml
PCB Congeners (8082)	1000	12	5	Hexane	2.0 (water) or 4.0 ml (solids and tissue)
PAH by HPLC (8310 & 610)	1000	15 NA for 610	30 NA for 610	Acetonitrile	5.0 (water), 1.0 (tissue/low-level water), 0.5 (solids)
Phenols (8041)	1000	N/A	N/A	N/A	1.0
OP Pesticides (8141A)	1000	15	12	Hexane	5.0 (water and solids) or 2.0 (tissue)

[3] Final Volumes will be ½ of the volume specified under Final Volume for Analysis if GPC Cleanup is performed (¼ if both Soxtherm® and GPC performed). GPC is required for all tissue analyses except PCBs, where it is recommended but optional if acid cleanup is performed.

[4] The values in ( ) under Initial Solid Wt. Are for the accelerated soxhlet procedures (Soxtherm®). All final volumes will be ½ of the volume listed under Final Volume for Analysis.

Table 3 Surrogate Spiking Solutions		
Analyte Group	**Surrogate Spike Solution ID**	**Volume (mL)[5]**
BNA (8270C or 625)	100/150 ppm (20/30 ppm for low-level analyses) BNA	0.5 (water/low-level solids), 0.25 (solids), 1.0 (low-level water)
BNA (8270C SIM)	5/7.5 ppm BNA	1.0
OP Pesticides (8141A)	50 ppm Tributyl Phosphate/Triphenyl Phosphate	0.2
PAHs (8310 or 610)	10.0/20.0 ppm Benzo(e)pyrene/p-terphenyl	1.0
Pesticides (8081A)	0.8 ppm DCB/TCX	1.0 (water), 0.2 (tissue), 0.5 solids), 0.025 (low-level waters)
Pesticides and PCB Aroclors (608)	0.2 ppm DCB/TCX	0.2
Phenols (8041)	200 ppm Dibromophenol	.25
PCB Congeners (8082)	0.08 ppm TCX/BZ165	0.2 (water) or 1.0 (solids/tissue)
PCB Aroclors (8082)	0.8 ppm DCB/TCX	1.0 (water), 0.2 (tissue), 0.5 (solids), 0.025 (low-level waters)

Table 4 Matrix Spike and LCS Solutions		
Analyte Group	**Matrix Spike Solution ID**	**Volume (mL)**
BNA (8270C)	100/150 ppm (20 ppm for low-level analyses) BNA	0.5 (water/low-level solids), 0.25 (solids), 1.0 (low-level water)
BNA TCLP (8270C)	BNA TCLP Spike	0.5
BNA 625	BNA NPDES Spike 100 PPM	0.5
BNA (8270C SIM)	BNA NPDES Spike-5 ppm	1.0
OP Pesticides (8141A)	10 ppm 8270 Appendix IX	0.5
PAHs (8310 or 610)	2.5/12.5 ppm PAH spike	2.0 (water), 1.0 (tissue), 0.5 (solids)
Pesticides (8081A)	1 ppm Pest	1.0, 0.5 (solids), 0.025 (low-level waters)
Pesticides TCLP (8081A)	Pest TCLP Spike	1.0
Pesticide 608	Pest NPDES Spike	0.2
PCB Congeners (8082)	0.05 ppm Congener Spike 26 compounds	0.2 (water) or 1.0 (solids/tissue)
Phenols (8041)	100 ppm Phenol Spike	0.25
PCB Aroclors 608	10 ppm PCB Spike	0.2
PCB Aroclors (8082)	40 ppm PCB Spike	1.0, 0.5 (solids), 0.025 (low-level waters)

[5] Solid samples being extracted using the Soxtherm® procedure will be spiked will ½ of the volume noted.

Table 5
Surrogate Spike Components

Type	Compounds	Solvent	Conc. (µg/mL)
BNA (8270C)	2-Fluorobiphenyl Nitrobenzene-d5 p-Terphenyl-d14 2-Fluorophenol Phenol-d6 2,4,6-Tribromophenol 1,2-Dichlorobenzene-d4 2-Chlorophenol-d4	Methanol	100, 20(low-level analyses) 100, 20(low-level analyses) 100, 20(low-level analyses) 150, 30(low-level analyses) 150, 30(low-level analyses) 150, 30(low-level analyses) 100, 20(low-level analyses) 150, 30(low-level analyses)
BNA (8270C SIM)	2-Fluorobiphenyl Nitrobenzene-d5 p-Terphenyl-d14 2-Fluorophenol Phenol-d6 2,4,6-Tribromophenol 1,2-Dichlorobenzene-d4 2-Chlorophenol-d4	Methanol	5 5 5 7.5 7.5 7.5 5 7.5
Pest/PCB Aroclors (8081A, 8082, 608)	Decachlorobiphenyl Tetrachloro-m-xylene	Acetone	0.2 0.2
Phenol (8041)	Dibromophenol	Acetone	200
PCB Congeners (8082)	BZ205 Tetrachloro-m-xylene	Acetone	0.025 0.025
PAHs (8310, 610)	Benzo(e)pyrene p-Terphenyl	Acetonitrile	10 20
OP Pesticides (8141A)	Tributyl phosphate Triphenyl phosphate	Acetone	50 50

Table 6
Matrix Spike Components

Type	Compounds	Solvent
BNA (8270C & 625)	See SOP PITT-MS-0001.	Methanol
BNA (8270C-SIM)	See SOP PITT-MS-0003	Methanol
BNA TCLP (8270C)	See SOP PITT-MS-0001	Methanol
Pesticides (8081A, 608)	See SOP PT-GC-001	Acetone
Pest TCLP (8081A)	See SOP PT-GC-001	Acetone
OP Pesticides (8141A)	See SOP PT-GC-001	Acetone
Phenol (8041)	See SOP PT-GC-001	Acetone
PAHs (8310 & 610)	See SOP PT-GC-001	Acetonitrile
PCB Congeners (8082)	See SOP PT-GC-001	Acetone
PCB Aroclors (8082 or 608)	See SOP PT-GC-001	Acetone

Table 7- Initial Extraction Weight Adjustments for Sediment Samples (based on % Solids)

Method 8270

If % Solids is:	Then the weight required to get 30 grams (dry weight) is:	Final Volume mL
≤ 54%	30.0	0.5
55-59%	27.3	0.5
60-64%	25.0	0.5
65-69%	23.1	0.5
70-74%	21.5	0.5
75-79%	20.0	0.5
80-84%	18.8	0.5
85-89%	17.7	0.5
90-94%	16.7	0.5
95-99%	15.8	0.5
100%	15.0	0.5

Table 8 - Method 8081A, 8082 and 8141

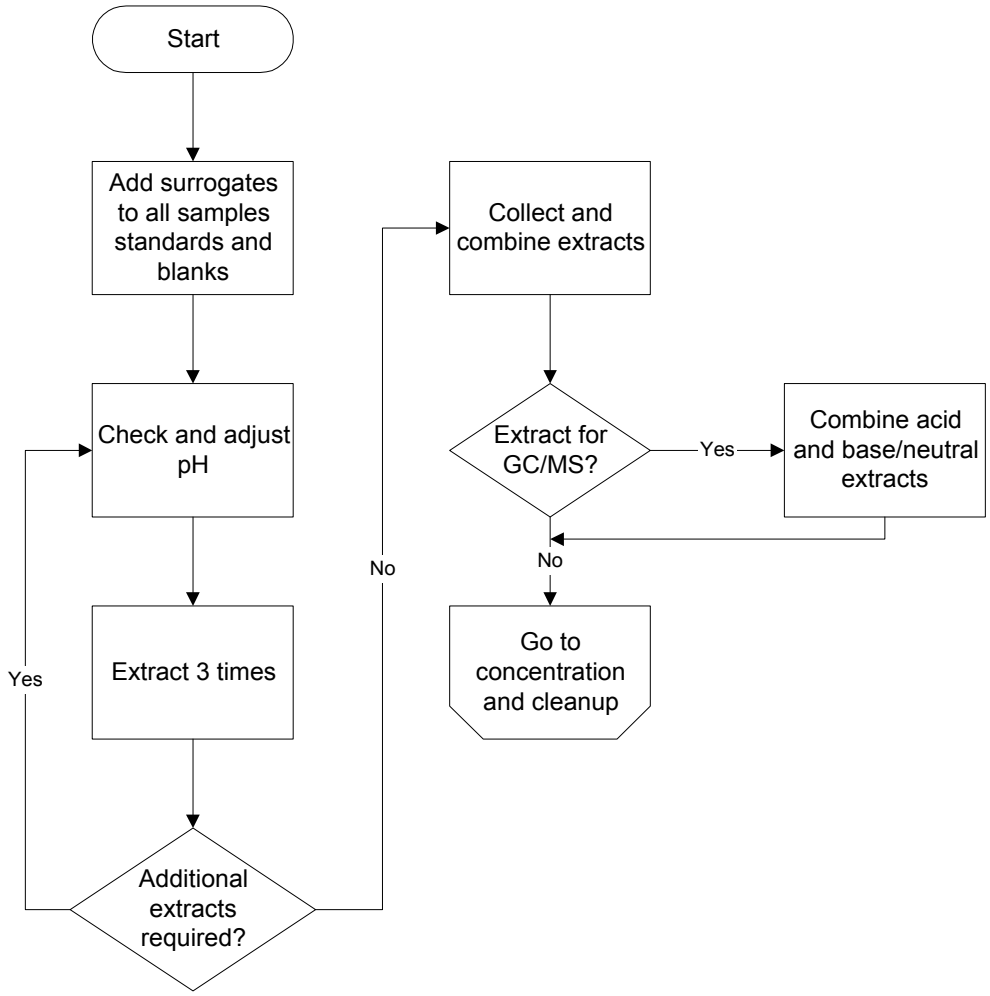
If % Solids is:	Then the weight required to get 30 grams (dry weight) is:	Final Volume 8081A/8082 (mL)	Initial and Final Volume 8141 (mL)
≤ 54%	15.0	10.0	24 g / 2.0 ml
55-59%	13.6	10.0	21.8 g / 2.0 ml
60-64%	12.5	10.0	20 g / 2.0 ml
65-69%	11.5	10.0	18.5 g / 2.0 ml
70-74%	10.7	10.0	17.1 g / 2.0 ml
75-79%	10.0	10.0	16 g / 2.0 ml
80-84%	9.38	10.0	15 g / 2.0 ml
85-89%	8.82	10.0	14.1 g / 2.0 ml
90-94%	8.33	10.0	13.3 g / 2.0 ml
95-99%	7.89	10.0	12.6 g / 2.0 ml
100%	7.5	10.0	12 g / 2.0 ml

Add 250 uL of surrogate for 8081A/8082. Add 200 mL of matrix spike for 8081. Add 250 uL of matrix spike for 8082. For 8141, add 80 uL of surrogate and 200 uL of matrix spike.

For PCB Congeners: Extract 12 grams with a 4.0 mL final volume. Add 400 uL of surrogate and matrix spike.

- 50/50 Sodium Sulfate/Magnesium Sulfate
- If multiple vessels needed, divide surrogate evenly among all vessels.

Figure 1 - Separatory Funnel Extraction



18.2.1 Figure 2 - Continuous Liquid/Liquid Extraction

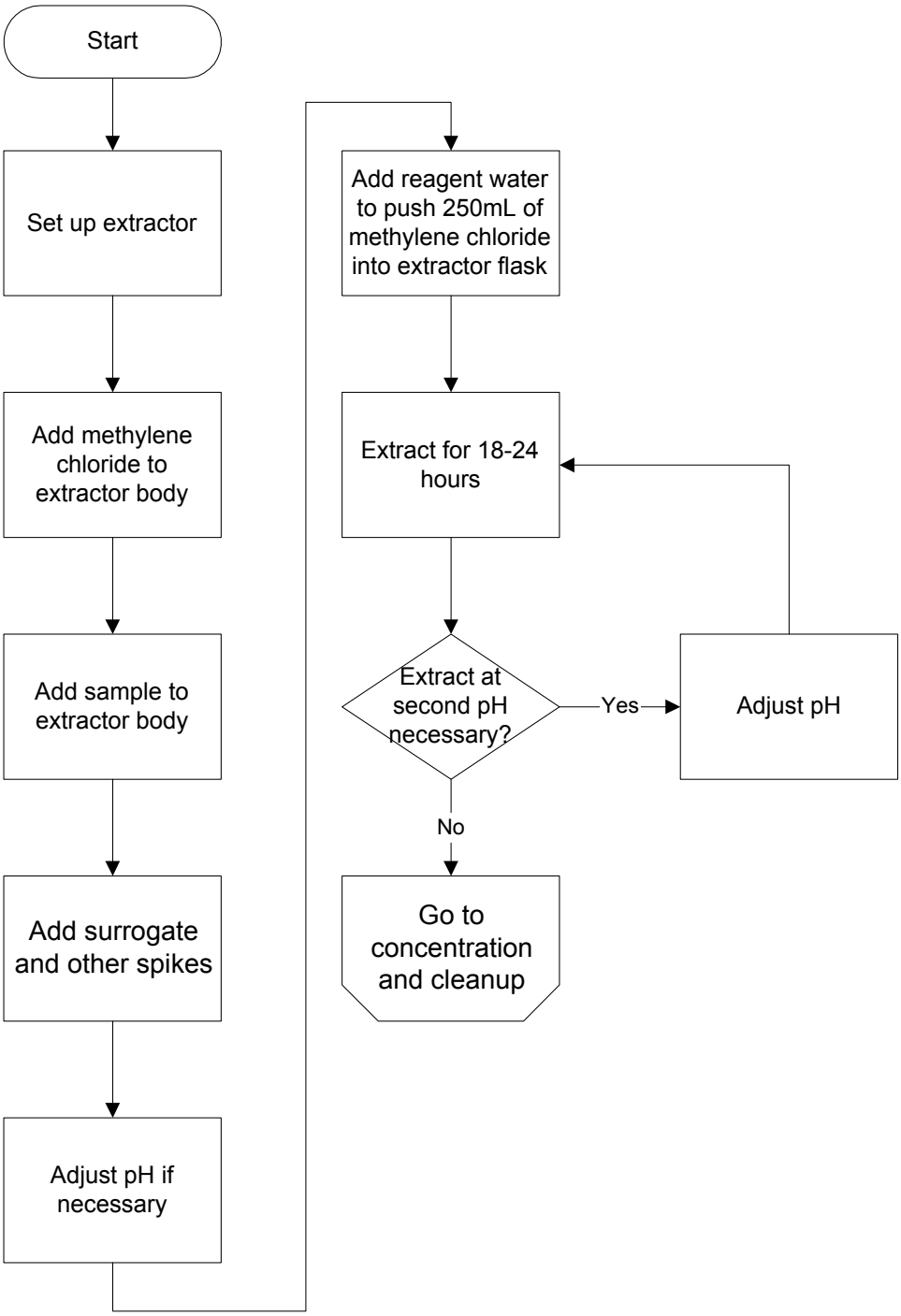
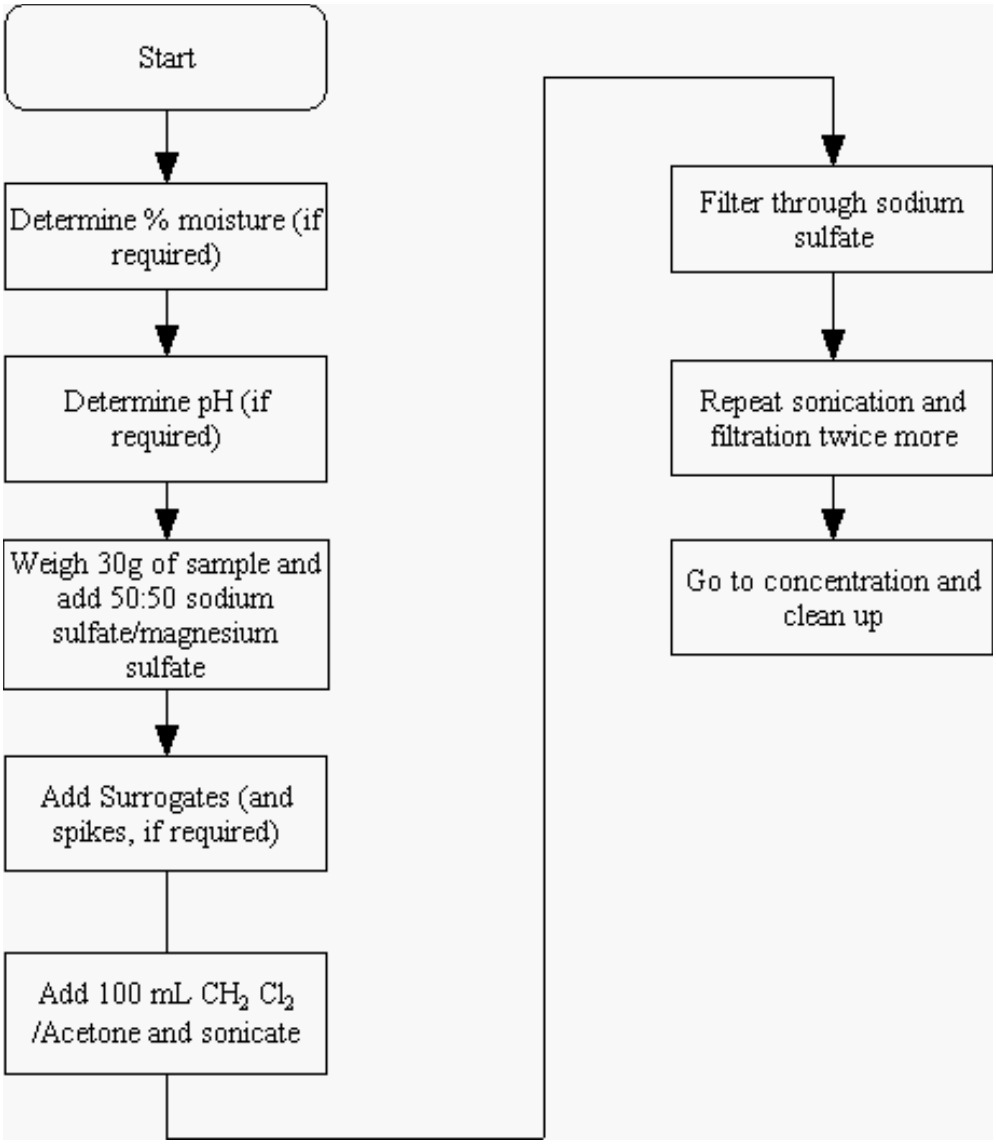
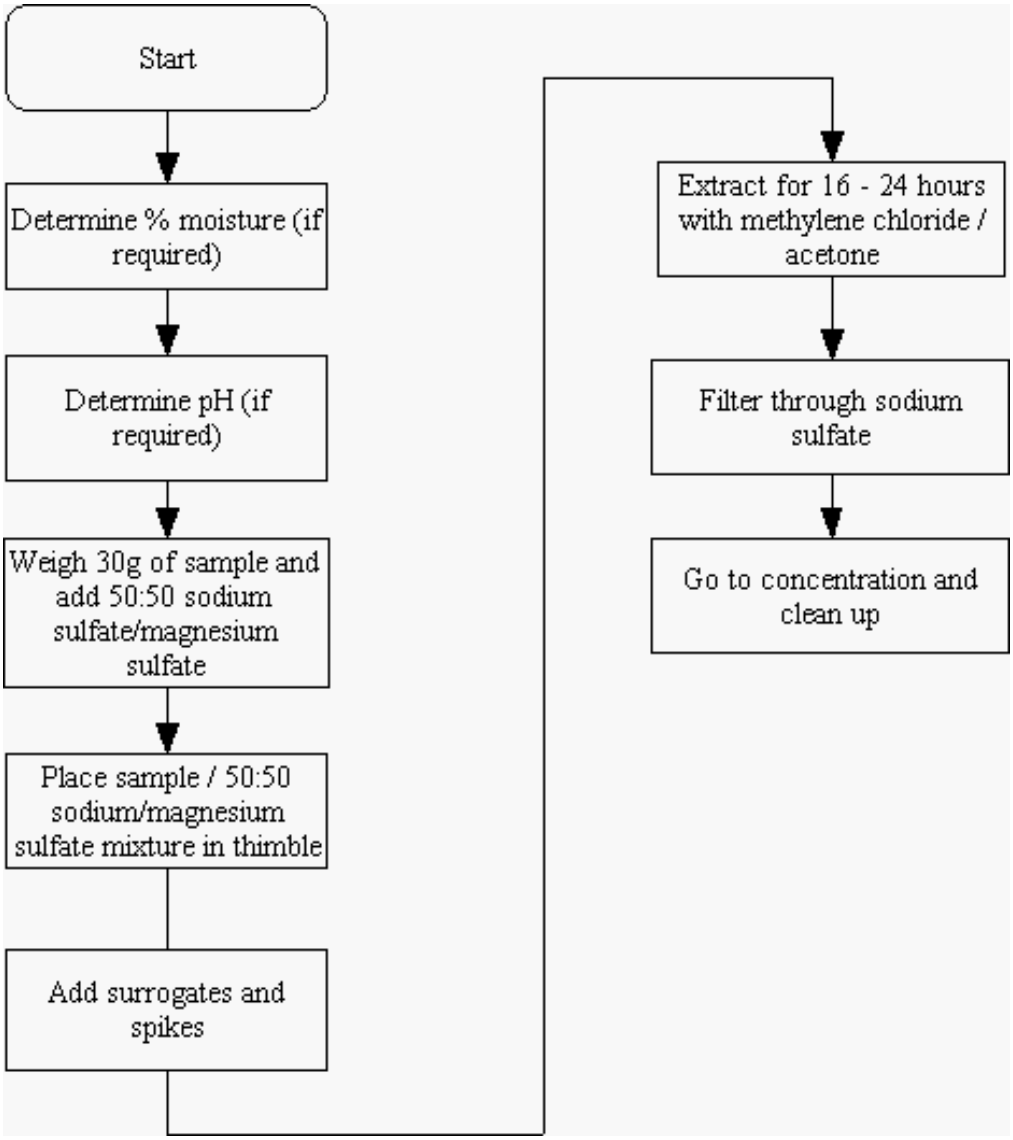


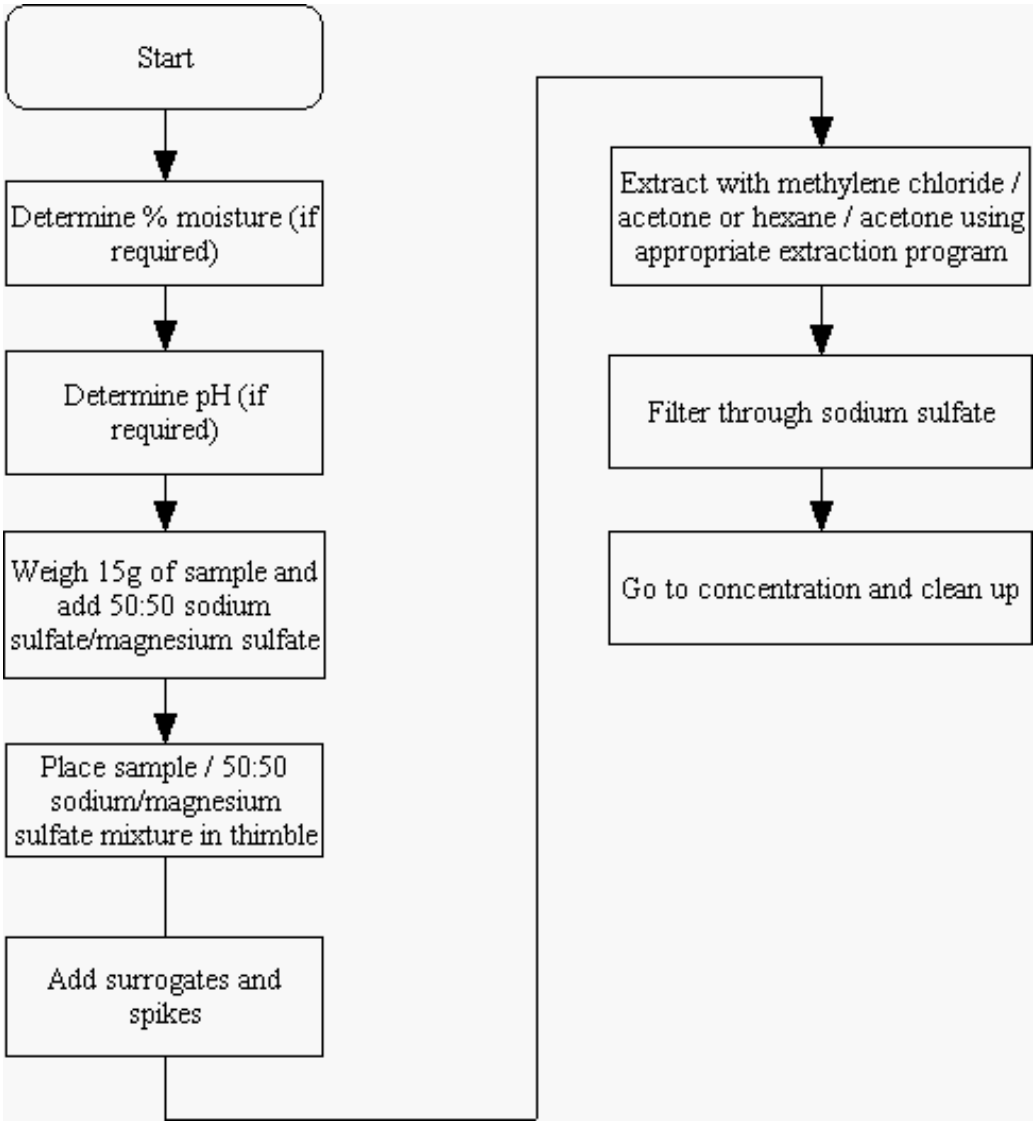
Figure 3 - Sonication Extraction



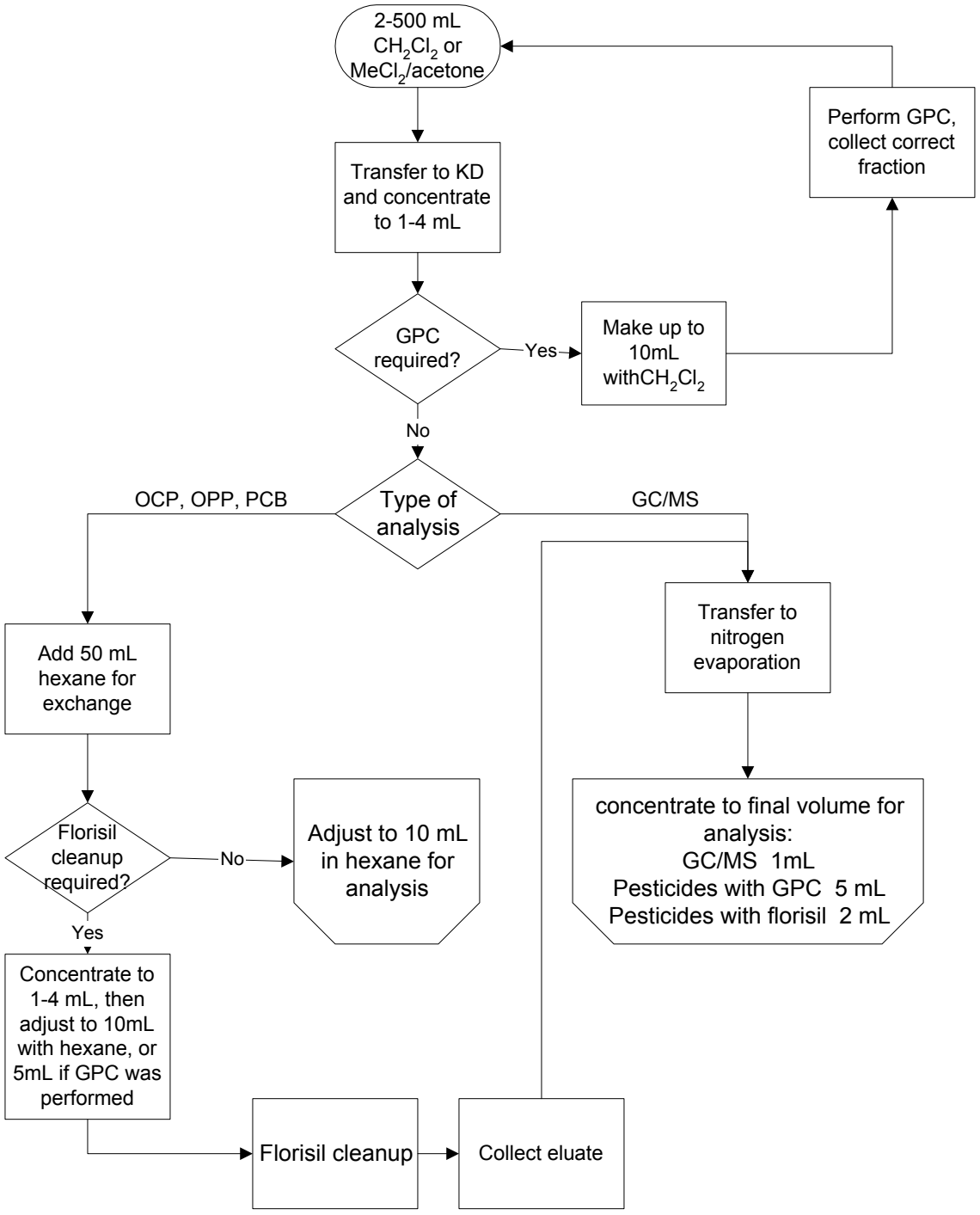
18.2.2 Figure 4 - Soxhlet Extraction



18.2.3 Figure 5 - Accelerated Soxhlet Extraction (Soxtherm®)



18.2.4 Figure 6 - Concentration and Cleanup



Appendix A – Herbicides by Method 8151A

19 SCOPE AND APPLICATION

This method is applicable to the extraction of chlorinated herbicides in waters, solids, oils, and TCLP extracts. Appropriate compounds for extraction by this method are listed in PT-GC-001, Gas Chromatography of Phenoxy Acid Herbicides based on Method 8151A.

20 SUMMARY OF METHOD

This method is based on SW846 method 8151A. Aqueous samples are hydrolyzed if esters and acids are to be determined, then washed with methylene chloride by a separatory funnel extraction. After acidifying the sample the free acids are extracted into diethyl ether. Solids are extracted into methylene chloride/ acetone by sonication. If esters and acids are to be determined, the extract is hydrolyzed and extracted into diethyl ether. For both soils and aqueous samples, the free acid herbicides in the ether extract are esterified. The final volume is adjusted to prepare the extract for gas chromatography.

21 DEFINITIONS

Refer to Section 3 of the main body of this SOP.

22 INTERFERENCES

Refer to Section 4 of the main body of this SOP.

23 SAFETY

23.1 Refer to Section 5 of the main body this SOP for basic safety information.

23.2 Diethyl ether is extremely flammable. It also tends to form peroxides when exposed to air. The peroxides can present an explosion hazard, especially when the ether is concentrated.

23.3 Diethyl ether must be free of peroxides as demonstrated by EM (or equivalent) Quant test strips. This test can be done every time the ether is used or once per week if the bottle is marked with the test date(s).

23.4 Concentrated potassium hydroxide solution is highly caustic.

24 EQUIPMENT AND SUPPLIES

24.1 Refer to Section 6 of the main body of this SOP for basic extraction equipment and supplies. Additional equipment and supplies needed for this procedure are listed below.

24.2 EM Peroxide test strips

25 REAGENTS AND STANDARDS

Reagents are listed in Section 7 of the main body of this SOP. Additional Reagents and standards needed for this procedure are listed below.

25.1 Derivitization of the stock standard must be documented in the extraction log and forwarded to the GC Department.

25.2 Reagents

25.2.1 Potassium hydroxide solution, 37% aqueous solution, (w/v): Dissolve 37 g of potassium hydroxide pellets in reagent water and dilute to 100 mL. **Caution:** Considerable heat will be generated. Other volumes of solution may be made up as convenient.

25.2.2 Sodium hydroxide solution, 6N. Dissolve 400 g NaOH in reagent water and dilute to 1.0L. **Caution:** Considerable heat will be generated. Other volumes of solution may be made up as convenient.

25.2.3 Sodium hydroxide solution, 0.1N. Dissolve 4g NaOH in reagent water and dilute to 1.0L. Other volumes of solution may be made up as convenient.

25.2.4 Sulfuric acid, 1:1 Slowly add 500 mL concentrated sulfuric acid to 500 mL water. **Caution:** Considerable heat will be generated. The acid must be added to the water. Wear protective clothing and safety glasses. Other volumes of solution may be made up as convenient.

25.2.5 Sodium sulfate, Na_2SO_4, Anhydrous, granular, acidified: Heat sodium sulfate in a shallow tray at 400°C for a minimum of 4 hours to remove phthalates and other interfering organic substances. In a large beaker, acidify by slurrying 1000 g sodium sulfate with just enough diethyl ether to cover. Add 2-5 mL of concentrated sulfuric acid and mix thoroughly. Place the mixture on a steam bath in a hood to evaporate the ether, or allow the ether to evaporate overnight. Larger or smaller batches of acidified sodium sulfate may be prepared using the reagents in the same proportions.

25.2.6 Sodium Chloride, NaCl

25.2.7 Acidified 5% sodium sulfate solution

Add 50 g of sodium sulfate to one liter of reagent water. Add 10 mL of concentrated H_2SO_4. (This reagent may be prepared in different quantities if the proportions are kept the same).

25.2.8 Diethyl ether, reagent grade.

25.2.9 Trimethylsilyldiazomethane solution (Aldrich 36,283-2)- 2.0M in hexanes (CAS # 18107-18-1).

25.2.10 Methanol, reagent grade.

25.2.11 Silicic acid

25.3 Standards

25.3.1 Surrogate Standard

See Table A3.

25.3.2 Matrix Spike and LCS standard

See Table A4.

26 SAMPLE COLLECTION PRESERVATION, SHIPMENT AND STORAGE

26.1 Sample collection and storage is described in Section 8 of the main body of this SOP.

27 QUALITY CONTROL

27.1 Refer to Section 9 of the main body of this SOP for Quality Control procedures.

28 PROCEDURE

28.1 Preparation of Aqueous Samples

28.1.1 The glassware must be acid washed prior to use to avoid alkaline reacting with acid herbicides. Mark the meniscus on the 1 liter sample bottle. Pour the entire contents into a 2 liter separatory funnel. The sample volume is determined by filling the sample bottle with reagent water up to the meniscus and measuring the volume in a graduated cylinder (note, this is done after the bottle is rinsed with solvent). Record to the nearest 10 mL. TCLP leachates, measure 100 mL of sample in a graduated cylinder and pour into the 2 liter separatory funnel (add reagent water to bring up to approximately 1 liter).

28.1.2 Spike each sample blank, LCS and MS with 1.0 mL of DCAA surrogate solution. Spike matrix spikes and LCS with 1 mL of herbicide matrix spiking solution. (Refer to Tables A1 and A2)

28.1.3 Add 250 g of NaCl to the sample and shake to dissolve the salt.

28.1.4 Hydrolysis

Use this step only if herbicide esters in addition to herbicide acids are to be determined. This is normally the case. If the herbicide esters are not to be determined, omit this step and go to 28.1.10.

Add 17 mL of 6N NaOH to the sample, seal and shake. Check the pH of the sample with pH paper. If the pH of the sample is not $\geq$12 adjust to $\geq$12 by adding more NaOH. Let the sample sit at room temperature for 2 hours to complete the hydrolysis.

28.1.5 Add 60 mL of methylene chloride to the sample bottle or graduated cylinder (TCLP samples). Rinse the bottle or graduated cylinder and add the methylene chloride to the separatory funnel.

28.1.6 Extract the sample by shaking or rotating vigorously for 2 minutes, venting as necessary. (An automatic shaker may be used). Allow the organic layer to separate from the aqueous layer. If an emulsion layer greater than one third of the solvent layer forms, use mechanical techniques to complete the phase separation. Suggested techniques are stirring, filtration through glass wool and centrifugation.

28.1.7 Discard the **methylene chloride** phase.

28.1.8 Add a second 60 mL of methylene chloride and repeat the extraction a second time, discarding the methylene chloride. Repeat the extraction a third time.

28.1.9 Add 17 mL of cold (4°C) 1:1 sulfuric acid to the sample. Seal, and shake to mix. Check the pH of the sample with pH paper. If the pH is not $\leq$ 2, add more acid to adjust the pH to $\leq$ 2.

Caution: Addition of acid may cause heat and / or pressure build up.

28.1.10 Add 120 mL diethyl ether to the sample and extract by shaking or rotating vigorously for 2 minutes, venting as necessary. (An automatic shaker may be used). Allow the organic layer to separate from the aqueous layer. If a emulsion layer greater than one third of the solvent layer forms, use mechanical techniques to complete the phase separation. Suggested techniques are stirring, filtration through glass wool and centrifugation.

28.1.11 Drain the aqueous layer into a clean flask or beaker. Collect the ether phase in a clean flask or bottle containing approximately 10g of acidified anhydrous sodium sulfate.

28.1.12 Return the aqueous phase to the separatory funnel, add 60 mL diethyl ether and repeat the extraction procedure a second time, combining the ether extracts. Repeat the extraction a third time with 60 mL diethyl ether. Discard the aqueous phase after the third extraction.

28.1.13 Allow the extract to remain in contact with the sodium sulfate for at least 2 hours, shaking periodically. (May be left overnight). The drying step is critical: if the sodium sulfate solidifies in a cake, add a few additional grams of acidified sodium sulfate. The amount of sodium sulfate is sufficient if some free flowing crystals are visible when the flask or bottle is swirled or shaken.

28.1.14 Proceed to Section 28.6; Concentration.

28.2 Extraction of Waste Samples

28.2.1 The glassware must be acid washed prior to use to avoid alkaline reacting with acid herbicides. Follow the Waste Dilution procedure in Section 11.7 of this SOP with the following exceptions:

- Use diethyl ether as the extraction solvent
- Use acidified sodium sulfate and acidified glasswool

- Spike 1.0 mL of the surrogate solution to all samples and 1.0 mL of the matrix spike solution to the MS, MSD, and LCS (see Tables A1 and A2 for details).

28.2.2 Transfer 1.0 ml of the extract to a 250 mL Erlenmyer flask with a ground glass joint at the neck. Proceed to Section 28.3.14.

28.3 Extraction of soil and sediment samples

28.3.1 The glassware must be acid washed prior to use to avoid alkaline reacting with acid herbicides. Decant and discard any water layer on a sediment/soil sample. Homogenize the sample by mixing thoroughly. Discard any foreign objects such as sticks, leaves and rocks, unless extraction of this material is required by the client. If the sample consists primarily of foreign materials consult with the client (via the Project Manager or Administrator). Document if a water layer was discarded.

28.3.2 Weigh 50.0 g of moist solid sample into a clean glass jar. Use 50 g of sodium sulfate for the Method Blank and the LCS. Acidify the sample with 5 mL of concentrated HCl.

28.3.3 There should be a small amount of liquid phase. If not, add reagent water until there is. Stir well with a spatula. (Note: This is not necessary for the method blank or LCS)

28.3.4 After 15 minutes, stir with a spatula and check the pH of the liquid phase. Add more acid if necessary to bring the pH to <2, repeating the stirring and standing time after each acid addition. (Note: The pH of the method blank and LCS are not determined.)

28.3.5 Add 60 g of acidified sodium sulfate and mix well. The sample should be free flowing. If not, add more sodium sulfate.

28.3.6 Spike each sample blank, LCS and MS with 1.0 mL of DCAA surrogate solution. Spike matrix spikes and LCS with 1 mL of herbicide matrix spiking solution. (Refer to Tables A1 and A2)

28.3.7 Add a minimum of 100 mL of 1:1 methylene chloride:acetone to the beaker.

28.3.8 Place the bottom surface of the appropriate disrupter horn tip approximately ½ inch below the surface of the solvent, but above the sediment layer.

28.3.9 Sonicate for 3 minutes, making sure the entire sample is agitated. If the W-380 or W-385 sonicator is used the output should be set at 6 for the 3/4 inch high gain (Q) horn or 10 for the 3/4 inch standard horn with mode switch on pulse, and percent-duty cycle knob set at 50%.

28.3.10 Loosely plug the stem of a 75 mm x 75 mm glass funnel with glass wool and/or line the funnel with filter paper. Add 10-20 g of anhydrous sodium sulfate to the funnel cup.

28.3.11 Place the prepared funnel on a collection apparatus. If the herbicide esters are *not* to be determined, the collection apparatus is a bottle or flask

containing approximately 10g of anhydrous acidified sodium sulfate. If the herbicide esters *are* to be determined, (normally the case) the collection apparatus is glassware suitable for the hydrolysis step, typically a KD flask.

28.3.12 Decant and filter extracts through the prepared funnel into the collection apparatus.

28.3.13 Repeat the extraction two more times with additional 100 mL minimum portions of methylene chloride / acetone each time. Decant off extraction solvent after each sonication. On the final sonication pour the entire sample (sediment and solvent) into the funnel and rinse with an additional 10 mL-20 mL of the methylene chloride/acetone.

Note: Alternatively, the three extracts may be collected together and then filtered through the sodium sulfate.

28.3.14 If the herbicide esters are not to be determined, dry the extract as described in Section 28.5 or go to cleanup, Section 28.4. If the herbicide esters are to be determined (normally the case) proceed to Section 28.3.15.

28.3.15 Add 5 mL of 37% aqueous potassium hydroxide and 30 mL of water to the extract. Check the pH with pH paper. If the pH is not $\geq$12, adjust with additional KOH.

28.3.16 Heat on a water bath at 60-65^{o}C for 2 hours. Allow to cool. Higher temperatures, up to 90^{o}C, may be used if needed to remove the ether layer within 2 hours.

28.3.17 Transfer the solution to a separatory funnel and extract three times with 100 mL portions of methylene chloride. **Discard the methylene chloride phase.** The aqueous solution contains the herbicides.

28.3.18 Adjust the pH of the solution to $\leq$ 2 with 1:1 sulfuric acid.

28.3.19 Extract once with 40 mL diethyl ether and twice with 20 mL diethyl ether.

28.3.20 Proceed to Section 28.4, Cleanup, if required, or Section 28.5, Extract drying.

28.4 Cleanup

This cleanup step may be necessary if the procedure for determining the herbicide acids only is being followed. (See Section 28.3.14) It is not normally required if the acids and esters are being determined (the usual case). If cleanup is not required, proceed to Section 28.5, Extract drying.

28.4.1 Prepare 45 mL of basic extraction fluid by mixing 30 mL of reagent water with 15 mL of 37% KOH. Use three 15 mL portions of this fluid to partition the extract from Section 28.3.14 or 28.3.20, using a small separatory funnel. **Discard the organic phase.**

28.4.2 Adjust the pH of the solution to $\leq$ 2 with cold (4^{o}C) sulfuric acid. (1:1). Extract once with 40 mL diethyl ether and twice with 20 mL diethyl ether.

Caution: Addition of acid may cause heat and / or pressure build up.

28.5 Extract drying

28.5.1 Combine the extracts and pour through a funnel containing acidified sodium sulfate into a flask or bottle containing approximately 10 g acidified sodium sulfate. Rinse the funnel with a little extra diethyl ether.

28.5.2 Allow the extract to remain in contact with the sodium sulfate for at least 2 hours, shaking periodically (may be left overnight). The drying step is critical: if the sodium sulfate solidifies in a cake, add a few additional grams of acidified sodium sulfate. The amount of sodium sulfate is sufficient if some free flowing crystals are visible when the flask or bottle is swirled or shaken. Proceed to Section 28.6, concentration.

28.6 Concentration

28.6.1 Transfer the ether extract by decanting, or through a funnel plugged with acid washed glass wool, into a 500 mL K-D flask equipped with a 10 mL concentrator tube. Use a stirring rod to crush the caked sodium sulfate during transfer. Rinse the flask or bottle with 20-30 mL ether to complete transfer.

28.6.2 Attach a three ball Snyder column to the K-D apparatus, pre-wet the column with a few mL of ether from the top, and place the apparatus on a water bath at approximately 60°C, not to exceed 65 °C. At the proper rate of distillation, the balls of the column will chatter, but the chambers will not flood. When the apparent volume reaches 15-20 mL, remove from the water bath and allow to completely cool. Add 20 mL of hexane and concentrate to 10 mL on the water bath. Then pour the sample into a centrifuge tube, blow down to 2 ml on the nitrogen bath.

28.6.3 The extract is now ready for esterification by the trimethylsilyldiazomethane solution method (28.7).

28.7 Esterification (trimethylsilyldiazomethane solution method)

28.7.1 To the extract (hexane), add 200 uL of methanol.

28.7.2 Add 100 uL of the Trimethylsilyldiazomethane solution.

28.7.2.1 The extract should turn a yellow color. If this does not occur, add an additional 100 uL of the trimethylsilyldiazomethane solution until the yellow color persists.

28.7.3 Allow the extract to sit for 1 hour at room temperature.

28.7.4 Add approximately 0.2 g of silicic acid to each extract. Allow to stand for an additional 20 minutes.

28.7.5 Adjust the volume to 10 mL with hexane. The sample is now ready for gas chromatography.

29 CALCULATIONS / DATA REDUCTION

Not applicable.

30 METHOD PERFORMANCE

Refer to the SOP PT-GC-001, Appendix D, for details of method performance.

31 POLLUTION CONTROL

Refer to Section 14 of the main body of this SOP.

32 WASTE MANAGEMENT

Refer to Section 15 of the main body of this SOP.

33 REFERENCES

33.1 SW-846, Test Methods for Evaluating Solid Waste, Third Edition, Update III, December 1996, Chlorinated Herbicides, Method 8151A.

33.2 PITT-QA-DoD-0001, Implementation of the DoD QSM Versions 3, January 2006.

34 ATTACHMENTS

34.1 Table A1 – Herbicide Surrogate Spiking Solutions

34.2 Table A2 – Herbicide Matrix Spike and LCS Solutions

34.3 Table A3 – Herbicide Surrogate Spike Components

34.4 Table A4 – Herbicide Matrix Spike Components

34.5 Figure A1 – Extraction of Aqueous Samples

34.6 Figure A2 – Extraction of Soils and Sediments

34.7 Figure A3 – Drying, Concentration and Esterification

35 REVISION HISTORY

35.1 Revision 9, 02/01/07

35.1.1 Removed the unused diazomethane solution procedure for esterification and added the trimethylsilyldiazomethane solution esterification method.

35.1.2 Added waste extraction procedure.

35.1.3 Several clarifications have been made.

35.1.4 Removed bubbler method.

35.2 Revision 10, 09/24/07

35.2.1 Added the requirement to document the derivitization of the stock standard in the extraction log and forward to the GC Department.

36 METHOD MODIFICATIONS

36.1 Directions to add sufficient reagent water to the soil sample so that the pH can be measured have been added (Section 28.2.3)

Table A1 Herbicide Surrogate Spiking Solutions		
Analyte Group	**Surrogate Spike Solution ID**	**Volume (mL)**
Chlorinated Acid Herbicides	Herbicides SS	1.0

Table A2 Herbicide Matrix Spike and LCS Solutions		
Analyte Group	**Matrix Spike Solution ID**	**Volume (mL)**
Chlorinated Acid Herbicides	Herbicides MS	1.0

Table A3 Herbicide Surrogate Spike Components			
Type	**Compounds[6]**	**Solvent**	**Conc. (ug/mL)**
Herbicides SS	2,4-DCAA	Methanol	10

Table A4 Herbicide Matrix Spike Components			
Type	**Compounds[7]**	**Solvent**	**Conc. (ug/mL)**
Herbicides MS	See SOP PT-GC-001	Methanol	See SOP PT-GC-001

[6] The surrogate is spiked as the free acid.

[7] The herbicide spiking solution contains the herbicides as the free acids.

Figure A1 – Extraction of Aqueous Samples

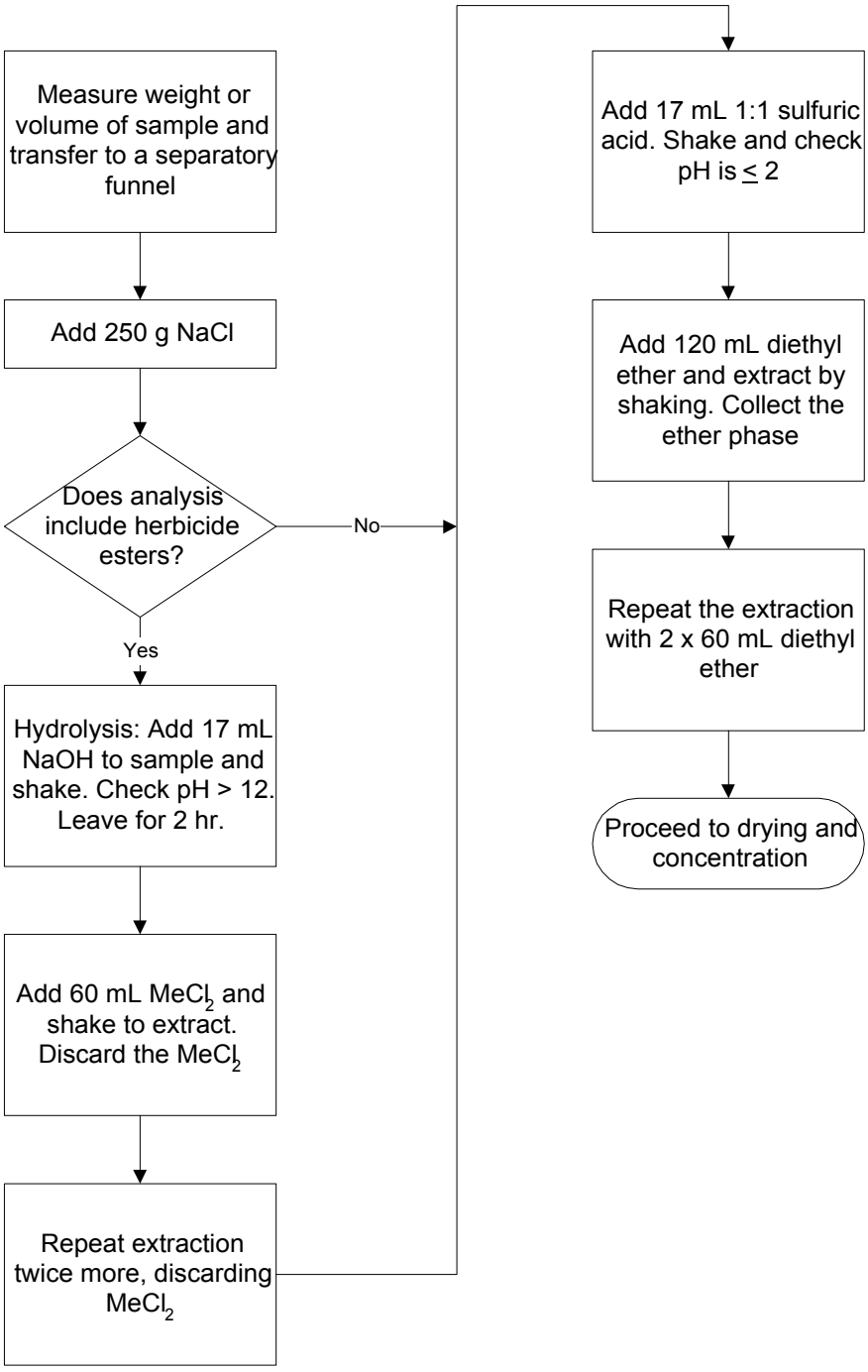


Figure A2 – Extraction of Soils and Sediments

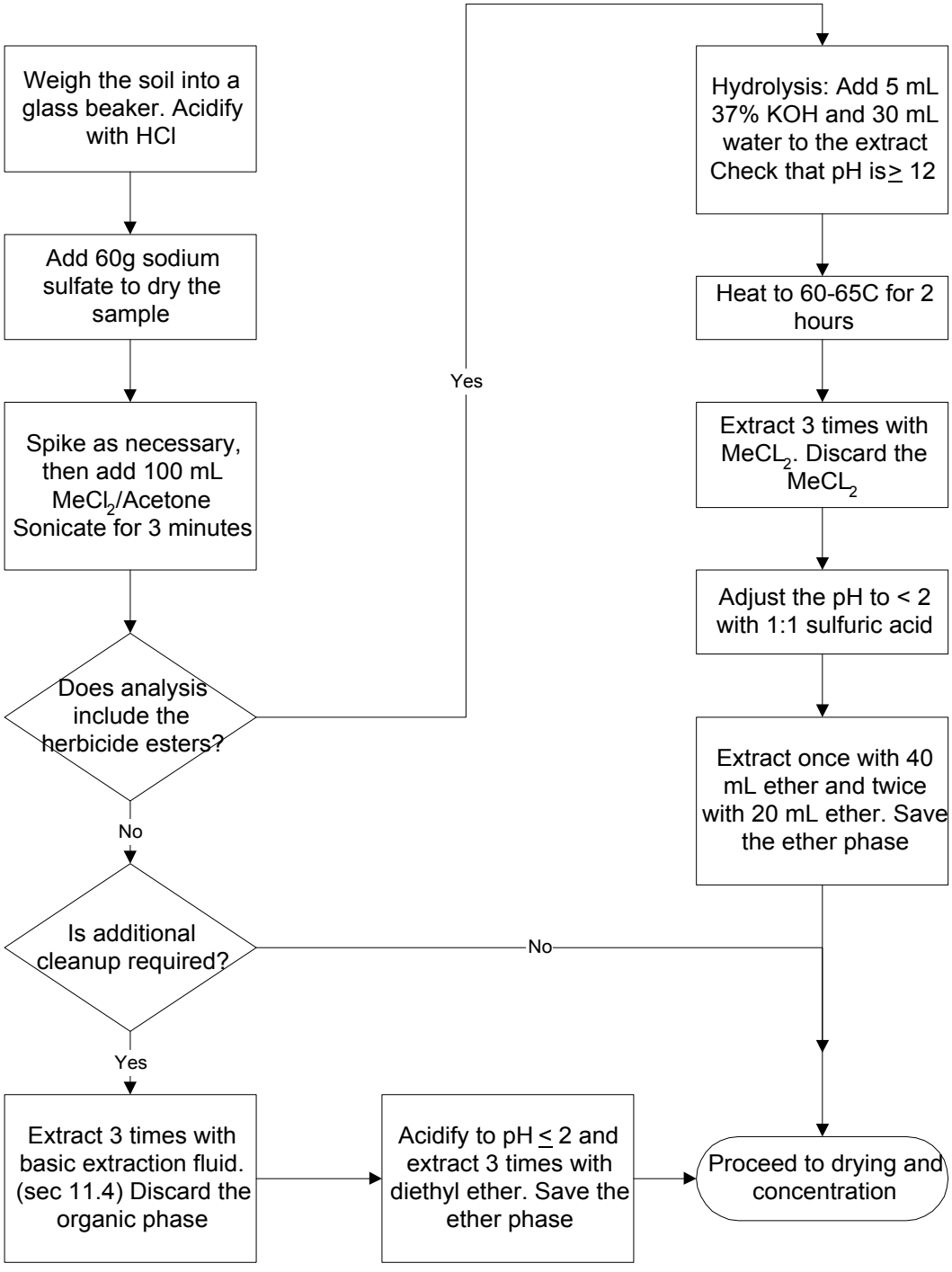
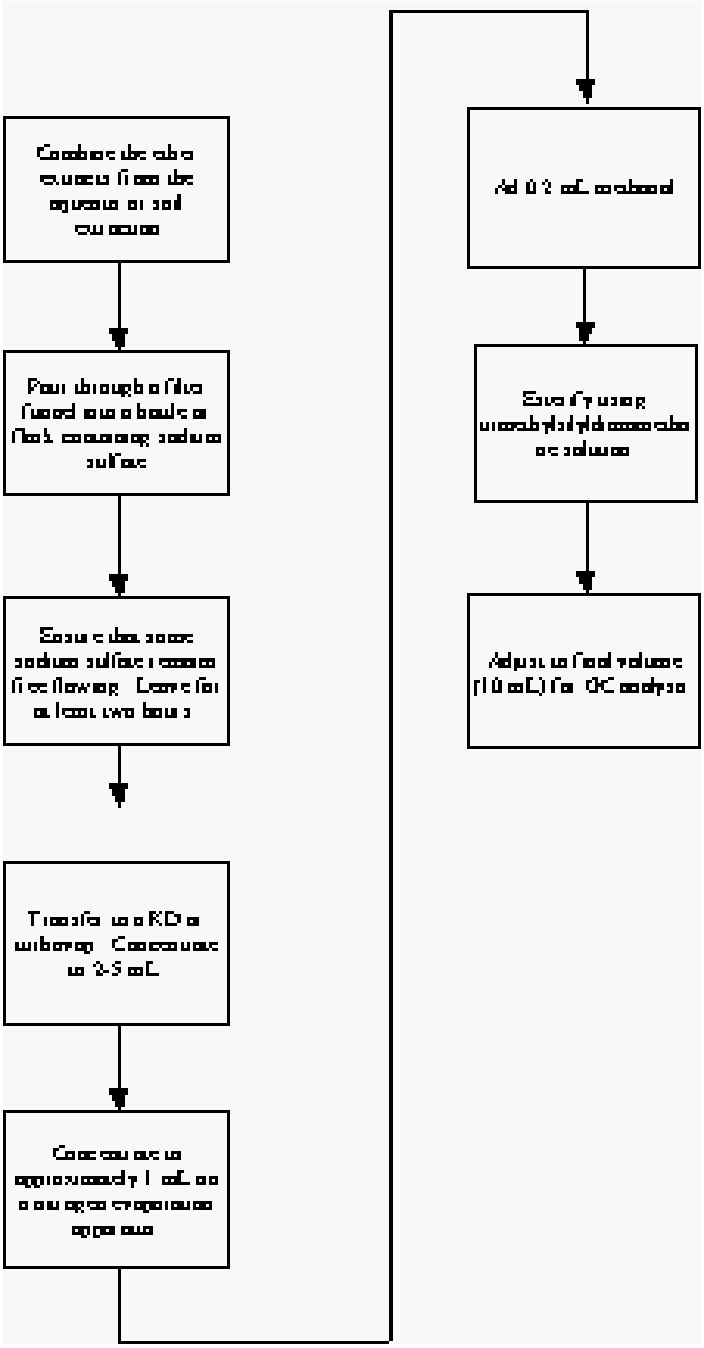


Figure A3 – Drying, Concentration and Esterification



APPENDIX 44
SOP FOR THE DETERMINATION OF MERCURY BY EPA 1631 (NC_MT_0001)

Controlled Copy
Copy No. _____

Implementation Date: 8/12/07

SOP No. NC-MT-0001
Revision No. 5.1
Revision Date: 07/29/07
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TESTAMERICA NORTH CANTON STANDARD OPERATING PROCEDURE

TITLE: PREPARATION AND ANALYSIS OF MERCURY IN AQUEOUS AND SOLID SAMPLES BY COLD VAPOR ATOMIC FLUORESCENCE, METHODS 1631E AND MCAWW 245.7

(SUPERSEDES: REVISION 5, REVISION DATE 01/17/05)

Approved by: Roger K. Scott — Technical Specialist — 8/7/07 Date

Approved by: Dorothy J. Reeson — Quality Assurance Manager — 8/12/07 Date

Approved by: _____ — Environmental, Health and Safety Coordinator — 8/8/07 Date

Approved by: _____ — Laboratory Director — 8/8/07 Date

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TABLE OF CONTENTS

LIST OF APPENDICES:

1. SCOPE AND APPLICATION

1.1. This procedure describes the preparation and analysis of mercury (Hg, CAS # 7439-97-6) by Cold Vapor Atomic Fluorescence Spectroscopy (CVAFS) using Method 1631E and MCAWW Method 245.7.

1.2. The associated LIMs method codes are PR (Method 1631E) and D5 (Method 245.7). The sample preparation code for all methods is D4 (BrCl Oxidation).

1.3. CVAFS analysis provides for the determination of total mercury (organic and inorganic). The oxidant, bromine monochloride has been found to give quantitative recovery with both types of compounds. Detection limits, sensitivity and optimum concentration ranges for mercury analysis will vary with the matrices, instrumentation and volume of sample used.

1.4. Method1631E (hereafter abbreviated to Method 1631 in this SOP) is applicable to the preparation and analysis of mercury in ground water, surface water, effluents and other aqueous samples. Appendix A to Method 1631 is applicable to the preparation and analysis of mercury in sediments, soils, biological media and other solid samples.All matrices require sample preparation prior to analysis.

1.5. Method 245.7 is applicable to the determination of mercury in drinking, surface and saline waters and domestic and industrial wastes. All matrices require sample preparation prior to analysis.

1.6. The TestAmerica North Canton reporting limit for mercury in aqueous matrices is 0.5 ng/L by Method 1631, and 5 ng/L by Method 245.7. The reporting limit for mercury by Method 1631 in solid matrices is 1.0 ug/kg.

2. SUMMARY OF METHOD

2.1. This SOP describes a technique for the determination of mercury in solids and aqueous solutions. The procedure is a physical method based on the absorption of radiation at 253.7 nm by mercury vapor and fluorescence at 253.7 nm. For aqueous samples, a representative portion of the sample is digested and oxidized in bromine monochloride. For solid samples, 1 gram of sample is digested with cold aqua regia, diluted, and further oxidized with bromine monochloride Excess free halogens in the digestate are then reduced with hydroxylamine hydrochloride. The mercury (+2) is reduced to its elemental state with stannous chloride and purged from solution with argon in a gas / liquid separator. For Method 1631, the mercury vapor is collected on a gold trap and then thermally desorbed to the detector. For Method 245.7, the mercury vapor is transported directly from the gas /

liquid separator to the detector. The mercury vapor passes through a cell positioned in the light path of an atomic fluorescence spectrophotometer. Fluorescence is measured as a function of mercury concentration. Concentration of the analyte in the sample is determined by comparison of the sample fluorescence to the calibration curve (fluorescence vs. concentration).

3. DEFINITIONS

3.1. Dissolved Metals: Those elements which pass through a 0.45 um membrane and are oxidized by bromine monochloride. (Sample is preserved after filtration).

3.2. Suspended Metals: Those elements which are retained by a 0.45 um membrane.

3.3. Total Metals: The concentration determined on an unfiltered sample following digestion and oxidation.

4. INTERFERENCES

Chemical and physical interferences may be encountered when analyzing samples using this method.

4.1. Gold, silver and iodide are known interferences. At mercury a concentration of 2.5 ng/L and at increasing iodide concentrations from 30 to 100 mg/L, test data have shown that mercury recovery will be reduced from 100 to 0 percent.

4.2. The use of a brominating digestion coupled with atomic fluorescence detection overcomes many of the chloride, sulfide and molecular absorbance interferences. No interferences have been noted for sulfide concentrations below 24 mg/L.

4.3. Water vapor may collect in the gold traps (Method 1631), and subsequently condense in the fluorescence cell upon desorption, giving a false peak due to scattering of the excitation radiation. Condensation can be avoided by predrying the gold trap and by discarding those traps that tend to absorb large quantities of water.

4.4. The fluorescent intensity is strongly dependent upon the presence of molecular species in the carrier gas that can cause *quenching* of the excited atoms.

4.5. The most common interference is laboratory contamination, which may arise from impure reagents, dirty glassware, improper sample transfers, dirty work areas, etc. Be aware of potential sources of contamination and take appropriate measures to minimize or avoid them. The analytical instrument and sample / standards preparation area should be protected from mercury vapor or particulates in the laboratory air. Samples, standards and

blanks should only be opened in a clean area. Gloves must be powder free and should be checked for mercury contamination. Do not use powdered nitrile gloves as they have been shown to have either low level mercury contamination or interferences. Only clean gloves should touch the instrument and other equipment used to process blanks, standards and samples.

4.6. Samples known to contain mercury concentrations greater than 200 ng/L should be diluted prior to bringing them into the clean work area dedicated to processing low level mercury samples.

5. SAFETY

5.1. Employees must abide by the policies and procedures in the Corporate Safety Manual and this document.

5.2. The following is a list of the materials used in this method, which have a serious or significant hazard rating. **NOTE: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Hydrochloric Acid	Corrosive Poison	5 ppm-Ceiling	Inhalation of vapors can cause coughing, choking, inflammation of the nose, throat, and upper respiratory tract, and in severe cases, pulmonary edema, circulatory failure, and death. Can cause redness, pain, and severe skin burns. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.

Nitric Acid	Corrosive Oxidizer Poison	2 ppm-TWA 4 ppm-STEL	Nitric acid is extremely hazardous; it is corrosive, reactive, an oxidizer, and a poison. Inhalation of vapors can cause breathing difficulties and lead to pneumonia and pulmonary edema, which may be fatal. Other symptoms may include coughing, choking, and irritation of the nose, throat, and respiratory tract. Can cause redness, pain, and severe skin burns. Concentrated solutions cause deep ulcers and stain skin a yellow or yellow-brown color. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
Bromine Monochloride	Corrosive Poison Oxidizer	0.1 (Br) ppm TWA	May be fatal if inhaled. Causes severe eye and skin burns. Causes damage to the following organs: Lungs, mucous membranes, respiratory tract, skin, central nervous system, eyes, lens or cornea.
Potassium Bromate	Oxidizer	0.1 Mg/M3 TWA	Irritates respiratory tract. May causecoughing and shortness of breath. Causes irritation to the skin. May cause redness, itching, and pain. In the presence of liquids, it is slowly absorbed in toxic amounts. Prolonged exposure may cause burns. Causes irritation to eyes with redness, pain. May cause eye damage.
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

5.3. Mercury is a highly toxic element that must be handled with care. The analyst must be aware of the handling and clean up techniques before working with mercury. Since mercury vapor is toxic, precaution must be taken to avoid its inhalation, ingestion or absorption through skin. All lines should be checked for leakage and the mercury vapor must be vented into a hood or passed through a mercury absorbing media such as a carbon filter.

5.4. Eye protection that protects against splash, laboratory coat, and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled. Cut resistant gloves must be worn doing any other task that presents a strong possibility of getting cut. Disposable gloves that have been contaminated will be removed and discarded; other gloves will be cleaned immediately.

5.5. Exposure to hazardous chemicals must be maintained **as low as reasonably achievable.** Therefore, unless they are known to be non-hazardous, all samples should be opened, transferred and prepared in a fume hood, or under other means of mechanical ventilation, where possible. All samples with stickers that read "Caution/Use Hood!" **must** be opened in the hood. Contact the EH&S Coordinator if this is not possible. Solvent and waste containers will be kept closed unless transfers are being made.

5.6. All work must be stopped in the event of a known or potential compromise to the health and safety of a TestAmerica North Canton associate. The situation must be reported **immediately** to the EH&S Coordinator and to a laboratory supervisor.

5.7. Do not look directly into the beam of the Hg lamp. The UV light that these lamps radiate is harmful to the eyes.

5.8. Cylinders of compressed gas must be handled with caution, in accordance with local regulations. It is recommended that, wherever possible, cylinders are located outside the laboratory and the gas led to the instrument through approved lines.

5.9. The CVAFS apparatus must be properly vented to remove potentially harmful fumes generated during sample analysis.

6. EQUIPMENT AND SUPPLIES

6.1. Atomic Fluorescence Spectrophotometer equipped with:

6.1.1. Fluorescence Cell with quartz ends. Dimensions of the cell must result in sufficient sensitivity to meet the SOP defined reporting limit. The quartz windows must be maintained to provide accurate measurements. Any scratches or fingerprints can alter the absorption of UV radiation.

6.1.2. Mercury specific hollow cathode lamp (HCL) or electrodeless discharge lamp (EDL).

6.1.3. Peristaltic pump.

6.1.4. Flowmeter.

6.1.5. Recorder or Printer.

6.1.6. Gas /Liquid separator:

6.1.7. Drying devices: Nafion Dryer (used for all methods), soda lime trap (Method 1631).

6.1.8. Gold traps (2): quartz tube containing gold coated sand.

6.2. Sample bottles, 40 mL borosilicate glass VOC vials, QEC or equivalent, < 0.5 ng/L contamination when used for Method 1631 samples. In actual practice, should contribute less than 0.1 ng/L to facilitate meeting method blank criteria. Unless tested by the manufacturer for cleanliness and accuracy, 12 vials from each lot must be gravimetrically tested at the 40 mL point. Cleanliness is assessed by adding 0.2 mL BrCl (Section 7.15). Store the test vials at room temperature for at least 12 hours and analyze as samples. All vial results must be less than the reporting limit.

6.3. Argon gas supply, high purity, or equivalent. A gold trap may be used in-line to further purify the argon.

6.4. Calibrated automatic pipettes.

6.5. Disposable cups or tubes, low mercury content.

6.6. Starch / iodine paper.

7. REAGENTS AND STANDARDS

7.1. Reagent water must be produced by a US Filter PureLab Plus deionized water system or equivalent. Reagent water must be free of mercury and interferences as demonstrated through the analysis of reagent and method blanks.

7.2. Stock (10 mg/L) mercury standards (in 5-10% HNO_3) are purchased. All standards must be stored in FEP fluorocarbon or previously unused polyethylene or polypropylene bottles. Stock standard solutions must be replaced prior to the expiration date provided by the manufacturer. If no expiration date is provided, the stock solutions may be used for up to one year and must be replaced sooner if verification from an independent source indicates a problem.

7.3. Intermediate mercury standard (10 µg/L): Fill a 100 mL volumetric flask about half full with reagent water. Add 0.5 mL of BrCl solution (Section 7.15). Add 0.10 mL of the stock mercury standard (Section 7.2) and dilute to 100 mL with reagent water. The intermediate mercury standard should be replaced every 9 months.

7.4. Working mercury standard (1 µg/L): Fill a 40 mL vial about half full with reagent water.

Add 0.2 mL of BrCl solution (Section 7.15). Add 4.0 mL of the intermediate mercury standard (Section 7.3) and dilute to 40 mL with reagent water. The working mercury standard should be replaced every 3 months.

7.5. The calibration standards listed in Table I must be prepared fresh daily from the working standard (Section 7.4) by transferring 0, 0.02, 0.04, 0.08, 0.2, 0.4, and 1.0 mL of a mercury standard into 40 mL vials and diluting to volume with reagent water; for Method 1631 use the working standard (Section 7.4), for 245.7 use the intermediate standard (Section 7.3). BrCl (Section 7.15) and $NH_2OH \bullet HCl$ (Section 7.13) reagent solutions are also added.

Note: Alternate approaches to standard preparation may be taken and alternate volumes of standard may be prepared as long as the accuracy and final standard concentrations as detailed in Table I are maintained. For example, some automated mercury systems may not require 40 mL of standard and therefore smaller volumes may be generated to reduce waste generation.

7.6. The initial calibration verification standard (QCS) must be made from a different manufacturer or lot than that of the calibration standards.

7.7. Refer to Table I (Appendix A) for details regarding the working standard concentrations for calibration, calibration verification and spiking solutions. All standards must be processed with all reagents that are used for sample preparation.

7.8. Hydrochloric acid (HCl), concentrated, trace metal grade and ultra trace mercury grade.

Note: Ultra trace mercury HCl (when commercially available) should be used to prepare the bromine monochloride solution. Trace metal grade HCl may be used to prepare the stannous chloride and 2% HCl rinse solutions provided that these solutions are purged with argon prior to use.

7.9. Autosampler rinse solution (2%): 400 mL trace metal grade HC1 diluted to 20 L reagent water. Purge overnight with argon.

7.10. Stannous chloride solution concentrate: Add 500 g of $SnCl_2 \bullet 2H_2O$ to 2.4 L trace metals concentrated hydrochloric acid. Allow the $SnCl_2 \bullet 2H_2O$ to completely dissolve. ACS Reagent grade suitable for mercury determination (< 1 ppb) recommended.

7.11. Stannous chloride working solution: Fill a 2.5 L glass bottle (HCl leached) with 2.25 L of reagent water. Add sufficient stannous chloride concentrate (Section 7.10) to bring the total volume to 2.5 L. This produces a reductant solution that is 10% HCl and 2%

$SnCl_2 \bullet 2H_2O$. Purge with argon (0.5 L/min) for at least 24 hours. Analyze a reagent blank with this solution prior to analysis of samples (Section 9.8).

7.12. Hydroxylamine hydrochloride solution: Dissolve 300 g of $NH_2OH \bullet HCl$ in reagent water. Dilute to 1 L. Add 1 mL of stannous chloride solution working solution and purge with argon (0.5 L/min) for at least 24 hours. Analyze a reagent blank made with this solution prior to analysis of samples (Section 9.8).

7.13. Potassium bromide: KBr, reagent grade, low mercury content is desirable. This dry reagent may be baked at 250°C for at least 8 hours to volatilize trace Hg(0) contamination.

7.14. Potassium bromate: $KBrO_3$, reagent grade, low mercury content is desirable. This dry reagent may be baked at 250°C for at least 8 hours to volatilize trace Hg(0) contamination.

7.15. Bromine monochloride preservative/oxidizing solution: In a ventilation hood, add 5.4 g KBr to 500 mL of ultra trace (low mercury) HCl. Allow the salt to dissolve. Slowly add 7.6 g $KBrO_3$. Halogen fumes will be emitted during this step. Adequate ventilation is essential to protect analyst safety. Analyze a reagent blank with this solution prior to analysis of samples (Section 9.8)

7.16. Nitric acid, concentrated, trace metal grade.

8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1. Preservation and Holding Time

8.1.1. Holding time from time of collection to the time of preservation is extended to 28 days when the oxidation step is performed in the sample bottle used for collection. Preservation/oxidation is verified by the persistence of the yellow color of the BrCl. Additional BrCl must be added if the preservative/oxidizer is consumed. Record any additional BrCl used (see Section 11.1.5). Samples to be analyzed for dissolved Hg must be filtered within 48 hours of collection, then preserved as above. Once preserved, holding time is 90 days from sample collection to analysis.

8.1.2. Solid sample holding time for Hg is one year from collection. The holding time for digested and preserved solid samples is 90 days from sample preparation

8.2. Collection and Storage

8.2.1. The clean hands/dirty hands procedure should be followed for collection. Samples are stored in a mercury clean area.

8.2.2. Solid samples may be stored in fluoropolymer or borosilicate glass or polyethylene bags.

9. QUALITY CONTROL

9.1. Table II (Appendix A) provides a summary of quality control requirements including type, frequency, acceptance criteria and corrective action.

9.2. Initial Demonstration of Capability

9.3. Prior to the analysis of any analyte using Method 1631 or Method 245.7, the following requirements must be met.

9.3.1. Method Detection Limit (MDL) - An MDL must be determined for each analyte/matrix prior to the analysis of any samples. The MDL is determined using seven replicates of reagent water, spiked with all the analytes of interest, that have been carried through the entire analytical procedure. MDLs must be redetermined in accordance with 40 CFR Part 136 Appendix B requirements. The spike level must be between the calculated MDL and 10X the MDL to be valid. The result of the MDL determination must be below both the TestAmerica North Canton reporting limit. In addition the MDL for Method 1631 must be ≤ 0.2 ng/L.

9.3.2. Initial Demonstration Study (initial precision and recovery study)- This requires the analysis of four QC check samples. The QC check sample is a well-characterized laboratory generated sample used to monitor method performance. The results of the initial demonstration study must be acceptable before analysis of samples may begin.

9.3.2.1. Four aliquots of the check sample (LCS) are prepared and analyzed using the procedures detailed in this SOP and the determinative SOPs.

9.3.3. Carryover determination – Analyte system blanks immediately after calibration solutions containing successively larger concentrations of Hg – from this test determine the amount of Hg that will carry >0.5 ng/L of Hg into a succeeding system blank. When a sample one half or more of this determined amount is analyzed then a system blank must be analyzed to demonstrate cleanliness at the RL. Samples with detectable Hg analyzed after the high sample but before the system blank must be reanalyzed.

9.4. Preparation Batch - A group of up to 20 samples that are of the same matrix and are processed together using the same procedures and reagents. The preparation batch must

contain a method blank, a LCS and a matrix spike/matrix spike duplicate (2 MS/MSD pairs if the batch has more than 10 samples). In some cases, at client request, it may be appropriate to process a matrix spike and sample duplicate in place of the MS/MSD. If clients specify specific samples for MS/MSD, the batch may contain multiple MS/MSD pairs.

9.5. Sample Count - Laboratory generated QC samples (Method Blanks, LCS, and MS/MSDs) are not included in the sample count for determining the size of a preparation batch.

9.6. Method Blank (MB): One method blank must be processed with each preparation batch. The method blank consists of reagent water containing all reagents specific to the method that is carried through the entire analytical procedure, including preparation and analysis. The method blank is used to identify any system and process interferences or contamination of the analytical system that may lead to the reporting of elevated analyte concentrations or false positive data. The method blank should not contain any analyte of interest at or above the reporting limit. The sample result must be a minimum of 20 times higher than the blank contamination level.

- If there is no analyte greater than the RL in the samples associated with an unacceptable method blank, the data may be reported with qualifiers. **Such action must be addressed in the project narrative.**

- Repreparation and reanalysis of all samples associated with an unacceptable method blank is required when reportable concentrations are determined in the samples (see exceptions noted above).

- If the above criteria are not met and reanalysis is not possible, then the sample data must be qualified. **This anomaly must be addressed in the project narrative and the client must be notified.**

9.7. If a sample requires additional BrCl beyond the normal amount (Section 11.1.5) an additional preparation blank should be prepared with the same amount of BrCl. The result of this prep blank will be added to the narrative of the associated sample if the result is ≥ the reporting limit. This prep blank does not have any specific acceptance criteria, but it should be proportional to the amount of BrCl used.

9.8. System / subtraction / reagent blank: The reagent blank consisting of all reagents used to prepare samples and standards will be used for background subtraction and system cleanliness monitoring. Three reagent blanks are prepared and analyzed with the daily initial calibration curve (ICal) . Apply the average calibration factor from the ICal to the average

raw response from these 3 reagent blanks. The calculated mercury concentration must be less than the reporting limit. The average raw response from these 3 calibration blanks will be subtracted from all raw response data from all other data prior to calculating concentration factor (for cal standards) or concentrations. Subsequent bubbler / reagent blanks are run as ICB and CCB in conjunction with the ICV (QCS) and CCV (OPR). These IC and CC blanks are used to monitor the cleanliness of the instrument and are calculated in the same manner as samples and are not used for background subtraction purposes. The absolute value of the calculated mercury concentration must be less than the reporting limit.

9.9. Laboratory Control Sample (LCS): One aqueous LCS must be processed with each preparation batch. The LCS is used to monitor the accuracy of the analytical process. On-going monitoring of the LCS results provides evidence that the laboratory is performing the method within acceptable accuracy and precision guidelines. The LCS must be carried through the entire analytical procedure. If the LCS is outside established control limits the system is out of control and corrective action must occur.

- In the instance where the LCS recovery is greater than the maximum and the sample results are < RL, the data may be reported with qualifiers**. Such action must be addressed in the case narrative.**

- In the event that an MS/MSD analysis is not possible, a Laboratory Control Sample Duplicate (LCSD) must be analyzed. The RPD of the LCS and LCSD must be compared to the matrix spike RPD limits.

- Corrective action will be repreparation and reanalysis of the batch unless the client agrees that other corrective action is acceptable.

9.10. Matrix Spike/Matrix Spike Duplicate (MS/MSD): One MS/MSD pair must be processed for each 10 samples in preparation batch. A matrix spike (MS) is a field sample to which known concentrations of target analytes have been added. A matrix spike duplicate (MSD) is a second aliquot of the same sample (spiked identically as the MS) prepared and analyzed along with the sample and matrix spike. Some client specific data quality objectives (DQO's) may require the use of sample duplicates in place of or in addition to MS/MSD's. The MS/MSD results are used to determine the effect of a matrix on the precision and accuracy of the analytical process. Due to the potential variability of the matrix of each sample, these results may have immediate bearing only on the specific sample spiked. Method 1631 requires that each matrix be spiked at a 10% frequency. Some regulatory agencies interpret each discharge or sampling point as a separate matrix. It is the client's responsibility to determine which sample(s) is to be matrix spiked each time samples are submitted for analysis. Samples identified as field blanks cannot be used for MS/MSD analysis. Spiking levels are provided in Table I (Appendix A).

- If analyte recovery or RPD falls outside the acceptance range, the recovery of that analyte must be in control for the LCS. Until in-house control limits are established, control limits of 71 - 125 % recovery and 24% RPD for 1631 aqueous, 70-130% recovery and 30% RPD for 1631 solid, and 76 – 111% recovery and 18% RPD for 245.7 must be applied to the MS/MSD. If the LCS recovery is within limits, then the laboratory operation is in control and the results may be accepted. If the recovery of the LCS is outside limits, corrective action must be taken. Corrective action will include repreparation and reanalysis of the batch. MS/MSD results, which fall outside the control limits, must be addressed in the narrative.

- If the native analyte concentration in the MS/MSD exceeds 4 times the spike level for that analyte, the recovery data are reported as NC (i.e., not calculated). If the reporting software does not have the ability to report NC then the actual recovery must be reported and narrated as follows: "Results outside of limits do not necessarily reflect poor method performance in the matrix due to high analyte concentrations in the sample relative to the spike level."

- If an MS/MSD is not possible due to limited sample volume, then a laboratory control sample duplicate (LCSD) should be analyzed. The RPD of the LCS and LCSD must be compared to the matrix spike RPD limits.

9.11. Initial Calibration Verification (ICV/ICB) (QCS – quality control sample): Calibration accuracy is verified by analyzing a second source standard (ICV). The ICV result must fall within 20% of the true value for that solution . An ICB is analyzed immediately following the ICV to monitor low level accuracy and system cleanliness. The ICB result must fall within +/- the reporting limit (RL) from zero. If either the ICV or ICB fail to meet criteria, the analysis should be terminated, the problem corrected and the instrument recalibrated. (See Section 11.3.5) for required run sequence). If the cause of the ICV or ICB failure was not directly instrument related the corrective action will include repreparation of the ICV, ICB, CCV, and CCB with the calibration curve.

9.12. Continuing Calibration Verification (CCV/CCB) (on-going precision and recovery - OPR): Calibration accuracy is monitored throughout the analytical run through the analysis of a known standard after every 10 samples. The CCV concentration must be at 5 ng/L for 1631. The CCV result must fall within 77-123% of the true value for that solution for 1631. A CCB is analyzed immediately following each CCV. (See Section 11.3.5 for required run sequence). The CCB (system/reagent blank) must fall within +/- the reporting limit (RL) from zero. Each CCV and CCB analyzed must reflect the conditions of analysis of all associated samples. Sample results may only be reported when bracketed by valid ICV/CCV and ICB/CCB pairs.

- In the instance where the CCV or CCB is greater than the maximum and the sample

results are < RL, the data may be reported. Such action must be addressed in the case narrative.

9.13. Method of Standard Addition (MSA) -This technique involves adding known amounts of standard to one or more aliquots of the sample prior to preparation. This technique compensates for a sample interferent that may enhance or depress the analyte signal, thus producing a different slope from that of the calibration standards. It will not correct for additive interferences, which cause a baseline shift. Refer to Appendix C for specific MSA requirements.

10. CALIBRATION AND STANDARDIZATION

10.1. Calibration standards must be processed through the preparation procedure as described in Section 11.1 except that the oxidation time need does not need to be a minimum of 12 hours and can be used immediately since the mercury is already in an oxidized state in the standard.

10.2. Due to the differences in calibration ranges separate calibration and calibration verification standards must be prepared for Methods 1631 and 245.7. See Section 7.5 and Table 1.

10.3. Calibration may be performed daily (every 24 hours), but is required only when indicated by instrument and preparation QC problems. The instrument calibration date and time must be included in the raw data.

10.4. Set up the instrument with the operating parameters recommended by the manufacturer (Table III). Allow the instrument to become thermally stable before beginning calibration (approximately 1-2 hours of warm-up is required if the lamp has been turned off). The most stable results are obtained if the lamp is left on full time. Refer to the CVAFS instrument manual for detailed setup and operation protocols.

10.5. Run 3 deionized water blanks to ensure that the instrument, reductant solution and rinse solutions are adequately clean.

10.6. Calibrate the instrument according to instrument manufacturer's instructions, using 6 standards and 3 calibration blanks. One standard must be at the TestAmerica North Canton reporting limit. Analyze standards in ascending order beginning with the blanks. Refer to Section 7.5 and Table I for additional information on preparing calibration standards and calibration levels.

10.7. The calibration factors must have less than 15% RSD or the instrument shall be stopped and recalibrated prior to running samples. Sample results can not be reported from a curve with

an unacceptable RSD. Also, the low standard must calculate back within ±25% of the true value.

10.8. Refer to Sections 9.11 and 9.12 for calibration verification procedures, acceptance criteria and corrective actions.

11. PROCEDURE

11.1. Aqueous Sample Preparation:

11.1.1. All calibration and calibration verification standards (ICV, ICB, CCV, CCB) are processed with the digestion reagents used for the field samples.

11.1.2. Open the outer sample bag, carefully dump the inner bag containing the sample bottles onto a clean bench top in the low level mercury area with a minimum of handling. Immediately discard the outer sample bag. Change gloves between each sample or work with another analyst using the clean hands-dirty hands technique.

11.1.3. Change gloves and open the remaining inner bag, remove the sample vials, label and place in the low level mercury prep area.

11.1.4. Remove ~2.7 mL from each sample vial. This will leave 40 mL in the bottle. Confirm by checking the meniscus and the 40mL calibration point. Set the cap back on the original vial. Repeat this process for all 40 mL vial aliquots of the sample. Transfer 1 mL of sample from a separate unpreserved "10X dilution" labeled tube and add 9 mL of reagent water. Reseal the original sample vial caps if it will be greater than 3 minutes before the next step of performed (Section 11.1.5)

Note: Typically two sample vials and one screening vial will be prepared per sample (six sample vials for client requested MS/MSD samples).

11.1.5. Temporarily lift the cap and add 0.20 mL of BrCl (Section 7.15) to the 40 mL sample vial, reseal and mix. If the yellow tint from the BrCl disappears add an additional aliquot of BrCl. This iterative process may be repeated until a maximum of 2 mL has been added. Record the amount of BrCl used on the bench sheet. If the 2 mL maximum was reached and the yellow BrCl color still does not persist consult supervisor to determine if sample dilution prior to preservation / oxidation is appropriate. At least one method preparation blank must be prepared for each different volume of BrCl added.

11.1.6. Add 0.05 mL BrCl to the dilution tube(s) from Section 11.1.4. Confirm the 10X

dilution tube has adequate BrCl. Add more as needed.

11.1.7. Store the sample vials at room temperature for at least 12 hours. If the yellow BrCl color disappears during the storage period, the oxidizer has been consumed. Add additional BrCl until the yellow color persists. Do not exceed a total of 2 mL. Consult laboratory Technical Director or supervisor if yellow color does not persist after 2 mL addition of BrCl. Record the total volume of BrCl added on the benchsheet. Starch / iodine paper may be used to detect excess halogens (i.e. BrCl) in colored samples where the yellow color of the BrCl can not be seen.

Note: To speed or improve oxidation, especially for samples with high organic content or known interferences, the vials may be heated at approximately 50°C. For samples requiring greater than 0.2 ml of BrCl, this can lessen preparation time.

Note: The 12 hour oxidation time is not required for the sample aliquots in the screening tubes.

11.1.8. Prepare method blank and LCS vials using the same reagents as used for the samples.

11.2.Solid sample Preparation:

11.2.1 Homogenize the sample then weigh 1 g into a 40 mL VOA vial. The VOA vial must come from a lot that has been pre-screened for Hg contamination (Sec. 6.2).

11.2.1.1 For the method blank, add approximately 1 mL of reagent water in lieu of 1 g of solid sample.

11.2.1.2 For the LCS, add 1.0 mL of the 10 ug/L intermediate mercury standard (Sec. 7.3) in lieu of 1 g of solid sample.

11.2.1.3 For the MS/MSD, add 1.0 mL of the 10 ug/L intermediate mercury standard (Sec. 7.3) in addition to the 1 g of solid sample.

11.2.2 In a fume hood, add 8 ml of concentrated HCl, swirl, and add 2 mL concentrated HNO_3 to the sample in the 40 mL vial. Cap and allow the sample to digest for at least 4 hours.

11.2.3 Add 1 ml of BrCl (Sec. 7.15) to the digestate, then dilute with reagent water (Sec. 7.15) to the 40 mL calibration point. Shake, then allow to settle until supernatant is

clear. Centrifuge or filter if necessary.

11.2.4 For screening, transfer 0.1 mL of the supernatant into a "5X dilution" 10 ml culture tube and dilute to 10 mL with reagent water. For analysis, transfer 2 mL of the supernatant into a pre-screened VOA vial and dilute to the 40 mL calibration point with reagent water, then cap and shake. The "5X dilution" aliquot may be analyzed as specified in Sec. 11.3. The 40 mL VOA vial sample is ready for analysis and may be analyzed as specified in Sec. 11.4. Based on sample matrix and/or historical results, a greater dilution may be required.

11.3. Sample screening

11.3.1. Add 0.05 mL of hydroxylamine solution (Section 7.12) and analyze the 5X screening aliquot of the sample using a single point calibration (10 ng/L) and Method 245.7.

11.3.2. If the sample response exceeds that of the 10 ng/L standard (i.e. sample concentration > 2000 ng/L), then low level analysis by either 245.7 or 1631 is not technically appropriate. Remove all vials associated with this sample from the low level prep and storage areas immediately. Consult supervisor.

11.3.3. If the estimated concentration is greater than 200 ng/L, consult supervisor about analysis by 245.7. If approved, calculate the appropriate dilution and proceed with 245.7 analysis. Alternately, prepare an appropriately large dilution of the sample before bringing it into the low level preparation area. Direct low level analysis by 1631 is not technically appropriate due to the likelihood of contamination.

11.3.4. If the sample response (Note: this is a 5X dilution) exceeds that of the 5 ng/L standard then the sample concentration is beyond the normal calibration range of Method 1631. Either analyze the sample 245.7 (if allowed by the client) or prepare the appropriate dilution for 1631 analysis.

11.3.5. If the 5X dilution screen response is non-detect at 5 ng/L then the sample may be analyzed without dilution by either 245.7, or Method 1631 depending on the reporting limit needed by the client unless matrix interferences warrant dilution.

11.4. Sample Analysis

11.4.1. When ready to begin analysis, add 0.10 mL of hydroxylamine hydrochloride solution (Section 7.12) to the samples to reduce the excess BrCl (the BrCl has been reduced when no yellow color remains). Cap and shake. Add the

hydroxylamine solution in 0.10 mL increments until the BrCl is completely reduced. Record the total volume used on the benchsheet.

Note: Spiking is done before the addition of the hydroxylamine hydrochloride reagent.

11.4.2. With instrument control parameters set to appropriate values (See Table III), load samples into autosampler. Use 40 mL vials for Method 1631 and 14 mL or 40 mL tubes for 245.7.

11.4.3. Start autosampler sequence.

11.4.4. All measurements must fall within the defined calibration range to be valid. Dilute and reanalyze all samples for analytes that exceed the highest calibration standard.

11.4.5. The following analytical sequence must be used:

Instrument Calibration
ICV (QCS)
ICB
CCV (OPR)
CCB
Maximum 10 samples
CCV
CCB
Repeat sequence of 10 samples between CCV/CCB pairs as required to complete run
CCV
CCB

Refer to Quality Control Section 3 and Table II (Appendix A) for the appropriate quality control criteria.

Note: Samples include the method blank, LCS, MS, MSD, duplicate, field samples and sample dilutions.

Note: Instrument calibration need not be performed if the run QC parameters indicate that the system is in control.

11.5. To facilitate the early identification of QC failures and samples requiring rerun it is strongly

recommended that sample data are reviewed periodically throughout the run.

11.6. Guidelines are provided in the appendices on procedures to minimize contamination of samples and standards, preventive maintenance and troubleshooting.

11.7. One time procedural variations are allowed only if deemed necessary in the professional judgment of supervision to accommodate variation in sample matrix, radioactivity, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using a Nonconformance Memo and is approved by the QA Manager. The Non-Conformance Memo shall be filed in the project file.

11.8. Any unauthorized deviations from this procedure must also be documented as a nonconformance, with a cause and corrective action described.

12. DATA ANALYSIS AND CALCULATIONS

12.1.Calibration Factors are calculated according to the equation:

$$CF(x) = \left(\frac{Area(x) - Area(b)}{Conc(x)} \right)$$

Where:
CF(x) = calibration factor of standard (x)
area(x) = area of standard (x)
conc(x) = concentration of standard (x)
area(b) = average area of 3 calibration blanks

12.2. ICV percent recoveries are calculated according to the equation:

$$\%R = 100 \left(\frac{Found(ICV)}{True(ICV)} \right)$$

12.3. CCV percent recoveries are calculated according to the equation:

$$\%R = 100 \left(\frac{Found(CCV)}{True(CCV)} \right)$$

12.4. Matrix spike recoveries are calculated according to the following equation:

$$\%\ R\ = 100\left(\frac{SSR - SR}{SA}\right)$$

Where:

SSR = Spike Sample Result
SR = Sample Result
SA = Spike Added

12.5. The LCS percent recovery is calculated according to the following equation:

$$\%R = 100\left(\frac{Found(LCS)}{True(LCS)}\right)$$

12.6. The relative percent difference (RPD) of matrix spike/matrix spike duplicates or sample duplicates are calculated according to the following equations:

$$RPD = 100\left[\frac{|MSD - MS|}{\left(\frac{MSD + MS}{2}\right)}\right]$$

Where:

MS = determined spiked sample concentration
MSD = determined matrix spike duplicate concentration

$$RPD = 100\left[\frac{|DU1 - DU2|}{\left(\frac{DU1 + DU2}{2}\right)}\right]$$

Where:

DU1 = Sample result
DU2 = Sample duplicate result

12.7. The final concentration for an aqueous sample is calculated as follows:

$$ng/L = \text{C x D}$$

Where:

C = Concentration (ng/L) from instrument readout
D = Instrument dilution factor

12.8. The final concentration for a solid sample is calculated as follows:

$$ug/kg = C \times D \times W \times P$$

Where:

C = Concentration (ng/L) from instrument readout

D = Instrument dilution factor

W = Weight/volume factor = 0.040, when 1 g of sample is digested and diluted to 40 mL.

P = Preparation factor = 20, when 2 mL of digestate is diluted to 40 mL.

12.9. Appropriate factors must be applied to sample values if dilutions are performed.

13. METHOD PERFORMANCE

13.1. Each laboratory must have initial demonstration of performance data on file for each analyte of interest as described in Section 9.3.

13.2. Method performance is determined by the analysis of method blanks and laboratory control samples. The method blanks must meet the criteria in Section 9.6. The laboratory control sample should recover within 25% of the true value until in house limits are established.

13.3. Training Qualification:

The group/team leader has the responsibility to ensure that this procedure is performed by an associate who has been properly trained in its use and has the required experience.

14. POLLUTION PREVENTION

14.1. This method allows for the proportional reduction of sample and reagent volumes to decrease waste generation.

15. WASTE MANAGEMENT

15.1. All waste will be disposed of in accordance with Federal, State and Local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this method and the policies in section 13 of the Corporate Safety Manual for “Waste Management and

Pollution Prevention."

15.2.Waste Streams Produced by the Method

15.2.1. The following waste streams are produced when this method is carried out.

15.2.1.1. **Acid Waste- Aqueous waste generated by the analysis.** Samples vials are collected and taken to the waste storage building. The vials are crushed and the liquid waste and glass are separated. The liquid waste is neutralized and released to the POTW. The glass is disposed of in the trash.

16. REFERENCES

16.1. References

16.1.1. Method 1631, Revision E: Mercury in Water by Oxidation, Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry, U.S. EPA, August 2002.

16.1.2. Appendix to Method 1631, Total Mercury in Tissue, Sludge, Sediment, and Soil by Acid Digestion and BrCl Oxidation, U.S. EPA, January 2001.

16.1.3. Method 245.7, Mercury in Water by Cold Vapor Atomic Fluorescence Spectrometry, U.S.EPA, January 2000.

16.1.4. Corporate Quality Management Plan (QMP), current version.

16.1.5. TestAmerica Laboratory Quality Manual (LQM), current version.

16.1.6. TestAmerica Corporate Safety Manual, M-E-0001 and TestAmerica North Canton Facility Addendum and Contingency Plan, current version.

16.2.Associated SOPs and Policies, latest version

16.2.1. QA Policy, QA-003

16.2.2. Glassware Washing, NC-QA-0014

16.2.3. Statistical Evaluation of Data and Development of Control Charts, NC-QA-0018

16.2.4. Method Detection Limits and Instrument Detection Limits, S-Q-003 and NC-QA-

0021

16.2.5. Supplemental Practices for DoD Project Work, NC-QA-0016

16.2.6. Standards and Reagents, NC-QA-0017

17. MISCELLANEOUS (TABLES, APPENDICES, ETC.)

17.1. Modifications/Interpretations from reference method.

17.1.1 Section 9.1.7 of the method requires three method blanks per analytical batch. The section also describes an analytical sequence that includes a CCV (OPR) only at the beginning and end of the sequence, and that includes no CCBs (system blanks) after calibration. This SOP requires only one method blank per preparation batch, but requires additional stability and cleanliness checks through the analysis of a CCV/CCB pair at the beginning, end and after every ten analyses during an analytical run.

17.1.2 Section 9.2.1 of the method recommends that an MDL be determined whenever a new operator begins work. At this laboratory, a new operator receives proper, documented training and must prove competence through an initial demonstration of performance that includes the successful analysis of (4) LCSs (See Section 9.3.2).

17.1.3 Conventional MS/MSD techniques and criteria have been maintained in contrast to Section 9.3.4 of the method (See Section 17.1.2.1 of this SOP).

17.1.4 Section 9.4.3.1 of the method requires reagent blank concentrations to be <0.2 ng/L. In this laboratory, reagent blanks are analyzed as system calibration blanks and are held to the system blank criteria of <0.5 ng/L (See Section 9.8 of this SOP).

17.1.5 Section 9.4.5.1 of the method recommends that field blank analysis immediately before analyzing samples from the batch. Field blanks are analyzed as normal samples in this laboratory with no particular run order requirement.

17.1.6 Section 9.4.7 of this method recommends that 5% of the bottles in a lot be monitored. Bottle cleanliness in this laboratory is verified by the initial analysis of 5% of the bottles from three boxes of a lot of 40 mL sample vials, and then monitored through the routine analyses of system blanks (calibration blanks).

17.1.7 The volume descriptions for the equation in Section 12.3.2 of the method includes

subtraction of the volume of reagent used in the standards and the samples. Since the volume of reagents used in samples and standards is typically the same (or differs insignificantly in rare cases), this subtraction is not included in the determination of Hg concentration in this laboratory.

17.2 Performance Based Modifications from Method 245.7.

17.2.1 The preservative / oxidizer solution (Section 7.15) from Method 1631B has been used in place of the bromate/bromide oxidizer solution (Section 7.7.4 in method).

17.2.2 The autosampler is rinsed with 2% HCI solution as recommended by the manufacturer rather than deionized water (Section 11.3.2 in method).

17.3 Other Interpretations and Differences from Method 245.7.

17.3.1 Reagent blank acceptance criteria is an absolute value less than the reporting limit (Section 9.8) rather than MDL (Section 9.2.1.3 in method)

17.3.2 Conventional fixed concentration matrix spiking has been used in this SOP (Section 9.10) rather than the variable concentration spiking described in the method (Section 9.5 in method). Also, batch acceptability is determined by method blank and LCS criteria and not MS/MSD recovery and RPD.

17.3.3 All standards are prepared using the same reagents as the samples rather than only in reagent water (Section 10.1.1.2 in method). (See Section 10.1)

17.3.4 The digested sample is used for dilution since no undigested sample (Section 11.3.4 in method) is available as the BrCl solution both preserves and oxidizes the sample. Also, this form of the sample should be more homogeneous for total mercury analysis.

17.4 Interpretations and Differences from Method 1631 Appendix A

17.4.1 In the method, after digestion with aqua regia is complete, the digestate is diluted with 0.07 N BrCl for elemental carbon-containing samples. In this SOP, all samples are diluted reagent water to which 1 mL of 0.2 N BrCl has been added. This presents a BrCl concentration in the diluted digestate comparable to the concentration achieved using the method technique. Also, since it is added to all digestates (not only those known to contain elemental carbon), the analyzed digestate will always contain some BrCl, and thereby be more comparable to the calibration standards.

17.5 Documentation and Record Management

17.5.1 The following documentation comprises a complete CVAFS raw data package:

- Raw data (direct instrument printout)
- Run log printout from instrument software. (A bench sheet may be substituted for the run log as long as it contains an accurate representation of the analytical sequence).
- Data review checklist - See Appendix B
- Standards Documentation (source, lot, date).
- Copy of digestion log.
- Non-conformance summary (if applicable).

Figure 1. Aqueous Sample Preparation - Mercury

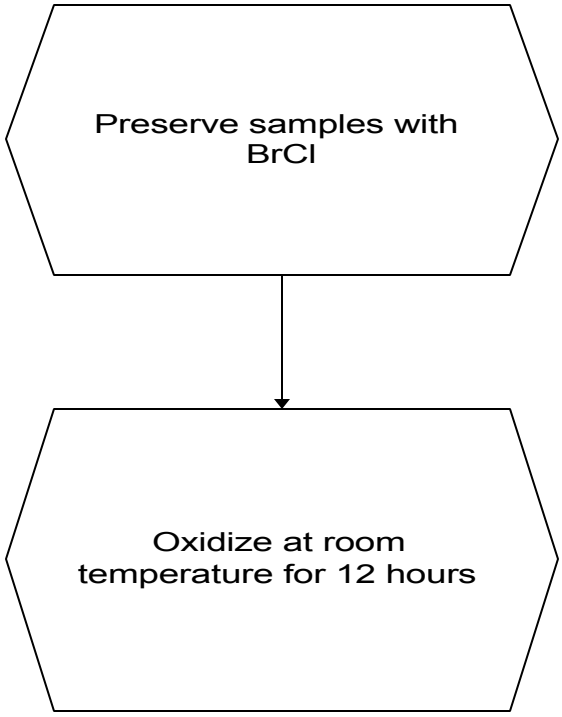
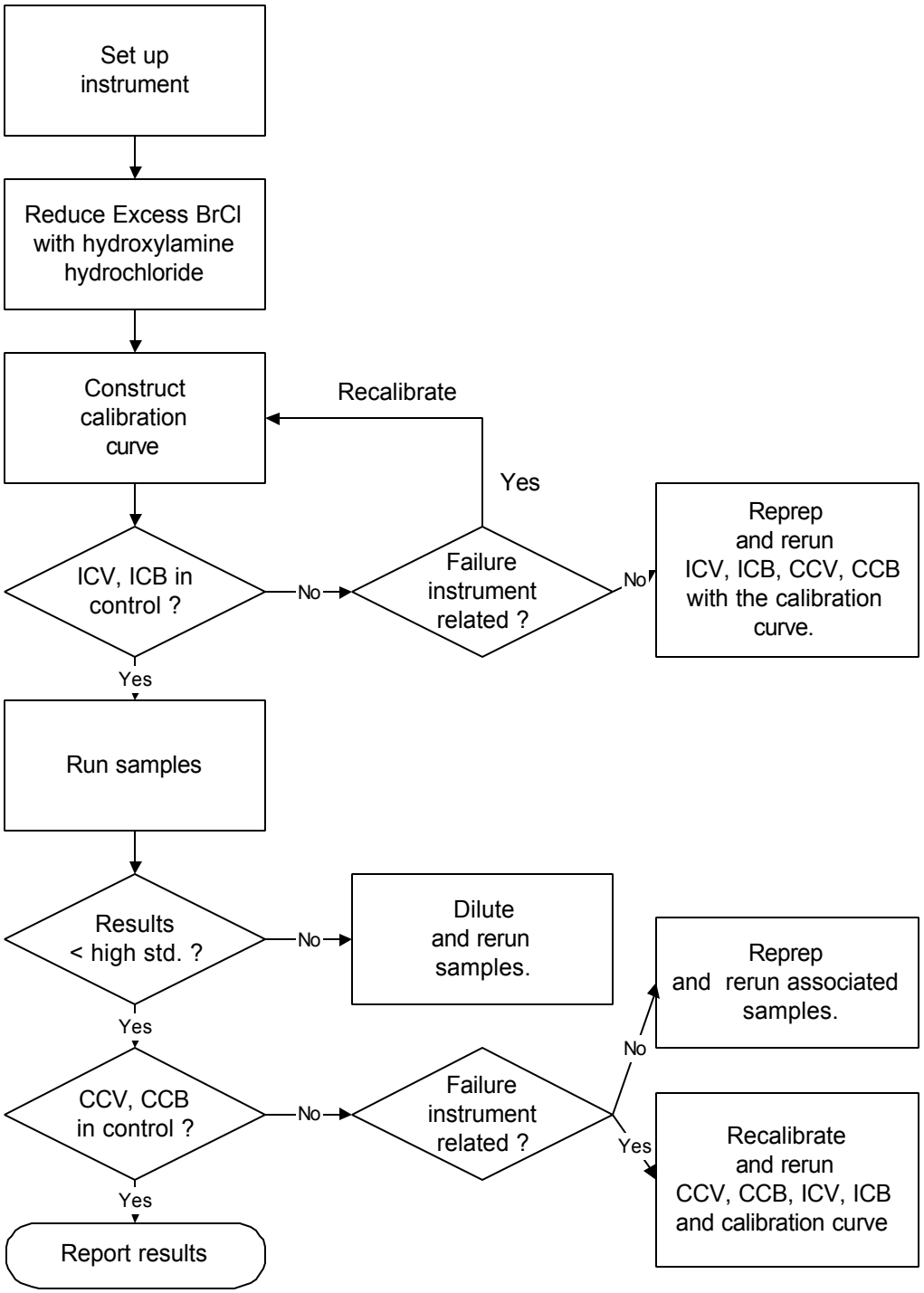


Figure 2. CVAF Mercury Analysis



APPENDIX A

TABLES

TABLE I
MERCURY REPORTING LIMITS, CALIBRATION STANDARD, QC STANDARD, AND SPIKING LEVELS (ng/L)

	1631E				245.7	
	Conc ng/L	**mL Std (Sec.7.4)**	**Conc ug/kg Solid**	**mL Std (Sec.7.3) Solid**		**mL Std (Sec.7.3)**
Standard Water RL	0.5				5	
Standard Solid RL			1.0		NA	
Std 1 (in triplicate)	0	0			0	0
Std 2	0.5	20			5	20
Std 3	1	40			10	40
Std 4	2	80			20	80
Std 5	5	200			50	200
Std 6	10	400			100	400
Std 7	25	1000			250	1000
ICV (QCS)	5	200 (Sec 7.6)			10	40 (Sec 7.6)
CCV (OPR)	5	200			10	40
LCS	5	200	10	1000		
MS/MSD	5	200	10	1000	10	40

TABLE II
SUMMARY OF QUALITY CONTROL REQUIREMENTS

QC PARAMETER	FREQUENCY *	ACCEPTANCE CRITERIA 1631	ACCEPTANCE CRITERIA 245.7	CORRECTIVE ACTION
ICV (QCS)	Beginning of every analytical sequence.	80-120 % recovery	80-120 % recovery	Terminate analysis; Correct the problem; Recalibrate or reprep with calibration curve. (see Section 9.11)
ICB	Beginning of every analytical run, immediately following the ICV	The result must be within +/- RL (0.5 ng/L for aqueous, 1.25 ng/L for solid)	The result must be within +/- RL (5 ng/L)	Terminate analysis; Correct the problem; Recalibrate or reprep with calibration curve (see Section 9.11)
CCV (OPR)	Every 10 samples and at the end of the run	77-123 % recovery	76-111 % recovery	Terminate analysis; Correct the problem; Recalibrate and rerun all samples not bracketed by acceptable CCV or reprep with calibration curve (Note exceptions in Section 9.12)
CCB	Immediately following each CCV	The result must be within +/- RL (0.5 ng/Lfor aqueous, 1.25 ng/L for solid)	The result must be within +/- RL (5 ng/L)	Terminate analysis; Correct the problem; Recalibrate and rerun all samples not bracketed by acceptable CCB or reprep with calibration curve (Note exceptions in Section 9.12)
Method Blank	One per sample preparation batch of up to 20 samples. Note: additional prep blank(s) required if additional BrCl needed in some sample(s)	The result must be within +/- RL Sample results greater than 20x the blank concentration are acceptable.	The result must be within +/- RL (5 ng/L)	Redigest and reanalyze samples Note exceptions under criteria section See Section 9.6 for additional requirements.

TABLE II

SUMMARY OF QUALITY CONTROL REQUIREMENTS (Cont'd)

QC PARAMETER	FREQUENCY *	ACCEPTANCE CRITERIA 1631	ACCEPTANCE CRITERIA 245.7	CORRECTIVE ACTION
Laboratory Control Sample (LCS)	One per sample preparation batch of up to 20 samples.	75-125 % recovery	75-125 % recovery	Terminate analysis; Correct the problem; Redigest and reanalyze all samples associated with the LCS (Note exception under Section 9.9)
Matrix Spike	Two per sample preparation batch of up to 20 samples.	71-125 % recovery for aqueous, 70-130% recovery for solid. If the MS/MSD is out for an analyte, it must be in control in the LCS	76-111 % recovery. If the MS/MSD is out for an analyte, it must be in control in the LCS.	In the absence of client specific requirements, flag the data; no flag required if the sample level is > 4x the spike added (see Section 9.10)
Matrix Spike Duplicate	See Matrix Spike	Same as Matrix Spike RPD ≤ 24% for aqueous, ≤30% for solid	76-111 %; RPD ≤ 18% (see MS)	See Corrective Action for Matrix Spike

*See Section 11.3.5 for exact run sequence to be followed

TABLE III
SUMMARY OF INSTRUMENT PARAMETERS
(LEEMAN LABS HYDRA AF GOLD +)

Instrument Parameter	**1631**	**245.7**
Argon flow (L/min)	0.5	0.4
Pump flow (mL/min)	10	10
Rinse (sec)	60	120
Uptake (sec)	240	35
Sample volume (mL)	40	11
Integration (sec)	0.70 (70 sec total)	35 sec total
Method	CVAFS with trap	CVAFS
Furnace 1 temp (°C)	450	
Furnace 2 temp (°C)	450	
Dry Time (sec)	5	
Desorption Time (sec)	70	
Stabilize Time (sec)	10	

APPENDIX B

EXAMPLE
TESTAMERICA NORTH CANTON Hg DATA REVIEW CHECKLIST

Example

TestAmerica North Canton Hg Data Review Checklist

Run/Project Information

Run Date: _____ Analyst:_____ Instrument:_____
Prep Batches Run:_____
Circle Methods used: 1631E : NC-MT-0001 Rev 4 **245.7 :** NC-MT-0001 Rev 4
245.7 screen : NC-MT-0001 Rev 4

Review Items

A. Calibration/Instrument Run QC	Yes	No	N/A	2ndLevel
1. Instrument calibrated per manufacturer's instructions and at SOP specified levels (including 3 initial calibration blanks)?				
2. ICV/CCV analyzed at appropriate frequency and within control limits?				
3. ICB/CCB analyzed at appropriate frequency and within +/- RL?				
B. Sample Results				
1. Were samples with concentrations > the high calibration standard diluted and reanalyzed?				
2. All reported results bracketed by in control QC?				
3. Sample analyses done within holding time?				
C. Preparation/Matrix QC				
1. Samples preserved within holding time at lab?				
2. LCS done per prep batch and within QC limits?				
3. Method blank done per prep batch and < RL?				
4. MS run at required frequency (1 per 10 samples) and within limits?				
5. MSD or DU run at required frequency (1 per 10 samples) and RPD within SOP limits?				
D. Other				
1. Are all nonconformances documented appropriately?				
2. Current MDL data on file?				
3. Calculations and Transcriptions checked for error?				
4. All client/ project specific requirements met?				
5. Date of analysis verified as correct?				

Analyst: _____ Date:_____
Comments:
_____
_____

2nd Level Reviewer : _____ Date:_____
_____
_____

Standard and Reagent Numbers

ICal/CCV _____ **ICV _____**

BrCl _____ NH2OH HCl _____ SnCl2 _____

APPENDIX C

MSA GUIDANCE

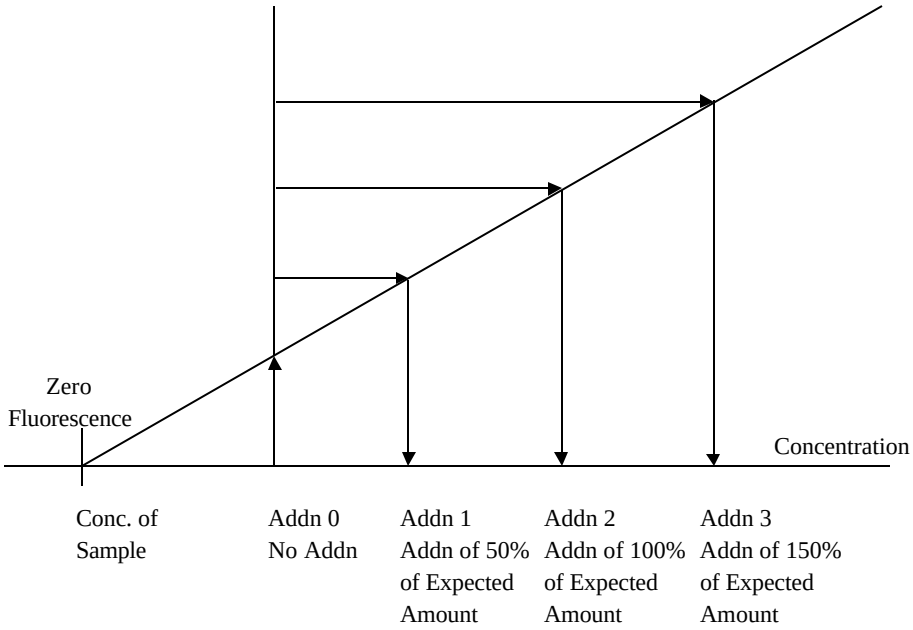
APPENDIX C. MSA GUIDANCE

Method of Standard Addition

Four equal volume aliquots of sample are measured and known amounts of standards are added to three aliquots. The fourth aliquot is the unknown and no standard is added to it. The concentration of standard added to the first aliquot should be 50% of the expected concentration. The concentration of standard added to the second aliquot should be 100% of the expected concentration and the concentration of standard added to the third aliquot should be 150% of the expected concentration. The volume of the unspiked and spiked aliquots should be the same (i.e., the volume of the spike added should be negligible in relation to the volume of sample).

To determine the concentration of analyte in the sample, the fluorescence (or response) of each solution is determined and a linear regression performed. On the vertical axis the fluorescence (or response) is plotted versus the concentrations of the standards on the horizontal axis using 0 as the concentration of the unspiked aliquot. An example plot is shown in Figure 1. When the resulting line is extrapolated back to zero fluorescence , the point of interception of the horizontal axis is the concentration of the unknown. Calculate the correlation coefficient (r) and the x-intercept (where y=0) of the curve. The concentration in the digestate is equal to the negative x-intercept.

Figure 1



- For the method of standard additions to be correctly applied, the following limitations must be taken into consideration.
- The plot of the sample and standards must be linear over the concentration range of concern. For best results, the slope of the curve should be similar to that of a plot of the aqueous standard curve.
- The effect of the interference should not vary as the ratio of the standard added to the sample matrix changes.

APPENDIX D

TROUBLESHOOTING GUIDE

APPENDIX D

TROUBLESHOOTING GUIDE

Problem	Possible Cause
Poor or No Fluorescence or Sensitivity Check failed	Incorrect wavelength Dirty windows Window loose Etched or dirty optics Wrong lamp Bad lamp Not enough or no sample introduced Empty sample cup Incorrectly made standards Gas leak EDL power supply set on "Continuous"
Erratic Readings	Source lamp not aligned properly Lamp not prewarmed Injection tip partially clogged Contaminated reagents Contaminated glassware Drying tube saturated Bad lamp Injection tip hitting outside of tube Injection tip coated or not set properly Leak in sample tubing Power fluctuations Air bubbles in tubing
EDL Won't Light	Lamp cable not plugged in Lamp power set at 0 Lamp is dead Power supply fuse is blown Short in cord
Standards reading twice or half normal fluorescence or concentration	Incorrect standard used Incorrect dilution performed Dirty cell

APPENDIX E

CONTAMINATION CONTROL GUIDELINES

APPENDIX E. CONTAMINATION CONTROL GUIDELINES

The following procedures are strongly recommended to prevent contamination:

All work areas used to prepare standards and spikes should be cleaned before and after each use.

All glassware should be washed with detergent and tap water and rinsed with 1:1 hydrochloric acid followed by deionized water.

Proper laboratory housekeeping is essential in the reduction of contamination in the metals laboratory. All work areas must be kept scrupulously clean.

Powdered Gloves must not be used in the mercury laboratory since the powder contains mercury, as well as other metallic analytes. Only powder free gloves should be used in the metals laboratory.

Glassware should be periodically checked for cracks and etches and discarded if found. Etched glassware can cause cross contamination of any metallic analytes.

Autosampler trays should be covered to reduce the possibility of contamination. Trace levels of elements being analyzed in the samples can be easily contaminated by dust particles in the laboratory.

The following are helpful hints in the identification of the source of contaminants:

Reagents or standards can contain contaminants or be contaminated with the improper use of a pipette.

Improper cleaning of glassware can cause contamination.

Separate glassware if an unusually high sample is analyzed and discard.

APPENDIX F

PREVENTIVE MAINTENANCE

APPENDIX F. PREVENTIVE MAINTENANCE

A maintenance log is used to record when maintenance is performed on instruments. When an instrument problem occurs indicate the date, time and instrument number, then identify the problem and corrective action in the maintenance log.

The following procedures are required to ensure that that the instrument is fully operational.

Cold Vapor Atomic Absorption (Leeman Labs Hydra AF gold plus) [(1)]

Daily	Semi-annually	As Needed
Check argon flow	Check Hg lamp intensity	Change Hg lamp
Check pump tubing		Change liquid/gas separator
Check drain		Change Nafion dryer
Check soda lime drying tube		

APPENDIX G

INSTRUMENT SET UP

Hg Analysis (Leeman Labs Hydra AF gold plus)

TO SET UP INSTRUMENT FOR ANALYSIS

1. WinHG Rack File editor

2. New Rack file

    A. Enter sample workorder # into corresponding "Sample name" (limit 8 chars, no spaces)

    B. Enter client ID into "Extended ID"

    C. Save file with Date/letter name (e.g. 0324a) (limit 8 characters, no spaces)

3. WinHg Database

    A. Select most recent calibration of appropriate method (1631 or 245.7)

    B. Save Protocol As, method / current date (e.g. 16310324) (limit 8 characters, no spaces)

    C. Clear calibration data from new protocol

    D. Apply (i.e. Save changes)

    E. Upload protocol to Runner

3. WinHg Runner

    A. Sample tab

    B. Select appropriate rack file(s), click auto sample

APPENDIX 45
SOP FOR THE ANALYSIS OF AROCLOR PCBS BY SW-846 8082 (NE148_06_R014)

Northeast Analytical, Inc.
2190 Technology Drive
Schenectady, NY 12308

STANDARD OPERATING PROCEDURE FOR THE DETERMINATION OF POLYCHLORINATED BIPHENYL (PCB) AROCLORS BY US-EPA SW-846 METHOD 8082

SOP Name: NE148_06.SOP
Revision: 06
Date Effective: February 19,2009
Issuing Section: GC Analysis

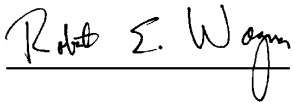
Controlled Copy #____

Reviewed and Approved By:

Chemist :

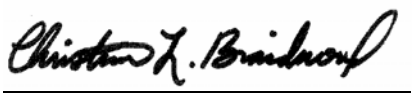
Kari Lantiegne — Date: 02/19/09

Laboratory Director:



Robert E. Wagner — Date: 02/19/09

QA/QC Director:



Christina L. Braidwood — Date: 02/19/09

Table of Contents

STANDARD OPERATING PROCEDURE FOR THE DETERMINATION OF POLYCHLORINATED BIPHENYL (PCB) AROCLORS BY US-EPA SW-846 METHOD 8082

1.0 Identification of Test Method

1.1 This method is used to determine Polychlorinated Biphenyl (PCB) by gas chromatography with electron capture detection and Total Aroclor Quantification using EPA SW 846 Method 8082- Polychlorinated Biphenyl (PCB) Aroclors by Capillary Column GC.

2.0 Applicable Matrix

2.1 This SOP is applicable in the determination and quantification of PCBs as outlined in EPA SW-846 Method 8082. It is applicable to the following matrices: water, soil, sediment, sludge, oil, fuel oil, waste solvent, fish, other aquatic animals, tissue samples, caulk, and air cassette samples including polyurethane foam (PUF) and associated filters for EPA Methods TO-4A and TO-10A.

3.0 Detection Limit

3.1 Detection Limit: Reporting Limits (RLs) and Method Detection Limits (MDLs) vary for each compound.

3.1.1 The following are default Reporting Limits based on the lowest calibration standard and global MDL /Reporting Limits based on MDL studies performed by NEA used for EPA Method 8082. See attachment G for example of MDL study. Reporting Limits (PQLs) are based on the Lowest Calibration Standard.

Matrix	Sample Mass/Volume Extracted	Calibration Curve Low Standard	Extract Volume	Global MDL* (All Aroclors)	RL (PQL) (all Aroclors)
Soil/Sediment Solid	10 g	20 ng/ml	25 mL	0.0115 mg/kg	0.050 mg/kg
Water	1 Liter	5 ng/ml	10 mL	0.0075 ug/L	0.050 ug/L
Biota	10 g (wet weight basis)	20 ng/mL	25 mL	0.0104 mg/kg	0.050 mg/kg
Polyurethane Foam Cassette (TO-4A/TO 10A)	1 PUF	20 ng/ml	5 mL	0.021 ug/Puf	0.100 ug/Puf
Waste Oil	0.5 g	20 ng/ml	25 mL	0.200 mg/kg	1.00 mg/kg
Wipe	1 Wipe	20 ng/ml	25 mL	0.115 ug/Wipe	0.500 ug/wipe

3.2 Individual MDLs and RLs are determined every two years for each instrument with matrix specific MDL studies for each extraction methodology. MDLs must be determined again whenever a major change in instrumentation or extraction methodology occurs.

3.3 MDLs are verified annually by the extraction and analysis of a low level MDL verification check sample. The Aroclor must be observed qualitatively in the MDL verification check sample

4.0 Scope and application, including components to be analyzed

4.1 This SOP is applicable in the determination and quantification of PCB as outlined in EPA SW-846 Method 8082. : water, soil, sediment, sludge, oil, fuel oil, waste solvent, fish, other aquatic animals, tissue samples, caulk, wipes and air cassette samples including polyurethane foam (PUF) and associated filters for EPA Methods TO-4A and TO-10A.

4.2 In general, samples are extracted, or in the case of oils and waste solvent diluted, with a pesticide grade solvent. Applicable extraction methods for solids and animal tissues include: SW-846 Method 3540 (Soxhlet), SW-846 Method 3545 (Pressurized Fluid Extraction), or SW-846 Method 3550 (Ultrasonic Extraction). Extraction methods for aqueous samples include SW-846 Method 3510 (Separatory Funnel), and SW-846 Method 3520 (Continuous Liquid Liquid Extraction). The extracts are further processed by concentrating or diluting, depending on the PCB concentration, and carried through a series of clean-up techniques. Applicable cleanup techniques include SW-846 Method 3620 (Florisil Cleanup), SW-846 Method 3660 (Sulfur Cleanup) and SW-846 Method 3665 (Sulfuric Acid/Permanganate Cleanup). The sample is then analyzed by direct injection onto a gas chromatographic system and detected by an electron capture detector.

4.3 This method provides detailed instructions for gas chromatographic conditions, calibration, and analysis of PCB by capillary column gas chromatography. Each matrix requires different sample handling or special preparation procedure before analysis can be performed. Each sample matrix will be covered separately in the extraction standard operating procedures.

5.0 Summary of Test Method

5.1 Samples are extracted with a pesticide analytical grade solvent. The extracts are further processed by concentration and a series of clean-up procedures. The sample extracts are then analyzed by injecting onto a gas chromatographic system and with an electron capture detector in series.

5.2 This purpose of this SOP is to provide a detailed written document for quantification of PCB according to SW-846 Method 8082 specification.

5.3 This SOP provides detailed instructions for gas chromatographic conditions, calibration, and analysis of PCBs by gas chromatography. Sample extraction and cleanup procedures are described separately in additional laboratory Standard Operating Procedures.

5.4 The following PCB Aroclors can be determined by this method*:

Compound	CAS Number
Aroclor 1016	12674-11-2
Aroclor-1221	11104-28-2
Aroclor-1232	11141-16-5
Aroclor-1242	53469-21-9
Aroclor-1248	12672-29-6
Aroclor-1254	11097-69-1
Aroclor-1260	11096-82-5

*Note: Additional PCB Aroclor mixtures including Aroclor 1262 and Aroclor 1268 may be analyzed by this method with minor modifications

5.4 Extensive knowledge of this SOP and EPA Method 8082 is required. The analysis portion of this method should be performed by a skilled chemist or by an analyst trained in the quantification of trace organics by gas chromatography.

6.0 Definitions

6.1 Accuracy – The nearness of a result or the mean of a set to the true value. Accuracy is assessed by analysis of references samples and percent recoveries.

6.2 Analytical Batch –The basic unit for analytical quality control is the analytical batch, which is defined as samples which are analyzed together with the sample method sequence and the same lots of reagents and with the manipulations common to each sample within the same time period or in continuous sequential time periods. Samples in each batch should be of similar matrices (e.g. water, sediment, soil, etc.).

6.3 Blank – A blank is an artificial sample designed to monitor the introduction of artifacts into the process. For aqueous samples, reagent water is used as a blank matrix, however, a universal blank matrix does not exist for solid samples, but sometimes sodium sulfate is used as a blank matrix. The blank is taken through the appropriate steps of the process. A

reagent blank is an aliquot of analyte-free water or solvent analyzed with the analytical batch. Field blanks are aliquots of analyte-free water or solvents brought to the field is sealed containers and transported back to the laboratory with the sample containers. Trip blanks and equipment blanks are two specific types of field blanks. Trip blanks are not opened in the field. They are a check on sample contamination originating from sample transport, shipping and from site conditions. Equipment blanks are opened in the field and the contents are poured appropriately over or through the sample collection device, collected in a sample container, returned to the laboratory as a sample. Equipment blanks are a check on sampling device cleanliness.

6.4 Continuing Calibration Check Standard (CCCS) –The continuing calibration check standard contains all target analytes found in the calibration standards and is used to verify that the initial calibration is prepared correctly and that the instrument system is correctly calibrated. Calibration check solutions are made from a stock solution which is different from the stock used to prepare standards

6.5 Calibration Standard (ICAL)– A series of known standard solutions used by the analyst for instrument calibration. Calibration standards are prepared from primary standard and/or stock standard solutions.

6.6 CAS Number – An assigned number used to identify a chemical. CAS stands for Chemical Abstracts Service, an organization that indexes information published in Chemical Abstracts by the American Chemical Society and that provides index guides by which information about particular substances may be located in the abstracts. Sequentially assigned CAS numbers identify specific chemicals, except when followed by an asterisk (*) which signifies a compound (often naturally occurring) of variable composition. The numbers have no chemical significance. The CAS number is a concise, unique means of material identification. (Chemical Abstracts Service, Division of American Chemical Society, Box 3012, Columbus, OH 43210: [614] 447-3600).

6.7 Duplicate– A second aliquot of a sample that is treated the same as the original sample in order to determine the precision of the method.

6.10 Environmental Sample – An environmental sample or field sample is a representative sample of any material (aqueous, non-aqueous, or multimedia) collected from any source for which determination of composition or contamination as requested or required.

6.11 Initial Calibration – Analysis of analytical standards for a series of different specified concentrations; used to define the linearity and dynamic range of the response of the analytical detector or method.

6.12 Instrument Calibration – Analysis of analytical standards for a series of different specified concentrations; used to define the quantitative response, linearity and dynamic range of the instrument to target analytes.

6.13 Laboratory Control Sample (LCS) – Also known as the Quality Control (QC) Check Standard or Quality Control (QC) Check Sample. The LCS consists of an aliquot or reagent water or other blank matrix to which known quantities of the method analytes are added. The LCS is extracted and analyzed exactly like a field sample, and its purpose is to determine whether the analysis is in control and whether the laboratory is capable of making accurate and precise measurements.

6.14 Laboratory Method Blank – An analytical control consisting of all reagents and surrogate standards that is carried through the entire analytical procedure. The method blank is used to define the level of laboratory background and reagent contamination.

6.15 Matrix – The predominant material of which the sample to be analyzed is composed. Matrix is not synonymous with phase (liquid or solid).

6.16 Matrix Spike – Aliquot of sample (water or soil) fortified (spiked) with known quantities of specific compounds and subjected to the entire analytical procedure in order to indicate the appropriateness of the method for the matrix by measuring recovery.

6.17 Matrix Spike Duplicate – A second aliquot of the same matrix as the matrix spike (above) that is spiked in order to determine the precision of the method.

6.18 Method Detection Limit (MDL) – The minimum constituent concentration that can be measured and reported with 99% confidence that the signal produced is different from the blank in a given matrix. The MDL is determined from a minimum

of seven replicate samples, taken through the entire preparation and analysis procedure. The standard deviation, *s*, of those replicates is multiplied by a student's t factor in order to calculate the MDL.

6.19 MSDS – Material Safety Data Sheet. OSHA has established guidelines for the descriptive data that should be concisely provided on a data sheet to serve as the basis for written hazard communication programs.

6.20 PCB Polychlorinated biphenyls (PCBs) are a class of 209 individual chemical compounds (congeners), in which one to ten chlorine atoms are attached to biphenyl. Use of PCBs has made them a frequent environmental pollutant.

6.21 Precision – The agreement between a set of replicate measurements without assumption of knowledge of the true value. Precision is assessed by means of duplicate/replicate sample analysis.

6.22 Quality Control – Set of measures within a sample analysis methodology to assure that the process is in control.

6.23 Standard Curve – A standard curve is a curve which plots concentrations of known analyte standards versus the instrument response to the analyte. Calibration standards are prepared by diluting the stock analyte solution in graduated amounts which cover the expected range of the samples being analyzed. Standards should be prepared at the frequency specified in the appropriate section. The calibration standards must be prepared using the same type of acid or solvent and at the same concentration as will result in the samples following sample preparation. This is applicable to organic and inorganic chemical analyses.

6.24 Stock Solution – Standard solution which can be diluted to derive the other standards.

6.25 Surrogate – Organic compounds which are similar to analytes of interest in chemical composition, extraction, and chromatography, but which are not normally found in environmental samples. These compounds are spiked into all blanks, calibration and check standards, samples (including duplicates and QC reference sample) and spiked samples prior to analysis. Percent recoveries are calculated for each surrogate.

6.26 Surrogate Standard – A pure compound added to a sample in the laboratory just before processing so that the overall efficiency of a method can be determined.

7.0 Interferences

7.1 Laboratory contamination can occur by the introduction of plasticizers (phthalate esters) into the samples through the use of flexible tubing. Samples and extracts should not be exposed to plastic materials. Phthalate esters exhibit response on electron capture detectors, usually as late eluting peaks, and can interfere in PCB quantification. Laboratory method blanks must be thoroughly reviewed for presence of non-target peaks and comparison of samples with blank chromatographic patterns.

7.2 Elemental sulfur (S_8) is readily extracted from soil samples and may cause chromatographic interferences in the determination of PCBs. Sulfur can be removed through the use of Method 3660.

7.3 Polychloroterphenyls (PCTs), polybrominatedbiphenyls (PBB), polychlorinated napthalenes (PCN), as well as dioxins can co-elute with PCBs. Carry-over from these compounds, when in high concentration, is common if clean-up procedures are not followed. These materials may be removed through the use of specified clean-up procedures.

7.4 Pesticides can be a source of contamination through breakdown into components such as hexachlorobenzene (HCB). This chlorinated compound can carry-over on the GC column, and contaminate samples. Specified clean-up procedures should be followed to eliminate this as a source of contamination when analyzing PCBs. High concentrations of pesticides can cause carry-over on GC columns.

8.0 Safety

8.1 Safety glasses and disposable gloves must be worn when handling samples and extracts.

8.2 All manipulations of sample extracts should be conducted inside a chemical fume hood. Manipulation of sample extracts outside of a fume hood should be minimized by the analyst.

8.3 Safe laboratory practices should be followed by the analyst at all times when conducting work in the lab. The analyst should refer to the reference file of material safety data sheets to familiarize themselves with the precautions for handling solvents and chemicals used to process samples. The analyst should refer to the laboratory chemical hygiene plan for further safety information.

8.4 Samples remaining after analysis should either be returned to the customer for disposal or disposed of through the laboratory's disposal plan. Refer to the sample custodian for assistance and also standard operating procedure NEO54, disposal of laboratory waste.

9.0 Equipment and Supplies

9.1 Gas Chromatograph: Complete system for high resolution, capillary column capability and all required accessories. Northeast Analytical, Inc. will use a Varian Model 3400 or 3800 (or equivalent) gas chromatograph (or equivalent), equipped with a Model 1077 or 1177 split/splitless injector (or equivalent), temperature programmable oven, Varian Model 8200, Varian Model 8400, or LEAP GC pal automatic sampler (or equivalent), and electron capture detector (or equivalent). A data system and integration of detector signal is interfaced to the gas chromatograph.

9.2 Chromatographic Data System: A data system for measuring peak height and peak area. An Empower computer network based workstation (Waters Corporation), will be employed to capture detector response and digitally store the chromatographic, electronic peak integration for precise calculations, database structuring of the analytical information, and archival capabilities.

9.3 Column (Primary): ZB-1, Phenomenex Cat. No. 7HG-G001-11; 30 m x 0.25mm x 0.25 um ; DB-1, J&W Part No. 122-1032; 30 m x 0.25 mm x 0.25 um ; or equivalent.

9.4 Column (Secondary): ZB-5, Phenomenex Cat. No. ZB-5-G002-11; 30m x 0.25mm x 0.25 um ; DB-5, J&W Part No. 122-5032; 30m x 0.25 mm x0.25 um; or equivalent.

9.5 Class A volumetric flasks: 5.0 – 100mL.

9.6 8 dram vials and 4 vials dram for sample extract storage.

9.7 Pasteur pipettes.

9.8 250ml and 100ml beakers, glass.

9.9 Disposable 1.0, 5.0, and 10.0 ml pipettes.

9.10 Hexane, Burdick and Jackson-Pest Grade.

9.11 Acetone, Burdick and Jackson.-Pest Grade

9.12 Toluene, Baker, (Cat.No. 9336-03)

9.13 Methylene Chloride, Burdick and Jackson, (Cat. No. 300-4)

9.13 Ferrules: 0.4mm graphite/vespel, Restek 20229, and ¼" graphite ferrules, Restek 20210 or equivalent.

9.14 Injector septa: Thermolite Septa, Restek 20365 or equivalent.

9.15 Injector liner: Low Pressure Drop Liner w/Glass Wool, Restek 21033 or equivalent.

9.16 SGE Injector Syringe 10.0 µL: SGE 002987 or equivalent

9.17 Auto sampler vials: Snap vial 12x32mm Clear w/P, Microliter 11-5200

9.18 Snap Caps: 11mm Natural Snap Cap PTFE, Microliter 11-0051N-B.

10.0 Reagents and Standards

10.1 Analytical Standard Solutions.

10.1.1 Aroclor Stock Standard Solutions

10.1.1.1 Polychlorinated Biphenyls - Neat commercial material for standard preparation. These materials are multi-component mixtures of PCB congeners and are the actual materials that were used in products such as electric power transformers and capacitors. Monsanto was the largest producer of PCB formulations and sold them under the trade name Aroclor. These standards should be compared to PCB reference materials to verify commercial materials. To be used as calibration standards, they must have the same pattern and congener distribution.

10.1.1.2 Stock standards are prepared from individual Aroclor formulations by weighing an exact amount of the neat material to the nearest 0.1 g, and dissolving and diluting to volume in a 100 mL volumetric flask with hexane. See Attachment A, Table 1 for exact weights of each compound.

10.1.1.3 The stock standards are transferred into Boston bottles and stored in a refrigerator at 0-6°C, protected from light.

10.1.1.4 The stock standards are transferred into screw-cap boston bottles and stored in a freezer 0°C , protected from light. Stock standards should be checked frequently for signs of evaporation, especially just prior to preparing calibration standards. Stock PCB standards must be replaced after one year, or sooner if a problem with instrument calibration is detected.

10.2 Calibration Standards

10.2.1 Calibration standards are prepared at five concentration levels using a prepared working standard. See Attachment A, Tables 2 and 3A AND 3B for the preparation and exact concentrations of the working standards. The following five standards make up the initial calibration curve standard set for a High Level curve : 20 ng/mL, 100 ng/mL, 250 ng/mL, 500 ng/mL, 1000 ng/mL. The following five standards make up the initial calibration curve set for a Low Level curve: 5 ng/mL, 10 ng/mL, 20 ng/mL, 50 ng/mL, 100 ng/mL.

10.2.1 The two surrogates Tetra-chloro-meta-xylene (TCMX) and Decachlorobiphenyl (DCBP) are included in the A1254 calibration standards. The standard for TCMX/DCBP is prepared by diluting 1 mL of TCMX/DCBP custom standard solution (ULTRA, cat.#CUS-4911, at 500/5000 ng/mL) into a 1000 mL volumetric flask resulting in a solution of TCMX/DCBP at 0.5/5.0 PPM

10.2.2 Refer to Attachment A, Tables 4A and 4B for instructions on preparation of the calibration standards containing A1254 and the surrogates. Refer to Attachment A, Tables 3A and 3B for instructions on preparing the remaining calibration standards.

10.2.3 Transfer all calibration standards to ASE vials and store in a refrigerator at 0-6°C, protected from light. Calibration standards must be replaced after six months, or sooner, if comparison with check standards indicates a problem.

10.3 Continuing Calibration Standards:

10.3.1 The surrogate compounds Tetra-chloro-meta-xylene (TCMX) and Decachlorobiphenyl (DCBP) are included in all Continuing Calibration Check Standards at a concentration near the mid-point of the surrogate calibration curve sequence. All continuing calibration standards are prepared independently from calibration standards, by using an alternate source purchased from standard vendors. Refer to Attachment B, Tables 1-3 for instructions on preparation of these standards.

11.0 Sample Collection, Preservation, Shipment and Storage

11.1 Sample Collection and Preservation:

11.1.1 Routine soil, sediment, sludge, solid, caulk, and concentrated liquid samples should be collected in 8 oz clear glass wide-mouth jars, fitted with a Teflon-lined cap. Aqueous samples should be collected in 1 liter amber glass bottles with a Teflon-lined cap. Project specific protocols may require that containers be pre-cleaned to EPA specification protocol A –. Protect samples from light.

11.1.2 All samples must be placed on ice or refrigerated at >0-6°C from the time they are collected until delivery to the lab.). Samples that are collected within driving distance of the laboratory and delivered the same day may not have reached temperature acceptance limits. These samples are deemed acceptable if evidence of cooling is present (i.e. they are received with ice in the cooler)

11.2 Sample Shipment:

11.2.1 Sample Shipment is accomplished through a carrier such as Federal Express or United Postal Service for overnight 1-day delivery to the lab. Shipment is normally handled by the field personnel collecting the samples and coordinated with sample receiving department at the lab. Samples can also be picked up by the lab courier service if samples are collected within driving distance to the lab.

11.3 Sample Storage:

11.3.1 The samples must be protected from light and refrigerated at >0-6°C from time of receipt until they are removed from storage for extraction. Remaining sample material will be stored protected from light and refrigerated at >0-6°C. Sample will be disposed of or stored / archived according to project specifications.

11.3.2 Routine soil, sediment, sludge, solid, liquid and concentrated liquid samples are stored in a refrigerator dedicated for this type of sample.

11.4 Sample Extract Storage:

11.4.1 Sample extracts must be protected from light and refrigerated at >0-6°C during the analysis. After analysis is complete, sample extracts will be discarded after 60 days or can be archived in a freezer at less than -20°C for longer periods of time depending on the program requirements.

11.4.2 Field samples, sample extracts, and calibration standards must be stored separately.

11.5 Required Hold Times

11.5.1 Extraction of solid samples by appropriate technique must be completed within fourteen days from sample collection.

11.5.2 Extraction of aqueous samples by appropriate technique must be completed within seven days from sample collection.

11.5.3 Sample extracts must be analyzed within forty days of sample extraction.

12.0 Quality Control

12.1 This section outlines the necessary quality control samples that need to be generated at the time of sample extraction. The results of the quality control measurement samples document the quality of the data generated.

The following table lists the Quality Control samples required for capillary gas chromatography analysis of PCBs.

Quality Control Requirements

QC Sample	Frequency
Method Blank	With each sample batch (up to 20 samples)
Lab Control Spike	With each sample batch (up to 20 samples)
Cont Cal Check Std	Analyzed prior to each sample batch and at a frequency or one per ten injections. Each analytical sequence must close with a Continuing Calibration Check Standard (CCCS).
Duplicate Analysis	Field generated sample – analyzed at discretion of client.
Matrix Spike	One matrix spike per 20 field samples or designated sample batch may be performed as specified in the client site plan.
Matrix Spike Duplicate	One matrix spike duplicate per 20 field samples or designated sample batch may be performed as specified in the client site plan.

12.2 Method Blank

12.2.1 With each batch of samples to be extracted a method blank is processed. The method blank is carried through all stages of sample preparation and measurement steps. For water samples and organic-free reagent water blank is processed. The method blank must exhibit PCB levels less than the matrix defined reporting limit (RL). If the method blank exhibits PCB contamination above the reportable RL, the samples associated with the contaminated blank should be re-extracted and analysis repeated. If there is no original sample available for re-extraction then the results should be flagged with a "B" indicating blank contamination. The value measured in the blank is reported for those samples associated with the particular blank out of criteria.

12.3 Laboratory Control Spike

12.3.1 A Laboratory Control Spike (LCS), also referred to as a QC reference check standard, is extracted with each batch of samples at a rate of one per 20 samples. For water sample, spike one liter of laboratory organic free water, extract and analyze. For solid and tissue samples spike 10 grams of sodium sulfate, extract and analyze. For oil samples spike 1 gram of PCB free oil, extract and analyze. An Aroclor is chosen for the LCS analyte, typically based on program requirements or expected sample contamination. Calculate the percent recovery for the PCB spike. If the percent recovery for the LCS is out of criteria, (70%-130%) the analysis is out of the control and the problem should be immediately corrected.

12.3.2 The following are default Laboratory Spikes Concentrations:

Aqueous Samples: .1.0 mL of A1242 @ 0.5 ug/mL (ppm) yielding a final sample concentration of 0.500 ug/L

Solid Samples: 1.0 mL of A1242 @ 12.5 ug/mL (ppm) yielding a final sample concentration of 10 ug/g

Note: Alternate spike concentrations and selection of Aroclors may be applicable based on project specific requirements.

12.4 Duplicate Analysis

12.4.1 Duplicate analysis of the same sample is performed to assess method precision. A duplicate can also be performed as a blind duplicate, so that identification with original sample is withheld. The analysis of a duplicate sample precludes that PCBs are to be found at appreciable levels in samples. If this is not known the analysis of matrix spike/matrix spike duplicates provide more consistent quality control information. The relative percent difference of the two measurements on the sample is calculated on total PCB concentration by the following equation:

RPD = (DUP1-DUP2)/AVG x 100

Where: RPD = Relative Percent Difference
DUP1 = The greater of the measured values
DUP2 = The lesser of the measured values
AVG = Average of the two analysis

The relative percent difference must be less than or equal to 30%.

12.5 Matrix Spike and Matrix Spike Duplicate (MS/MSD)

12.5.1 A matrix spike is to be analyzed at a rate of one matrix spike per every 20 samples. Also matrix spike duplicate or duplicate sample is to be analyzed at a rate of one per every 20 samples. Duplicate samples may be appropriate in place of matrix spike duplicate, for soil and waste samples, where detectable amounts of organics are present.

12.5.2 The following are default Laboratory Matrix Spike Concentrations:

Aqueous Samples: .1.0 mL of A1242 @ 0.5 ug/mL (ppm) yielding a final sample added concentration of 0.500 ug/L

Solid Samples: 1.00 mL of A1242 @ 100 ug/mL (ppm) yielding a final sample added concentration of 10 ug/g

Note: Alternate spike concentrations and selection of Aroclors may be applicable based on project specific requirements.

12.5.3 Analyze one unspiked and one spiked sample. Calculate the percent recovery based on PCB concentration of both samples as follow:

P = A-B/T x 100

Where: P = Percent recovery, %
A = concentration of analyte in the spike sample aliquot
T = Know true values of the spike concentration
B = Background concentration of PCB in the unspiked sample aliquot

12.5.4 Matrix spike recovery information is used to assess the long-term precision and accuracy of the method for each encountered matrix. Matrix spike/matrix spike duplicate results are not used alone to qualify an extraction batch. Generally, percent recovery for MS/MSD samples should be greater than or equal to 70% and less than or equal to 130% based on the total PCB concentration. If the percent recovery is outside the limits, all calculations should be checked and the data should be narrated to describe possible matrix interference.

12.6 Surrogates

12.6.1 A surrogate compound is added to each sample, matrix spike, matrix spike duplicate, duplicate, method blank, and LCS at time of extraction. The surrogate compounds chosen for this method are Tetra-chloro-meta-xylene (TCMX) and Decachlorobiphenyl (DCBP). The following are typical surrogate amounts added to normal encountered matrices. These amounts can be adjusted if the PCB background levels are high and the surrogate is being diluted out of analysis range.

12.6.1.1 Soil, sediment, sludge, oil, fuel oil, waste solvent, fish, other aquatic animals, tissue samples: 0.5ml of 0.5ppm TCMX/ 5.0ppm DCBP set to 25ml final extract volume.

12.6.1.2 Water: 1.0ml of 0.05ppm TCMX/ 0.5ppm DCBP set to 10ml final extract volume.

12.6.2 Only one surrogate analyte needs to meet established control limits for the analysis to be valid. The recovery must fall within lab established limits of 60-140% if lab limits are not available for the analysis to be valid. If percent surrogate recovery is not within laboratory established limits for either surrogate, the following steps are required.

12.6.2.1 Review calculations that were used to generated surrogate percent recovery values to make certain there are no errors.

12.6.2.2 Check by GC analysis surrogate solutions used during sample extraction steps to ensure that no problems exist with spiking solutions.

12.6.2.3 Review data for chromatographic interferences.

12.6.2.4 Re-extraction and/or re-analysis of samples may be indicated if problems persist with surrogate recoveries. If the surrogate percent recovery is out of limits on the re-extracted samples, low or high surrogate recovery is due to matrix affects and the data can be reported as estimated. If above steps do not lead to satisfactory results then consult with organics manager to resolve the situation.

12.7 Continuing Calibration Check Standard (CCCS)

12.7.1 The initial CCCS is from an alternative source independent of the calibration check standards. It is prepared at a concentration approximately equal to the midlevel standard. This standard is analyzed after the initial calibration standards, every tenth injection, and at the end an analytical sequence. One check standards must be run with a 24 hour time period. The percent recover must be $\pm$15% of the true value.

12.7.2 If the criterion is exceeded, the analyst should inspect the system to determine the cause and perform maintenance as necessary. The system can then be recalibrated and sample analysis can proceed. Note that all samples which are not bracketed by valid check standards must be re-analyzed when the system is in-control.

12.8 Retention Time

12.8.1 The retention time (RT) windows are established from the Continuing Calibration Check Standard (CCS) peak retention times. The CCS is analyzed three times over a 72-hour period and the standard deviation is calculated from the three retention time measurements. The standard deviation is multiplied by three and this establishes the retention time window for each quantified peak (±3SD). Use the retention time for a peak in the continuing calibration check standard to determine the mid point of the retention time window for the analysis sequence. If the continuing calibration checks fall outside of these windows update the windows using the previous check standard. If the retention times are still outside the established windows instrument maintenance must be performed and recalibration may be required.

12.8.2 This function is performed in the chromatography software graphically as vertical dropdown retention time markers with retention time window brackets. Besides using the retention time window to assign peaks for quantification, the analyst should also rely on their experience in pattern recognition of multi-response sample analysis.

12.8.2 See attachment F for an example of calculated retention time windows.
Retention Time Window Study for GC18F Column DB-1

12.9 Analytical Sequence Queue:

12.9.1 The following is an example of the order that initial calibration standards, continuing calibration check standards, method blanks, QC samples, and samples are placed in an analytical sequence. A continuing calibration check standard is run after every nine samples in the analytical sequence. All analytical sequences must end with a continuing calibration check standard regardless of the number of samples. Below is an example of an analytical sequence:

Injections	Material Injected
1	Hexane Blank
2-36	Initial Calibration Standards
37-43	Continuing Calibration Check Standard
44-52	Samples analyses, including method blanks, matrix spikes, matrix duplicates, matrix spike duplicates, and QC reference check standard. A maximum of nine samples between continuing calibration check standards.
53	Continuing calibration check standard
54 and higher	repeat inject. 44-53 sequence

12.10 PCB Aroclor Qualitative Identification and Secondary GC Column Confirmation:

12.10.1 Positive identification of PCB Aroclors is based on comparison of retention time of the five selected quantitation peaks and major non-quantitation peaks for the unknown sample with retention time of reference standards (continuing calibration verification standards). Additionally pattern recognition is used for comparison of unknown samples with reference standards for positive identification. Confirmation of Aroclor presence by secondary GC column analysis may be necessary for highly altered/degraded PCB patterns or for programs including PCB air monitoring, US-EPA CLP protocol and other projects as specified in the site sampling and analysis quality assurance plan.

12.10.1.1 Dual Column/Confirmatory Column Analysis by GC:

Inject samples under same operating conditions and analytical run QA/QC parameters on a secondary GC column of dissimilar phase (e.g ZB-1 and ZB-5). Note: If using dual GC column system, samples are injected sequentially through separate injection ports onto both columns. Samples are analyzed and concentration results are reported.

12.10.1.2 Dual Column/Confirmatory Column Laboratory Default by SW-846:

12.10.1.2. 1 Report **highest** concentration of the 2 column results for each individual Aroclor on the merged EDD, Form 1 or Certificate of Analysis (Note: This is appropriate for Aroclor regulated projects. E.g. Air Monitoring for EPA TO-10A alternative reporting may be based upon total PCB values for PCB- Total regulated projects).

12.10.1.2.2 If **RPD percent** exceeds 40% report the highest concentration result of the two analyses unless observed chromatographic interference or instrumental analysis QA/QC indicates the lower value may be more accurate. P-flag all excursions > 40% and describe interferences or rationale for reporting lower value in Data Narrative.

12.10.1.2.3 If a concentration is above the PQL on one column and below the PQL on the second column, the qualitative presence is not confirmed and the sample is reported as not detected. **Note: If reporting to the MDL is required do the following:**

For reporting the MDL:

a) If one result is greater than the PQL and other result is < PQL (J-flag) Report the **highest** result as confirmed (*unless interference or QC reasons indicate lower value*)

b) If one result is above MDL (J-Flag) and second is Not Detected report the concentration as **not detected**. (Presence not confirmed).

c) If both results are J-Flag values (< PQL) report the **highest** value of the two.

12.10.1.3 **USEPA-CLP/ASP Program Protocols**

a) Report **Lowest** Value of the 2 column results for each individual Aroclor on the merged EDD, Form 1 or Certificate of Analysis (Note: This is appropriate for Aroclor regulated projects. E.g. Air Monitoring for EPA TO-10A alternative reporting may be based upon total PCB values for PCB- Total regulated projects).

b) If **Percent Difference** (not RPD%) exceeds 25% then P-flag all excursions > 25%. Note any chromatographic interferences present in Case Narrative.

c) If one result is greater than PQL and other result is < PQL (J-Flag) Report the **lowest** result (J-Flagged) value (*confirmed hit*).

d) If one result is above MDL (J-Flag) and second is Not detected, report the concentration as **not detected** (*presence not confirmed*).

13.0 Calibration and Standardization

13.1 Gas chromatographic operation parameters: See Attachment C

13.3 Initial GC Calibration

13.3.1 GC calibration is performed by the internal standard calibration procedure. Prior to running samples the system must be calibrated and system performance must be verified.

13.3.2 Establish the gas chromatographic operating parameters outlined in the Procedure section and prepare the calibration standards at the five concentrations outlined in the Reagent and Standard section. Inject each calibration standard using the GC Autosampler and the parameters outlined in the Procedure section. Note: The same parameters are used for actual samples.

13.3.3 For each Aroclor, 5 peaks are selected to prepare calibration curves. The peaks selected from the multi-component Aroclor formulations were based on maximizing the separation for each Aroclor (i.e., minimizing peak overlap in retention time). Consideration was also given to selecting peaks that normally did not have problems with co-elution with interfering peaks or possible co-elution with

organochlorine pesticides. The determined area of the five peaks selected for calibration is processed by the data workstation as a group, combining the area for calculations of the calibration factors. The following table lists the Aroclors that are included in the initial calibration and the peak numbers used.

Aroclor	Peak Numbers
A1016	6 , 7 , 8 , 9 , 10
A1221	1 , 2 , 3 , 4 , 5
A1232	5 , 7 , 8 , 9 , 10
A1242	6 , 7 , 8 , 9 , 10
A1248	11 , 12 , 13 , 14 , 15
A1254	16 , 17 , 18 , 19 , 20
A1260	20 , 21 , 22 , 23 , 24

13.3.4 For the initial calibration curve to be considered valid, the percent relative standard deviation of response factors must be less than 20% over the working range if average calibration factor quantitation is used. Note: the % RSD is a useful check for linearity through the origin and is used as a data quality indicator. In general an inverse weighted linear calibration curve with intercept is used for quantitation and is not replaced with the average calibration factor. For linear calibration curve the Correlation Coefficient R must be greater than 0.99.

13.3.5 Our laboratory uses a computer based chromatography software module (Water Corporation, Empower software) interfaced to the gas chromatograph. The workstation processes the detector signal, performs an analog to digital conversion, and stores the digitized chromatograms on the computer hard disk. Integration of peak areas and production of chromatograms is performed in the Empower software. All data analysis will be carried out on specialized software developed at Northeast Analytical including calculating calibration curves/response factors, report generation, and archival of data.

13.3.6 If a re-calibration is performed, the CCCS must be analyzed again and values calculated using the new relative response factors. If the CCCS fails to meet the percent difference criteria after re-calibration, sample analysis must not proceed until the problem is found and corrected (*i.e.,* GC gas leak, autosampler lines plugged, broken injector liner).

13.4 Retention Time Windows

13.4.1 The GC system should be checked by the analyst to make sure it is functioning properly before establishing retention time windows. Select a calibration standard and inject three times within a 72-hour time period.

13.4.2 For each peak calculate the standard deviation resulting from the variation in the three retention times for that peak.

13.4.3 The retention time window is defined as plus or minus three times the standard deviation of the three retention time determination.

13.5.3 If the standard deviation of the selected peak is zero, the standard deviation of the peak eluting after it is used. If it is the last eluting peak that the zero for the standard deviation, then substitute the standard deviation of the peak eluting before the last peak.

14.0 Procedure

14.1 Sample Extraction and Preparation

14.1.1 The following SOP's detail sample extraction procedures that are utilized in preparing samples for analysis by this analytical method:

SOP NAME	TITLE	EPA Method
NE005	Soxhlet Extraction/ Extract Prep	8082, 3540C
NE017	Fish and Biota Extraction	8082
NE088	PCB Extraction Of Wipe	8082, 3540A
NE111	Waste Dilution EPA 3580 for PCB 8082	8082, 3580A
NE120	Extraction and cleanup of PCB by SW-846 3550B	8082, 3550B
NE140	PCB Screening by GC	3510C, 3520C, 3545
NE141	SW-846 3510C H2O PCB extraction	8082, 608, 3510C
NE143	EPA 3545 extraction for 8082 PCB	8082, 3545
NE144	EPA 3545 extraction of wipe for 8082 PCB	8082, 3545
NE151	PUF Extraction for 8082 analysis	8082, 3540C/ TO-10A
NE158	% Lipid Determination Fish & Biota	3540, 3500, 2500A
NE194	High Level PCB extraction for 8082 by SepFunnel	8082, 3510C

14.2 Gas Chromatographic Procedures

14.2.1 Prescreening of sample extracts: See standard operating procedure NE140 for details on the PCB screening procedures used prior to final analysis by this method. Prescreening is a fast and effective way to determine if re-extracts are required and dilutions for over ranged samples. The GC will be standardized by using Aroclor 1221, Aroclor 1242, and Aroclor 1260. These three Aroclor formulations incorporate most environmental PCBs found in sample extracts and provide a good estimate of PCB amount for final dilution for this determinative method. A three level calibration curve is utilized (0.50ug/ml, 2.5ug/ml, and 5.0ug/ml standards). The concentration of each Aroclor (grouped as Aroclor 1221, Aroclor 1242, and Aroclor 1260 only) in a sample will be calculated based on the extract volume (not the sample weight or volume) to supply solution concentration values that show if the extract needs to be diluted for final capillary GC analysis. If a dilution is necessary, sample extracts are diluted to a solution concentration near 0.500ug/g, so ensuring each sample quantifies in the middle of the calibration curve.

14.2.2 Approximately 1.0ml of the final dilution extract is then transferred into a labeled autosampler vial.

14.2.3 The sequence of the analytical queue is set up in the NEA LIMS as a unique batch file. This file contains the exact order in which standards, instrument blanks, and samples will be analyzed. Once the sample set is uploaded into the Empower acquisition/run screen and saved, the sample set is printed and the samples are loaded into the GC autosampler tray in the order specified by the sample set queue.

14.2.4 The following labeling will be used on the autosampler vial and for the sample set file created for the analytical queue.

14.2.4.1 The initial calibration standard will be labeled as 040516A, 040516B, etc. Substitute the actual date of analysis and the Aroclor used in the file name.

14.2.4.2 The instrument blanks will be labeled 070405B01, B02, B03, etc. Substitute the actual date of analysis in the file name.

14.2.4.3 The Continuing calibration check standards will be labeled CS160405A CS160405B, etc. Substitute the actual date of analysis and the Aroclor used in the file name.

14.2.4.4 Samples are labeled with the laboratory identification number on the autosampler vial. In the sample set file the laboratory identification number, along with the client identification, sample weight, set volume and dilution are entered.

14.2.5 At this point the chromatography software can be initiated to start data collection. The gas chromatograph is placed into run mode and sample analysis is performed until the analytical queue is complete.

14.2.6 Peak Identification

14.2.6.1 Target peaks are identified in unknown samples based upon Retention Time (RT). The retention time of an unknown peak must fall within the retention time windows established.

14.2.6.2 Besides using retention time windows to assign peak IDs, the analyst should also rely on their own experience in recognition of multi-response PCB chromatograms. Caution should be exercised when identifying peaks which elute near interferences present in samples and blanks. Comparison of sample chromatograms with method blank and field blank chromatograms is useful in determining chromatographic interferences.

14.2.6.3 This method should be applied with caution when used in determining PCB of interest in unknown sample for which no prior historical information exists. In this case confirmatory column analysis or confirmation by GC/MS analysis may be advised.

14.3 Data Reduction/Reporting

14.3.1 Final peak assignments and quantitation calculations are performed within the software along with the current instrument calibration. The final concentration results are provided in the reporting section of the software. Final concentration results are reviewed by QA department or other approved manager before release to the client.

14.3.2 Data Qualifiers:

Sample Concentration Reports (Certificates of Analysis, Data Package Form 1's and Electronic Data Deliverables (EDDs) are generated using the appropriate data qualifiers as follows:

U – Denotes analyte not detected at concentration greater than or equal to the Practical Quantitation Limit (PQL). Note: PQLs are adjusted for sample weight/volume and dilution factors.

J - Denotes an estimated concentration. The concentration result is greater than or equal to the Method Detection Limit (MDL) but less than the Practical Quantitation Limit (PQL).

P - Indicates relative percent difference between primary and secondary GC column analysis exceeds 40 %.

C- Denotes analyte confirmed by secondary GC column analysis.

B - Denotes analyte observed in associated method blank. Analyte concentration should be considered as estimated.

E - Denotes analyte concentration exceeded calibration range of instrument. Sample could not be re-analyzed at secondary dilution due to insufficient sample amount, quick turn-around request, sample matrix interference or hold time excursion. Concentration result should be considered as estimated.

Z - Laboratory Reserved Qualifier (explained in associated Case Narrative)

15.0 Calculations

15.1 Calibration curve calculation:

15.1.1 PCB Solution concentration calculation from initial Calibration by Linear Regression $Yi = aXi + b$

Xi = Calibrated Solution Concentration (ng/mL)
Yi = total area response of 5 PCB quant. peaks (uV-Sec.)
a = slope
b = intercept

Unknown Solution Conc. X = (Y –b) a

Y = Total area response of PCB Chromatogram (uV-Sec.)
a = slope of ICAL by linear regression
b = intercept of ICAL by linear regression

15.2 Capillary GC: Sample calculations

15.2.1 The concentration of each identified PCB Aroclor in a sample will be calculated based on the sample weight or volume.

15.2.2 The PCB solution concentration of the extract is calculated as follows:

Solution Conc. = (Y –b)/a

Where:

Y = Total area response of PCB Chromatogram (uV-Sec.)
a = slope of ICAL by linear regression
b = intercept of ICAL by linear regression

15.3 Final concentration of samples:

15.3.1 Calculations of final PCB concentrations will vary upon matrix, calculations are as follows:

(1.) Soil/Sediment/Solids:

Final Conc. = (Sol. Conc.) * (V)*DF/ (M)* (%Total Solids) (1/1000) ug/g

Where: Sol Conc. = Solution Concentration (ng/mL)
V = concentrated extract volume (mL)
DF = analytical dilution factor
M = mass extracted (g)

(2.) Water:

Final Conc.= (Sol. Conc.) * V*DF/[(Vt)](1/1000) ug/L

Where: Sol Conc. = Solution Concentration (ng/mL)
V = concentrated extract volume (mL)
DF = analytical dilution factor
Vt= Total Volume Extraction (L)

(3.) Biota Tissue

Final Conc. = (Sol. Conc.) * (V)*DF/(M)(1/1000) ug/g

Where: Sol Conc. = Solution Concentration (ng/mL)
V = concentrated extract volume (mL)
DF = analytical dilution factor

M = mass extracted (g)

(4.) PUF Cassette

Final Conc. = (Sol. Conc.) * (V)*DF/ (Va) ng/cubic meter

Where: Sol Conc. = Solution Concentration (ng/mL)
V = concentrated extract volume (mL)
DF = analytical dilution factor
Va = volume of air sampled (cubic meters)

(5.) Waste Oil

Final Conc. = (Sol. Conc.) * (V)*DF/ (M)*(%Total Solids) (1/1000) ug/g

Where: Sol Conc. = Solution Concentration (ng/mL)
V = concentrated extract volume (mL)
DF = analytical dilution factor
M = mass extracted (g)

15.3 The calculated concentration for each PCB aroclor will be compared to its respective sample-specific reporting limit (RL) and method detection limit (MDL). The results with concentrations at or above the MDL but below RL will be reported as detects and flagged as estimated J. The results for peaks with concentrations at or above the RL would be reported as unqualified numeric values.

16.0 Method Performance
Method Performance is Assessed by Initial/Continuing Demonstration of Proficiency Studies and MDL Determinations

16.1 Initial Demonstration of Performance (IDOP) Procedure:

16.1.1 Prepare 4 replicates of a fortified laboratory blank sample (using laboratory reagent water or sodium sulfate) by spiking each sample with 1.0 mL of 0.500 ug/mL Aroclor solution (typically Aroclor 1242) for water samples and 0.100 mL of 100 ug/mL Aroclor 1242 solution for solid samples. Prepare one method blank sample with the batch. Extract and analyze each aliquot according to procedures beginning in Section 14.0 below.

16.1.2 For each replicate the recovery value of the sample must fall in the range of 70±30 % (or established lab limits) and the percent RSD must be < 20 % for the method performance to be considered acceptable. See Section 23 Attachment G for example IDOP study.

16.1.3 This procedure must be repeated using four fresh samples until satisfactory performance has been demonstrated. The initial demonstration of capability is used primarily to preclude the laboratory from analyzing unknown samples via a new, unfamiliar method prior to obtaining some experience with it. It is expected that as laboratory personnel gain experience with this method the quality of data will improve beyond those required here.

16.2 Continuing Demonstration of Performance Procedure:

16.2.1 Annual continuing demonstration of performance may be satisfied by a repeat Initial Demonstration of Performance, the acceptable analysis of an unknown samples (for example PT test sample), or the acceptable analysis of 4 consecutive Laboratory Control Spike samples. Records of continuing demonstration of performance are maintained by the laboratory Quality Assurance Department.

16.2.2 With each batch of samples to be extracted a method blank is processed. The method blank is carried through all stages of sample preparation and measurement steps. For water samples an organic-free reagent water blank is processed.

16.2.3 The method blank should exhibit PCB levels less than the practical quantification limit or reporting limt (PQL or RL). If the method blank exhibits PCB contamination above the reportable quantitation limit, the samples associated with the contaminated blank should be re-extracted and analysis repeated when appropriate. If there is no original sample available for re-extraction or if the associated sample concentrations greatly exceed the blank concentration, then all positive concentration results for the associated samples should be flagged with a "B" indicating blank contamination and a case narrative describing the situation prepared.

16.2.4 A matrix spike is to be analyzed at a rate of 1 matrix spike per every 10 samples. A duplicate sample may be prepared in lieu of a matrix spike when detectable PCB concentrations are known to be present.

16.3 Method Detection Limit

16.3.1 A method detection limit will be determined for this method whenever major modification to the extraction or analysis procedures are made or at a minimum frequency of every 2 years. A minimum of seven laboratory organic free water samples or sodium sulfate will be prepared and spiked with chlorinated PCB methyl esters mixture, at a low level and taken through all extraction and analytical procedures.

$MDL = S * t_{(n-1,\ 1\text{-}alpha=0.99)}$

Where:

S = Standard deviation of the replicate analyses
n = Number of replicates
$t_{(n-1,\ 1\text{-}alpha=0.99)}$ = Student's t value for the 99% confidence level with n-1

For example: t for 8 replicates = $t_{(7,0.99)} = 2.998$

16.3.2 The determined MDL must be less than the concentration spiked but greater than one tenth (1/10) the spiked concentration. If not, repeat the MDL determination at an appropriate spike concentration for affected analytes.

17.0 Pollution Prevention

17.1 Pollution prevention is practiced in the laboratory by minimizing usage of solvents and chemicals, so that disposal of waste generated is held to the smallest amount possible. This is directly linked to the types of extraction procedures in place at the laboratory to reduce the volumes of solvents used for semi-volatile extraction procedures. Northeast Analytical employs extraction procedures such as continuous liquid/liquid and solid phase extraction methods to reduce solvent requirements for water extraction protocols and ASE and Soxhlet extractions for solid matrices.

17.2 Pollution prevention also relies on minimizing to the best extent the chemicals and solvents required to perform extraction and analysis procedures. The laboratory personnel strive to purchase chemicals and standards that will be consumed based on anticipated workload. For additional information about laboratory pollution prevention, please refer to laboratory SOP NE168.

18.0 Data Assessment and Acceptance Criteria for Quality Control Measures

18.1 The GC analyst is responsible for generating the data and also is the initial individual to review the data. This would include inspection of the chromatographic data, processing the raw data, producing all required data forms, inspection of calibration curves for compliance, surrogate recovery, laboratory control spike recovery, matrix spike/matrix spike duplicate recovery, and continuing calibration compliance.

18.2 Once the initial review of the data is performed by the analyst, decisions are made at that time to accept the data if all criteria are met or to reject sample data if any of the quality control parameters or limits are out of control. Depending on the situation, samples requiring re-extraction will be notified to the appropriate extraction personnel, sample extracts requiring re-injection will be queued for analysis, new calibrations may have to be performed, or samples re-analyzed due to failing continuing check standards.

18.3 The analyst may also consult with the quality control officer as to the best form of action to take or if the situation warrants corrective action beyond routine practices. If no recourse is available and the data is to be reported out of criteria, a Case Narrative Report is generated and the deviation is documented and reported to the client. The Case Narrative Report is filed with the data and is also useful for production of case narratives that are issued with the final data reports. If a problem exists that requires follow-up to rectify, a Corrective Action Report (CAR) is issued to document the problem found, steps taken to resolve the problem, and what samples were affected. This CAR form is filed by the quality control officer and reviewed by management to verify that appropriate actions have been taken to correct the problem.

18.4 Please see Table 19.1 below for specific Quality Assurance Acceptance Criteria.

19.0 Corrective Action for Out-Of-Control Data

19.1 The table below outlines the data assessment, acceptance criteria, and corrective action procedures for out-of-control data.

Quality Control Acceptance Criteria and Corrective Action Plan

Quality Control Item	Frequency	Acceptance Criteria	Corrective Action
Initial Calibration	The five point calibration is analyzed initially and when Continuing Calibration Check standard fails criteria.	- %RSD≤20% for the relative response factors for the calibration standards if using average response factor calibration. Correlation Coefficient R must be >0.99 for Linear Regression.	- Re-analyze the initial calibration standard and/or evaluate/correct instrument malfunction to obtain initial calibration and continuing calibration check standards that meet criteria.
Continuing Calibration Check Standard (CCCS)	- Initially analyze a CCCS immediately following an initial calibration. - After the initial CCCS of the sequence, a CCCS must be analyzed after 9 samples. - Analytical sequence must end with analysis of a CCCS.	- Calibration factor for the continuing calibration check must ±15% of the true value. - Retention time of all quantitated peaks must be within RT window (reset with each initial CCCS of a sequence). - All samples must be bracketed by a CCCS that meet all criteria stated above.	- If the reason for the failure of the CCCS appears to be a poor injection (or a degraded standard solution), the CCCS will be re-injected (or re-prepared and re-injected) immediately following the failed CCCS. This can only occur if the instrument is being attended by an analyst. If upon re-injection, the CCCS meets all the acceptance criteria and there is no apparent impact on the sample data the analytical sequence will continue and samples will not be reanalyzed. The associated sample data will be reported. - If CCCS failure was not due to a poor injection (or degraded standard solution) or the instrument was unattended at the time of the CCCS failure, correct system, if necessary, and recalibrate. Initial calibration and CCS criteria must be met before sample analysis may begin. Samples that are not bracketed by complaint CCCSs must be reanalyzed. -If acceptable CCCSs are observed later in the sequence, samples bracketed by acceptable CCCSs will be reported. Samples between the failed CCS and prior/ subsequent complaint CCCS will be re-analyzed.

-Retention Time (RT)	- Use the retention time for peak in the CCSs to determine midpoint of the relative retention time window for the analysis sequence. -Each sample analysis: Rely on RT windows to identify PCB Aroclor to report. Also use pattern recognition and professional judgment for peaks that shift from RT windows, because compound composition may shift RT for GC peaks.	- Each quantitated peak and surrogate peak should be with established windows.	-Inspect chromatographic system for malfunction, correct problem. Perform re-analysis if necessary.
Method Blank	-One per extraction batch of ≤20 samples of the same matrix per day. -Must be analyzed on each instrument used to analyze associated samples. -Must undergo all sample preparative procedures.	- Concentration does not exceed the RL for any PCB Aroclor. - Must meet surrogate criteria of 60-140% recovery.	- Re-analyze method blank to determine if instrument contamination was the cause. If method blank re-analysis passes, then report samples. -If method blank is found to contain PCB contamination above the RL for any PCB Aroclor compound , then re-extract and re-analyze all associated samples. If no sample exists for re-extraction, report data B flagged to indicate method blank contamination.
Laboratory Control Spike (LCS)	- One per extraction batch of ≤20 samples per matrix per day.	-Percent recovery must be within method limits. - Must meet Aroclor spike criteria of 70-130% recovery -Must meet surrogate criteria of 60-140% recovery.	-Re-analyze LCS to determine if instrument was the cause. If LCS passes, then report samples. -If LCS recovery is still out of limits, the re-extract and re-analyze all associated samples. If no sample exists for re-extraction, report data flagged to indicate LCS failed recovery.
Matrix Spike/Matrix Spike Duplicate (MS/MSD)	-Normal method procedure is to extract and analyze a matrix spike sample. One MS per extraction batch of ≤20 samples per matrix per day. -If requested, an MSD can be extracted and analyzed. The MSD would follow the above criteria as for the MS.	- Percent recovery for MS must be within method limits - If MS/MSD is analyzed, relative percent difference (RPD) should be within 30%. - Must meet Aroclor spike criteria of 70-130% recovery -Must meet surrogate criteria of 60-140% (unless original unspiked sample is also outside of criteria)	-Re-analyze MS and/or MSD to determine if instrument was the cause. If MS and/or MSD pass, then report samples. -Check for errors such as calculations and spike preparation. -Check original unspiked sample results and surrogate recovery for indications of matrix effects. -If no errors are found, and the associated LCS is within limits, then sample matrix effects are likely the cause. Note exceedance in case narrative.
Surrogates	-Surrogates are added to all samples and QC samples.	- Percent recovery for the surrogate should be 60-140%.	-Re-analyze the affected sample or QC sample to

	Tetra-chloro-meta-xylene (TCMX) and Decachlorobiphenyl (DCBP) solution.		determine if instrument was the cause. If surrogate passes, then report samples. -Check for errors in surrogate calculation and surrogate solutions. -If no problem is found, then re-extract and re-analyze the sample. -If re-extraction is within limits and sample extract holding time, then report only the re-analysis. -If the re-extraction is within limits, but out of extraction holding time, then report both sets of data. -If the re-extraction produces surrogate recovery still out of limits, then report both sets of data. -If no sample exists for re-extraction, report data flagged to indicate surrogate failed recovery or have a client re-sample.

20.0 Contingencies for Handling Out-Of-Control or Unacceptable Data

20.1 Data that is detected to be out-of-control for any reason, when compared to method acceptance criteria, will addressed in the following manner:

20.1.1 If the problem exists with the gas chromatographic instrumentation, appropriate action will be taken to repair and perform maintenance to bring the instrument back to operation condition. Once the instrumentation is determined to be correctly operating analysis can begin again.

20.1.2 If the problem exists with calibration standard solutions, the analyst will prepare new standards and discard the standard solutions that are suspect. Instrument calibration can be performed and analysis can begin once system is control.

20.1.3 If the problem exists with sample extraction and extract preparation, the extraction step that is producing the out of-control situation will be diagnosed and rectified. Once the troubleshooting procedures correct the problem extraction can once again occur and analysis can continue.

20.1.4 In situations where data is reported under out-of-control conditions, the data will be annotated with data qualifiers and/or appropriate descriptive comments defining the nature of the excursion in the sample case narrative. If warranted, a corrective action report (CAR) will be issued to define the problem, steps to correct the problem, and final resolution.

21.0 Waste Management

21.1 All applicable federal and state rules and regulations governing hazardous waste will be followed when disposing of laboratory waste generated during the execution of this method.

21.2 Please refer to standard operating procedures NE089 and NE054 regarding how hazardous waste is handled and disposed of by the laboratory.

22.0 References:

22.1 U.S. EPA SW-846 "Test Methods for Evaluating Solid waste; Volume 1B Laboratory Manual Physical/Chemical Methods", Office of Solid Waste and Emergency Response, Third Edition, Final Update III, December 1996.

22.2 U.S. EPA 40 CFP Part 136, "Guidelines Establishing Test Procedures of the Analysis of Pollutants", July, 1988.

22.3 "Standard Methods for the Examination of Water and Waste Water", 19th Edition 1995, American Public Health Association, American Water Works Association, Water Pollution Control Federation.

22.4 New York State Department of Health, "Environmental Laboratory Approval Program Certification Manual", Wadsworth Center for laboratories and Research, 1996.

22.5 Guide to Environmental Analytical Methods", third edition, Genium Publishing Corporation, 1997.

23.0 Tables, Diagrams, Flowcharts and Validation Data

Attachment A: PCB Stock Standard/Calibration Standard Preparation

Attachment B: Continuing Calibration Check Standard Preparation

Attachment C: GC Operating Parameters

Attachment D: Chromatograms

Attachment E: Example Retention Time Window Study

Attachment F: Example MDL Studies

Attachment A-PCB Stock Standards Prep Table:

Table 1

PCB Stock Standard Preparation Table

PCB Formulation	Supplier	Catalog #	Standard weight(mg)	Conc. (PPM)
A1016	Monsanto Neat Archive	NA	100.0	1000.0
A1221	Monsanto Neat Archive	NA	100.0	1000.0
A1232	Monsanto Neat Archive	NA	100.0	1000.0
A1242	Monsanto Neat Archive	NA	100.0	1000.0
A1248	AccuStandard	C-248N-50mg	100.0	1000.0
A1254	Monsanto Neat Archive	NA	100.0	1000.0
A1260	Monsanto Neat Archive	NA	100.0	1000.0
TCMX/DCBP (Surrogate)	Ultra Scientific	CUS-4911*	0.5/5.0	500/5000

Unless otherwise noted hexane is the solution used to make all dilutions. *Custom Order

Table 2

PCB Calibration Standard Preparation Table (High Level Calibration Curve)

Initial Volume (mL)	Initial Conc. (ug/mL)	Final Volume (mL)	Final Concentration (PPM)					
			A1016	A1221	A1232	A1242	A1248	A1260
5.0	(10.0)	50.0	1.000	1.000	1.000	1.000	1.000	1.000
2.5	(10.0)	50.0	0.500	0.500	0.500	0.500	0.500	0.500
1.25	(10.0)	50.0	0.250	0.250	0.250	0.250	0.250	0.250
1.00	(10.0)	50.0	0.200	0.200	0.200	0.200	0.200	0.200
0.500	(10.0)	50.0	0.100	0.100	0.100	0.100	0.100	0.100
5.0	(0.200)	50.0	0.020	0.020	0.020	0.020	0.020	0.020

Actual Concentration, see Table 1 for actual working standard concentrations for each Aroclor.
See Table 3 for A1254 Standard Preparation (high level)

Table 2A

PCB Calibration Standard Preparation Table (Low Level Calibration Curve)

Init. Volume (mL)	Initial Conc. (ug/ml)	Final Volume (mL)	Final Concentration (PPM)					
			A1016	A1221	A1232	A1242	A1248	A1260
0.5	(10.0)	50.0	0.100	0.100	0.100	0.100	0.100	0.100
2.5	(1.0)	50.0	0.050	0.050	0.050	0.050	0.050	0.050
1.0	(1.0)	50.0	0.020	0.020	0.020	0.020	0.020	0.020
1.0	(0.500)	50.0	0.010	0.010	0.010	0.010	0.010	0.010
0.50	(0.500)	50.0	0.005	0.005	0.005	0.005	0.005	0.005

Actual Concentration, see Tables 1 and 2 for actual working standard concentrations for each Aroclor.
See Table 3A for A1254 Standard Preparation (low level)

Table 3

PCB A1254 Calibration Standard Preparation Table (for High Level Curve)

Initial Volume (mL) A1254	Initial Conc. (ug/mL) A1254	Initial Volume (mL) 0.5/5.0 -PPM Surrogate	Final Volume (mL)	Final Concentration (PPM)		
				A1254	TCMX	DCBP
5.0	10.0	0	50	1.000	0	0
2.5	10.0	0	50	0.500	0	0
10.0	10.00	4.0	100	1.000	0.020	0.200
25.0*	1.000		50	0.500	0.010	0.100
1.25	10.0	0.800	50	0.250	0.008	0.080
0.500	10.0	0.500	50	0.100	0.005	0.050
1.000**	1.000	0.200	50	0.020	0.002	0.020

*This initial volume is of the A1254 1.000 ppm calibration standard WITH surrogates.
**This initial volume is of the A1254 1.000 ppm secondary stock solution WITHOUT surrogates.

Table 3A
PCB A1254, TCMX and DCBP Calibration Standard Preparation Table (for Low Level Curve)

Initial Volume A1254 (mL)	Initial Conc. A1254 (ug/mL)	Initial Volume (mL) 0.5/5.0 -PPM Surrogate	Final Volume (mL)	Final Concentration (PPM)		
				A1254	TCMX	DCBP
5.00	1.000	0.80	50	0.100	0.00800	0.0800
2.50	1.000	0.50	50	0.050	0.00500	0.0500
1.0	1.000	0.40	50	0.020	0.00400	0.0400
1.0	0.500	0.250	50	0.010	0.00250	0.0250
0.50	0.500	0.100	50	0.005	0.00100	0.0100

ATTACHMENT B: PCB Continuing Calibration Standards

Table 1
PCB Continuing Calibration Working Standards
prepared from 1000 PPM Stock Standards

PCB	Stock Source	Initial Volume (mL)	Final Volume (mL)	Concentration (PPM)
A1016	Chem Service Cat # F107AS	1.0	100	10.0
A1221	Chem Service Cat # F108AS	1.0	100	10.0
A1232	Chem Service Cat# F113AS	1.0	100	10.0
A1242	Chem Service Cat# F109AS	1.0	100	10.0
A1248	Chem Service Cat# F110AS	1.0	100	10.0
A1254	Chem Service Cat# F111AS	1.0	100	10.0
A1260	Chem Service Cat# F112AS	1.0	100	10.0

Table 2
PCB Continuing Calibration Standards (High Level)
prepared from 10 PPM CCV Working Standards and all contain surrogates

PCB	Surr. Volume* (mL)	Initial Volume (mL)	Final Volume (mL)	Surrogate Concentration TCMX/DCBP (PPM)	Aroclor Concentration (PPM)
A1016	2.0	5.0	100	0.010/0.100	0.500
A1221	2.0	5.0	100	0.010/0.100	0.500
A1232	2.0	5.0	100	0.010/0.100	0.500
A1242	2.0	5.0	100	0.010/0.100	0.500
A1248	2.0	5.0	100	0.010/0.100	0.500
A1254	2.0	5.0	100	0.010/0.100	0.500
A1260	2.0	5.0	100	0.010/0.100	0.500

*Surrogate stock solution 0.500 PPM TCMX and 5.0 PPM DCBP

Table 3
PCB Continuing Calibration Standards (low Level)
prepared from 10.0 PPM CCV Working Standards and all contain surrogates.

PCB	Surr. Volume* (mL)	Initial Volume (mL)	Final Volume (mL)	Surrogate Concentration TCMX/DCBP (PPM)	Aroclor Concentration (PPM)
A1016	1.0	0.500	100	0.005/0.050	0.050
A1221	1.0	0.500	100	0.005/0.050	0.050
A1232	.1.0	0.500	100	0.005/0.050	0.050
A1242	.1.0	0.500	100	0.005/0.050	0.050
A1248	.1.0	0.500	100	0.005/0.050	0.050
A1254	1.0	0.500	100	0.005/0.050	0.050
A1260	1.0	0.500	100	0.005/0.050	0.050

*Surrogate stock solution 0.500 PPM TCMX and 5.0 PPM DCBP

Attachment C: GC Operating Parameters

GC-19 Low Level PCB Method

GC #:	**19**
Method:	**608/8082 Low Level PCB**
GC Method #:	**5**
Date:	**10/27/2006**
Analyst:	**AJM**
File Name:	**S:\FORMS\LOG\GC\[GC19_Parameters.xls]8082 LL M5**
Column:	**19F ZB-1**
	19B ZB-5

Sample Delivery:

Single Method **Method 5**

CP-8400

Injection Mode:	**User**		
Sample Penetration Depth (%)	95	Viscosity Delay (sec)	1.0
Solvent Penetration Depth (%)	95	Plunger Speed During Fill (ul/sec)	1.0
		Plunger Speed During Injection (ul/sec)	5.0
Air Plug after Sample (ul)	1.0	Pre Injection Delay (sec)	3.0
Sample Air Gap	No	Post Injection Delay (sec)	3.0
Number of Fill Strokes	0		
Fill Volume for Fill Strokes	5.0		

Default Clean

Default Clean Vial	I
Default Clean Volume (ul)	5
Number of Clean Strokes	1
Default Clean Drawup Spped (ul/sec)	5

Clean Mode

Number of Pre-Injection Solvent Clean Flushes	1
Number of Post-Injection Solvent Clean Flushes	1
Number of Pre-Injection Sample Clean Flushes	0
Clean Solvent Source Vial	I+II

Solvent Plug

Vial for Solvent Plug	III
Solvent Plug Size (ul)	0.2
Solvent Drawup Speed (ul/sec)	5.0
Solvent Pause Time	1.0
Solvent Air Gap	NO

Select Edit

Select Automation Mode:	Single Method		
Edit Single Method Automation			
Method:	5		
Initial Sample:	0	Injection Possition	Both
Final Sample:	99	First Injector used	Pos. 1
Injections / Sample:	1	Use Injection Delay	No
First Injection Volume (ul):	1.1*	Delay between Injections	0.5
Second Injection Volume (ul):	1.3*	Advance Carrousel between Injections	No
	*can vary	Clean between Injections	Yes

Column Oven:

Step	Temp (°C)	Rate (°C/min)	Hold (min)	Total (min)
Initial	140	-------	2.00	2.00
2	200	10	0.00	8.00
3	245	5	13.23	30.23

Stabilization Time (min): 0.20

Injector Front CP-

1177 Oven	O
1177 Temperature	30

Tim	Split State	Split Ratio
Initial	ON	20

Flow/PSI (Front EFC, Type

Step	Pres (psi)	Rate (psi/min)	Hold (min)	Total (min)
Initial	*23.1**	-------	30.30	30.30

*last

Constant Flow Mode	N
Column Flow Rate	1.

Injector Middle CP-

1177 Oven	O
1177 Temperature	30

Tim	Split State	Split Ratio
Initial	ON	20

Flow/PSI (Front EFC, Type

Step	Pres (psi)	Rate (psi/min)	Hold (min)	Total (min)
Initial	*29.5**	-------	30.30	30.30

Constant Flow Mode	N
Column Flow Rate	1.

Detector **Front** **Middle**

ECD Oven	O	**OF**
Temperature	30	5
Electronics	O	O
Range	1	1

Tim	Range	Autozero
Initial	1	YE

Tim	Range	Autozero
Initial	1	YE

Front ECD		
Time Constant:	Fas	Fas
Cell Current:	CAP	CAP
Contact Potential (mV):	-	-
Date of last adjustment	5/2/200	5/2/200
Make-Up Flow (ml/min):	manually set and measured.	

Analog

Detectors	Front:
	Middle:
	Rear:

Tim	Signal Source	Attenuation
Initial	Front Detector	1
Tim	Signal Source	Attenuation
Initial	Middle Detector	1
Tim	Signal Source	Attenuation
Initial	Rear Detector	1

Valve

Time	1 Non	2 Non	3 Non	4 Non	5 Non	6 Non	7 None
Initia	----	----	----	----	----	----	-----

Initial valve

GC-19 8082 High Level PCB Method

GC #:	**19**
Method:	**8082 High Level PCB**
GC Method #:	**7**
Date:	**2/15/2006**
Analyst:	**KLL**
File Name:	**S:\FORMS\LOG\GC\[GC19_Parameters.xls]8082 HL M7**
Column:	**19F ZB-1**
	19B ZB-5

Sample Delivery:

Single Method **Method 7**

CP-8400

Injection Mode:	**User**		
Sample Penetration Depth (%)	95	Viscosity Delay (sec)	1.0
Solvent Penetration Depth (%)	95	Plunger Speed During Fill (ul/sec)	1.0
		Plunger Speed During Injection (ul/sec)	5.0
Air Plug after Sample (ul)	1.0	Pre Injection Delay (sec)	3.0
Sample Air Gap	No	Post Injection Delay (sec)	3.0
Number of Fill Strokes	0		
Fill Volume for Fill Strokes	5.0		

Default Clean

Default Clean Vial	I
Default Clean Volume (ul)	5
Number of Clean Strokes	1
Default Clean Drawup Spped (ul/sec)	5

Clean Mode

Number of Pre-Injection Solvent Clean Flushes	1
Number of Post-Injection Solvent Clean Flushes	1
Number of Pre-Injection Sample Clean Flushes	0
Clean Solvent Source Vial	I+II

Solvent Plug

Vial for Solvent Plug	III
Solvent Plug Size (ul)	0.2
Solvent Drawup Speed (ul/sec)	5.0
Solvent Pause Time	1.0
Solvent Air Gap	NO

Select Edit

Select Automation Mode:	Single Method		
Edit Single Method Automation Method:	7		
Initial Sample:	0	Injection Possition	Both
Final Sample:	99	First Injector used	Pos. 1
Injections / Sample:	1	Use Injection Delay	No
First Injection Volume (ul):	1	Delay between Injections	0.5
Second Injection Volume (ul):	1	Advance Carrousel between Injections	No
		Clean between Injections	Yes

Column Oven:

Step	Temp (°C)	Rate (°C/min)	Hold (min)	Total (min)
Initial	140	-------	2.00	2.00
2	200	10	0.00	8.00
3	245	5	13.23	30.23

Stabilization Time (min): 0.20

Injector: Front CP-1177

1177 Oven Power:	ON
1177 Temperature (°C)	300

Time	Split State	Split Ratio
Initial	ON	35

Flow/PSI(Front EFC, Type 1):

Injector: Middle CP-1177

1177 Oven Power:	ON
1177 Temperature (°C)	300

Time	Split State	Split Ratio
Initial	ON	35

Flow/PSI(Front EFC, Type 1):

Leap GC Pal Parameters 3/9/2007					
Sample injection Methods					
Method	**GC Dual**	**GC Duals**		**Method**	**GC Inj s**
Cylcle	GC Dual	GC Dual		**Cylcle**	GC Inj S
Syringe	10 ul	10 ul		**Syringe**	10 ul
1. Sample Vol	1.0 ul	1.0 ul		**1. Sample Vol**	1.0 ul
1. Air Vol	1.0 ul	1.0 ul		**Solvent Plug**	200 nl
1. Inject to	GC Inj 1	GC Inj 1		**Slv Source**	Standard
Inj Time Diff	0s	0s		**Int Standard**	0 nl
2. Sample Offs	1	0		**Std Source**	Standard
2. Sample Vol	1.0 ul	1.0 ul		**Air Gap (s)**	1.0 ul
2. Air Vol	1.0 ul	1.0 ul		**1. Air Vol Ndl**	1.1 ul
2. Inject to	GC Inj 2	GC Inj 2		**Pre Cln Slv 1**	2
Pre Cln Slv 1	2	2		**Pre Cln Slv 2**	2
Pre Cln Slv 2	2	2		**Fill Speed**	5.0 ul/s
Pre Cln Sp 1	0	0		**Pull Up Delay**	1.0 s
Int Cln Slv 1	2	2		**Inject to**	GC Inj 1
Int Cln Slv 2	2	2		**Inject Speed**	5.0 ul/s
Pst Cln Slv 1	2	2		**Pre Inj Del**	0 ms
Pst Cln Slv 2	2	2		**Pst Inj Del**	0 ms
Fill Volume	10 ul	10 ul		**Pst Cln Slv 1**	2
Fill Speed	2.5 ul/s	2.5 ul/s		**Pst Cln Slv 2**	2
Fill Stroke	0	0			
Pull Up Delay	500ms	500ms			
Inject Speed	10 ul/s	10 ul/s			
Pre Inj Del	0 ms	0 ms			
Pst Inj Del	0 ms	0 ms			

ATTACHMENT D ZB5 Chromatograms

FIGURE 1. A1016 @ 0.500PPM PLOT

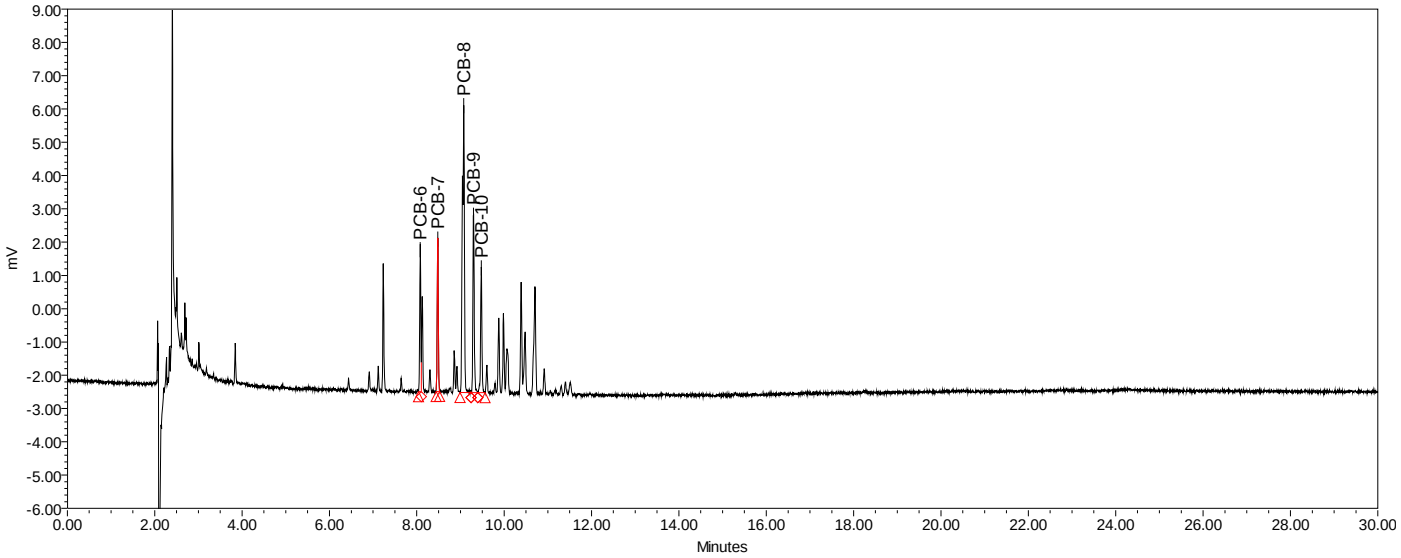


FIGURE 2. A1221 @ 0.500PPM PLOT

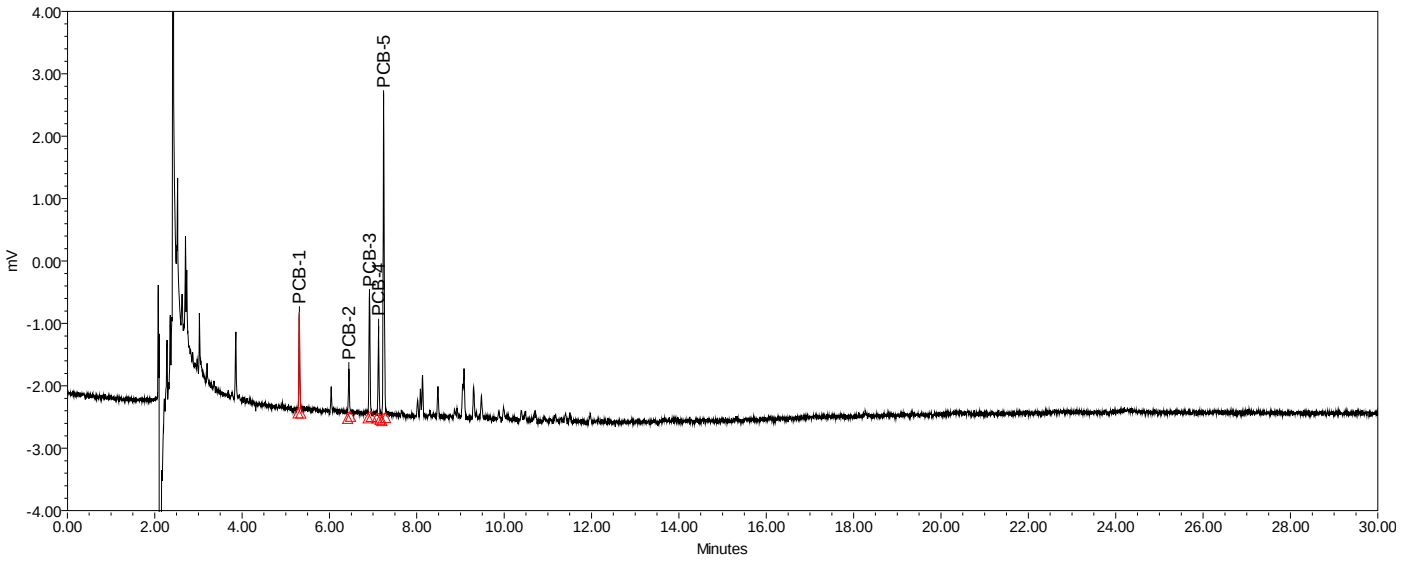


FIGURE 3. A1232 @ 0.500PPM PLOT

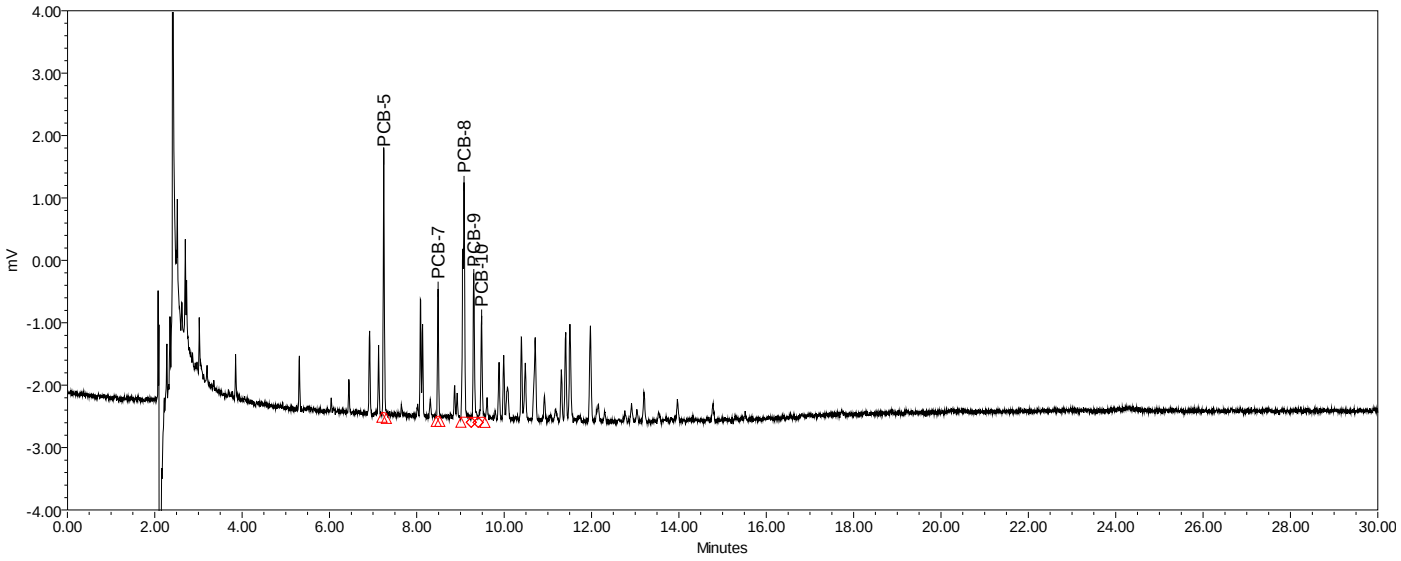


FIGURE 4. A1242 @ 0.500PPM PLOT

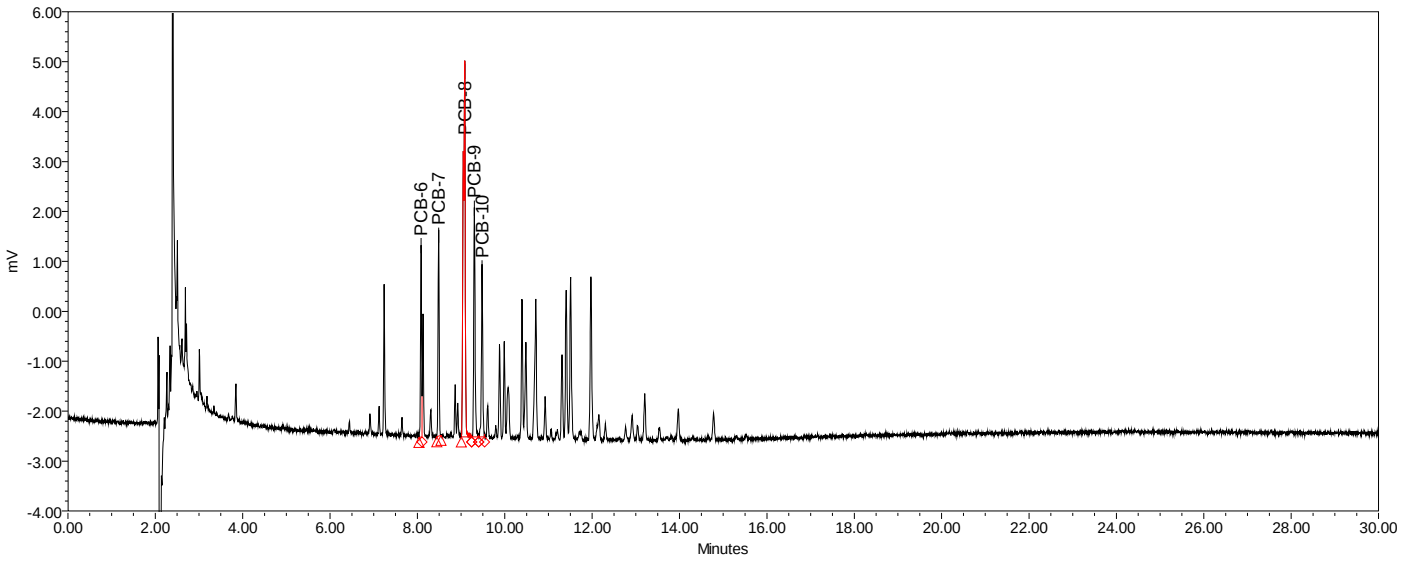


FIGURE 5. A1248 @ 0.500PPM PLOT

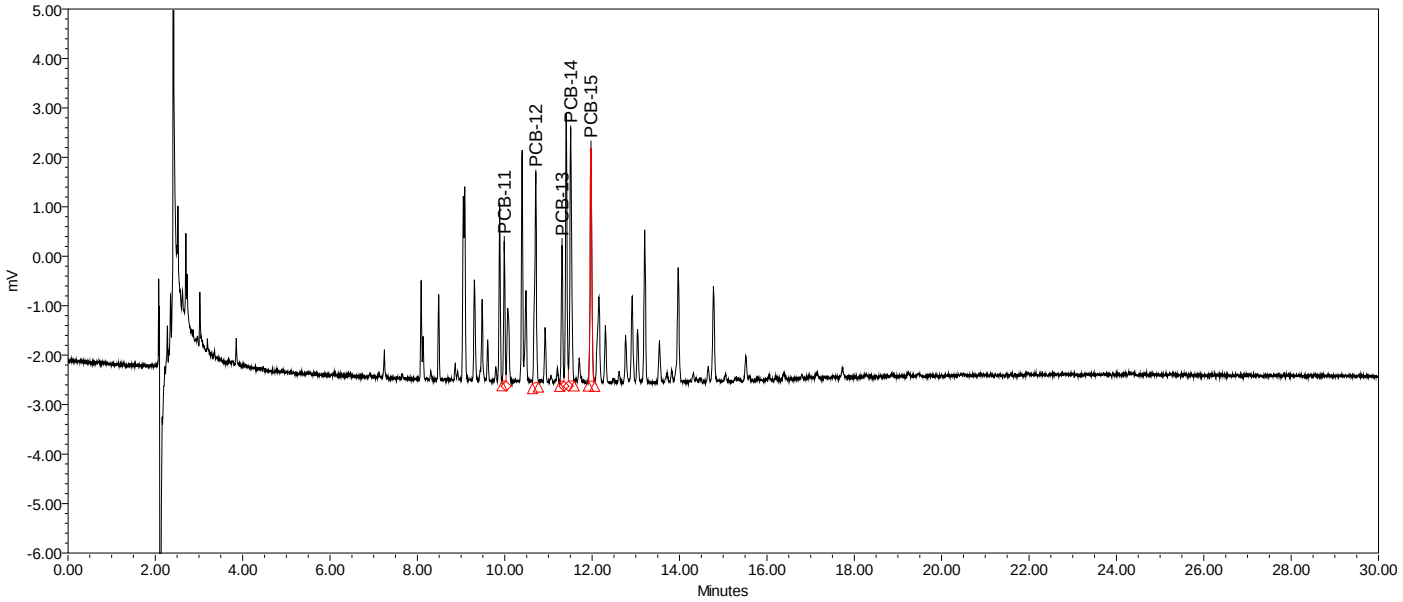


FIGURE 6. A1254 @ 0.500PPM w/ TCMX & DCBP @ 10/100PPB PLOT

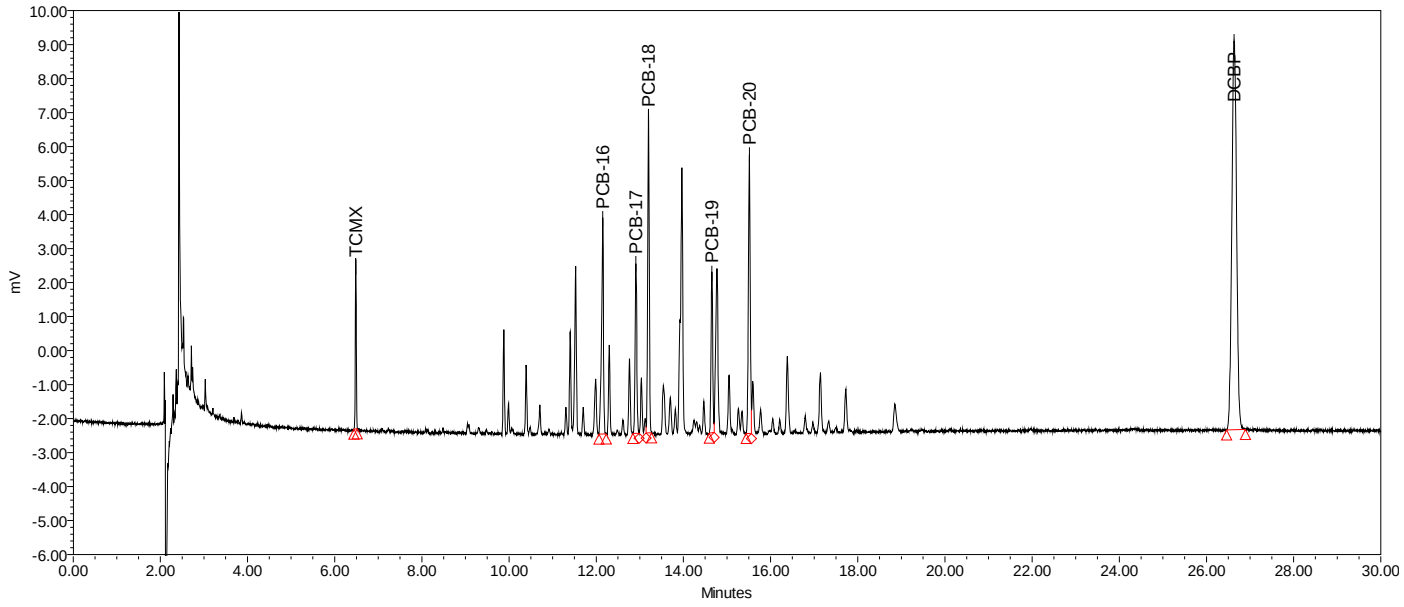
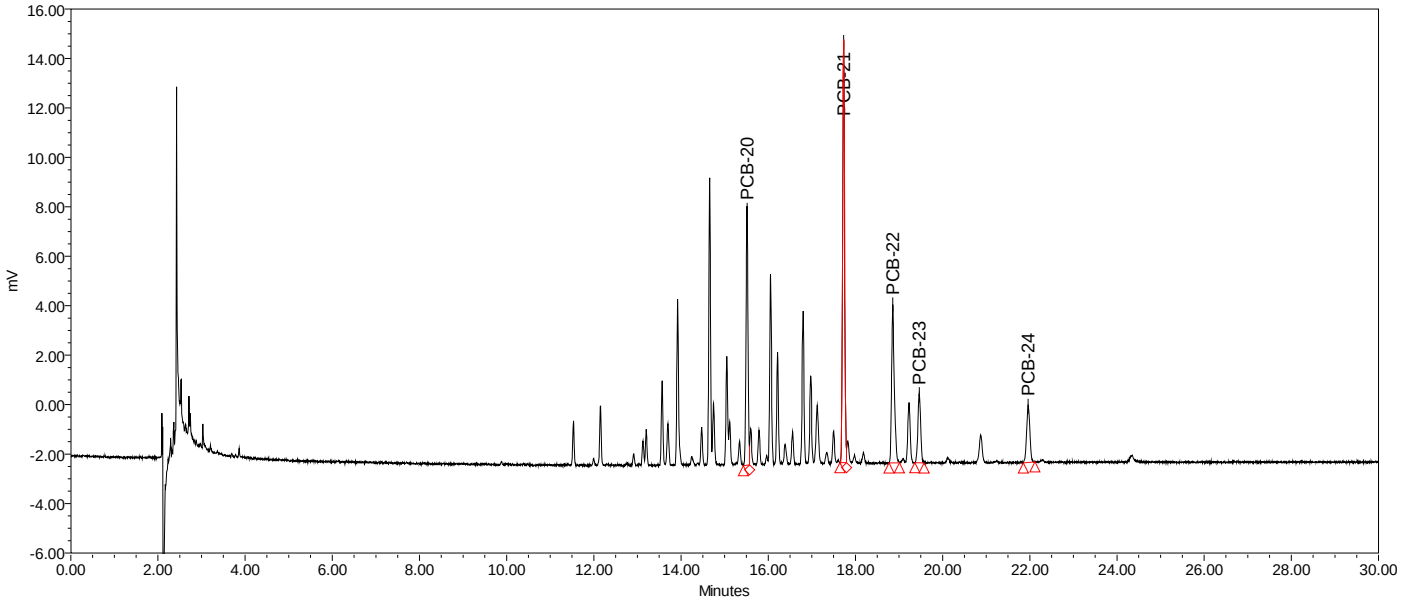


FIGURE 7. A1260 @ 0.500PPM PLOT



ATTACHMENT D cont' ZB1 Chromatograms

FIGURE 1. A1016 @ 0.500PPM PLOT

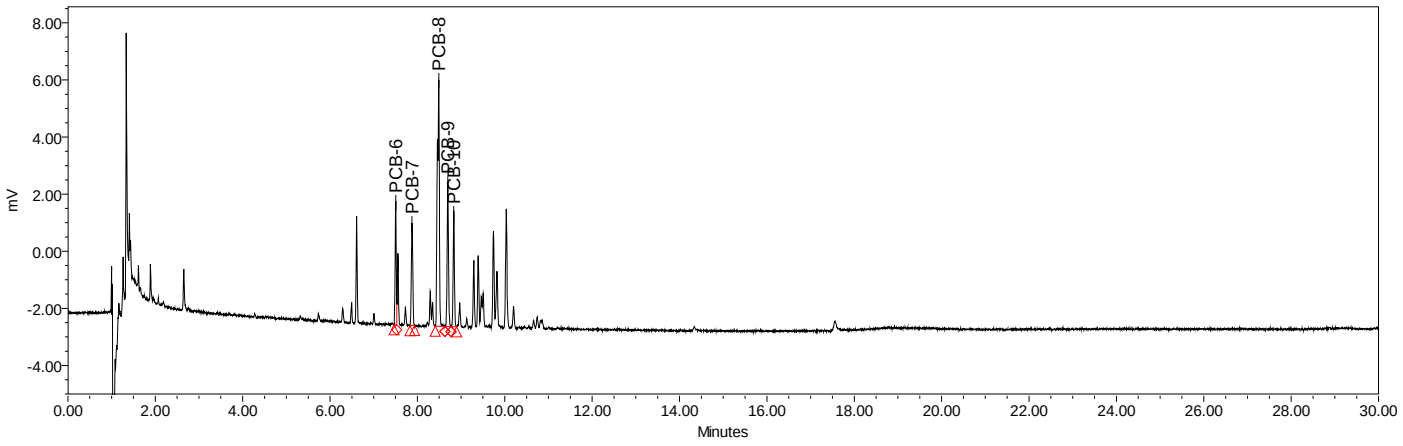


FIGURE 2. A1221 @ 0.500PPM PLOT

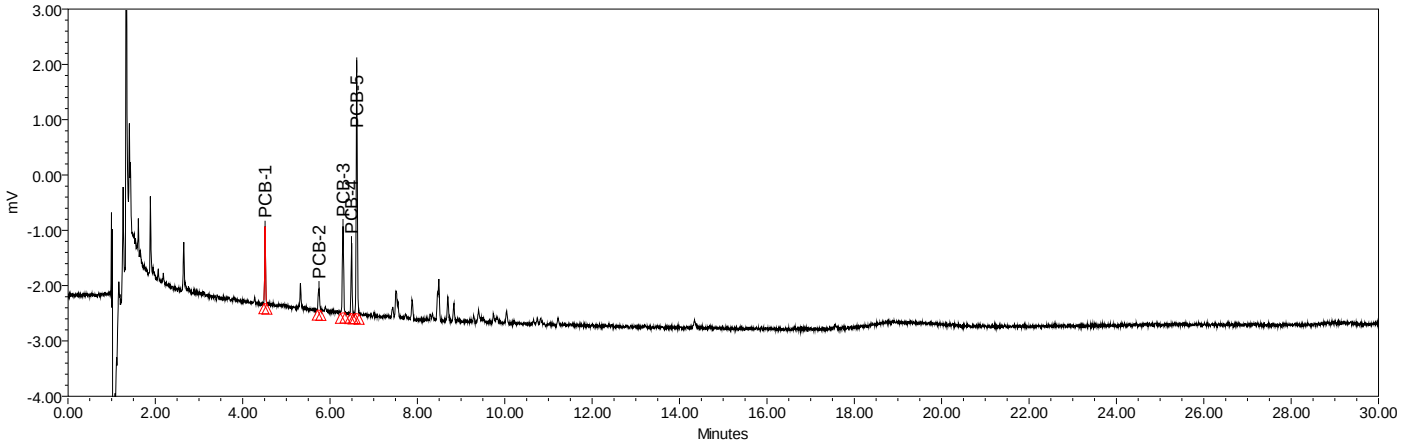


FIGURE 3. A1232 @ 0.500PPM PLOT

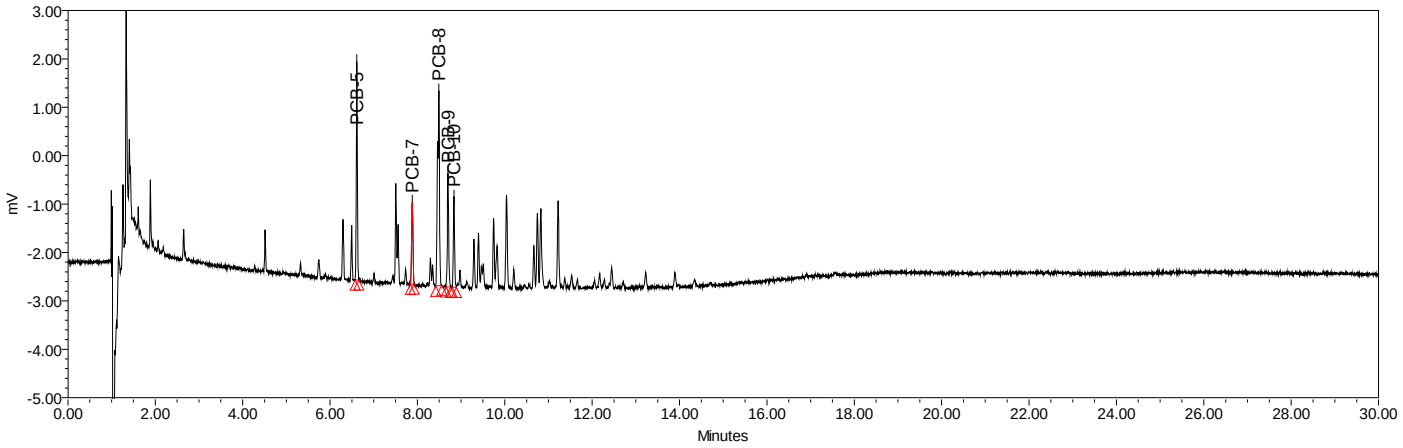


FIGURE 4. A1242 @ 0.500PPM PLOT

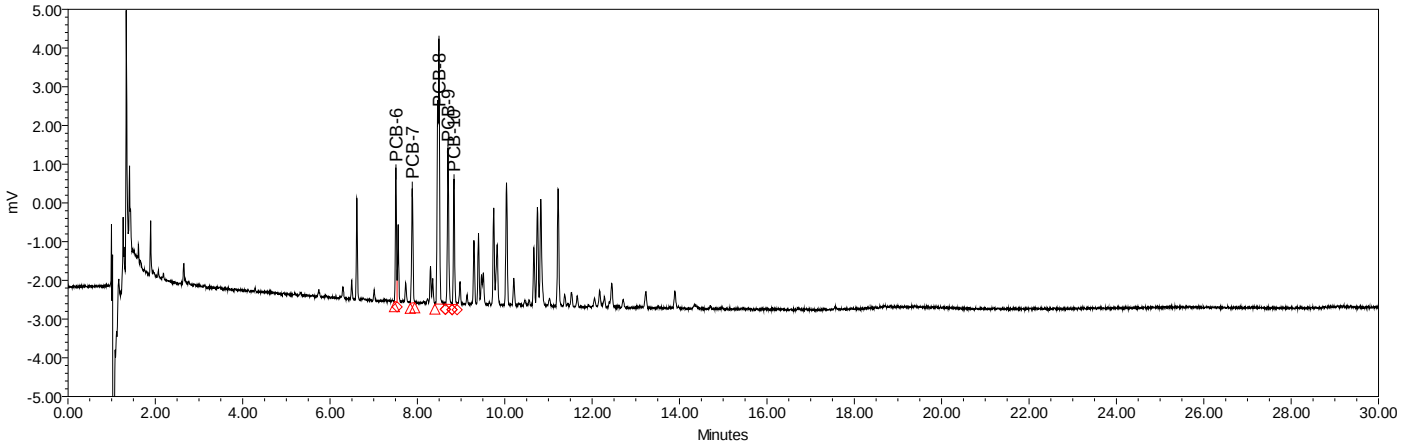


FIGURE 5. A1248 @ 0.500PPM PLOT

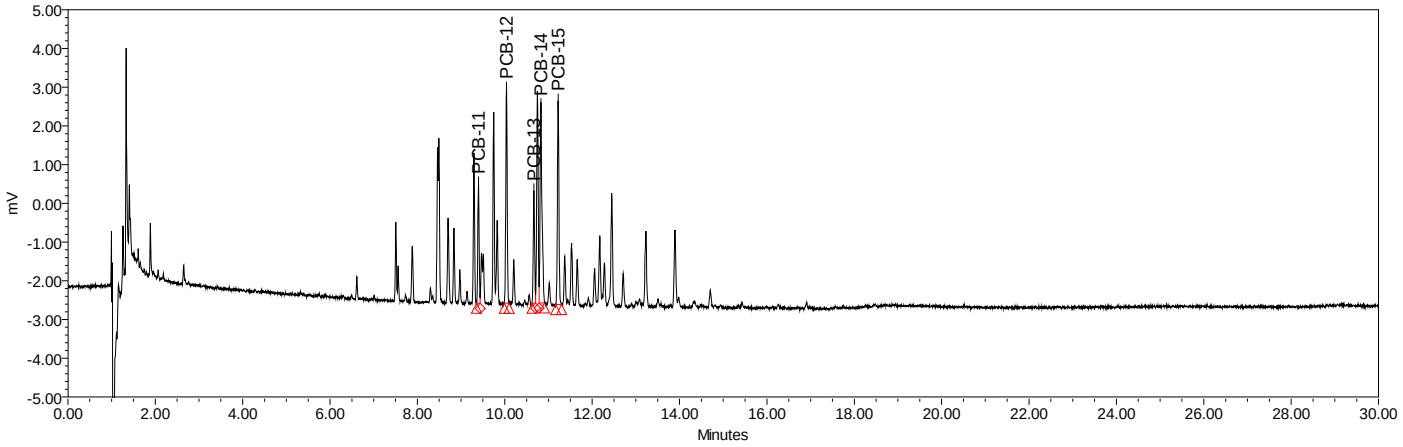


FIGURE 6. A1254 @ 0.500PPM w/ TCMX & DCBP @ 10/100PPB PLOT

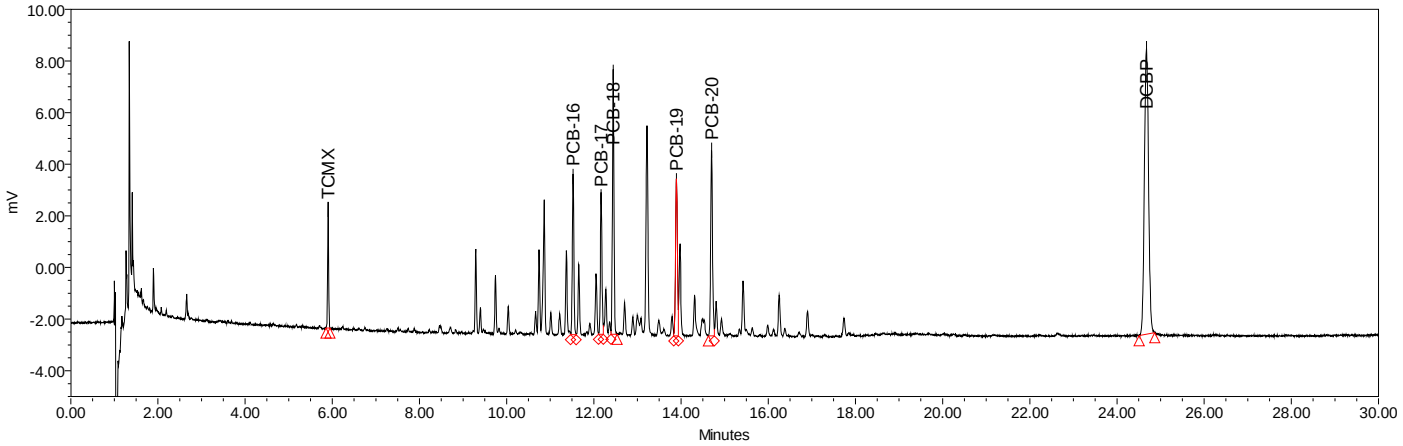
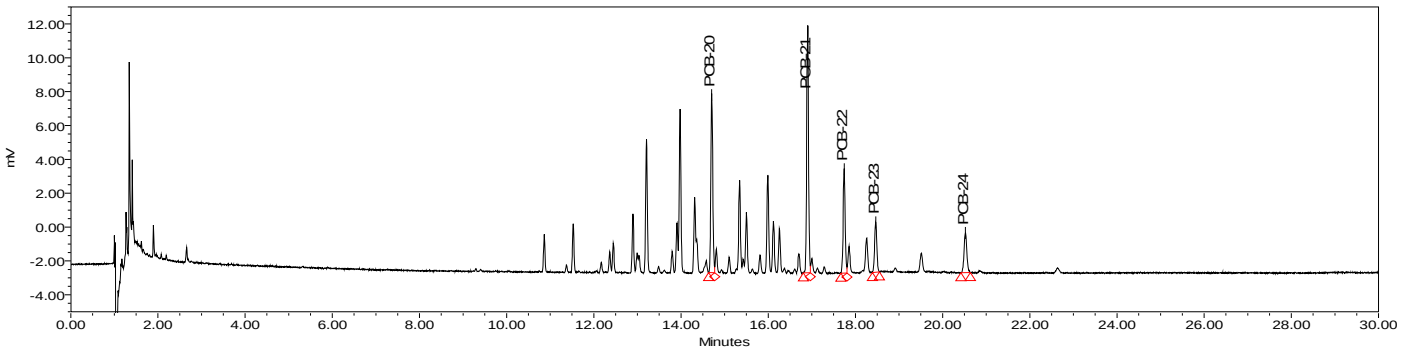


FIGURE 7. A1260 @ 0.500PPM PLOT



Attachment E Retention Time Windows: ZB-1 Column

Attachment E Retention Time Windows: ZB-1

Retention Time Window Study
for Aroclors (PCB) by GC/ECD

Instrument: GC 19F
Column: ZB-1

Analyte	PEAK	Standard 1 500 PPB R.T. Min	Standard 2 50/500 PPB R.T. Min	Standard 3 500 PPB R.T. Min	STD. DEV Min	%RSD	Window +/- Min.
		CS_0327B/A	CS_0328A	CS_0329A			
Aroclor 1016	6	7.927	7.922	7.921	0.0032	0.0406	0.010
	7	8.317	8.312	8.312	0.0029	0.0347	0.009
	8	8.961	8.956	8.956	0.0029	0.0322	0.009
	9	9.178	9.172	9.172	0.0035	0.0378	0.010
	10	9.321	9.317	9.317	0.0023	0.0248	0.007
Aroclor 1221	1	4.894	4.892	4.893	0.0010	0.0204	0.003
	2	6.142	6.142	6.145	0.0017	0.0282	0.005
	3	6.706	6.703	6.705	0.0015	0.0228	0.005
	4	6.904	6.900	6.902	0.0020	0.0290	0.006
	5	7.024	7.021	7.023	0.0015	0.0218	0.005
Aroclor 1232	5	7.025	7.026	7.022	0.0021	0.0296	0.006
	7	8.315	8.318	8.312	0.0030	0.0361	0.009
	8	8.961	8.963	8.957	0.0031	0.0341	0.009
	9	9.178	9.179	9.173	0.0032	0.0350	0.010
	10	9.322	9.324	9.318	0.0031	0.0328	0.009
Aroclor 1242	6	7.925	7.928	7.922	0.0030	0.0379	0.009
	7	8.314	8.318	8.311	0.0035	0.0422	0.011
	8	8.959	8.963	8.956	0.0035	0.0392	0.011
	9	9.176	9.180	9.173	0.0035	0.0383	0.011
	10	9.320	9.324	9.317	0.0035	0.0377	0.011
Aroclor 1248	11	9.906	9.900	9.901	0.0032	0.0325	0.010
	12	10.577	10.573	10.571	0.0031	0.0289	0.009
	13	11.231	11.225	11.225	0.0035	0.0309	0.010
	14	11.396	11.390	11.390	0.0035	0.0304	0.010
	15	11.808	11.803	11.803	0.0029	0.0245	0.009
Arolcor 1254	16	12.121	12.116	12.115	0.0032	0.0265	0.010
	17	12.793	12.786	12.785	0.0044	0.0341	0.013
	18	13.075	13.069	13.070	0.0032	0.0246	0.010
	19	14.572	14.567	14.566	0.0032	0.0221	0.010
	20	15.394	15.389	15.389	0.0029	0.0188	0.009
Arolcor 1260	20	15.396	15.398	15.392	0.0031	0.0198	0.009
	21	17.668	17.670	17.664	0.0031	0.0173	0.009
	22	18.611	18.613	18.606	0.0036	0.0194	0.011
	23	19.417	19.421	19.415	0.0031	0.0157	0.009
	24	21.729	21.731	21.722	0.0047	0.0218	0.014
TCMX (SURROGATE)	Surr.	6.311	6.307	6.307	0.0023	0.0366	0.007
DCB (SURROGATE)	Surr.	26.432	26.421	26.421	0.0064	0.0240	0.019

Attachment E cont' Retention Time Windows: ZB-5 Column

Retention Time Window Study
for Aroclors (PCB) by GC/ECD

Instrument: GC 19B
Column: ZB-5

Analyte	PEAK	Standard 1 500 PPB R.T. Min	Standard 2 500 PPB R.T. Min	Standard 3 500 PPB R.T. Min	STD. DEV Min	%RSD	Window +/- Min.
		CS_0327B/A	CS_0328A	CS_0329A			
Aroclor 1016	6	8.260	8.256	8.256	0.0023	0.0280	0.007
	7	8.669	8.665	8.665	0.0023	0.0266	0.007
	8	9.277	9.272	9.272	0.0029	0.0311	0.009
	9	9.502	9.498	9.498	0.0023	0.0243	0.007
	10	9.685	9.680	9.679	0.0032	0.0332	0.010
Aroclor 1221	1	5.480	5.479	5.476	0.0021	0.0380	0.006
	2	6.618	6.615	6.611	0.0035	0.0531	0.011
	3	7.086	7.084	7.084	0.0012	0.0163	0.003
	4	7.291	7.289	7.288	0.0015	0.0210	0.005
	5	7.410	7.406	7.407	0.0021	0.0281	0.006
Aroclor 1232	5	7.408	7.412	7.409	0.0021	0.0281	0.006
	7	8.667	8.671	8.667	0.0023	0.0266	0.007
	8	9.278	9.278	9.274	0.0023	0.0249	0.007
	9	9.502	9.505	9.501	0.0021	0.0219	0.006
	10	9.684	9.686	9.681	0.0025	0.0260	0.008
Aroclor 1242	6	8.258	8.261	8.255	0.0030	0.0363	0.009
	7	8.667	8.670	8.664	0.0030	0.0346	0.009
	8	9.275	9.279	9.272	0.0035	0.0379	0.011
	9	9.501	9.506	9.498	0.0040	0.0425	0.012
	10	9.682	9.686	9.679	0.0035	0.0363	0.011
Aroclor 1248	11	10.202	10.196	10.198	0.0031	0.0300	0.009
	12	10.936	10.930	10.932	0.0031	0.0279	0.009
	13	11.545	11.540	11.541	0.0026	0.0229	0.008
	14	11.748	11.743	11.742	0.0032	0.0274	0.010
	15	12.219	12.215	12.217	0.0020	0.0164	0.006
Arolcor 1254	16	12.402	12.397	12.397	0.0029	0.0233	0.009
	17	13.175	13.170	13.168	0.0036	0.0274	0.011
	18	13.469	13.463	13.461	0.0042	0.0309	0.012
	19	14.942	14.935	14.934	0.0044	0.0292	0.013
	20	15.812	15.805	15.805	0.0040	0.0256	0.012
Arolcor 1260	20	15.808	15.810	15.804	0.0031	0.0193	0.009
	21	18.082	18.085	18.079	0.0030	0.0166	0.009
	22	19.272	19.274	19.268	0.0031	0.0159	0.009
	23	19.911	19.910	19.912	0.0010	0.0050	0.003
	24	22.558	22.557	22.552	0.0032	0.0143	0.010
TCMX (SURROGATE)	Surr.	6.658	6.653	6.653	0.0029	0.0434	0.009
DCB (SURROGATE)	Surr.	27.519	27.509	27.498	0.0105	0.0382	0.032

Attachment F Example of MDL Study: ZB-1 Column

Compound:	Aroclor 1254		Analysis:	SW-846 8082	
Matrix:	Solid		Instrument:	GC-19F	
Extraction:	Ase		Column:	DB-1	
Spike conc:	75.0	ug/Kg	Detector:	ECD	
			LRF:	09010025	

NEA Sample ID	Extraction Date	File Name	Analysis Date	Measured Concentration ug/Kg	Percent Recovery (%)
AM00103	01/08/09	1221/1254 #1 ASE	01/23/09	68.9	91.9%
AM00104	01/08/09	1221/1254 #2 ASE	01/23/09	70.2	93.5%
AM00105	01/08/09	1221/1254 #3 ASE	01/23/09	76.8	102.4%
AM00106	01/08/09	1221/1254 #4 ASE	01/23/09	67.0	89.4%
AM00107	01/08/09	1221/1254 #5 ASE	01/23/09	75.2	100%
AM00108	01/08/09	1221/1254 #6 ASE	01/23/09	67.3	89.7%
AM00109	01/08/09	1221/1254 #7 ASE	01/23/09	69.9	93.2%
AM00110	01/08/09	1221/1254 #8 ASE	01/23/09	69.3	92.4%

		Number (n):	8	
One sided Student's t values (t)		AVG:	70.6	ug/Kg
at the 99% confidence level.		STD (s):	3.55	ug/Kg
Number (n)	(t) value	%RSD:	5.04%	
7	3.143	MDL:	10.7	ug/Kg
8	2.998	PQL:	53.3	ug/Kg
		VALID:	valid	

Attachment F cont' Example of MDL Study: ASE extraction ZB-5 Column

Compound:	Aroclor 1254		Analysis:	SW-846 8082	
Matrix:	Solid		Instrument:	GC-19B	
Extraction:	Ase		Column:	ZB-5	
Spike conc:	75.0	ug/Kg	Detector:	ECD	
			LRF:	09010025	

NEA Sample ID	Extraction Date	File Name	Analysis Date	Measured Concentration ug/Kg	Percent Recovery (%)
AM00103	01/08/09	1221/1254 #1 ASE	01/23/09	73.9	98.5%
AM00104	01/08/09	1221/1254 #2 ASE	01/23/09	74.8	99.7%
AM00105	01/08/09	1221/1254 #3 ASE	01/23/09	79.9	107%
AM00106	01/08/09	1221/1254 #4 ASE	01/23/09	75.8	101%
AM00107	01/08/09	1221/1254 #5 ASE	01/23/09	78.6	105%
AM00108	01/08/09	1221/1254 #6 ASE	01/23/09	77.7	104%
AM00109	01/08/09	1221/1254 #7 ASE	01/23/09	70.1	93.5%
AM00110	01/08/09	1221/1254 #8 ASE	01/23/09	78.9	105%

		Number (n):	8	
One sided Student's t values (t)		AVG:	76.2	ug/Kg
at the 99% confidence level.		STD (s):	3.24	ug/Kg
Number (n)	(t) value	%RSD:	4.25%	
7	3.143	MDL:	9.72	ug/Kg
8	2.998	PQL:	48.6	ug/Kg
		VALID:	valid	

Attachment F cont' Example of MDL Study: SOX extraction ZB-1 Column

Compound:	A1221	Analysis:	EPA METHOD 8082
Matrix:	SOIL/SOLID	Instrument:	GC-18F/LEAP GC PAL
Extraction:	SOX	Column:	ZB-1
Spike conc:	75.00 ug/kg		

NEA Sample ID	Extraction Date	File Name	Analysis Date	Measured Concentration ug/kg	Percent Recovery (%)
AJ00234	01/17/06	1221/1254 #1 SOX	04/19/06	81.0	108.0%
AJ00235	01/17/06	1221/1254 #2 SOX	04/19/06	79.4	106%
AJ00236	01/17/06	1221/1254 #3 SOX	04/19/06	77.0	102.7%
AJ00237	01/17/06	1221/1254 #4 SOX	04/19/06	81.1	108.1%
AJ00238	01/17/06	1221/1254 #5 SOX	04/19/06	77.1	102.8%
AJ00239	01/17/06	1221/1254 #6 SOX	04/19/06	73.7	98%
AJ00240	01/17/06	1221/1254 #7 SOX	04/19/06	71.8	95.7%
AJ00241	01/17/06	1221/1254 #8 SOX	04/19/06	77.4	103%

One sided Student's t values (t) at the 99% confidence level.

Number (n)	(t) value
7	3.143
8	2.998

Number (n):	8	
AVG:	77.31	ug/kg
STD (s):	3.293	ug/kg
%RSD:	4.26%	
MDL:	9.871	ug/kg
PQL:	49.36	ug/kg
VALID:	valid	

Attachment F cont' Example of MDL Study: SOX extraction ZB-5 Column

Compound:	A1221	Analysis:	EPA METHOD 8082
Matrix:	SOIL/SOLID	Instrument:	GC-18B/LEAP GC PAL
Extraction:	SOX	Column:	ZB-5
Spike conc:	75.00 ug/kg		

NEA Sample ID	Extraction Date	File Name	Analysis Date	Measured Concentration ug/kg	Percent Recovery (%)
AJ00234	01/17/06	1221/1254 #1 SOX	07/01/06	79.2	105.7%
AJ00235	01/17/06	1221/1254 #2 SOX	07/01/06	74.7	100%
AJ00236	01/17/06	1221/1254 #3 SOX	07/01/06	80.2	107.0%
AJ00237	01/17/06	1221/1254 #4 SOX	07/01/06	79.8	106.3%
AJ00238	01/17/06	1221/1254 #5 SOX	07/01/06	81.9	109.2%
AJ00239	01/17/06	1221/1254 #6 SOX	07/01/06	78.3	104%
AJ00240	01/17/06	1221/1254 #7 SOX	07/01/06	85.2	113.6%
AJ00241	01/17/06	1221/1254 #8 SOX	07/01/06	82.6	110%

Number (n):	8	
AVG:	80.23	ug/kg
STD (s):	3.146	ug/kg
%RSD:	3.92%	
MDL:	9.432	ug/kg
PQL:	47.16	ug/kg
VALID:	valid	

One sided Student's t values (t) at the 99% confidence level.

Number (n)	(t) value
7	3.143
8	2.998

Attachment F cont' Example of MDL Study: PUF extraction ZB-1 Column

Compound:	A1221	Analysis:	EPA METHOD 8082
Matrix:	PUF	Instrument:	GC-19F/8400
Extraction:	SOX	Column:	ZB-1
Spike conc:	0.150 ug		

NEA Sample ID	Extraction Date	File Name	Analysis Date	Measured Concentration ug	Percent Recovery (%)
AJ00508	02/08/06	TO-10A 1221/1254 #1	02/10/06	0.138	91.8%
AJ00509	02/08/06	TO-10A 1221/1254 #2	02/10/06	0.130	86.8%
AJ00510	02/08/06	TO-10A 1221/1254 #3	02/10/06	0.141	93.7%
AJ00511	02/08/06	TO-10A 1221/1254 #4	02/10/06	0.150	99.8%
AJ00512	02/08/06	TO-10A 1221/1254 #5	02/10/06	0.135	90.2%
AJ00513	02/08/06	TO-10A 1221/1254 #6	02/10/06	0.142	94.6%
AJ00514	02/08/06	TO-10A 1221/1254 #7	02/10/06	0.140	93.1%
AJ00515	02/08/06	TO-10A 1221/1254 #8	02/10/06	0.134	89.2%

	Number (n):	8	
One sided Student's t values (t)	AVG:	0.139	ug
at the 99% confidence level.	STD (s):	0.006	ug
	%RSD:	4.25%	
	MDL:	0.018	ug
	PQL:	0.088	ug
	VALID:	valid	

Number (n)	(t) value
7	3.143
8	2.998

Attachment F cont' Example of MDL Study: PUF extraction ZB-5 Column

Compound:	A1221	Analysis:	EPA METHOD 8082
Matrix:	PUF	Instrument:	GC-19B/8400
Extraction:	SOX	Column:	ZB-5
Spike conc:	0.150 ug		

NEA Sample ID	Extraction Date	File Name	Analysis Date	Measured Concentration ug	Percent Recovery (%)
AJ00508	02/08/06	TO-10A 1221/1254 #1	02/10/06	0.143	95.3%
AJ00509	02/08/06	TO-10A 1221/1254 #2	02/10/06	0.127	84.8%
AJ00510	02/08/06	TO-10A 1221/1254 #3	02/10/06	0.135	90.2%
AJ00511	02/08/06	TO-10A 1221/1254 #4	02/10/06	0.134	89.0%
AJ00512	02/08/06	TO-10A 1221/1254 #5	02/10/06	0.134	89.1%
AJ00513	02/08/06	TO-10A 1221/1254 #6	02/10/06	0.136	90.4%
AJ00514	02/08/06	TO-10A 1221/1254 #7	02/10/06	0.143	95.2%
AJ00515	02/08/06	TO-10A 1221/1254 #8	02/10/06	0.140	93.3%

Number (n):	8	
AVG:	0.136	ug
STD (s):	0.005	ug
%RSD:	3.91%	
MDL:	0.016	ug
PQL:	0.080	ug
VALID:	valid	

One sided Student's t values (t) at the 99% confidence level.

Number (n)	(t) value
7	3.143
8	2.998

STANDARD OPERATING PROCEDURE REVIEW

SOP Name	Review Number	Reviewers	Title	QAO Approval	Effective Date
NE148_06	01	Kari Lantiegne Christina L. Braidwood Robert E. Wagner	Chemist QAO Lab Director	Christina Braidwood	02/19/09

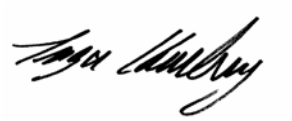
APPENDIX 46
SOP FOR THE ANALYSIS OF PCB CONGENERS BY NEA013_09

STANDARD OPERATING PROCEDURE FOR CONGENER-SPECIFIC POLYCHLORINATED BIPHENYL (PCB) ANALYSIS BY GREEN BAY MASS BALANCE METHOD

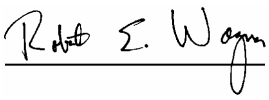
NE013_09.SOP
Revision 09
February 20th, 2009

Northeast Analytical, Inc.
2190 Technology Drive
Schenectady, NY 12308

Reviewed and Approved By:



Inga Hotaling
Chemist
Date: 02/20/09



Robert E. Wagner
Laboratory Director
Date: 02/20/09

Christina L. Braidwood
Quality Assurance Officer
Date: 02/20/09

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METHOD FOR CONGENER-SPECIFIC POLYCHLORINATED BIPHENYL (PCB) QUANTIFICATION AND IDENTIFICATION BY CAPILLARY COLUMN/GAS CHROMATOGRAPHY WITH ELECTRON CAPTURE DETECTION

1.0 Identification of Test Method

1.1 Congener Specific Method for Congener-Specific Polychlorinated Biphenyl (PCB) Quantification and Identification by Capillary Column/Gas Chromatography with Electron Capture Detection.

2.0 Applicable Matrix

2.1 This method is applicable for the determination of PCB Congeners in soils, sediments, biota, oils, water and other solid and liquid matrices.

3.0 Detection Limit

3.1 Detection Limit: Reporting Limits (RLs) and Method Detection Limits (MDLs) vary for each matrix and are based on total PCB concentration.

3.2 MDL and RL are the following:

3.2.1 Aqueous matrix, 1L final volume 5mL, MDL = 9.34ng/L Total PCB ; RL 32.3ng/L Total PCB.

3.2.2 Solid Matrix: 10g final volume to 25mL, MDL = 0.0135 ug/g Total PCB ; RL 0.312ug/g Total PCB.

3.3 Individual peak MDLs and RLs are determined every two years with matrix specific MDL studies or as required when a major equipment change occurs. See Appendix E for MDL values.

4.0 Scope and application, including components to be analyzed

4.1 This method is applicable in the determination and quantification of Polychlorinated Biphenyls (PCB) in sediments, soils, biota, oils, water, and other solid and liquid matrices. This method is a congener-specific determination, employing a high resolution fused-silica capillary chromatographic column. The method has been, in part, developed from the following documents:

4.2 "Quality Assurance Plan, Green Bay Mass Balance Study, 1. PCBs and Dieldrin, US EPA Great Lakes National Program Office", prepared by Deborah L. Swackhamer, Quality Assurance Coordinator, Field and Analytical Methods Committees, University of Minnesota, December 11, 1987. This document outlines quality assurance and quality control procedures to be followed by laboratories participating in the Green Bay Mass Balance Study. Where applicable, Northeast Analytical, Inc., will incorporate and utilize this information in quality control of data generated. Instrumental analysis and conditions (Mullin, M.D., 1985, PCB Workshop, US EPA Large Lakes Research Station, Gross Ile, MI, June.) cited in the Green Bay Mass Balance Study document will be refined to be applicable to an in-house data management software package.

4.3 "Comprehensive, Quantitative, Congener-Specific Analyses of Eight Aroclors and Complete PCB Congener Assignments on DB-1 Capillary GC Columns", George M. Frame, Robert E. Wagner, James C. Carnahan, John F. Brown, Jr., Ralph J. May, Lynn A. Smullen, and Donna L. Bedard, Chemosphere, Vol. 33, No. 4, pp. 603-623, 1996. This journal publication provides complete assignment of all 209 PCB congeners to the GC peaks separable on a DB-1 capillary column. It also provides weight percent information for PCB congeners in Aroclor formulations used in labeling protocols for reporting purposes.

4.4 "Standard Operating Procedure for the Gas Chromatographic Analysis of Hydrophobic Organic Contaminant Extracts from Great Lakes Water Samples", US EPA Great Lakes National Program Office, 77 West Jackson Boulevard, Chicago, IL 60604-2590, GLNPO Organics SOP – 10, 6/1/94:Revision 2. This USEPA SOP summarizes M. Mullin's congener composition of the mixed Aroclor standard used for calibration.

4.5 "Biphenyls and Halogenated Pesticides by High Resolution Gas Chromatography", M.D. Mullin, Large Lakes Research Station, LLRS-SOP-ORG-013, revision 2, August 3, 1990, p 1-10. This LLRS SOP written by M. Mullin summarizes the calibration composition of the mixed Aroclor standard reported in "Mullin, M.D., PCB Workshop, U.S. EPA Large Lakes Research Station, Grosse Ile, MI, June 1985.

4.6 This gas chromatographic capillary column method, utilizing an electron capture detector, will effectively separate 112 or more peaks representing 209 PCB congeners.

5.0 Summary of Test Method

5.1 This method provides detailed instructions for gas chromatographic conditions for the analysis of PCBs by capillary gas chromatography.

5.2 This method utilizes a mixed Aroclor standard (Aroclor 1232/1248/1262 in the ratio of 25:18:18) for calibration. Method detection limit and practical quantitation limit will be established experimentally using the procedure in USEPA 40 CFR, Part 136, App.B.

5.3 In general, samples are first extracted with a pesticide-grade solvent. The extracts are further processed through a series of clean-up techniques. The sample is then analyzed by direct liquid injection onto the gas chromatographic column and detected by an electron capture detector. This method should be performed by a skilled chemist or by an analyst trained in the quantification of trace organics by gas chromatography.

5.4 A key component of this method is the importance placed on the chromatographic separation that must be achieved for this congener specific technique. A total of 112 chromatographic peaks are detected, containing 209 PCB congeners in various ratios. This allows an almost complete profile of environmentally occurring PCBs.

6.0 Definitions

6.1 Accuracy – The nearness of a result or the mean of a set to the true value. Accuracy is assessed by analysis of reference samples and measurement of percent recoveries.

6.2 Analytical Batch –The basic unit for analytical quality control is the analytical batch, which is defined as samples which are analyzed together with the sample method sequence and the same lots of reagents and with the manipulations common to each sample within the same time period or in continuous sequential time periods. Samples in each batch should be of similar matrices (e.g. water, sediment, soil, etc.).

6.3 Aroclor – Polychlorinated Biphenyls (PCBs) were commercially produced for a variety of uses including, transformers, capacitors, inks, paints, dust control agents, and pesticides. Monsanto Corporation was a major producer and sold PCBs under the trade name Aroclor.

6.4 Blank – A blank is an artificial sample designed to monitor the introduction of artifacts into the process. For aqueous samples, reagent water is used as a blank matrix, however, a universal blank matrix does not exist for solid samples, but sometimes sodium sulfate is used as a blank matrix. The blank is taken through the appropriate steps of the process. A reagent blank is an aliquot of analyte-free water or solvent analyzed with the analytical batch. Field blanks are aliquots of analyte-free water or solvents brought to the field is sealed containers and transported back to the laboratory with the sample containers. Trip blanks and equipment blanks are two specific types of field blanks. Trip blanks are not opened in the field. They are a check on sample contamination originating from sample transport, shipping and from site conditions. Equipment blanks are opened in the field and the contents are poured appropriately over or through the sample collection

device, collected in a sample container, returned to the laboratory as a sample. Equipment blanks are a check on sampling device cleanliness.

6.5 Calibration Standard (ICAL)– A series of known standard solutions used by the analyst for instrument calibration. Calibration standards are prepared from primary standard and/or stock standard solutions.

6.6 Congener – Any of the 209 Chlorinated Biphenyl compounds of varying degree of chlorination, mono through decachlorobiphenyl.

6.7 Continuing Calibration Check Standard(CC) –The continuing calibration check standard contains all the target analytes found in the calibration standards and is used to verify that the initial calibration is prepared correctly and that the instrument system is correctly calibrated. Calibration check solutions are made from a stock solution which is different from the stock used to prepare standards (not independent for CQCS-PCB).

6.8 CAS Number – An assigned number used to identify a chemical. CAS stands for Chemical Abstracts Service, an organization that indexes information published in Chemical Abstracts by the American Chemical Society and that provides index guides by which information about particular substances may be located in the abstracts. Sequentially assigned CAS numbers identify specific chemicals, except when followed by an asterisk (*) which signifies a compound (often naturally occurring) of variable composition. The numbers have no chemical significance. The CAS number is a concise, unique means of material identification. (Chemical Abstracts Service, Division of American Chemical Society, Box 3012, Columbus, OH 43210: [614] 447-3600).

6.9 Duplicate– A second aliquot of a sample that is treated the same as the original sample in order to determine the precision of the method.

6.10 Environmental Sample – An environmental sample or field sample is a representative sample of any material (aqueous, non-aqueous, or multimedia) collected from any source for which determination of composition or contamination as requested or required. Environmental samples are normally classified as follows:

6.10.1 Drinking water -delivered (treated or untreated) water designated as potable water.

6.10.2 Water/Wastewater -raw source waters for public drinking water supplies, ground waters, municipal influents/effluents, and industrial influents/effluent.

6.10.3 Sludge -municipal sludge and industrial sludge.

6.10.4 Waste –aqueous and non-aqueous liquid wastes, chemical solids, contaminated soils, and industrial liquid and solid wastes.

6.11 Homolog – Any of the ten sets of PCB congeners of the same degree of chlorination.

6.12 Initial Calibration – Analysis of analytical standards for a series of different specified concentrations; used to define the linearity and dynamic range of the response of the analytical detector or method.

6.13 Instrument Calibration – Analysis of analytical standards for a series of different specified concentrations; used to define the quantitative response, linearity and dynamic range of the instrument to target analytes.

6.14 Laboratory Control Sample (LCS) – Also known as the Quality Control (QC) Check Standard or Quality Control (QC) Check Sample. The LCS consists of an aliquot or reagent water or other blank matrix to which known quantities of the method analytes are added. The LCS is extracted and analyzed exactly like a field sample, and its purpose is to determine whether the analysis is in control and whether the laboratory is capable of making accurate and precise measurements.

6.15 Laboratory Method Blank – An analytical control consisting of all reagents, internal standards and surrogate standards, that is carried through the entire analytical procedure. The method blank is used to define the level of laboratory background and reagent contamination.

6.16 Matrix – The predominant material of which the sample to be analyzed is composed. Matrix is not synonymous with phase (liquid or solid).

6.17 Matrix Spike – Aliquot of sample (water or soil) fortified (spiked) with known quantities of specific compounds and subjected to the entire analytical procedure in order to indicate the appropriateness of the method for the matrix by measuring recovery.

6.18 Matrix Spike Duplicate – A second aliquot of the same matrix as the matrix spike (above) that is spiked in order to determine the precision of the method.

6.19 Method Detection Limit (MDL) – The minimum constituent concentration that can be measured and reported with 99% confidence that the signal produced is different from the blank in a given matrix. The MDL is determined from a minimum of seven replicate samples, taken through the entire preparation and analysis procedure. The standard deviation, *s*, of those replicates is multiplied by a student's t factor in order to calculate the MDL.

6.20 MSDS – Material Safety Data Sheet. OSHA has established guidelines for the descriptive data that should be concisely provided on a data sheet to serve as the basis for written hazard communication programs.

6.21 PCB – Polychlorinated Biphenyl (PCBs) are a class of 209 individual chemical compounds (congeners), in which one to ten chlorine atoms are attached to biphenyl. Use of PCBs has made them a ubiquitous environmental pollutant.

6.22 Practical Quantitation Limit (PQL) – The minimum constituent concentration that can be determined with 95% confidence to be at the value stated. It is calculated by multiplying three to five times the MDL.

6.23 Precision – The agreement between a set of replicate measurements without assumption of knowledge of the true value. Precision is assessed by means of duplicate/replicate sample analysis.

6.24 Primary Standard Solution – A solution of several analytes prepared from stock solutions that can be diluted as needed to prepare calibration solutions and to prepare other standard solutions.

6.25 Quality Control – Set of measures within a sample analysis methodology to assure that the process is in control.

6.26 Sample Matrix Spike/Sample Matrix Spike Duplicate (MS/MSD) – An aliquot of a field sample that is fortified with known quantities of the method analytes and subjected to the entire analytical procedure. Its purpose is to assess the appropriateness of the method for the matrix by measuring recovery.

6.27 Standard Curve – A standard curve is a curve which plots concentrations of known analyte standards versus the instrument response to the analyte. Calibration standards are prepared by diluting the stock analyte solution in graduated amounts which cover the expected range of the samples being analyzed. Standards should be prepared at the frequency specified in the appropriate section. The calibration standards must be prepared using the same type of acid or solvent and at the same concentration as will result in the samples following sample preparation. This is applicable to organic and inorganic chemical analyses.

6.28 Stock Solution – Standard solution which can be diluted to derive the other standards.

6.29 Surrogate – Organic compounds which are similar to analytes of interest in chemical composition, extraction, and chromatography, but which are not normally found in environmental samples. These compounds are spiked into all blanks, calibration and check standards, samples (including duplicates and QC reference sample) and spiked samples prior to analysis. Percent recoveries are calculated for each surrogate.

6.30 Surrogate Standard – A pure compound added to a sample in the laboratory just before processing so that the overall efficiency of a method can be determined.

7.0 Interferences

7.1 One of the major sources of interference in the analysis of PCBs is co-extracted organochlorine pesticides. Several of the commonly found pesticides and associated pesticide degradation products (e.g. PP-DDT, PP-DDE, PP-DDD) overlap the

PCB profile envelope and co-elute with several PCB peaks causing inaccurate measurement. The analyst must be careful to review the chromatographic pattern and peak retention times and flag peaks that are suspected of containing interference so that they are not included in the total PCB values generated. Rigorous cleanup of sample extracts (i.e. sulfuric acid cleanup and florisil cleanup) removes many non-target pesticides.

7.2 Laboratory contamination can occur by the introduction of plasticizers (phthalate esters) into the samples through the use of flexible tubing. Samples and extracts should not be exposed to plastic materials. Phthalate esters exhibit response on electron capture detectors, usually as late eluting peaks, and can interfere in PCB quantification. Laboratory method blanks must be thoroughly reviewed for presence of non-target peaks and comparison of samples with blank chromatographic patterns.

7.3 The sample matrix itself is also a potential source for method analyte interference. Sample preparation, extraction procedures, and extract clean-up protocols are covered in separate SOPs that deal exclusively with sample extraction.

8.0 Safety

8.1 Safety glasses and disposable gloves must be worn when handling samples and extracts.

8.2 All manipulations of sample extracts should be conducted inside a chemical fume hood. Manipulation of sample extracts outside of a fume hood should be minimized by the analyst.

8.3 Safe laboratory practices should be followed by the analyst at all times when conducting work in the lab. The analyst should refer to the reference file of material safety data sheets to familiarize themselves with the precautions for handling solvents and chemicals used to process samples. The analyst should refer to the laboratory chemical hygiene plan for further safety information.

8.4 Samples remaining after analysis should either be returned to the customer for disposal or disposed of through the laboratory's disposal plan. Refer to the sample custodian for assistance and also standard operating procedure NEO54, disposal of laboratory waste.

9.0 Equipment and Supplies

9.1 Gas Chromatograph: Complete system for high resolution, capillary column capability and all required accessories. Northeast Analytical, Inc. will use an Agilent Model 6890 gas chromatograph (or equivalent), equipped with capillary split/splitless injector (or equivalent), temperature programmable oven, Model 7683 automatic sampler (or equivalent), and micro-electron capture detector (or equivalent). A data system and integration of detector signal is interfaced to the gas chromatograph.

9.2 Chromatographic Data System: A data system for measuring peak height and peak area. An Empower computer network based workstation (Waters Corporation), will be employed to capture detector response and digitally store the chromatographic, electronic peak integration for precise calculations, database structuring of the analytical information, and archival capabilities.

9.3 GC Column: The gas chromatograph column to be used for analysis will be a DB-1 (J&W Company) or a ZB-1 (Phenomenex), bonded polydimethylsilicone, 30 meter fused silica capillary column with an internal diameter of 0.25mm and phase coating thickness of 0.25 microns. This column is capable of resolving 112 chromatographic peaks from the full spectrum of all PCB congeners that could be expected in an environmental sample. Refer to Appendix A and Appendix B for a complete description of PCB congeners identified in each GC chromatographic peak and achievable chromatographic separations.

9.4 Volumetric Flasks – 10, 50 and 100mL, ground-glass stopper. For standard preparation.

9.5 Micro syringe – 10uL for internal standard addition.

9.6 Hamilton Syringes – 50, 100, 250, 500, 1000 and 2000uL for standard preparation.

9.7 Class A volumetric pipettes – 1mL, 5mL, 10mL

9.8 Pasteur pipettes.

9.9 250ml and 100ml beakers, glass.

9.10 Disposable 1.0, 5.0, and 10.0 ml pipettes.

9.11 Vials – Glass, 10 and 20mL capacity for sample extracts.

9.12 Bottles – Glass , 120mL capacity for standard storage.

9.11 Autosampler Vials – 2ml capacity vials with PTFE septa.

9.12 Ferrules: 0.4mm graphite/vespel, Agilent or equivalent.

9.13 Injector septa – Restek Ice Blue Septa or equivalent.

9.14 Injector liner – Agilent Split/Splitless Liner w/ glass wool or equivalent.

9.15 Viton Fluorocarbon O-ring – Agilent or equivalent.

9.16 Autosampler Vials – 2ml capacity vials with PTFE septa.

10.0 Reagents and Standards

10.1 Solvents – Pesticide grade quality. Hexane, Acetone, Toluene, Methylene chloride. Obtained form Burdick & Jackson or equivalent.

10.2 Octachloronaphthalene (Internal Standard): Obtained from Ultra Scientific (Hope, RI) or AccuStandard with purity greater than 95%.

10.3 Polychlorinated Biphenyls: Neat commercial material or solutions for standard preparation. These materials are multi-component mixtures of PCB congeners and are the actual materials that were used in products such as transformers and capacitors. Monsanto was the largest producer of PCB formulations and sold them under the trade name Aroclor.

10.4 PCB Congeners: A complete set of all 209 PCB congeners to individually verify the exact elution order on the chosen chromatographic system. A subset of congeners are also used as a secondary supplemental calibration standard for those congeners that do not exist at a high enough level in the Aroclor based calibration standard. Congener Set obtained from AccuStandard or Ultra Scientific.

10.5 Stock Standard Solutions

10.5.1 Stock standards are prepared from individual neat Aroclor formulations by weighing approximately 0.1000g to the nearest 0.2 mg and dissolving and diluting to volume in a 100mL volumetric flask with hexane. This will give a stock concentration of 1,000ug/mL.

10.5.2 The stock standard is transferred into screw-cap 120mL boston bottles and stored in a freezer (≤0°C), protected from light. Stock standards should be checked at frequent intervals for signs of evaporation, especially just prior to preparing calibration standards.

10.5.3 Stock PCB standards must be replaced after one year or sooner if comparison with continuing calibration check standards indicate a problem.

10.5.4 Stock standards for the following are prepared by the above procedure:

Aroclor 1232
Aroclor 1248
Aroclor 1262

10.6 Mixed Aroclor Stock Standard at 62.7ug/mL: A primary stock standard is prepared at 62.7ug/mL that is used for preparing secondary stock standards and calibration standards. This stock standard is prepared by combining Aroclor 1232, Aroclor 1248, and Aroclor 1262 in a 25:18:18 ratio with a final mixture concentration of 25.7ug/mL, 18.6ug/mL, and 18.4ug/mL respectively (total=62.7ug/mL). These ratios are strictly maintained so that the percent composition data remains applicable, since it was developed for use under these fixed mixture parameters. The final concentration of the mixed standard may vary to accommodate instrument sensitivity or more closely represent sample concentrations, but the same ratio values must be maintained. Using a 5.0mL Class A pipette, accurately add 2.49mL of stock Aroclor 1232 standard (1,033ug/mL) to a 100mL volumetric flask. Using a 2.0mL Class A pipette, accurately add 1.82mL of stock Aroclor 1248 standard (1,019ug/mL) and 1.80mL of stock Aroclor 1262 standard (1,024ug/mL) to the same 100mL volumetric flask. Make volume to the 100mL mark with hexane.

10.6.1 Store the Mixed Aroclor Stock Standard at 62.7ug/mL in a refrigerator (4 ± 2°C) or freezer (≤0°C) in a tightly capped bottle. This standard must be replaced after one year, or sooner, if comparison with the continuing check standard indicates a problem.

10.6.2 Linearity Study Standards: The Linearity Standards are all prepared from the 62.7ug/mL mixed Aroclor stock standard. The following standard concentrations are needed. 31.35ug/mL w/OCN; 6.27ug/mL w/o OCN, 6.27ug/mL w/OCN; 1.25ug/ml w/o OCN; 1.25ug/ml w/OCN and 0.125ug/mL w/OCN.

10.6.2.1 Linearity Study Standard at 31.35ug/mL: Using a 5.0mL Class A pipette, accurately add 5.0mL of the 62.7 stock standard into a 10mL volumetric flask. Using a 10 microliter syringe add 9.0uL of 202ug/mL Octachloronaphthalene into the same 10mL volumetric flask and set to volume with hexane. The Octachloronaphthalene is used as an internal standard for instrument calibration. Transfer the standard solution to a 10ml vial and store in a refrigerator (4 ± 2°C) or freezer (≤0°C).

10.6.2.2 Linearity Study Standard at 6.27ug/mL w/o OCN: Using a 1.0mL Class A pipette, accurately add 1.0mL of the 62.7 stock standard into a 10mL volumetric flask and set to volume with hexane. Transfer the standard solution to a 10ml vial and store in a refrigerator (4 ± 2°C) or freezer (≤0°C).

10.6.2.3 Linearity Study Standard at 6.27ug/mL w/OCN: Using a 1.0mL Class A pipette, accurately add 1.0mL of the 62.7 stock standard into a 10mL volumetric flask. Using a 10 microliter syringe add 9uL of 202ug/mL Octachloronaphthalene into the same 10mL volumetric flask and set to volume with hexane. The Octachloronaphthalene is used as an internal standard for instrument calibration. Transfer the standard solution to a 10ml vial and store in a refrigerator (4 ± 2°C) or freezer (≤0°C).

10.6.2.4 Linearity Study Standard at 1.25ug/mL w/OCN: Using a 5.0mL Class A pipette, accurately add 2.0mL of the 6.27ug/mL standard w/o OCN (10.6.2.2) into a 10mL volumetric flask. Using a 10 microliter syringe add 9uL of 202ug/mL Octachloronaphthalene into the same 10mL volumetric flask and set to volume with hexane. The Octachloronaphthalene is used as an internal standard for instrument calibration. Transfer the standard solution to a 10ml vial and store in a refrigerator (4 ± 2°C) or freezer (≤0°C).

10.6.2.5 Linearity Study Standard at 1.25ug/mL w/o OCN: Using a 5.0mL Class A pipette, accurately add 2.0mL of the 6.27ug/mL standard w/o OCN (10.6.2.2) into a 10mL volumetric flask and set to volume with hexane. Transfer the standard solution to a 10ml vial and store in a refrigerator (4 ± 2°C) or freezer (≤0°C).

10.6.2.6 Linearity Study Standard at 0.125ug/mL w/ OCN: Using a 1.0mL Class A pipette, accurately add 1.0mL of the 1.27ug/mL standard w/o OCN (10.6.2.5) into a 10mL volumetric flask. Using a 10 microliter syringe add 9uL of 202ug/mL Octachloronaphthalene into the same 10mL volumetric flask and set to volume with hexane. The Octachloronaphthalene is used as an internal standard for instrument calibration. Transfer the standard solution to a 10ml vial and store in a refrigerator (4 ± 2°C) or freezer (≤0°C).

10.6.3 All Linearity Study standards must be replaced after 6 month

10.7 Mixed Aroclor Calibration Standard at 6.27ug/mL: The calibration standard is prepared from the 62.7ug/mL mixed Aroclor stock standard (10.6). Using a 10.0mL Class A pipette, accurately add 10.0mL of the 62.7 stock standard into a 100mL volumetric flask. Using a 100 microliter syringe add 90.0uL of 202ug/mL Octachloronaphthalene into the same 100mL volumetric flask and set to volume with hexane. The Octachloronaphthalene is used as an internal standard for instrument calibration. Transfer the standard solution to a 120-ml boston bottle and store in a freezer (≤0°C).

10.7.1 The 6.27ug/mL Mixed Aroclor Calibration Standard must be replaced after 6 month, or sooner, if comparison with continuing check standards indicates a problem.

10.8 Supplemental Congener Standard: A Supplemental Congener Standard is analyzed along with the 6.27ug/mL Mixed Aroclor Calibration Standard. This standard contains congeners that exist at low levels in the mixed Aroclor standard and comprises congeners that are not typically found in Aroclor formulations, but could become important in by-product PCB analysis or the study of model experiments that use unusual PCB congeners. This standard is analyzed to supply accurate retention time information and response factors for quantification.

10.8.1 Supplemental Congener Stock Standard at 2.00ug/mL: All stock standards are purchased as solutions at 100ug/mL from Ultra Scientific or equivalent. All supplemental congeners are diluted together (except 3-Chlorobiphenyl) to 2.00ug/mL. For each congener, using a 2000uL syringe, transfer 2.0mL of the 100ug/mL stock standard into the same 100mL volumetric flask and set to volume with hexane. The 3-Chlorobiphenyl, due to its low ECD response, will be added to the secondary stock standard. Transfer the standard solution to a 120mL boston bottle and store in a refrigerator (4 ± 2°C) or freezer (≤0°C). This stock standard must be replaced after one year.

10.8.1.1 This standard can also be purchased as a custom mix with a concentration of 100ug/mL per congener. The preparation remains the same as in 10.8.1.

10.8.1.2 Supplemental Congener Secondary Stock Standard at 0.0500ug/mL: Into a 50mL volumetric flask combine, using a 2000uL syringe, 1.25mL of the Supplemental Congener Stock Standard, using a 1000uL syringe, 1.0mL of the 3-Chlorobiphenyl purchased stock standard at 100ug/mL and using a 50uL syringe, 45uL of the Octachloronaphthalene Stock Standard at 202ug/mL. Set to volume with hexane and transfer the standard solution to a 120mL boston bottle and store in a refrigerator (4 ± 2°C) or freezer (≤0°C). The Octachloronaphthalene is used as an internal standard for instrument calibration and is at a concentration of 0.1818ug/mL in the standard. The standard concentration is 2.00ug/mL for 3-Chlorobiphneyl and 0.050ug/mL for all other congeners in the standard.

Supplemental Congener Standard

DB-1 Peak Number	IUPAC Congener Number	(IUPAC #) PCB Congener Analyzed	Conc ug/mL
3	2	(2) 3-Chlorobiphenyl	2.000
9	14	(14) 3,5-Dichlorobiphenyl	0.050
11	30	(30) 2,4,6-Trichlorobiphenyl	0.050
12	11	(11) 3,3'-Dichlorobiphenyl	0.050
19	23,34,54	(34) 2',3,5-Trichlorobiphenyl	0.050
28	36	(36) 3,3',5-Trichlorobiphenyl	0.050
30	39	(39) 3,4',5-Trichlorobiphenyl	0.050
35	62,65	(65) 2,3,5,6-Tetrachlorobiphenyl	0.050
36	35	(35) 3,3',4-Trichlorobiphenyl	0.050
41	68,96	(96) 2,2',3,6,6'-Pentachlorobiphenyl	0.050
43	57,103	(103) 2,2',4,5',6-Pentachlorobiphenyl	0.050

62	154	(154) 2,2'4,4',5,6'-Hexachlorobiphenyl	0.050
68	123	(123) 2',3,4,4',5-Pentachlorobiphenyl	0.050
70	140	(140) 2,2',3,4,4',6'-Hexachlorobiphenyl	0.050
76	127,168,184	(127) 3,3',4,5,5'-Pentachlorobiphenyl	0.050

10.9 Internal Standard Stock Standard at 202ug/mL: The internal standard used for capillary gas chromatography of PCBs will be Octachloronaphthalene (OCN). Weigh, 10.1mg of solid Octachloronaphthalene (OCN) into a 5mL vial. Quantitatively transfer the OCN using six successive 2-mL washings of toluene to a 50mL volumetric flask. Be sure to rinse the 5mL vial walls carefully so that all OCN is completely transferred to the 50mL volumetric flask. Make the solution to volume using toluene and mix the internal standard solution by shaking the flask several times. This will give a concentration of OCN of 202ug/mL. Carefully transfer the internal standard solution to 25mL vials, tightly cap, and store in a refrigerator (4 ± 2°C) or freezer (≤0°C). A portion of the internal standard is transferred to a 5mL reacti-vial with a Teflon syringe-valve cap to use on a daily basis. The react-vial minimizes evaporation since the cap does not have to be removed.

10.9.1 The internal standard is added to all calibration standards, continuing check standards, blanks, samples, and QC samples at the same amount. In most cases this will be achieved by spiking 9.0uL of OCN internal standard solution to 10mL of standard or sample extract to give a solution concentration of 0.1818ug/mL.

10.9.2 The internal standard will be added to calibration standards, sample extracts, blanks, and QC samples prior to gas chromatographic analysis. Thus, the internal standard is used as a quantification spiking standard and will eliminate sample injection volume variations, but will not correct for analytical losses during sample preparation.

10.9.3 OCN internal stock standard must be replaced after one year. Working standards are replaced every 6 month.

10.10 Surrogate Stock Standard (2,2',3,3',4,4',5,6,6'-Nonachlorobiphenyl) at 100ug/mL:The surrogate stock standard is prepared from a solid standard. Weigh 5.0mg of the neat Standard material into a solvent rinsed 10mL vial. Quantitatively transfer the surrogate standard using six successive 2-mL washings of hexane to a 50mL volumetric flask. Be sure to rinse the 10mL vial walls carefully so that the entire surrogate standard is completely transferred to the 50mL volumetric flask. Make to volume with hexane and mix the surrogate standard solution by shaking the flask several times. This will give a concentration of surrogate standard of 100ug/mL. Carefully transfer the surrogate standard solution to a 125mL boston bottle, tightly cap, and store in a freezer (≤0°C) or refrigerator (4 ± 2°C). The surrogate standard must be replaced after one year.

10.10.1 Surrogate Calibration Standard (2,2',3,3',4,4',5,6,6'-Nonachlorobiphenyl) at 50.0ng/mL with Internal Standard at 181.8ng/mL: The Surrogate Calibration Standard is prepared from the 100ug/mL Surrogate Stock Standard and the 202ug/mL Internal Standard Stock Standard. Into a 100mL volumetric flask, using a 50-microliter syringe, transfer 50uL of the Surrogate Stock Standard at 100ug/mL. Into the same 100mL volumetric flask transfer, using a 100-microliter syringe, 90 microliters of the 202ug/mL Internal Standard Stock Standard. Make to volume with hexane and transfer the standard solution to a 125mL boston bottle, tightly cap, and store in a freezer (≤0°C) or refrigerator (4 ± 2°C). This will give a concentration of Surrogate Calibration Standard of 50ng/mL and Internal Standard (OCN) of 181.8ng/mL. This Standard must be replaced after six months.

10.10.2 Surrogate Calibration Standard (2,2',3,3',4,4',5,6,6'-Nonachlorobiphenyl) at 20.0ng/mL with Internal Standard at 181.8ng/mL: The Surrogate Calibration Standard is prepared from the 100ug/mL Surrogate Stock Standard and the 202ug/mL Internal Standard Stock Standard. Into a 100mL volumetric flask, using a 50-microliter syringe, transfer 20-miroliter of the Surrogate Stock Standard at 100ug/mL. Into the same 100mL volumetric flask transfer, using a 100-microliter syringe, add 90 microliters of the 202ug/mL Internal Standard Stock Standard. Make to volume with hexane and transfer the standard solution to a 125mL boston bottle, tightly cap, and store in a refrigerator (4 ± 2°C). This will give a concentration of Surrogate Calibration Standard of 20ng/mL and Internal Standard (OCN) of 181.8ng/mL. This Standard must be replaced after six months.

10.11 Continuing Calibration Check Standards (CCCS): Continuing calibration check standards at 1.27ug/mL and 0.127ug/mL are prepared from Aroclor solutions obtained from a different source (ULTRA Scientific or equivalent) than the

calibration standard. The continuing calibration check standard is a mixed Aroclor 1232, 1248, and 1262 in the fixed ratio used to prepare the calibration standard and must be strictly adhered to.

10.11.1 50.0ug/mL Continuing Calibration Check Stock Standards: Aroclor 1232, Aroclor 1248, and Aroclor 1262 are obtained from ULTRA Scientific or equivalent at 1000ug/mL in isooctane. Using a 500-microliter syringe, 500-microliter of 1000ug/mL Aroclor 1232 is transferred to a 10.0mL volumetric flask and made to volume with hexane. This procedure is repeated for Aroclor 1248 and Aroclor 1262. The 50ug/mL stock standards are each transferred to an individual 10mL vial, tightly capped and stored in a freezer (≤0°C) or refrigerator (4 ± 2°C). These stock standards must be replaced after one year.

10.11.2 1.27ug/mL Continuing Calibration Check Standard with OCN: Using a 1.0mL syringe transfer 1.0mL of 50.0ug/mL Aroclor 1232, 0.720mL of 50.0ug/mL Aroclor 1248, and 0.720mL of 50.0ug/mL Aroclor 1262 into a 100mL volumetric flask. Using a 100-mircoliter syringe, add 90.0-microliter of OCN internal standard (final concentration of 0.1818ug/mL). Set to volume with hexane and mix well by shaking and inverting flask several times. The prepared continuing calibration check solution will contain a total of 1.27ug/mL PCB (0.500ug/mL Aroclor 1232, 0.360ug/mL Aroclor 1248, and 0.360ug/mL Aroclor 1262).

10.11.3 Transfer the 1.27ug/mL Continuing Calibration Check Standard with OCN to a 120mL boston bottle, cap tightly, and store in a freezer (≤0°C) or refrigerator (4 ± 2°C). A new continuing check standard must be prepared every six months.

10.11.4 1.27ug/mL Continuing Calibration Check Standard without OCN: Using a 1.0mL syringe transfer 1.0mL of 50.0ug/mL Aroclor 1232, 0.720mL of 50.0ug/mL Aroclor 1248, and 0.720mL of 50.0ug/mL Aroclor 1262 into a 100mL volumetric flask. Make to volume with hexane and mix well by shaking and inverting flask several times. The prepared continuing check solution will contain a total of 1.27ug/mL PCB (0.500ug/mL Aroclor 1232, 0.360ug/mL Aroclor 1248, and 0.360ug/mL Aroclor 1262).

10.11.5 Transfer the 1.27ug/mL Continuing Calibration Check Standard without OCN to a 120mL boston bottle, cap tightly, and store in a freezer (≤0°C). A new continuing calibration check standard must be prepared every six months. This continuing check standard without OCN is used to prepare the 0.127ug/mL Continuing Calibration Check Standard with OCN.

10.11.6 0.127ug/mL Continuing Calibration Check Standard with OCN: Using a 10.0mL Class A pipette transfer 10.0mL of 1.27ug/mL Continuing Calibration Check Standard without OCN to a 100mL volumetric flask. Using a 100-microliter syringe, add 90.0uL of OCN internal standard (final concentration of 0.1818ug/mL). Make to volume with hexane and mix well by shaking and inverting flask several times. The prepared continuing calibration check solution will contain a total of 0.127ug/mL PCB (0.050ug/mL Aroclor 1232, 0.036ug/mL Aroclor 1248, and 0.036ug/mL Aroclor 1262).

10.11.7 Transfer the 0.127ug/mL Continuing Calibration Check Standard with OCN to a 120mL boston bottle, cap tightly, and store in a freezer (≤0°C) or refrigerator (4 ± 2°C). A new Continuing Calibration Check Standard must be prepared every six months.

11.0 Sample Collection, Preservation, Shipment and Storage

11.1 Sample Collection and Preservation:

11.1.1 Routine soil, sediment, sludge, solid and concentrated liquid samples should be collected in 8 oz clear glass wide-mouth jars, fitted with a Teflon-lined cap. Aqueous samples should be collected in 1 liter amber glass bottles with a Teflon-lined cap. Project specific, the jars maybe required to be pre-cleaned to EPA specification protocol A – recommended for extractable organic, semivolatile and pesticide analysis. Protect samples from light.

11.1.2 All samples must be placed on ice or refrigerated at 4°C (± 2°C) from the time they are collected until delivery to the lab. Samples collected and delivered to the laboratory on the same day may not reach 4± 2°C. Sample cooling is considered adequate if samples are received on ice.

11.2 Sample Shipment:

11.2.1 Sample Shipment is accomplished through a carrier such as Federal Express or United Postal Service for overnight 1-day delivery to the lab. Shipment is normally handled by the field personnel collecting the samples and coordinated with sample receiving department at the lab. Samples can also be picked up by the lab courier service if samples are collected within driving distance to the lab.

11.3 Sample Storage:

11.3.1 The samples must be protected from light and refrigerated at 4°C (± 2°C) from time of receipt until they are removed from storage for extraction. Remaining sample material will be stored protected from light and refrigerated at 4°C (± 2°C). Sample will be disposed of or stored / archived according to project specifications.

11.3.2 Routine soil, sediment, sludge, solid, liquid and concentrated liquid samples are stored in a refrigerator (4 ± 2°C) dedicated for this type of sample.

11.4 Sample Extract Storage:

11.4.1 Sample extracts must be protected from light and stored refrigerated at 4°C (± 2°C) during the analysis. After analysis is complete, sample extracts will be discarded after 60 days or can be archived in a freezer (≤0°C) and at less than -20°C for longer periods of time depending on the project requirements.

11.4.2 Field samples, sample extracts, and calibration standards must be stored separately.

11.5 Required Hold Time:

11.5.1 Extraction of solid samples by appropriate technique must be completed within fourteen days from sample collection.

11.5.2 Extraction of aqueous samples by appropriate technique must be completed within seven days from sample collection.

11.5.3 Sample extracts must be analyzed within forty days of sample extraction.

12.0 Quality Control

12.1 This section outlines the necessary quality control samples that need to be generated at the time of sample extraction. The results of the quality control measurement samples document the quality of the data generated. The following table lists the Quality Control samples required for capillary gas chromatography analysis of PCBs.

Quality Control Requirements

QC Sample	Frequency
Method Blank	With each sample batch (up to 20 samples)
Lab Control Spike	With each sample batch (up to 20 samples)
Cont Cal Check Std	Analyzed prior to each sample batch and at a Frequency or one per ten injections. Each analytical sequence must close with a Continuing Calibration Check Standard (CCCS).
Duplicate Analysis	Field generated sample – analyzed at discretion of client.
Matrix Spike	One matrix spike per 20 field samples or

	designated sample batch may be performed as specified in the client site plan.
Matrix Spike Duplicate	One matrix spike duplicate per 20 field samples or designated sample batch may be performed as specified in the client site plan.

12.2 Method Blank:

12.2.1 With each batch of samples to be extracted a method blank is processed. The method blank is carried through all stages of sample preparation and measurement steps. For water samples and organic-free reagent water blank is processed. For soil, sediment, solid, fish, and other tissue sample a laboratory clean sodium sulfate is processed. For oil samples, a PCB-free blank control oil is processed. The method blank must exhibit PCB levels less than the matrix defined reporting limit (RL). If the method blank exhibits PCB contamination above the reporting limit, the samples associated with the contaminated blank should be re-extracted and analysis repeated. If there is no original sample available for re-extraction, then the results should be flagged with a "B" indicating blank contamination. The value measured in the blank is reported for those samples associated with the particular blank out of criteria.

12.3 Laboratory Control Spike:

12.3.1 A Laboratory Control Spike (LCS), also referred to as a QC reference check standard, is extracted with each batch of samples at a rate of one per 20 samples. For water sample, spike one liter of laboratory organic free water, extract and analyze. For solid and tissue samples spike 10 grams of sodium sulfate/ hydromatrix, extract and analyze. For oil samples spike 0.50 gram of PCB free oil, extract and analyze. An Aroclor is chosen for the LCS analyte, typically based on program requirements or expected sample contamination. Calculate the percent recovery for the PCB spike. If the percent recovery for the LCS is out of criteria, (60%-140%) the analysis is out of the control for that analyte and the problem should be immediately corrected. If there is sufficient sample, the samples associated with the Laboratory Control Spike that failed must be re-extracted and re-analyzed. If no more sample material is available, the data must be flagged to indicate low or high Control Spike recovery.

12.4 Duplicate Analysis:

12.4.1 Duplicate analysis of the same sample is performed to assess method precision. A duplicate can also be performed as a blind duplicate, so that identification with original sample is withheld. The analysis of a duplicate sample precludes that PCBs are to be found at appreciable levels in samples. If this is not known the analysis of matrix spike/matrix spike duplicates provide more consistent quality control information. The relative percent difference of the two measurements on the sample is calculated on total PCB concentration by the following equation:

$$RPD = (DUP1-DUP2)/AVG \times 100$$

Where: RPD = Relative Percent Difference
DUP1 = The greater of the measured values
DUP2 = The lesser of the measured values
AVG = Average of the two analysis

The relative percent difference must be less than or equal to 30%.

12.5 Matrix Spike and Matrix Spike Duplicate (MS/MSD)

12.5.1 Spiked sample matrix data are analyzed to assess analytical accuracy and recovery of analytes of interest. Thus the sample is spiked and carried through sample analytical procedures including extraction, clean up, and GC analysis. Depending on the specific project plans and at the discretion of the client a matrix spike or matrix spike and matrix spike duplicate can be analyzed.

12.5.2 There must be sufficient sample for analysis of matrix spike/matrix spike duplicate samples and the sample must be homogeneous in PCB distribution for valid data to be produced. Spike MS and/or MSD samples with the Aroclor matrix spike standard at a concentration approximately two to five times the sample concentration. Extract and analyze the two spiked samples following procedures used for actual sample analysis. Calculate the percent recovery of the matrix spike/matrix spike duplicate by the following equation:

$$P = A-B/T \times 100$$

Where: P = Percent recovery, %
A = concentration of analyte in the spike sample aliquot
T = Know true values of the spike concentration
B = Background concentration of PCB in the unspiked sample aliquot

12.5.3 Matrix spike recovery information is used to assess the long-term precision and accuracy of the method for each encountered matrix. Matrix spike/matrix spike duplicate results are not used alone to qualify an extraction batch. Generally, percent recovery for MS/MSD samples should be greater than or equal to 60% and less than or equal to 140% based on the total PCB concentration. If the percent recovery is outside the limits, all calculations should be checked and the data should be narrated to describe possible matrix interference.

12.6 Surrogate:

12.6.1 Surrogate-spiking compounds monitor the extraction efficiency and sample processing procedures for each sample. Surrogate compounds are chosen which do not chromatographically interfere with the PCB target congeners and which behave similarly to the target PCB congeners during extraction and sample processing.

12.6.2 A surrogate compound is added to each sample, matrix spike, matrix spike duplicate, duplicate, method blank, and laboratory control spike at the time of extraction. The surrogate compound chosen for this method is 2,2',3,3',4,4',5,6,6' – Nonachlorobiphenyl, Accu Standard Cat. No. C-206S-TP (this congener is not present or found at trace amounts in Aroclor formulations). The following are typical surrogate amounts added to normally encountered matrices. These amounts can be adjusted by the analyst, if PCB background levels are high and surrogates are being diluted out of analysis range.

12.6.2.1 Water: 0.50ml of 0.20ppm 2,2',3,3',4,4',5,6,6'-Nonachlorobiphenyl

12.6.2.2 Soil/Sediment/Solid/Fish: 1.00ml of 1.25ppm 2,2',3,3',4,4',5,6,6'-Nonachlorobipenyl

12.6.3 Surrogate recovery measurements are used for advisory purposes, if surrogate recovery is not within laboratory establish limits, the following steps are required. The laboratory established limits for surrogate recovery are 60%-140%.

12.6.3.1 Review calculations that were used to generated surrogate percent recovery values to make certain there are no errors.

12.6.3.2 Check by GC analysis surrogate solutions used during sample extraction steps to ensure that no problems exist with spiking solutions.

12.6.3.3 Review data for chromatographic interferences.

12.6.3.4 Re-extraction and/or re-analysis of samples may be indicated if problems persist with surrogate recoveries. If the surrogate percent recovery is out of limits on the re-extracted samples, low or high surrogate recovery is due to matrix affects and the data can be reported as estimated.

12.7 Continuing Calibration Check Standard (CCCS):

12.7.1 As outlined in Section 12.9.1, a CCCS will be analyzed on each working day prior to sample analysis and at an interval of one CCCS per 10 samples. The CCCS must meet the acceptance criteria established in Section 13.3. If the CCCS Standard fails to meet the acceptance criteria, the following guidance must be followed.

12.7.2 If samples are being run using an autoanalyzer (i.e., the instrument is unattended) and a CCCS that fails to meet the acceptance criteria is present in the analytical sequence but acceptable CCCSs are observed later in the analytical sequence, samples bracketed by acceptable CCCSs will be reported.

12.7.3 If the reason for the failure of the CCCS appears to be a poor injection (or a degraded standard solution), the CCCS will be re-injected (or re-prepared and re-injected) immediately following the failed CCCS. This can only occur if the instrument is being attended by an analyst. If upon re-injection, the CCCS meets all the acceptance criteria established in Section 13.3. and there is no apparent impact on the sample data (i.e., acceptable internal standard areas and surrogate recoveries are observed), the analytical sequence will continue and samples will not be reanalyzed. The associated sample data will be reported.

12.7.4 If the CCCS fails to meet the acceptance criteria, the initial calibration standards must be re-analyzed and new response factors generated. After re-calibration, the CCCS must be analyzed again and compared to the acceptance criteria. If the CCCS fails to meet the acceptance criteria after re-calibration, sample analysis must not proceed until the problem is corrected.

12.7.5 All samples that were analyzed directly before or after the CCCS exceeded established criteria must be re-analyzed.

12.8 Retention Time Windows:

12.8.1 Refer to the table entitled “Quality Control Acceptance Criteria and Corrective Action Plan” in Section 19.0 for retention time window and retention time shift acceptance criteria and corrective action.

12.8.2 The Initial CCCS of each analytical sequence is used to establish the retention time window for each analyte. The retention time window equals the absolute retention time of the Initial CCCS for a given batch of samples ±0.07 minutes.

12.8.3 Besides using the retention time window to assign peaks for quantification, the analyst should also rely on their experience in pattern recognition of multi-response sample analysis.

12.9 Analytical Sequence Queue:

12.9.1 A typical analytical sequence is as follows:

Injections	Material Injected
1-2	Hexane Instrument Blanks
3	Initial Calibration Standard 6.27 ppm

4	Hexane Blank
5	Supplemental Congener Standard
6	Hexane Blank
7-8	Surrogate Calibration Standards
9	Hexane Blank
10	Continuing Calibration Check Standard (CCCS)
11	Method Blank
12	Lab Control Spike
13-19	Samples (including Duplicates, MS/MSD)
20	Continuing Calibration Check Standard (CCCS)
21-29	Samples (including Duplicates, MS/MSD)
30	Continuing Calibration Check Standard (CCCS); repeat 21 to 30

13.0 Calibration and Standardization

13.1 Calibration:

13.1.1 Gas chromatographic operation parameters:

13.1.1.1 GC Column: DB-1 or ZB-1 (J&W or Phenomenex, bonded polydimethylsilicone), 30 meters, 0.25 mm internal diameter, 0.25 micron phase coating.

13.1.1.2 Oven Temperature Program: 50°C for 2.5 min hold time, 50°C to 150°C at 15.0°C/min, hold 0.01minutes, 150°C to 220°C at 4.3°C/minute, hold at 220°C for 35.1 minutes.

13.1.1.3 GC Column Velocity: Approximately 30 cm/sec Helium. Column flow adjusted to elute OCN Internal Standard between 42.0 and 48.0 minutes.

13.1.1.4 Detector: Electron Capture Detector (micro-ECD), attenuation 0, range 3. (adjustable based on signal sensitivity).

13.1.1.5 Detector Temperature: 300°C.

13.1.1.6 Injector Temperature Program: 250°C , pulsed split injection, initial pressure at 25.0PSI, pulsed pressure at 40PSI, pulsed time 0.75 minutes, split ratio 25 (adjustable based on signal sensitivity).

13.1.1.7 Detector Make-up Gas: Approximately 65mL/min Nitrogen. Adjusted for signal sensitivity.

13.1.1.8 Autosampler: 1.0uL sample volume (adjustable based on signal sensitivity). Sample pumps 4, viscosity delay 3, sample wash 2, solvent A 2 washes, solvent B 2 washes, slow plunger OFF, sampling offset OFF, solvent A pre-wash 1, solvent B pre-wash 1.

13.2 Initial GC Calibration:

13.2.1 Prior to running samples the system must be calibrated and the Initial Continuing Calibration Check Standard must be verified.

13.2.2 Establish the gas chromatographic operation parameters outlined in Section 13.1.1 and prepare the appropriate calibration standards composed of a mixture of Aroclor 1232, 1248, and 1262 as outlined in Sections 10.6 through 10.11.

13.2.3 Chromatographic Resolution Criteria: Chromatographic resolution is measured by peak height to valley height for two pairs of closely eluting peaks. The peak valley height formed between DB-1/ZB-1 peaks 14 and 15 must be equal to or less than the half height of peak 15. The peak valley height formed

between DB-1/ZB-1 peaks 74 and 75 must be equal to or less than one-third the height of peak 74. This peak resolution must be established initially and maintained throughout sample analysis.

13.2.4 Initial High Level Linearity Verification: The gas chromatograph must undergo a linearity study. A high-level three-point initial calibration check for linearity is analyzed and calculated relative response factors must meet a limit for relative standard deviation for each GC peak of less than 20%. This high level linearity verification is associated with samples with medium to high levels of PCBs for sample matrices such as biota, sediment, soil, oil, and other solid or liquid samples that contain appreciable levels of PCBs. The high level initial linearity is comprised of the following standards: 31.35ug/mL w/OCN Standard (10.6.2.1) the 6.27ug/mL w/OCN Standard (10.6.2.3) and the 1.27ug/mL w/OCN Standard (10.6.2.4). See Appendix C.

13.2.5 Initial Low Level Linearity Verification: The gas chromatograph must undergo a linearity study. A low-level three-point initial calibration check for linearity is analyzed and calculated relative response factors must meet a limit for relative standard deviation for each GC peak of less than 20%. This low level linearity verification is associated with samples with low levels of PCBs for sample matrices such as water and other solid or liquid samples that contain low levels of PCBs. The low-level initial linearity is comprised of the following standards: 6.27ug/mL w/OCN Standard (10.6.2.3), the 1.27ug/mL w/OCN Standard (10.6.2.4), and the 0.127ug/mL w/OCN Standard (10.6.2.6). See Appendix C.

13.2.6 Initial 72-Hour Retention Time Window Measurement: An initial retention time study must be performed to establish retention time windows to assist in PCB peak assignment. Three high level Continuing Calibration Check standards (prepared at a concentration of 1.27 ug/ml as described in Section 10.11, must be analyzed over at least a 72-hour period. In addition, the Supplemental Congener Standard is analyzed three times over at least a 72-hour period. The mean retention time is calculated from these standards along with the standard deviation for each GC peak. The retention time window is established as ±3 times the determined standard deviation. If the 3 times the standard deviation value is less than 0.07 minutes a default of 0.07 minutes is applied to that GC peak. The default 0.07 minutes retention time window is the default window used in Contract Laboratory Program, Statement of Work for Organic Analysis for PCB/Pesticide analysis. See Appendix C.

13.2.7 Our laboratory uses a computer based chromatography software module (Water Corporation, Empower software) interfaced to the gas chromatograph and a In House LIMS System for data handling, reporting and packaging. The Empower workstation acquires and processes the analog detector signal, which is then digitally converted. Empower then stores the digitized chromatograms in a database on a designated Server. All phases of integration of peak areas, quantitation and production of chromatograms and raw data reports is performed within the Empower software. This data then can be captured by the LIMS system for further data handling, scoring, reporting, packaging and data distribution as requested by the client.

13.2.8 After the above criteria are met system calibration for sample analysis can be performed. Appendix A identifies which congener and or congeners compose each resolvable GC peak in the calibration standard, along with the amount that each congener or co-eluting group of congeners are represented in the calibration standard. Throughout this document the IUPAC PCB numbering system will be used for congener identification. Appendix B is an example of an acceptable chromatogram of the calibration standard, along with peak congener labels for cross-reference to data in Appendix A. Analyze the 6.27ug/mL Calibration Standard to initiate calibration of the GC system. Also analyze the Supplemental Congener Standard to calculate relative response factors for congeners that do not exist in the 6.27ug/mL Calibration Standard. Response factors are calculated relative to the internal standard by the following equation:

$$RRF = (Ax/Ais)x(Cis/Cx)$$

Where:	RRF	=	Relative response factor of congener(s).
	Ax	=	Area of peak for the congener(s).
	Ais	=	Area of peak for the internal standard.
	Cx	=	Concentration of the congener(s).

Cis = Concentration of the internal standard.

13.3 Continuing Calibration:

13.3.1 Chromatographic Resolution: Chromatographic resolution is measured by peak height to valley height for two pairs of closely eluting peaks. The peak valley height formed between DB-1/ZB-1 peaks 14 and 15 must be equal to or less than the half height of peak 15. The peak valley height formed between DB-1/ZB-1 peaks 74 and 75 must be equal to or less than one-third the height of peak 74. This peak resolution must be established initially and maintained throughout sample analysis.

13.4 Response Factor Verification:

13.4.1 The relative response factors calculated from the calibration standard will be verified on each working day by analyzing a CCCS, calculating the selected congener concentrations and comparing to their known concentration. The CCCS concentration is either 1.27ug/mL or 0.127ug/mL depending on the expected concentrations of PCB in the sample. A subset of six congeners and Total PCBs will be used to verify the relative response factors before samples are processed. The Percent Difference for Total PCBs must be <15%. The six congeners include:

DB-1 PEAK NUMBER	IUPAC CONGENER NUMBER	RELATIVE PEAK LEVEL IN CALIBRATION STANDARD	PEAK CONC 1.27ug/mL or 0.127ug/mL CONTINUING CALIBRATION STD (ng/mL)	PERCENT DIFFERENCE LIMITS
7	6	Low level peak in	14.10 / 1.41	<30
116	205	Low level peak in	0.820 / 0.082	<30
47	70	Medium level peak in	25.22 / 2.52	<15
93	174, 181	Medium level peak in	23.74 / 2.37	<15
37	104, 44	high level peak in	31.90 / 3.19	<15
102	180	high level peak in	45.26 / 4.53	<15

13.4.2 After the Continuing Calibration Check Standard is analyzed, calculate the amount for these six congeners and Total PCBs and compare those values to the known concentrations by the following equation:

Percent Difference = [Amt(1)-Amt(2)]/Amt(2) x 100

Where: Amt(1) = Amount calculated for congener or Total PCBs.
Amt(2) = Known amount for congener or Total PCBs.

13.4.3 A percent difference greater than ± 30% for the two low-level peaks (7 and 116) indicate an instrument problem or unacceptable relative response factors. A percent difference greater than ± 15% for the medium level (47 and 93) and high level (37 and 102) peaks also indicates an instrument problem or unacceptable relative response factors. If any of the evaluation congeners or Total PCBs fails to meet the percent difference acceptance criteria, the guidance provided in Section 18.3. must be followed.

13.4.4 The percent recovery for the internal standard Octachloronaphthalene (OCN) in the CCCS must be within 50-150% of the OCN area in the associated calibration standard. If the OCN area fails to meet the acceptance criteria, the guidance provided in Section 18.3. must be followed.

13.4.5 If re-calibration is performed, the CCCS must be analyzed again and values calculated using the new relative response factors. If the CCCS fails to meet the percent difference criteria after re-calibration, sample analysis must not proceed until the problem is found and corrected (i.e., GC gas leak, autosampler lines plugged, broken injector liner).

14.0 Procedure

14.1 Sample Extraction and Preparation:

14.1.1 The following SOPs detail sample extraction procedures that are utilized in preparing samples for analysis by this analytical method:

SOP NAME	TITLE
NE005	SOXHLET EXTRACTION : SOLIDS
NE006	WATER EXTRACTION
NE017	FISH & BIOTA EXTRACTION
NE088	WIPE EXTRACTION FOR PCB
NE111	WASTE DILUTION FOR PCB
NE124	CLLE PCB WATER EXTRACTION
NE132	FISH/BIOTA GRINDING PROCEDURES
NE140	PCB SCREENING BY GC
NE143	ASE EXTRACTION FOR PCB: SOLIDS
NE144	ASE EXTRACTION FOR WIPE: PCB
NE158	% LIPID DETERMINATION: FISH & BIOTA

14.2 Gas Chromatographic Procedures:

14.2.1 Pre-secreening of sample extracts: See standard operating procedure NE140 for details on the PCB screening procedures used prior to final analysis by this method. The GC will be standardized by using Aroclor 1221, Aroclor 1242 and Aroclor 1260. These three Aroclor formulations incorporate most environmental PCBs found in sample extracts and provide a good estimate of PCB amount for final dilution for capillary analysis. A three level calibration curve is utilized (0.50ug/mL, 2.5ug/mL and 5.0 ug/mL standards). The concentration of each Aroclor (grouped as Aroclor 1221, Aroclor 1242 and Aroclor 1260 only) in a sample will be calculated based on the extract volume (not the sample weight or volume) to supply solution concentration values that show if the extract needs to be diluted for final capillary GC analysis. If a dilution is necessary, sample extracts are diluted to a solution concentration between 0.60ug/ml to 1.0 ug/mL depending of the Aroclor pattern from the pre-screening results. Preferable solution set volumes are 5mL and 10mL as the internal standard (OCN) is added at this time to give a solution concentration of 0.1818ug/mL in the final dilution.

Dilution Scheme Examples

Dilution Factor based on 25x final extract volume	Amount of original Sample Transferred (mL)	Amount of Hexane added (ml)	Final Volume of diluted Sample (ml)	Amount of 202 ppm OCN Added for final analysis
e31.3 x	4	1	5	4.5 uL
41.7 x	3	2	5	4.5 uL
50.0 x	2.5	2.5	5	4.5 uL
62.5 x	2	3	5	4.5 uL
83.3 x	1.5	3.5	5	4.5 uL
125 x	1.0	4.0	5	4.5 uL
167 x	1.5	8.5	10	9.0 uL
250 x	1	9	10	9.0 uL
500 x	0.5	9.5	10	9.0 uL

Should higher dilutions be needed, a dilution sequence is performed, utilizing the dilution examples above without the addition of OCN. The OCN is only added to the final dilution used for analysis.

14.2.2 Approximately 1.0mL of the final dilution extract is then transferred into a labeled autosampler vial.

14.2.3 The sequence of the analytical queue is set up in the NEA LIMS as a unique batch file. This file contains all the sample extraction information such as sample name, client ID, sample volume extracted, set volume and the exact order in which standards, instrument blanks, and samples will be analyzed. Once the sample set is uploaded into the Empower acquisition/run screen and saved, the sample set is printed and the samples are loaded into the GC autosampler tray in the order specified by the sample set queue.

14.2.4 The following labeling will be used on the autosampler vial and for the sample set file created for the analytical queue.

14.2.4.1 The initial Calibration Standard will be labeled as ICAL0301. Substitute the actual date of analysis in the file name.

14.2.4.2 The Supplemental Congener Calibration Standard will be labeled as SC0301. Substitute the actual date of analysis in the file name.

14.2.4.3 The Surrogate Standard will be labeled SS0301. Substitute the actual date of analysis in the file name.

14.2.4.4 The Instrument blanks will be labeled 070301B01, B02, B03, etc. Substitute the actual date of analysis in the file name.

14.2.4.5 The Continuing Calibration Check Standards will be labeled CCCS0301A, CCCS0301B, etc. Substitute the actual date of analysis in the file name.

14.2.4.6 Samples are labeled with the laboratory identification number on the autosampler vial. In the sample set file the laboratory identification number along with the client identification, sample weight, set volume and dilution are entered.

14.2.5 At this point the chromatography software can be initiated to start data collection. The gas chromatograph is placed into run mode and sample analysis is performed until the analytical queue is complete.

14.3 Peak Integration and Analyte Identification:

14.3.1 Due to the complex nature of the PCB patterns encountered and the range of peak intensities that can occur in the sample chromatograms, manual peak integration is performed to accurately integrate the samples. Manual peak integration is also performed on standards to best address the changing signal intensities. Manual integration provides for better peak start and peak end positioning, better control of peak baselines and more accurate data.

14.3.2 Analytes are identified by matching retention time to the calibrated peak in the initial calibration standard that are within the retention time window of ±0.07 minutes. The analyst must also use judgment in pattern recognition.

14.3.3 The PCB congener composition of DB-1/ ZB-1 peaks is identified in Appendix A. Peaks may include one or more co-eluting PCB congeners.

14.3.3.1 In the case of some peaks, the congeners assigned to the peak consist of co-eluting congeners and a congener that is resolved or is just slightly out of the normal retention time window of ± 0.07 minutes. With exception of congeners IUPAC 77 and 122, the resolved peaks are found

at trace levels in Aroclor (and, therefore, not present in the calibration standards) and are addressed in this method in the event they are detected. If these congeners are detected in a sample, the retention time window of the assigned peak is set to ensure the congener is quantitated. A standard comment is included on the Congener Weight and Mole Report (see Appendix C) identifying this issue. If detection of one of the resolved congeners occurs, a comment will be included in the report narrative indicating that the assigned DB-1/ZB-1 peak includes the presence of the resolved congener. The peaks consisting of co-eluting congeners and a congener that is resolved are as follows:

DB-1/ZB-1 Peak[1]	Resolved Congener (IUPAC #)
37 (**44**, *104*)	*104*
48 (**66**, *76*, *98*, *80*, *93*, **95**, **102**, *88*)	*80*, *88*, *93*
56 (*78*, **83**, *112*, *108*)	*108*
61 (**77**, **110**, 148)	**77**
72 (**122**, 131, 133, 142)	**122**
89 (**128**, *162*)	*162*
105 (**200**, *169*)	*169*

1 - IUPAC congener numbers listed in boldface font were found to be present in at least one of the Aroclor at or above 0.05 weight percent. These congeners should be considered the primary congeners existing in a peak composed of co-eluting congeners. IUPAC congener numbers listed in italic font were absent or present below 0.05 weight percent.

14.3.4 If uncertainty in analyte identification exists, analysis by secondary methodology such as NEA Comprehensive Quantitative Congener Specific Method or GC/MS Method 680.

15.0 Calculations

15.1 Screening GC - External Standard Calibration:

15.1.1 The GC screening analysis will be done by the external standard calibration technique. See standard operating procedure NE140 for details on the PCB screening procedures used prior to final analysis by this method. The calibration curves for each section of the PCB elution profile will be calculated using the following formula:

$$\text{Calibration factor} = \frac{\text{Amount (ug) of Aroclor}}{\text{Total area of Aroclor}}$$

15.1.2 The calibration curve will be a linear fit forced through zero.

15.2 Screening GC - Sample Calculations:

15.2.1 The concentration of each Aroclor (grouped as Aroclor 1221, Aroclor 1242 and Aroclor 1260 only) in a sample will be calculated based on the extract volume (not the same weight or volume) to supply solution concentration values that show if the extract needs to be diluted for final capillary GC analysis.

The solution concentration of Aroclor 1221, Aroclor 1242, or Aroclor 1260 (or all 3) in a sample is calculated as follows.

Concentration (ug/mL) = (Ax) x (CF)
Where:
Ax = Area of Aroclor of interest in sample
CF =Calibration factor in standard

15.3 Capillary GC - Internal Standard Calibration:

15.3.1 The capillary column GC analysis will be performed by the internal standard calibration technique. Octachloronaphthalene (OCN) is added to all calibration standards, CCCS and samples at a concentration of 181.8 ng/mL.

15.3.2 Relative Response Factors for each separated and identified peak in the standard will be calculated using the following formula:

RRF = (Ax/Ais)x(Cis/Cx)
Where:
RRF = Relative response factor of congener(s).
Ax = Area of peak for the congener(s).
Ais = Area of peak for the internal standard.
Cx = Concentration of the congener(s).
Cis = Concentration of the internal standard

15.4 Capillary GC - Sample calculations:

15.4.1 The concentration of each identified PCB peak in a sample will be calculated based on the sample dry weight in the case of soils, sediment, and wet weight for fish and biota samples.

15.4.2 The sample PCB concentration of each standardized PCB peak is calculated as follows:

$$\text{Concentration (ng/g or ng/L)} = \frac{[(Ax)(Cis)(V)(D)}{[(Ais)(RRF)(Ws \text{ or } Ls)]}$$

Where:
Ax = Peak area for congener(s) being measured.
Cis = Amount of internal standard added to sample extract.
D = Dilution factor, if sample was diluted prior to analysis.
V = Extract volume.
Ais = Peak area of added internal standard
RRF = Relative response factor for congener(s) being measured.
Ws = Dry or wet weight of sample.
Ls = Volume of sample extracted

15.5 The calculated PCB concentration for each PCB peak will be compared to its respective sample-specific reporting limit (RL) and method detection limit (MDL). The results for peaks with concentrations at or above the MDL but below RL will be reported as detected and flagged as estimated with a "J" Flag. The results for peaks with concentrations at or above the RL would be reported as unqualified numeric values.

15.6 The Total PCB concentration will be calculated and reported as follows.

15.6.1 All peak results above their respective MDL (both "J" flagged and unqualified results) will be summed and compared to the sample-specific Total PCB MDL and RL.

15.6.2 If no peaks are detected above their respective MDL, the Total PCB results will be reported as not detected at or above the sample-specific Total PCB MDL.

15.6.3 If the summed peaks from Section 15.6.1 are below the Total PCB MDL the result would be reported as less than ("<") the sample-specific Total PCB MDL.

15.6.4 If the summed peaks from Section 15.6.1 are at or above the Total PCB MDL but below the Total PCB RL, the summed result will be flagged as estimated ("J").

15.6.5 If the summed peaks from Section 15.6.1 are at or above the Total PCB RL, the Total PCB result will be reported as the unqualified numeric value.

15.7 Data Output and Reporting Format:

15.7.1 Several specialized software routines have been developed for high resolution PCB analysis to aid the data user in understanding and organizing the complex data generated from this extremely detailed analysis. Appendix C contains examples of the sample hard copy format that will be used in reporting sample information. This data is also available in electronic format as a PDF file.

16.0 Method Performance

16.1 Precision and Accuracy Determination: Precision and accuracy data is obtained for the method by analyzing four laboratory control spikes at a reasonable concentration above the calibration standard and below the calibration standard 1. The analyte will be added to a laboratory organic free water sample, sodium sulfate or hydro matrix and taken through all extraction and analytical procedures. Aroclor 1242 is used as the analyte and recovery on a total basis is used to calculate percent recovery. To be valid, Aroclor 1242 will be recovered between the limits of 70 to 130 percent. Also, a percent relative standard deviation will be calculated for the replicates will be less than or equal to 20% to be valid. An initial Precision and Accuracy Determination is required for each analyst/technician combination.

16.2 Method Detection Limit: A method detection limit will be determined for this method whenever major modification to the extraction or analysis procedures are made or at a minimum frequency of every 2 years. A minimum of seven laboratory organic free water samples, sodium sulfate or hydromatrix will be prepared with the mixed Aroclor calibration standard at a low level and taken through all extraction and analytical procedures. Method detection limit data will be determined for each chromatographic peak (comprising one or more PCB congeners) based on the following equation:

MDL = S * t(n-1, 1-alpha=0.99)
Where:

S = Standard deviation of the replicate analyses
n = Number of replicates
t(n-1, 1-alpha=0.99) = Student's t value for the 99% confidence level with n-1

For example: t for 8 replicates = t(7,0.99) = 2.998

16.2.1 The determined MDL must be less than the concentration spiked but greater than one tenth (1/10) the spiked concentration. If not, repeat the MDL determination at an appropriate spike concentration for affected analytes.

17.0 Pollution Prevention

17.1 Pollution prevention is practiced in the laboratory by minimizing usage of solvents and chemicals, so that disposal of waste generated is held to the smallest amount possible. This is directly linked to the types of extraction procedures in place at the laboratory to reduce the volumes of solvents used for semi-volatile extraction procedures. Northeast Analytical employs extraction procedures such as continuous liquid/liquid and solid phase extraction methods to reduce solvent requirements for water extraction protocols and ASE and Soxhlet extractions for solid matrices.

17.2 Pollution prevention also relies on minimizing to the best extent the chemicals and solvents required to perform extraction and analysis procedures. The laboratory personnel strive to purchase chemicals and standards that will be consumed based on anticipated workload. For additional information about laboratory pollution prevention, please refer to laboratory SOP NE168.

18.0 Data Assessment and Acceptance Criteria for Quality Control Measures

18.1 The GC analyst is responsible for generating the data and also is the initial individual to review the data. This would include inspection of the chromatographic data, processing the raw data, producing all required data forms, inspection of calibration curves for compliance, surrogate recovery, laboratory control spike recovery, matrix spike/matrix spike duplicate recovery, and continuing calibration compliance. See table 19.1 for Acceptance Criteria.

18.2 Once the initial review of the data is performed by the analyst, decisions are made at that time to accept the data if all criteria are met or to reject sample data if any of the quality control parameters or limits are out of control. Depending on the situation, samples requiring re-extraction will be notified to the appropriate extraction personnel, sample extracts requiring re-injection will be queued for analysis, new calibrations may have to be performed, or samples re-analyzed due to failing continuing check standards.

18.3 The analyst may also consult with the quality control officer as to the best form of action to take or if the situation warrants corrective action beyond routine practices. If no recourse is available and the data is to be reported out of criteria, a Case Narrative Report is generated and the deviation is documented and reported to the client. The Case Narrative Report is filed with the data and is also useful for production of case narratives that are issued with the final data reports. If a problem exists that requires follow-up to rectify, a Corrective Action Report (CAR) is issued to document the problem found, steps taken to resolve the problem, and what samples were affected. This CAR form is filed by the quality control officer and reviewed by management to verify that appropriate actions have been taken to correct the problem.

19.0 Corrective Action for Out-Of-Control Data
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19.1 The table below outlines the data assessment, acceptance criteria, and corrective action procedures for out-of-control data.

Quality Control Acceptance Criteria and Corrective Action Plan

Quality Control Item	Frequency	Acceptance Criteria	Corrective Action
Linearity Verification and Initial Calibration	• Initially verify linearity through the High- and Low-Level Linearity Verifications. • The initial calibration checks for linearity are each at 3 concentration levels. • A single-point calibration is analyzed initially and when	• %RSD≤20% for among the relative response factors for each peak in the linearity verifications. • Relative response factors are to be calculated using area for each quantifiable peak with internal standard method.	• Re-analyze the initial calibration standard and/or evaluate/correct instrument malfunction to obtain initial calibration and continuing calibration check standards that meet criteria. • Sample results above highest linearity verification standard

	Continuing Calibration Check standard fails criteria.		concentration require dilution and re-analysis.
eContinuing Calibration Check Standard (CCC)	• Initially analyze a CCC immediately following a calibration standard analysis. • After the initial CCC of the sequence, a CCC must be analyzed after every 9 samples. • Analytical sequence must end with analysis of a CCC.	• ≤ 30% difference based on "true" concentration for peaks 7, 116. • ≤ 15% difference based on "true" concentration for peaks 37, 47, 93, and 102 and Total PCBs • Retention time of all quantitated peaks must be within RT window (reset with each initial CCC of a sequence) • The percent recovery for the internal standard (OCN) in the Continuing Calibration Check Standard must be within 50-150% of the OCN area of the associated initial calibration standard. • All samples must be bracketed by CCCs that meet all criteria stated above	• If the reason for the failure of the CCC appears to be a poor injection (or a degraded standard solution), the CCC will be re-injected (or re-prepared and re-injected) immediately following the failed CCC. This can only occur if the instrument is being attended by an analyst. If upon re-injection, the CCC meets all the acceptance criteria and there is no apparent impact on the sample data (*i.e.,* acceptable OCN areas and surrogate recoveries are observed), the analytical sequence will continue and samples will not be reanalyzed. The associated sample data will be reported. • If CCC failure was not due to a poor injection (or degraded standard solution) or the instrument was unattended at the time of the CCC failure, correct system, if necessary, and recalibrate. Initial calibration and CCC criteria must be met before sample analysis may begin. Samples that are not bracketed by complaint CCCs must be re-analyzed. • If acceptable CCCs are observed later in the sequence, samples bracketed by acceptable CCCs will be reported. Samples between the failed CCC and prior/ subsequent complaint CCC will be re-analyzed.

Quality Control Acceptance Criteria and Corrective Action Plan

Quality Control Item	Frequency	Acceptance Criteria	Corrective Action
Retention Time (RT) Windows	• Initial RT windows are established to assist in PCB peak assignment. Three high-level CCC standards and three Supplemental Congener Standards are analyzed over at	•	•

	least 72-hours. The mean RT and the standard deviation of each of the GC peaks are calculated. RT window is ± 3× the determined standard deviation or a default of 0.07 minute is applied (whichever is larger). • RT windows are re-centered based on the initial CCC analyzed after calibration curve or if using the first CCC of the day to start a new sequence.		
Retention Time (RT) shift	• Each CCC analysis: RT of all quantitated peaks in the CCC is evaluated against the initial CCC following the initial calibration curve. • Each sample analysis: Rely on RT windows to identify PCB congeners to report. Also use pattern recognition and professional judgment for peaks that shift from RT windows, because congener composition may shift RT for GC peaks.	• Each quantitated peak and surrogate peak should be with established windows.	• Inspect chromatographic system for malfunction, correct problem. Perform re-analysis if necessary.
Method Blank	• One per extraction batch of ≤20 samples of the same matrix per day. • Must be analyzed on each instrument used to analyze associated samples. • Must undergo all sample preparative procedures.	• Concentration does not exceed the total PCB method reporting limit. • Must meet surrogate criteria of 60 to 140 % recovery.	• Re-analyze method blank to determine if instrument contamination was the cause. If method blank re-analysis passes, then report samples. • If method blank is found to contain PCB contamination above total PCB reporting limit, then re-extract and re-analyze all associated samples. If no sample exists for re-extraction, report data flagged (B) to indicate method blank contamination or have client re-sample if possible.

Quality Control Acceptance Criteria and Corrective Action Plan

Quality Control Item	Frequency	Acceptance Criteria	Corrective Action
Laboratory Control Spike (LCS)	• One per extraction batch of ≤20 samples per matrix per day. The LCS is typically Aroclor 1242.	• Percent recovery of Aroclor 1242 on a total PCB basis must be within method limits of 60 to 140% • Must meet surrogate criteria of 60 to 140% recovery.	• Re-analyze LCS to determine if instrument was the cause. If LCS passes, then report samples. • If LCS recovery is still out of limits, then re-extract and re-analyze all associated samples. If no sample exists for re-

			extraction, report data flagged to indicate LCS failed recovery or have client re-sample if possible.
Matrix Spike/Matrix Spike Duplicate (MS/MSD)	• Normal method procedure is to extract and analyze a matrix spike sample. One MS per extraction batch of ≤20 samples per matrix per day. The MS is typically Aroclor 1242. • If requested, an MSD can be extracted an analyzed. The MSD would follow the above criteria as for the MS.	• Percent recovery for MS on a total PCB basis should be 60 to 140% • If MS/MSD is analyzed, relative percent difference (RPD) should be within 20%. • Must meet surrogate criteria of 60 to 140%(unless original unspiked sample is also outside of criteria).	• Re-analyze MS and/or MSD to determine if instrument was the cause. If MS and/or MSD pass, then report samples. • Check for errors such as calculations and spike preparation. • Check original unspiked sample results and surrogate recovery for indications of matrix effects. • If no errors are found, and the associated LCS is within 70 to 130%, then sample matrix effects are likely the cause. Note exceedence in case narrative.

20.0 Contingencies for Handling Out-Of-Control or Unacceptable Data

20.1 Data that is detected to be out-of-control for any reason, when compared to method acceptance criteria, will addressed in the following manner:

20.1.1 If the problem exists with the gas chromatographic instrumentation, appropriate action will be taken to repair and perform maintenance to bring the instrument back to operation condition. Once the instrumentation is determined to be correctly operating analysis can begin again.

20.1.2 If the problem exists with calibration standard solutions, the analyst will prepare new standards and discard the standard solutions that are suspect. Instrument calibration can be performed and analysis can begin once system is control.

20.1.3 If the problem exists with sample extraction and extract preparation, the extraction step that is producing the out-of-control situation will be diagnosed and rectified. Once the troubleshooting procedures correct the problem extraction can once again occur and analysis can continue.

20.1.4 In situations where data is reported under out-of-control conditions, the data will be annotated with data qualifiers and/or appropriate descriptive comments defining the nature of the excursion in the sample case narrative. If warranted, a corrective action report (CAR) will be issued to define the problem, steps to correct the problem, and final resolution.

21.0 Waste Management

21.1 All applicable federal and state rules and regulations governing hazardous waste will be followed when disposing of laboratory waste generated during the execution of this method.

21.2 Please refer to standard operating procedures NE089 and NE054 regarding how hazardous waste is handled and disposed of by the laboratory.

22.0 References:

22.1 US EPA 40 CFR Part 136, "Guidelines Establishing Test Procedures for the Analysis of Pollutants," July, 1988.

22.2 Standard Methods for the Examination of Water and Wastewater, 19th Edition, Published by: American Public Health Association, American Water Works Association, Water Pollution Control Federation, 1995.

22.3 US EPA SW-846, "Test Methods for Evaluating Solid Waste Physical/Chemical Methods," Office of Solid Waste and Emergency Response, 3rd Edition, 1986 and its updates.

22.4 New York State Department of Health, "Environmental Laboratory Approval Program Certification Manual," Wadsworth Center for Laboratories and Research, 1988.

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22.6 M. Zell, K. Ballschmiter, Baseline Studies of the Global Pollution, III. Trace Analysis of Polychlorinated Biphenyls (PCB) by ECD Glass Capillary Gas Chromatography in Environmental Samples of Different Trophic Levels, Fresenius Z. Anal. Chem., 304, 337-349, 1980.

22.7 M.D. Mullin, C.M. Pochini, S. McCrindle, M. Romkes, S.H. Save, "High-Resolution PCB Analysis: Synthesis and Chromatographic Properties of All 209 PCB Congeners," Environ. Sci. Technol., Vol 18, No. 6, pp 468-476, 1984.

22.8 D.L. Swackhamer, "Quality Assurance Plan, Green Bay Mass Balance Study, 1. PCBs and Dieldrin, US EPA Great Lakes National Program Office" Quality Assurance Coordinator, Field and Analytical Methods Committees, University of Minnesota, December 11, 1987.

22.9 George M. Frame, Robert E. Wagner, James C. Carnahan, John F. Brown, Jr., Ralph J. May, Lynn A. Smullen, and Donna L. Bedard, "Comprehensive, Quantitative, Congener-Specific Analyses of Eight Aroclors and Complete PCB Congener Assignments on DB-1 Capillary GC Columns ", Chemosphere, Vol. 33, No. 4, pp. 603-623, 1996.

22.10 "Standard Operating Procedure for the Gas Chromatographic Analysis of Hydrophobic Organic Contaminant Extracts from Great Lakes Water Samples", USEPA Great Lakes National Program Office, 77 West Jackson Boulevard, Chicago, IL 60604-2590, GLNPO Organics SOP – 10, 6/1/94:Revision 2

22.11 "Biphenyls and Halogenated Pesticides by High Resolution Gas Chromatography", M.D. Mullin, Large Lakes Research Station, LLRS-SOP-ORG-013, revision 2, August 3, 1990, p 1-10.

22.12 Contract Laboratory Program – Statement of Work for Organic Analysis, Multi-Media, Multi-Concentration. Document OLM3.2, 1996.

23.0 Tables, Diagrams, Flowcharts and Validation Data

APPENDIX A
Congener Composition of Multi-Aroclor Calibration Standard (6.27 ug/mL)

Congener Composition of Mixed Aroclor High-level Standard (6270ng/mL)
(Aroclor 1232, 1248, 1262 in a ratio of 25:18:18)

Number	DB-1 Peak Number [1]	IUPAC # [2]	Amount ng/mL
1	2	**001**	438.57
2	3	**002**	-
3	4	**003**	255.84
4	5	**004 010**	124.26
5	6	**007 009**	43.85
6	7	**006**	69.40
7	8	**005 008**	511.66
8	9	*014*	-
9	10	**019**	10.24
10	11	*030*	-
11	12	**011**	-
12	13	**012 013**	9.75
13	14	**015 018**	135.22
14	15	**017**	135.22
15	16	**024 027**	9.50
16	17	**016 032**	142.53
17	19	*023* **034** *054*	-
18	20	**029**	1.94
19	21	**026**	26.32
20	22	**025**	11.69
21	23	**031**	150.68
22	24	**028** *050*	192.86
23	25	**020** *021* **033 053**	145.16
24	26	**022 051**	105.99
25	27	**045**	32.52
26	28	*036*	-
27	29	**046**	14.62
28	30	*039*	-
29	31	**052** *069 073*	174.33
30	32	**043 049**	84.06
31	33	*038* **047**	36.55
32	34	**048** *075*	36.55
33	35	*062 065*	-
34	36	**035**	-
35	37	*104* **044**	157.16
36	38	**037 042 059**	95.03
37	39	**041 064 071** *072*	149.85
38	41	*068* **096**	-
39	42	**040**	34.36
40	43	**057** *103*	-
41	44	*058* **067** *100*	4.02
42	45	**063**	7.68
43	46	**074** *094 061*	69.44

Number	DB-1 Peak Number [1]	IUPAC # [2]	Amount ng/mL
44	47	**070**	124.26
45	48	**066** *076 098 080 093* **095 102** *088*	263.14
46	49	*055* **091** *121*	18.64
47	50	**056 060**	127.91
48	51	**084 092** *155*	65.78
49	52	**089**	3.66
50	53	**090 101**	65.78
51	54	*079* **099** *113*	27.04
52	55	**119** *150*	1.02
53	56	*078* **083** *112 108*	5.48
54	57	**097** *152 086*	20.46
55	58	*081* **087** *117 125* **115** *145*	42.39
56	59	*111 116* **085**	25.59
57	60	*120* **136**	27.41
58	61	**077 110** *148*	77.84
59	62	*154*	-
60	63	**082**	16.08
61	64	**151**	62.15
62	65	**124 135**	10.60
63	66	**144**	21.93
64	67	*107* **109** *147*	4.75
65	68	*123*	-
66	69	*106* **118** *139* **149**	146.19
67	70	*140*	-
68	71	**114 134** *143*	7.38
69	72	**122 131 133** *142*	1.06
70	73	**146** *165 188*	14.26
71	74	**105 132** *161*	49.52
72	75	**153**	107.64
73	76	*127 168 184*	-
74	77	**141**	62.13
75	78	**179**	53.36
76	79	**137**	2.74
77	80	**130 176**	9.50
78	82	**138 163 164**	98.68
79	83	**158** *160 186*	9.13
80	84	*126* **129**	0.47
81	85	*166* **178**	40.20
82	87	**175** *159*	7.31
83	88	*182* **187**	131.57
84	89	**128** *162*	3.66
85	90	**183**	62.13
86	91	**167**	1.79
87	92	**185**	17.17
88	93	**174** *181*	116.95

Number	DB-1 Peak Number [1]	IUPAC # [2]	Amount ng/mL
89	94	**177**	62.13
90	95	**156 171**	28.88
91	96	**157 202**	2.41
92	98	**173**	1.39
93	99	**201**	14.26
94	100	**172** *204*	20.46
95	101	*192* **197**	4.02
96	102	**180**	222.94
97	103	**193**	15.35
98	104	**191**	4.38
99	105	**200** *169*	15.71
100	106	**170**	46.78
101	107	**190**	15.35
102	108	**198**	4.38
103	109	**199**	153.50
104	110	**196 203**	157.16
105	111	**189**	1.46
106	112	**195**	20.21
107	113	**208**	9.02
108	114	*207*	3.40
109	115	**194**	65.78
110	116	**205**	4.02
111	117	**206**	24.85
112	118	*209*	0.44

1 - Note that 5 DB-1/ZB-1 peaks (PK18, PK40, PK81, PK86, PK97) have been removed from the DB-1/ZB-1 peak numbering scheme. The following low-level congeners that were designated as separately eluting peaks have been determined to co-elute with another congener. The DB-1/ZB-1 peak numbers are no longer required for these congeners, but the original DB-1/ZB-1 numbering system has remained intact for all other peaks.
PK 18 (23) now elutes in PK 19 (23,34,54)
PK 40 (68) now elutes in PK 41 (68,96)
PK 81 (176) now elutes in PK 80 (130,176)
PK 86 (166) now elutes in PK 85 (166,178)
PK 97 (157) now elutes in PK 96 (157,202)

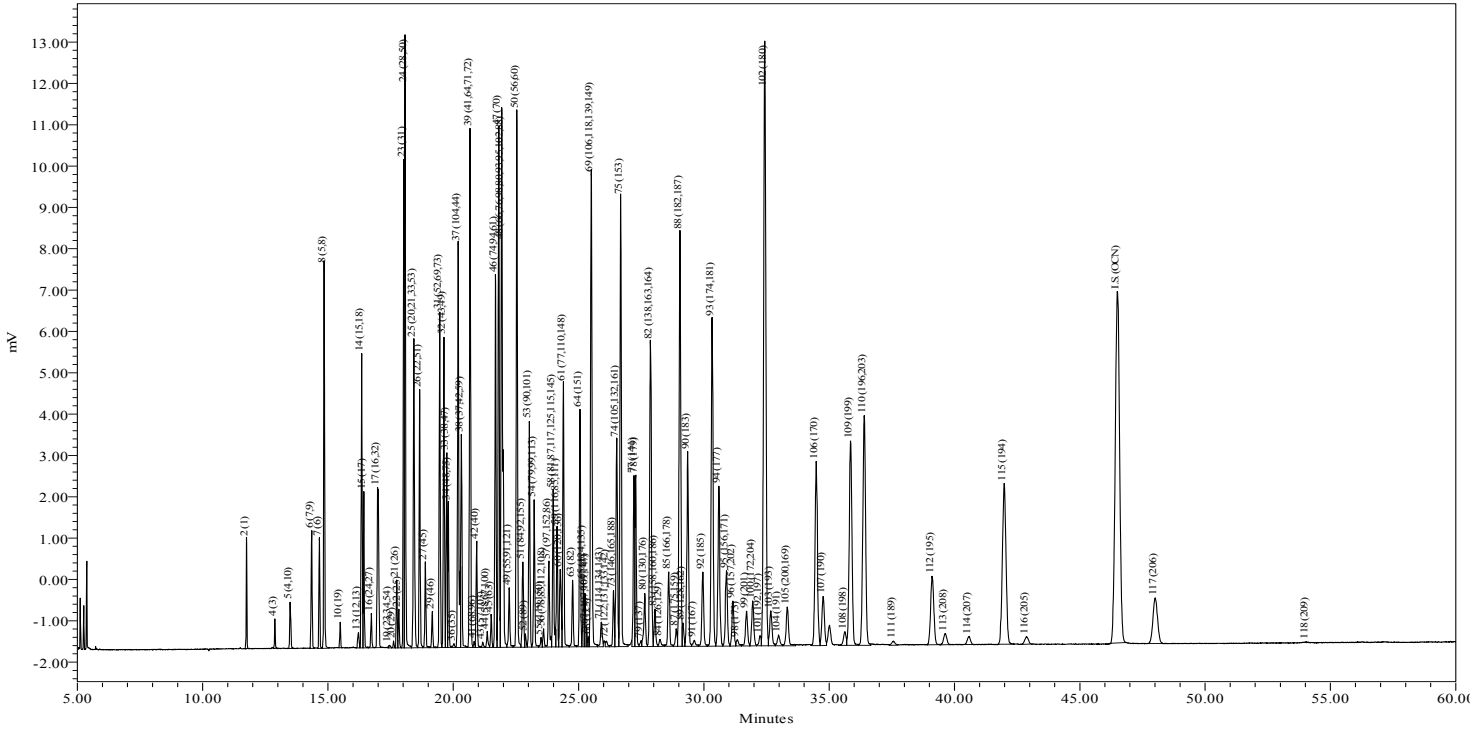
2 - IUPAC congener numbers listed in boldface font were found to be present in at least one of the Aroclor at or above 0.05 weight percent. These congeners should be considered the primary congeners existing in a peak composed of co-eluting congeners. IUPAC congener numbers listed in italic font were absent or present below 0.05 weight percent.

APPENDIX B

DB-1/ ZB-1 Capillary GC Chromatograms:

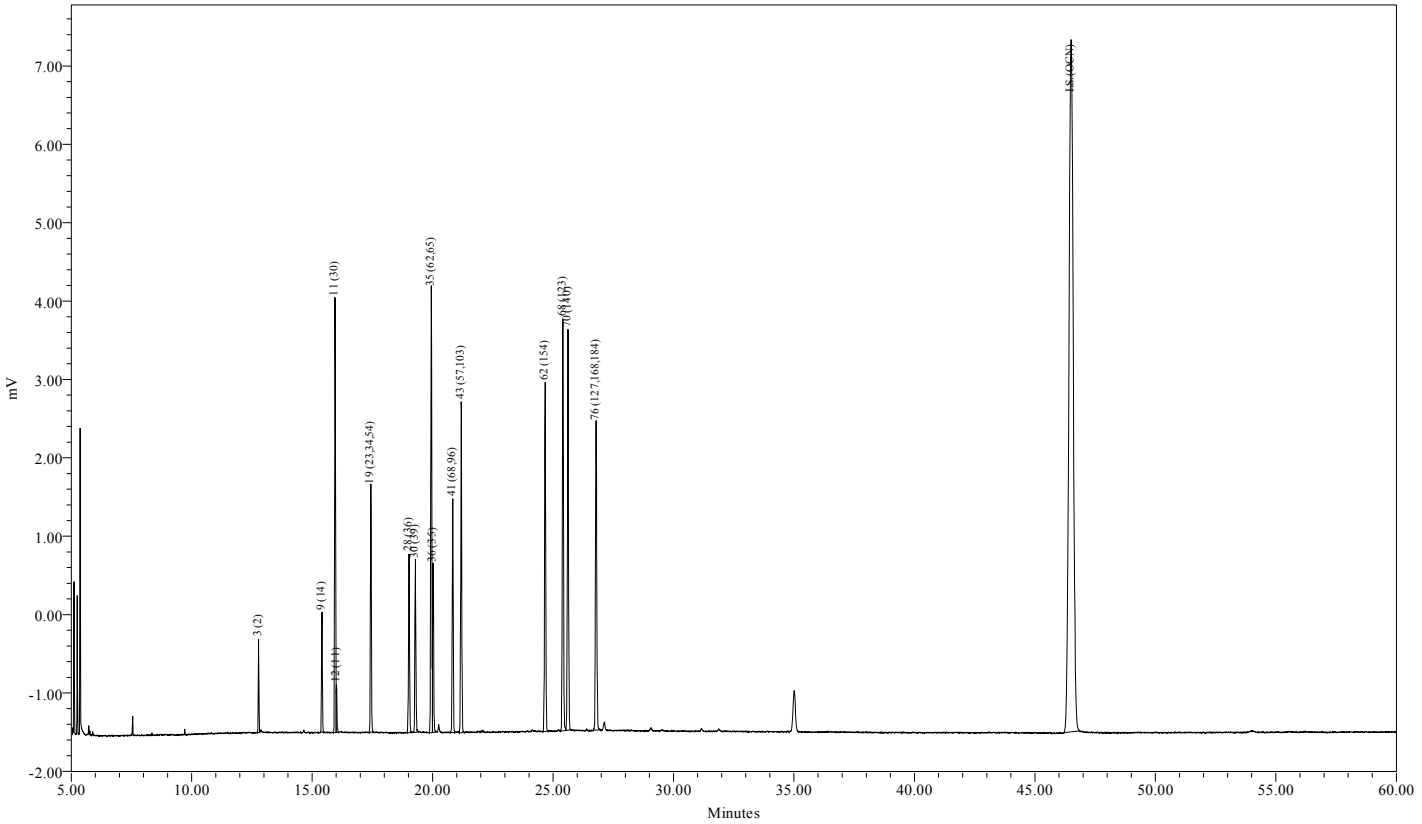
1.) 6.27 ug/mL Calibration Standard

Chromatogram Report Congener Specific PCB Green Bay
Northeast Analytical, Inc., 2190 Technology Drive, Schenectady, NY 12308
Phone: (518) 346-4592 Fax: (518) 381-6055



2.) Supplemental Congener Standard

Chromatogram Report Congener Specific PCB Green Bay
Northeast Analytical, Inc., 2190 Technology Drive, Schenectady, NY 12308
Phone: (518) 346-4592 Fax: (518) 381-6055



Sample Name:	**SC0926A**	**Sample Amount:**	**1**
Sample ID:	**SUP CONG STD 2000/50 ng/mL**	**Dilution:**	**1**
Date Acquired:	**09/26/2006 23:21:18**	**Processing Method:**	**CSGB_HL_092606**

APPENDIX C

Example of Reporting Format

Northeast Analytical, Inc.
2190 Technology Drive
Schenectady, NY 12308
(518) 346-4592 Fax (518) 381-6055

PCB Congener Amount Report

Customer: CLIENT NAME
Sample Description: SAMPLE IDENTIFICATION
Comment: PROJECT INFORMATION
Date Acquired: 09/27/2006 13:46:46
Lab Sample ID: AJ11122
LRF ID: 0609110-05
Lab File ID: GC17-80-17

Type for Mixed Peak Deconvolution = S

Total PCBs in sample = 8.76 ug/g

PCB Homolog Distribution

Homologs	Weight %	Mole %
Mono	0.12	0.18
Di	0.83	1.11
Tri	14.17	16.28
Tetra	51.77	53.12
Penta	22.98	20.99
Hexa	7.78	6.56
Hepta	1.83	1.39
Octa	0.48	0.33
Nona	0.05	0.03
Deca	0.00	0.00

Nominal 'Aroclor' Distribution

Aroclor	Indicator Peak (PK # / IUPAC #)	Amount ug/g	Percent Sediment	Percent Biota
A1221	2/001	0.0101	0.913	0.767
A1242	23+24/31+28	0.7014	63.3	53.2
A1254SED	61/100	0.3591	32.4	
A1254BIO	69+75+82/149+153+138	0.5695		43.2
A1260	102/180	0.0341	3.08	2.59
A1268	115/194	0.0025	0.228	0.192

Ortho Cl / biphenyl Residue = 1.64
Meta + Para Cl / biphenyl Residue = 2.57
Total Cl / biphenyl Residue = 4.21

Northeast Analytical, Inc.
2190 Technology Drive
Schenectady, NY 12308
(518) 346-4592 Fax (518) 381-6055

PCB Congener Amount Report

Customer: CLIENT NAME
Sample Description: SAMPLE IDENTIFICATION
Comment: PROJECT INFORMATION
Date Acquired: 09/27/2006 13:46:46
Lab Sample ID: AJ11122
LRF ID: 0609110-05
Lab File ID: GC17-80-17

Type for Mixed Peak Deconvolution = S

DB-1 Peak Number	Retention Time	Molecular Weight	Peak Area	Amount (ug/g)	Sample	MDL (ug/g)	RL (ug/g)	Qual
2	11.75	188.7	7	0.0101	0.0536	0.00672	0.160	J
3	12.78	188.7				0.167	36.6	U
4	12.88	188.7				0.00287	0.0936	U
5	13.51	223.1	98	0.0546	0.245	0.00197	0.0455	B
6	14.36	223.1	14	0.00121	0.00543	0.000789	0.0160	J
7	14.64	223.1	26	0.00456	0.0205	0.000808	0.0254	JB
8	14.84	223.1	33	0.0110	0.0494	0.00613	0.187	J
9	15.40	223.1				0.00195	0.915	U
10	15.49	257.5	63	0.00685	0.0266	0.00161	0.00374	
11	15.95	257.5				0.00169	0.915	U
12	16.01	223.1				0.00457	0.915	U
13	16.22	223.1				0.00146	0.00357	U
14	16.38	249.0	37	0.00382	0.0153	0.00250	0.0495	J
15	16.42	257.5	33	0.00711	0.0276	0.00146	0.0495	JB
16	16.73	257.5	81	0.00502	0.0195	0.000162	0.00347	
17	16.97	257.5	17	0.00200	0.00778	0.00190	0.0521	J
19	17.43	267.9	122	0.0120	0.0449	0.00117	0.915	J
20	17.63	257.5	20	0.00129	0.00500	0.000259	0.000710	
21	17.74	257.5	1358	0.126	0.487	0.000532	0.00963	
22	17.82	257.5	282	0.0197	0.0765	0.000192	0.00428	
23	18.02	257.5	3061	0.236	0.917	0.00274	0.0551	
24	18.07	257.5	6708	0.465	1.81	0.00303	0.0706	
25	18.40	259.5	190	0.0168	0.0647	0.00267	0.0531	J
26	18.66	258.7	1380	0.127	0.491	0.00163	0.0388	B
27	18.88	292.0	358	0.0293	0.100	0.000483	0.0119	B
28	19.02	257.5				0.00134	0.915	U
29	19.16	292.0	6			0.00226	0.00535	U
30	19.28	257.5				0.00170	0.915	U
31	19.45	292.0	7735	0.876	3.00	0.00311	0.0638	
32	19.62	292.0	7769	0.442	1.51	0.00150	0.0308	
33	19.74	292.0	4969	0.201	0.689	0.000556	0.0134	B
34	19.80	292.0	287	0.0164	0.0563	0.000470	0.0134	B
35	19.94	292.0				0.00195	0.915	U
36	20.01	257.5				0.00124	0.915	U

DB-1 Peak Number	Retention Time	Molecular Weight	Peak Area	Amount (ug/g)	Sample	MDL (ug/g)	RL (ug/g)	Qual
37	20.19	292.0	5094	0.368	1.26	0.00188	0.0575	
38	20.32	272.4	4204	0.389	1.43	0.00170	0.0348	B
39	20.67	292.0	5889	0.338	1.16	0.00166	0.0548	B
41	20.84	326.4	313	0.0289	0.0887	0.00185	0.915	J
42	20.93	292.0	1074	0.0723	0.248	0.000624	0.0126	
43	21.17	298.9	257	0.0169	0.0566	0.00115	0.915	J
44	21.36	298.9	404	0.0183	0.0613	0.000370	0.00147	
45	21.51	292.0	1015	0.0492	0.169	0.00134	0.00281	
46	21.68	292.0	6784	0.262	0.898	0.000807	0.0254	
47	21.81	292.0	8579	0.419	1.43	0.00197	0.0455	
48	21.93	293.5	12842	0.932	3.18	0.00295	0.0963	
49	22.23	324.7	1416	0.0822	0.253	0.000251	0.00682	B
50	22.54	292.0	7587	0.361	1.24	0.00144	0.0468	
51	22.79	326.4	2486	0.309	0.947	0.000639	0.0241	
52	22.87	326.4	10	0.000566	0.00173	0.000524	0.00134	J
53	23.03	326.4	4934	0.283	0.868	0.000660	0.0241	
54	23.23	326.4	2847	0.104	0.318	0.000444	0.00989	
55	23.51	326.4	196	0.00379	0.0116	0.000139	0.000375	
56	23.60	326.4	599	0.0348	0.107	0.000817	0.00200	
57	23.81	326.4	2069	0.0877	0.269	0.000276	0.00749	
58	23.99	326.4	4055	0.206	0.630	0.000582	0.0155	B
59	24.14	326.4	2241	0.0936	0.287	0.000369	0.00936	
60	24.29	360.9	327	0.0164	0.0453	0.000528	0.0100	B
61	24.39	326.4	6279	0.359	1.10	0.00126	0.0285	
62	24.66	360.9				0.00751	0.915	U
63	24.76	326.4	1130	0.0498	0.153	0.000248	0.00588	
64	25.05	360.9	685	0.0358	0.0993	0.000590	0.0227	B
65	25.20	350.5	509	0.0158	0.0450	0.000177	0.00388	
66	25.23	360.9	216	0.0179	0.0495	0.000251	0.00802	
67	25.32	336.8	719	0.0376	0.112	0.0000683	0.00174	
68	25.41	326.4	199	0.00982	0.0301	0.00131	0.915	J
69	25.52	337.5	6659	0.321	0.952	0.00155	0.0535	
70	25.61	360.9				0.00127	0.915	U
71	25.92	347.8	458	0.0175	0.0503	0.000747	0.00270	
72	26.12	336.8	216	0.00450	0.0134	0.000151	0.000416	
73	26.39	360.9	556	0.0243	0.0673	0.000155	0.00522	
74	26.51	347.8	4239	0.147	0.422	0.000654	0.0181	
75	26.68	360.9	2402	0.0938	0.260	0.00128	0.0394	
76	26.78	360.9				0.000917	0.915	U
77	27.20	360.9	649	0.0391	0.108	0.000644	0.0227	
78	27.28	395.3	102	0.00526	0.0133	0.000501	0.0195	J
79	27.49	360.9	235	0.0167	0.0462	0.000498	0.00100	
80	27.57	360.9	246	0.00572	0.0158	0.000193	0.00347	
82	27.86	360.9	3760	0.154	0.427	0.00146	0.0361	
83	28.05	360.9	449	0.0154	0.0427	0.000180	0.00334	
84	28.26	360.9	188	0.00123	0.00340	0.0000598	0.000173	
85	28.60	395.3	190	0.0138	0.0350	0.000467	0.0147	J
87	28.85	395.3	29	0.00168	0.00426	0.00111	0.00267	J
88	29.04	395.3	627	0.0269	0.0680	0.00126	0.0481	J
89	29.16	360.9	768	0.0182	0.0506	0.0000432	0.00134	
90	29.34	395.3	224	0.00953	0.0241	0.000668	0.0227	J
91	29.61	360.9	127	0.00326	0.00903	0.000306	0.000656	

DB-1 Peak Number	Retention Time	Molecular Weight	Peak Area	Amount (ug/g)	Sample	MDL (ug/g)	RL (ug/g)	Qual
92	29.96	394.3	48	0.00137	0.00348	0.000368	0.00628	J
93	30.33	394.3	289	0.0124	0.0316	0.00146	0.0428	J
94	30.60	394.3	262	0.0124	0.0314	0.000735	0.0227	J
95	30.89	382.2	680	0.0294	0.0770	0.000313	0.0106	
96	31.15	429.8	211	0.00128	0.00297	0.0000432	0.000883	
98	31.30	395.3	33	0.000698	0.00177	0.000256	0.000508	
99	31.71	429.8	28	0.00119	0.00278	0.000168	0.00522	J
100	31.95	395.3				0.000312	0.00749	U
101	32.19	429.8	59	0.00256	0.00596	0.000493	0.00147	
102	32.42	395.3	907	0.0341	0.0863	0.00271	0.0816	J
103	32.64	395.3	72	0.00306	0.00774	0.000159	0.00562	J
104	33.01	395.3	57	0.00204	0.00516	0.000613	0.00160	
105	33.31	429.8	47	0.00176	0.00409	0.000197	0.00575	J
106	34.48	395.3	583	0.0138	0.0348	0.000617	0.0171	J
107	34.74	395.3	134	0.00365	0.00924	0.000185	0.00562	J
108	35.61	429.8	25	0.000673	0.00157	0.000502	0.00160	J
109	35.86	429.8	225	0.0139	0.0324	0.00150	0.0562	J
110	36.38	429.8	300	0.0168	0.0392	0.00149	0.0575	J
111	37.52	395.3	67	0.00159	0.00402	0.000244	0.000584	
112	39.13	429.8	40	0.000840	0.00195	0.000229	0.00739	J
113	39.64	464.2	51	0.00293	0.00631	0.00181	0.00330	J
114	40.57	464.2						U
115	41.97	429.8	98	0.00253	0.00589	0.000800	0.0241	J
116	42.86	429.8	11			0.000799	0.00147	U
117	48.02	464.2	48	0.00130	0.00279	0.000470	0.00909	J
118	54.01	498.6				0.0000781	0.000162	U
	Total Concentration = 8.76 ug/g					0.0988596	2.29255	

Total Millimoles = 0.029

Average Molecular Weight = 299.1

Number of Calibrated Peaks Found = 96

Internal Standard Retention Time = 46.50 minutes

Internal Standard Peak Area = 123355.5

Northeast Analytical, Inc.
2190 Technology Drive
Schenectady, NY 12308
(518) 346-4592 Fax (518) 381-6055

PCB Congener Amount Report

Customer: CLIENT NAME
Sample Description: SAMPLE IDENTIFICATION
Comment: PROJECT INFORMATION
Date Acquired: 09/27/2006 13:46:46
Lab Sample ID: AJ11122
LRF ID: 0609110-05
Lab File ID: GC17-80-17

Type for Mixed Peak Deconvolution = S

DB-1 Peak [1] Number	Retention Time	T-CL:O-CL	IUPAC # [2]	RRT	Congeners [3]	Weight Percent	Mole Percent
2	11.75	1:1	**001**	0.2527	2	0.115	0.183
3	12.78	1:0	**002**		3	-	-
4	12.88	1:0	**003**		4	-	-
5	13.51	2:2	**004 010**	0.2905	2-2; 26	0.624	0.836
6	14.36	2:1	**007 009**	0.3088	24; 25	0.014	0.019
7	14.64	2:1	**006**	0.3148	2-3	0.052	0.070
8	14.84	2:1	**005 008**	0.3191	23; 2-4	0.126	0.169
9	15.40	2:0	*014*		35	-	-
10	15.49	3:3	**019**	0.3331	26-2	0.078	0.091
11	15.95	3:2	*030*		246	-	-
12	16.01	2:0	**011**		3-3	-	-
13	16.22	2:0	**012 013**		34; 3-4	-	-
14	16.38	2:0 3:2	**015 018**	0.3523	4-4; 25-2	0.044	0.052
15	16.42	3:2	**017**	0.3531	24-2	0.081	0.094
16	16.73	3:2	**024 027**	0.3598	236; 26-3	0.057	0.067
17	16.97	3:2	**016 032**	0.3649	23-2; 26-4	0.023	0.027
19	17.43	3:1 4:4	*023* **034** *054*	0.3748	235; 35-2; 26-26	0.137	0.153
20	17.63	3:1	**029**	0.3791	245	0.015	0.017
21	17.74	3:1	**026**	0.3815	25-3	1.433	1.665
22	17.82	3:1	**025**	0.3832	24-3	0.225	0.261
23	18.02	3:1	**031**	0.3875	25-4	2.698	3.134
24	18.07	3:1 4:3	**028** *050*	0.3886	24-4; 246-2	5.312	6.170
25	18.40	3:1 4:3	**020** *021* **033 053**	0.3957	23-3; 234; 34-2; 25-26	0.192	0.221
26	18.66	3:1 4:3	**022 051**	0.4013	23-4; 24-26	1.452	1.678
27	18.88	4:3	**045**	0.4060	236-2	0.334	0.342
28	19.02	3:0	*036*		35-3	-	-
29	19.16	4:3	**046**		23-26	-	-
30	19.28	3:0	*039*		35-4	-	-
31	19.45	4:2	**052** *069 073*	0.4183	25-25; 246-3; 26-35	10.007	10.251
32	19.62	4:2	**043 049**	0.4219	235-2; 24-25	5.047	5.170
33	19.74	4:2	*038* **047**	0.4245	345; 24-24	2.298	2.354
34	19.80	4:2	**048** *075*	0.4258	245-2; 246-4	0.188	0.192
35	19.94	4:2	*062 065*		2346; 2356	-	-
36	20.01	3:0	**035**		34-3	-	-
37	20.19	5:4 4:2	*104* **044**	0.4342	246-26; 23-25	4.200	4.302
38	20.32	3:0 4:2	**037 042 059**	0.4370	34-4; 23-24; 236-3	4.442	4.878
39	20.67	4:2	**041 064 071** *072*	0.4445	234-2; 236-4; 26-34; 25-35	3.860	3.954

DB-1 Peak [1] Number	Retention Time	T-CL:O-CL	IUPAC # [2]	RRT	Congeners [3]	Weight Percent	Mole Percent
41	20.84	5:4	*068* **096**	0.4482	24-35; 236-26	0.330	0.303
42	20.93	4:2	**040**	0.4501	23-23	0.826	0.846
43	21.17	4:1 5:3	**057** *103*	0.4553	235-3; 246-25	0.193	0.193
44	21.36	4:1 5:3	*058* **067** *100*	0.4594	23-35; 245-3; 246-24	0.209	0.210
45	21.51	4:1	**063**	0.4626	235-4	0.562	0.576
46	21.68	4:1 5:3	**074** *094 061*	0.4662	245-4; 235-26; 2345	2.994	3.067
47	21.81	4:1	**070**	0.4690	25-34	4.785	4.901
48	21.93	4:1 5:3	**066** *076 098 080 093* **095 102** *088*	0.4716	24-34; 345-2; 246-23; 35-35; 2356-2; 236-25; 245-26; 2346-2	10.646	10.850
49	22.23	4:1 5:3	*055* **091** *121*	0.4781	234-3; 236-24; 246-35	0.939	0.865
50	22.54	4:1	**056 060**	0.4847	23-34; 234-4	4.123	4.224
51	22.79	5:3 6:4	**084 092** *155*	0.4901	236-23; 235-25; 246-246	3.530	3.235
52	22.87	5:3	**089**	0.4918	234-26	0.006	0.006
53	23.03	5:2	**090 101**	0.4953	235-24; 245-25	3.235	2.964
54	23.23	5:2	*079* **099** *113*	0.4996	34-35; 245-24; 236-35	1.187	1.088
55	23.51	5:2 6:4	**119** *150*	0.5056	246-34; 236-246	0.043	0.040
56	23.60	5:2	*078* **083** *112 108*	0.5075	345-3; 235-23; 2356-3; 2346-3	0.397	0.364
57	23.81	5:2 6:4	**097** *152 086*	0.5120	245-23; 2356-26; 2345-2	1.001	0.918
58	23.99	5:2	*081* **087** *117 125* **115** *145*	0.5159	345-4; 234-25; 2356-4; 345-26; 2346-4; 2346-26	2.347	2.151
59	24.14	5:2	*116* **085** *111*	0.5191	23456; 234-24; 235-35	1.069	0.980
60	24.29	6:4	*120* **136**	0.5224	245-35; 236-236	0.187	0.155
61	24.39	5:2	**077 110** *148*	0.5245	34-34; 236-34; 235-246	4.100	3.758
62	24.66	6:3	*154*		245-246	-	-
63	24.76	5:2	**082**	0.5325	234-23	0.569	0.521
64	25.05	6:3	**151**	0.5387	2356-25	0.409	0.339
65	25.20	5:1 6:3	**124 135**	0.5419	345-25; 235-236	0.180	0.154
66	25.23	6:3	**144**	0.5426	2346-25	0.204	0.169
67	25.32	5:1 6:3	*107* **109** *147*	0.5445	234-35; 235-34; 2356-24	0.430	0.382
68	25.41	5:1	*123*	0.5465	345-24	0.112	0.103
69	25.52	5:1 6:3	*106* **118** *139* **149**	0.5488	2345-3; 245-34; 2346-24; 236-245	3.671	3.253
70	25.61	6:3	*140*		234-246	-	-
71	25.92	5:1 6:3	**114 134** *143*	0.5574	2345-4; 2356-23; 2345-26	0.200	0.172
72	26.12	5:1 6:3	**122 131 133** *142*	0.5617	345-23; 2346-23; 235-235; 23456-2	0.051	0.046
73	26.39	6:2	**146** *165 188*	0.5675	235-245; 2356-35; 2356-246	0.278	0.230
74	26.51	5:1 6:3	**105 132** *161*	0.5701	234-34; 234-236; 2346-35	1.677	1.442
75	26.68	6:2	**153**	0.5738	245-245	1.071	0.888
76	26.78	6:2	*127 166 184*		345-35; 246-345; 2346-246	-	-
77	27.20	6:2	**141**	0.5849	2345-25	0.447	0.370
78	27.28	7:4	**179**	0.5867	2356-236	0.060	0.045
79	27.49	6:2	**137**	0.5912	2345-24	0.191	0.158
80	27.57	6:2 7:4	**130 176**	0.5929	234-235; 2346-236	0.065	0.054
82	27.86	6:2	**138 163 164**	0.5991	234-245; 2356-34; 236-345	1.761	1.460
83	28.05	6:2	**158** *160 186*	0.6032	2346-34; 23456-3; 23456-26	0.176	0.146
84	28.26	6:2	*126* **129**	0.6077	345-34; 2345-23	0.014	0.012
85	28.60	7:3	*166* **178**	0.6151	23456-4; 2356-235	0.158	0.119
87	28.85	7:3	**175** *159*	0.6204	2346-235; 2345-35	0.019	0.015
88	29.04	7:3	*182* **187**	0.6245	2345-246; 2356-245	0.307	0.232
89	29.16	6:2	**128** *162*	0.6271	234-234; 235-345	0.208	0.173
90	29.34	7:3	**183**	0.6310	2346-245	0.109	0.082
91	29.61	6:1	**167**	0.6368	245-345	0.037	0.031
92	29.96	7:3	**185**	0.6443	23456-25	0.016	0.012
93	30.33	7:3	**174** *181*	0.6523	2345-236; 23456-24	0.142	0.108
94	30.60	7:3	**177**	0.6581	2356-234	0.142	0.107
95	30.89	6:1 7:3	**156 171**	0.6643	2345-34; 2346-234	0.336	0.263
96	31.15	8:4	**157 202**	0.6699	234-345; 2356-2356	0.015	0.010
98	31.30	7:3	**173**	0.6731	23456-23	0.008	0.006
99	31.71	8:4	**201**	0.6819	2346-2356	0.014	0.009
100	31.95	7:2	**172** *204*		2345-235; 23456-246	-	-
101	32.19	8:4	*192* **197**	0.6923	23456-35; 2346-2346	0.029	0.020
102	32.42	7:2	**180**	0.6972	2345-245	0.390	0.295
103	32.64	7:2	**193**	0.7019	2356-345	0.035	0.026
104	33.01	7:2	**191**	0.7099	2346-345	0.023	0.018
105	33.31	8:4	**200** *169*	0.7163	23456-236; 345-345	0.020	0.014
106	34.48	7:2	**170**	0.7415	2345-234	0.157	0.119

DB-1 Peak [1] Number	Retention Time	T-CL:O-CL	IUPAC # [2]	RRT	Congeners [3]	Weight Percent	Mole Percent
107	34.74	7:2	**190**	0.7471	23456-34	0.042	0.032
108	35.61	8:3	**198**	0.7658	23456-235	0.008	0.005
109	35.86	8:3	**199**	0.7712	2345-2356	0.159	0.111
110	36.38	8:3	**196 203**	0.7824	2345-2346; 23456-245	0.192	0.134
111	37.52	7:1	**189**	0.8069	2345-345	0.018	0.014
112	39.13	8:3	**195**	0.8415	23456-234	0.010	0.007
113	39.64	9:4	**208**	0.8525	23456-2356	0.033	0.022
114	40.57	9:4	*207*		23456-2346	-	-
115	41.97	8:2	**194**	0.9026	2345-2345	0.029	0.020
116	42.86	8:2	**205**		23456-345	-	-
117	48.02	9:3	**206**	1.033	23456-2345	0.015	0.010
118	54.01	10:4	*209*		23456-23456	-	-

Concentration = 8.76 ug/g

Total Millimoles = 0.029

Average Molecular Weight = 299.1

Number of Calibrated Peaks Found = 96

[1] - Note that five DB-1 peaks (PK18, PK40, PK81, PK86, PK97) have been removed from the DB-1 peak numbering scheme. The following low level congeners that were designated as separately eluting peaks have been determined to co-elute with another congener. The DB-1 peak numbers are no longer required for these congeners, but the original DB-1 numbering system has remained intact for all other peaks.

PK 18 (23) now elutes in PK 19 (23,34,54)
PK 40 (68) now elutes in PK 41 (68,96)
PK 86 (166) now elutes in PK 85 (166,178)
PK 97 (157) now elutes in PK 96 (157,202)

[2] - IUPAC congener numbers listed in **boldface** font were found to be present in at least one of the Aroclors at or above 0.05 weight percent. These congeners should be considered the primary congeners existing in a peak composed of co-eluting congeners. IUPAC congener numbers listed in *italic* font were absent or present below 0.05 weight percent.

[3] - PCB congener identification is denoted by position of the chlorine atoms on each ring of the biphenyl molecule. Designation used in this report has unprimed chlorines separated from primed chlorines by a hyphen that represents separation of the biphenyl rings.

[4] - DB-1 peaks may include one or more coeluting PCB congeners. In the case of some peaks, the congeners assigned to the peak consist of coeluting congeners and a congener that is resolved or is just slightly out of the normal retention time window of ± 0.07 minutes. If detection of one of the resolved congeners occurs, a comment will be included in the report narrative indicating the assigned DB-1 peak includes the presence of the resolved congener. The DB-1 peaks consisting of coeluting congeners and a congener that is resolved are as follows:

DB-1 Peak	Resolved Congener (IUPAC #)
37 (**44**,104)	*104*
48 (**66**,76,98,80,93,**95**,**102**,88)	*80,88,93*
56 (78,**83**,112,108)	*108*
61 (**77**,**110**,148)	**77**
72 (**122**,131,133,142)	**122**
89 (**128**,162)	*162*
105(**200**,169)	*169*

Appendix D
High Level Linearity Study

PCB STANDARD EVALUATION SUMMARY
THREE POINT INITIAL CALIBRATION CHECK FOR LINEARITY

LAB NAME: NORTHEAST ANALYTICAL, INC.

LAB CODE: NYS ELAP #11078

INSTRUMENT ID: GC #17

GC COLUMN ID: J&W, DB-1, 30 METER

STANDARD A:	FILENAME: CS0222A	AMT: 31.35 PPM	DATE: 02/22/07	TIME: 18:44
STANDARD B:	FILENAME: CS0222B	AMT: 6.27 PPM	DATE: 02/22/07	TIME: 20:58
STANDARD C:	FILENAME: CS0222C	AMT: 1.25 PPM	DATE: 02/23/07	TIME: 01:26

STANDARD D:	FILENAME: SCS0222	AMT: SEE LIST	DATE: 02/22/07	TIME: 23:12

Peak # (IUPAC#)	PCB Congener Analyzed	Conc. ppm
3 (2)	3-Chlorobiphenyl	2.000
9 (14)	3,5-Dichlorobiphenyl	0.050
11 (30)	2,4,6-Trichlorobiphenyl	0.050
12 (11)	3,3'-Dichlorobiphenyl	0.050
19 (23,34,54)	2',3,5-Trichlorobiphenyl	0.050
28 (36)	3,3',5-Trichlorobiphenyl	0.050
30 (39)	3,4',5-Trichlorobiphenyl	0.050
35 (62,65)	2,3,5,6-Tetrachlorobiphenyl	0.050
36 (35)	3,3',4-Trichlorobiphenyl	0.050
41 (68,96)	2,2',3,6,6'-Pentachlorobiphenyl	0.050
43 (57,103)	2,2',4,5',6-Pentachlorobiphenyl	0.050
62 (154)	2,2'4,4',5,6'-Hexachlorobiphenyl	0.050
68 (123)	2',3,4,4',5-Pentachlorobiphenyl	0.050
70 (140)	2,2',3,4,4',6'-Hexachlorobiphenyl	0.050
76 (127,168,184)	3,3',4,5,5'-Pentachlorobiphenyl	0.050

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PCB STANDARD EVALUATION SUMMARY
THREE POINT INITIAL CALIBRATION CHECK FOR LINEARITY

	DB-1 PEAK NUMBER (IUPAC Congener Number)	RRF STD A CS0222A	RRF STD B CS0222B	RRF STD C CS0222C	RRF STD D SCS0222	% RSD (< 20%)
1	2 (1)	0.02259	0.02901	0.02853		13.4
2	3 (2)*				0.00446	N/A
3	4 (3)	0.01321	0.01493	0.01349		6.66
4	5 (4,10)	0.05826	0.06745	0.06532		7.56
5	6 (7,9)	0.38172	0.46862	0.46682		11.3
6	7 (6)	0.17915	0.22338	0.22642		12.6
7	8 (5,8)	0.09096	0.11552	0.12834		17.0
8	9 (14)*				0.18206	N/A
9	10 (19)	0.32003	0.36149	0.33953		6.09
10	11 (30)*				0.70230	N/A
11	12 (11)*				0.06035	N/A
12	13 (12,13)	0.31192	0.31599	0.30304		2.13
13	14 (15,18)	0.29075	0.37005	0.40785		16.8
14	15 (17)	0.14609	0.18520	0.19256		14.3
15	16 (24,27)	0.55026	0.57808	0.58698		3.35
16	17 (16,32)	0.25978	0.32568	0.33834		13.7
17	18 **					**
18	19 (23,34,54)*				0.41549	N/A
19	20 (29)	0.49480	0.55272	0.50063		6.18
20	21 (26)	0.35075	0.41316	0.38550		8.16
21	22 (25)	0.48053	0.53416	0.49565		5.49
22	23 (31)	0.40680	0.49337	0.57867		17.4
23	24 (28,50)	0.45800	0.56209	0.62389		15.3
24	25 (20,21,33,53)	0.34347	0.43008	0.46038		14.8
25	26 (22,51)	0.34392	0.42267	0.44250		12.9
26	27 (45)	0.39420	0.47862	0.45889		9.9
27	28 (36)*				0.31903	N/A
28	29 (46)	0.36506	0.40325	0.38531		4.97
29	30 (39)*				0.31248	N/A
30	31 (52,69,73)	0.25601	0.33054	0.37383		18.6
31	32 (43,49)	0.52016	0.66698	0.74572		17.8
32	33 (38,47)	0.74962	0.96631	1.02130		15.7
33	34 (48,75)	0.54881	0.68828	0.68535		12.4
34	35 (62,65)*				0.83100	N/A
35	36 (35)*				0.29514	N/A
36	37 (104,44)	0.36042	0.45293	0.51976		18.0
37	38 (37,42,59)	0.42451	0.53545	0.55697		14.1
38	39 (41,64,71,72)	0.54586	0.66667	0.76262		16.5
39	40 **					**
40	41 (68,96)*				0.45828	N/A
41	42 (40)	0.48041	0.57885	0.56415		9.8
42	43 (57,103)*				0.62202	N/A
43	44 (58,67,100)	0.71833	0.71304	0.75228		2.93
44	45 (63)	0.69737	0.74557	0.74217		3.69
45	46 (74,94,61)	0.77442	0.96318	1.10146		17.3
46	47 (70)	0.59976	0.74962	0.87831		18.8

PCB STANDARD EVALUATION SUMMARY
THREE POINT INITIAL CALIBRATION CHECK FOR LINEARITY

	DB-1 PEAK NUMBER (IUPAC Congener Number)	RRF STD A CS0222A	RRF STD B CS0222B	RRF STD C CS0222C	RRF STD D SCS0222	% RSD (< 20%)
47	48 (66,76,98,80,93,95,102,88)	0.41348	0.51326	0.58991		17.5
48	49 (55,91,121)	0.54714	0.61399	0.57185		5.85
49	50 (56,60)	0.65387	0.77954	0.88680		15.1
50	51 (84,92,155)	0.25851	0.31137	0.32020		11.2
51	52 (89)	0.56478	0.54114	0.51399		4.71
52	53 (90,101)	0.49978	0.63772	0.72282		18.2
53	54 (79,99,113)	0.81510	1.01092	1.08160		14.2
54	55 (119,150)	1.53563	1.41040	1.58224		5.89
55	56 (78,83,112,108)	0.55891	0.55436	0.59615		4.02
56	57 (97,152,86)	0.73973	0.86278	0.86263		8.64
57	58 (81,87,117,125,115,145)	0.61771	0.74809	0.78074		12.1
58	59 (116,85,111)	0.76791	0.92249	0.93681		10.7
59	60 (120,136)	0.61615	0.74495	0.72593		10.0
60	61 (77,110,148)	0.51319	0.63536	0.70638		15.8
61	62 (154)*				0.74795	N/A
62	63 (82)	0.71358	0.81117	0.80435		7.02
63	64 (151)	0.55138	0.70086	0.77696		17.0
64	65 (124,135)	0.98386	1.18822	1.15365		9.9
65	66 (144)	0.41292	0.47150	0.44515		6.62
66	67 (107,109,147)	0.60733	0.53180	0.59399		6.98
67	68 (123)*				0.75721	N/A
68	69 (106,118,139,149)	0.59020	0.73584	0.87010		19.1
69	70 (140)*				0.81617	N/A
70	71 (114,134,143)	0.80053	0.80142	0.69286		8.16
71	72 (122,131,133,142)	1.18199	1.05810	1.46624		16.9
72	73 (146,165,188)	0.68697	0.78770	0.74836		6.85
73	74 (105,132,161)	0.85755	1.06403	1.12667		13.9
74	75 (153)	0.69524	0.87548	1.03850		19.7
75	76 (127,168,184)*				0.64655	N/A
76	77 (141)	0.48575	0.60953	0.63916		14.1
77	78 (179)	0.56653	0.72179	0.79553		16.8
78	79 (137)	0.37594	0.33346	0.33330		7.07
79	80 (130,176)	1.37320	1.52945	1.48899		5.54
80	81 **					**
81	82 (138,163,164)	0.68712	0.86463	0.97953		17.5
82	83 (158,160,186)	0.90898	0.97112	0.91740		3.62
83	84 (126,129)	3.59383	3.08366	2.81965		12.4
84	85 (166,178)	0.40833	0.47983	0.46097		8.24
85	86 **					**
86	87 (175,159)	0.52810	0.49041	0.42845		10.43
87	88 (182,187)	0.65075	0.82073	0.95553		18.9
88	89 (128,162)	1.21993	1.23308	1.22205		0.58
89	90 (183)	0.68082	0.84977	0.89965		14.2
90	91 (167)	0.81120	0.63450	0.85094		15.1
91	92 (185)	1.07086	1.24739	1.21824		8.03
92	93 (174,181)	0.65708	0.82060	0.93214		17.2

PCB STANDARD EVALUATION SUMMARY
THREE POINT INITIAL CALIBRATION CHECK FOR LINEARITY

	DB-1 PEAK NUMBER (IUPAC Congener Number)	RRF STD A CS0222A	RRF STD B CS0222B	RRF STD C CS0222C	RRF STD D SCS0222	% RSD (< 20%)
93	94 (177)	0.61058	0.75928	0.78218		13.0
94	95 (156,171)	0.71013	0.82515	0.77090		7.49
95	96 (157,202)	5.18082	5.76783	5.67256		5.69
96	97 **					**
97	98 (173)	1.19321	1.15191	0.91430		13.9
98	99 (201)	0.71911	0.77792	0.70789		5.12
99	100 (172,204)	0.64149	0.70896	0.66601		5.08
100	101 (192,197)	0.68289	0.69665	0.54763		12.8
101	102 (180)	0.73096	0.90383	1.07371		19.0
102	103 (193)	0.69292	0.74744	0.67318		5.46
103	104 (191)	0.72973	0.68096	0.64063		6.5
104	105 (200,169)	0.82643	0.86874	0.82524		2.95
105	106 (170)	1.21127	1.51047	1.59284		14.0
106	107 (190)	1.12545	1.25639	1.16608		5.67
107	108 (198)	1.12881	1.11950	1.11999		0.5
108	109 (199)	0.44072	0.56377	0.61375		16.5
109	110 (196,203)	0.48403	0.61754	0.68149		17.0
110	111 (189)	1.11803	1.05317	1.17492		5.46
111	112 (195)	1.46810	1.70680	1.73800		9.02
112	113 (208)	0.59157	0.55924	0.71851		13.5
113	114 (207)	1.17903	1.15468	1.43212		12.2
114	115 (194)	1.09041	1.37671	1.44694		14.5
115	116 (205)	0.97903	0.96908	1.07212		5.65
116	117 (206)	1.13252	1.28657	1.25055		6.59
117	118 (209)	1.48415	1.50043	1.53298		1.65

* - A separate PCB congener calibration standard is analyzed for these PCB congeners that do not exist at measurable levels in the Green Bay multi-Aroclor calibration. These so-called non-Aroclor PCB congeners (with the exception of peak 3(2)) are analyzed to provide accurate retention time information and relative response factors in the event they need to be quantified.

* *- Refinements in the elution position of several congeners has occurred due to the availability of individual congener standards. The following low level congeners that were designated as separately eluting peaks have been determined to co-elute with another congener. The DB-1 peak numbers are no longer required for these congeners, but the original DB-1 numbering system has remained intact for all other peaks.

PK 18 (23) now elutes in PK 19 (23,34,54)
PK 40 (68) now elutes in PK 41 (68,96)
PK 81 (176) now elutes in PK 80 (130,176)
PK 86 (166) now elutes in PK 85 (166,178)
PK 97 (157) now elutes in PK 96 (157,202)

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Low Level Linearity Study

PCB STANDARD EVALUATION SUMMARY
THREE POINT INITIAL CALIBRATION CHECK FOR LINEARITY

LAB NAME: NORTHEAST ANALYTICAL, INC.

LAB CODE: NYS ELAP #11078

INSTRUMENT ID: GC #17

GC COLUMN ID: J&W, DB-1, 30 METER

STANDARD A:	FILENAME: CS0222B	AMT: 6.27 PPM	DATE: 02/22/07	TIME: 20:58
STANDARD B:	FILENAME: CS0222C	AMT: 1.25 PPM	DATE: 02/23/07	TIME: 01:26
STANDARD C:	FILENAME: CS0222D	AMT: 0.125 PPM	DATE: 02/23/07	TIME: 03:39

STANDARD D:	FILENAME: SCS0222	AMT: SEE LIST	DATE: 02/22/07	TIME: 23:12

Peak # (IUPAC#)	PCB Congener Analyzed	Conc. ppm
3 (2)	3-Chlorobiphenyl	2.000
9 (14)	3,5-Dichlorobiphenyl	0.050
11 (30)	2,4,6-Trichlorobiphenyl	0.050
12 (11)	3,3'-Dichlorobiphenyl	0.050
19 (23,34,54)	2',3,5-Trichlorobiphenyl	0.050
28 (36)	3,3',5-Trichlorobiphenyl	0.050
30 (39)	3,4',5-Trichlorobiphenyl	0.050
35 (62,65)	2,3,5,6-Tetrachlorobiphenyl	0.050
36 (35)	3,3',4-Trichlorobiphenyl	0.050
41 (68,96)	2,2',3,6,6'-Pentachlorobiphenyl	0.050
43 (57,103)	2,2',4,5',6-Pentachlorobiphenyl	0.050
62 (154)	2,2'4,4',5,6'-Hexachlorobiphenyl	0.050
68 (123)	2',3,4,4',5-Pentachlorobiphenyl	0.050
70 (140)	2,2',3,4,4',6'-Hexachlorobiphenyl	0.050
76 (127,168,184)	3,3',4,5,5'-Pentachlorobiphenyl	0.050

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PCB STANDARD EVALUATION SUMMARY
THREE POINT INITIAL CALIBRATION CHECK FOR LINEARITY

	DB-1 PEAK NUMBER (IUPAC Congener Number)	RRF STD A CS0222B	RRF STD B CS0222C	RRF STD C CS0222D	RRF STD D SCS0222	% RSD (< 20%)
1	2 (1)	0.02891	0.02853	0.03116		4.82
2	3 (2)*				0.00446	N/A
3	4 (3)	0.01488	0.01349	0.01604		8.61
4	5 (4,10)	0.06723	0.06532	0.06747		1.77
5	6 (7,9)	0.46710	0.46682	0.50184		4.21
6	7 (6)	0.22265	0.22642	0.25201		6.84
7	8 (5,8)	0.11515	0.12834	0.12603		5.72
8	9 (14)*				0.18206	N/A
9	10 (19)	0.33737	0.33953	0.37428		5.91
10	11 (30)*				0.70230	N/A
11	12 (11)*				0.06035	N/A
12	13 (12,13)	0.31497	0.30304	0.33470		5.04
13	14 (15,18)	0.36884	0.40785	0.39877		5.21
14	15 (17)	0.18459	0.19256	0.18529		2.35
15	16 (24,27)	0.57620	0.58698	0.64280		5.94
16	17 (16,32)	0.32462	0.33834	0.33041		2.08
17	18 **					**
18	19 (23,34,54)*				0.41549	N/A
19	20 (29)	0.55092	0.50063	0.59326		8.46
20	21 (26)	0.41182	0.38550	0.40880		3.58
21	22 (25)	0.53243	0.49565	0.61153		10.8
22	23 (31)	0.49177	0.57867	0.57412		8.92
23	24 (28,50)	0.56027	0.62389	0.68446		9.97
24	25 (20,21,33,53)	0.42868	0.46038	0.44000		3.63
25	26 (22,51)	0.42130	0.44250	0.40433		4.52
26	27 (45)	0.47706	0.45889	0.47536		2.13
27	28 (36)*				0.31903	N/A
28	29 (46)	0.40194	0.38531	0.34615		7.58
29	30 (39)*				0.31248	N/A
30	31 (52,69,73)	0.32947	0.37383	0.39498		9.13
31	32 (43,49)	0.66481	0.74572	0.78145		8.18
32	33 (38,47)	0.96317	1.02130	1.05106		4.42
33	34 (48,75)	0.68605	0.68535	0.72837		3.52
34	35 (62,65)*				0.83100	N/A
35	36 (35)*				0.29514	N/A
36	37 (104,44)	0.45146	0.51976	0.49730		7.11
37	38 (37,42,59)	0.53371	0.55697	0.54218		2.16
38	39 (41,64,71,72)	0.66450	0.76262	0.77092		8.08
39	40 **					**
40	41 (68,96)*				0.45828	N/A
41	42 (40)	0.57697	0.56415	0.67780		10.3
42	43 (57,103)*				0.62202	N/A
43	44 (58,67,100)	0.71072	0.75228	0.72095		2.97
44	45 (63)	0.74315	0.74217	0.81364		5.35
45	46 (74,94,61)	0.96005	1.10146	1.11723		8.17
46	47 (70)	0.74718	0.87831	0.98003		13.4

PCB STANDARD EVALUATION SUMMARY
THREE POINT INITIAL CALIBRATION CHECK FOR LINEARITY

	DB-1 PEAK NUMBER (IUPAC Congener Number)	RRF STD A CS0222B	RRF STD B CS0222C	RRF STD C CS0222D	RRF STD D SCS0222	% RSD (< 20%)
47	48 (66,76,98,80,93,95,102,88)	0.51160	0.58991	0.60042		8.55
48	49 (55,91,121)	0.61200	0.57185	0.64033		5.66
49	50 (56,60)	0.77700	0.88680	0.88717		7.47
50	51 (84,92,155)	0.31036	0.32020	0.33427		3.74
51	52 (89)	0.53938	0.51399	0.46349		7.64
52	53 (90,101)	0.63565	0.72282	0.68050		6.41
53	54 (79,99,113)	1.00764	1.08160	0.96150		5.96
54	55 (119,150)	1.40582	1.58224	1.42089		6.65
55	56 (78,83,112,108)	0.55256	0.59615	0.66361		9.26
56	57 (97,152,86)	0.85998	0.86263	0.92393		4.10
57	58 (81,87,117,125,115,145)	0.74566	0.78074	0.80426		3.80
58	59 (116,85,111)	0.91949	0.93681	0.98626		3.66
59	60 (120,136)	0.74253	0.72593	0.72858		1.22
60	61 (77,110,148)	0.63330	0.70638	0.79548		11.4
61	62 (154)*				0.74795	N/A
62	63 (82)	0.80854	0.80435	0.92210		7.91
63	64 (151)	0.69859	0.77696	0.75194		5.39
64	65 (124,135)	1.18436	1.15365	1.10157		3.65
65	66 (144)	0.46997	0.44515	0.44728		3.03
66	67 (107,109,147)	0.53007	0.59399	0.60092		6.79
67	68 (123)*				0.75721	N/A
68	69 (106,118,139,149)	0.73345	0.87010	0.91065		11.1
69	70 (140)*				0.81617	N/A
70	71 (114,134,143)	0.79881	0.69286	0.67134		9.46
71	72 (122,131,133,142)	1.05467	1.10365	1.21482		7.30
72	73 (146,165,188)	0.77338	0.74836	0.84851		6.60
73	74 (105,132,161)	1.05376	1.12667	1.09001		3.34
74	75 (153)	0.86842	1.03850	1.06451		10.8
75	76 (127,168,184)*				0.64655	N/A
76	77 (141)	0.60452	0.63916	0.56596		6.07
77	78 (179)	0.71594	0.79553	0.82721		7.35
78	79 (137)	0.28921	0.33330	0.37882		13.4
79	80 (130,176)	1.50600	1.48899	1.73451		8.70
80	81 **					**
81	82 (138,163,164)	0.86057	0.97953	0.98015		7.33
82	83 (158,160,186)	0.96156	0.91740	1.02119		5.39
83	84 (126,129)	3.02729	2.81965	2.86788		3.74
84	85 (166,178)	0.47828	0.46097	0.43324		4.97
85	86 **					**
86	87 (175,159)	0.48882	0.42845	0.47475		6.81
87	88 (182,187)	0.81807	0.95553	0.98900		9.84
88	89 (128,162)	1.22907	1.22205	1.27093		2.13
89	90 (183)	0.84701	0.89965	1.00533		8.79
90	91 (167)	0.63244	0.70415	0.65569		5.51
91	92 (185)	1.24334	1.21824	1.13498		4.73
92	93 (174,181)	0.81793	0.93214	0.95125		8.01

PCB STANDARD EVALUATION SUMMARY
THREE POINT INITIAL CALIBRATION CHECK FOR LINEARITY

	DB-1 PEAK NUMBER (IUPAC Congener Number)	RRF STD A CS0222B	RRF STD B CS0222C	RRF STD C CS0222D	RRF STD D SCS0222	% RSD (< 20%)
93	94 (177)	0.75682	0.78218	0.68315		6.95
94	95 (156,171)	0.82247	0.77090	0.71856		6.74
95	96 (157,202)	5.74911	5.64512	5.50993		2.13
96	97 **					**
97	98 (173)	1.14817	1.04452	1.13947		5.18
98	99 (201)	0.77539	0.70789	0.66887		7.51
99	100 (172,204)	0.70666	0.66601	0.64435		4.70
100	101 (192,197)	0.69439	0.57289	0.57592		11.3
101	102 (180)	0.90090	1.07432	1.10591		10.7
102	103 (193)	0.74501	0.67521	0.64895		7.20
103	104 (191)	0.67875	0.64063	0.72364		6.10
104	105 (200,169)	0.86592	0.82524	0.82689		2.74
105	106 (170)	1.50556	1.59284	1.77012		8.31
106	107 (190)	1.25231	1.16608	1.23789		3.79
107	108 (198)	1.11587	1.11999	1.08282		1.84
108	109 (199)	0.56194	0.61375	0.56994		4.79
109	110 (196,203)	0.61553	0.68149	0.61836		5.84
110	111 (189)	1.04975	1.17492	1.22129		7.73
111	112 (195)	1.70125	1.73800	1.45485		9.44
112	113 (208)	0.55743	0.59984	0.61475		5.03
113	114 (207)	1.15093	1.16468	1.19848		2.09
114	115 (194)	1.37224	1.44694	1.36265		3.31
115	116 (205)	0.96593	1.07212	1.07089		5.88
116	117 (206)	1.28240	1.25055	1.23288		2.00
117	118 (209)	1.49555	1.53298	1.59618		3.30

* - A separate PCB congener calibration standard is analyzed for these PCB congeners that do not exist at measurable levels in the Green Bay multi-Aroclor calibration. These so-called non-Aroclor PCB congeners (with the exception of peak 3(2)) are analyzed to provide accurate retention time information and relative response factors in the event they need to be quantified.

* *- Refinements in the elution position of several congeners has occurred due to the availability of individual congener standards. The following low level congeners that were designated as separately eluting peaks have been determined to co-elute with another congener. The DB-1 peak numbers are no longer required for these congeners, but the original DB-1 numbering system has remained intact for all other peaks.

PK 18 (23) now elutes in PK 19 (23,34,54)
PK 40 (68) now elutes in PK 41 (68,96)
PK 81 (176) now elutes in PK 80 (130,176)
PK 86 (166) now elutes in PK 85 (166,178)
PK 97 (157) now elutes in PK 96 (157,202)

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Retention Time Study

PCB RETENTION TIME SUMMARY
INITIAL 72-HOUR RETENTION TIME WINDOW MEASUREMENT

LAB NAME: NORTHEAST ANALYTICAL, INC.

LAB CODE: NYS ELAP #11078

INSTRUMENT ID: GC #17

GC COLUMN ID: J&W, DB-1, 30 METER

STANDARD #1:	FILENAME:	CCCS0222B	DATE:	02/23/07	TIME:	17:02
STANDARD #2:	FILENAME:	CCCS0227A	DATE:	02/27/07	TIME:	19:14
STANDARD #3:	FILENAME:	CCCS0301A	DATE:	03/01/07	TIME:	15:58
STANDARD #4:	FILENAME:	SC0222	DATE:	02/22/07	TIME:	23:12
STANDARD #5:	FILENAME:	SC0227	DATE:	02/27/07	TIME:	17:00
STANDARD #6:	FILENAME:	SC0301	DATE:	03/01/07	TIME:	13:44

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PCB RETENTION TIME SUMMARY
INITIAL 72-HOUR RETENTION TIME WINDOW MEASUREMENT

DB-1 PEAK NUMBER (IUPAC Congener Number)	MEAN R.T.	+/- 3SD	R.T. WINDOW FROM	TO
2 (1)	11.74	0.07	11.67	11.81
3 (2)*	12.77	0.07	12.70	12.84
4 (3)	12.87	0.07	12.80	12.94
5 (4,10)	13.48	0.07	13.41	13.55
6 (7,9)	14.35	0.07	14.28	14.42
7 (6)	14.65	0.07	14.58	14.72
8 (5,8)	14.84	0.07	14.77	14.91
9 (14)*	15.40	0.07	15.33	15.47
10 (19)	15.49	0.07	15.42	15.56
11 (30)*	15.95	0.07	15.88	16.02
12 (11)*	16.01	0.07	15.94	16.08
13 (12,13)	16.21	0.07	16.14	16.28
14 (15,18)	16.34	0.07	16.27	16.41
15 (17)	16.43	0.07	16.36	16.50
16 (24,27)	16.73	0.07	16.66	16.80
17 (16,32)	16.98	0.07	16.91	17.05
18 **				
19 (23,34,54)*	17.44	0.07	17.37	17.51
20 (29)	17.63	0.07	17.56	17.70
21 (26)	17.75	0.07	17.68	17.82
22 (25)	17.83	0.07	17.76	17.90
23 (31)	18.03	0.07	17.96	18.10
24 (28,50)	18.08	0.07	18.01	18.15
25 (20,21,33,53)	18.43	0.07	18.36	18.50
26 (22,51)	18.66	0.07	18.59	18.73
27 (45)	18.89	0.07	18.82	18.96
28 (36)*	19.03	0.07	18.96	19.10
29 (46)	19.17	0.07	19.10	19.24
30 (39)*	19.29	0.07	19.22	19.36
31 (52,69,73)	19.46	0.07	19.39	19.53
32 (43,49)	19.63	0.07	19.56	19.70
33 (38,47)	19.75	0.07	19.68	19.82
34 (48,75)	19.81	0.07	19.74	19.88
35 (62,65)*	19.95	0.07	19.88	20.02
36 (35)*	20.03	0.07	19.96	20.10
37 (104,44)	20.20	0.07	20.13	20.27
38 (37,42,59)	20.33	0.07	20.26	20.40
39 (41,64,71,72)	20.68	0.07	20.61	20.75
40 **				
41 (68,96)*	20.84	0.07	20.77	20.91
42 (40)	20.94	0.07	20.87	21.01
43 (57,103)*	21.20	0.07	21.13	21.27
44 (58,67,100)	21.36	0.07	21.29	21.43
45 (63)	21.52	0.07	21.45	21.59
46 (74,94,61)	21.69	0.07	21.62	21.76
47 (70)	21.82	0.07	21.75	21.89

PCB RETENTION TIME SUMMARY
INITIAL 72-HOUR RETENTION TIME WINDOW MEASUREMENT

DB-1 PEAK NUMBER (IUPAC Congener Number)	MEAN R.T.	+/- 3SD	R.T. WINDOW FROM	TO
48 (66,76,98,80,93,95,102,88)	21.94	0.07	21.87	22.01
49 (55,91,121)	22.24	0.07	22.17	22.31
50 (56,60)	22.55	0.07	22.48	22.62
51 (84,92,155)	22.78	0.07	22.71	22.85
52 (89)	22.89	0.07	22.82	22.96
53 (90,101)	23.05	0.07	22.98	23.12
54 (79,99,113)	23.24	0.07	23.17	23.31
55 (119,150)	23.51	0.07	23.44	23.58
56 (78,83,112,108)	23.61	0.07	23.54	23.68
57 (97,152,86)	23.83	0.07	23.76	23.90
58 (81,87,117,125,115,145)	24.00	0.07	23.93	24.07
59 (116,85,111)	24.15	0.07	24.08	24.22
60 (120,136)	24.27	0.07	24.20	24.34
61 (77,110,148)	24.40	0.07	24.33	24.47
62 (154)*	24.69	0.07	24.62	24.76
63 (82)	24.77	0.07	24.70	24.84
64 (151)	25.07	0.07	25.00	25.14
65 (124,135)	25.20	0.07	25.13	25.27
66 (144)	25.27	0.07	25.20	25.34
67 (107,109,147)	25.33	0.07	25.26	25.40
68 (123)*	25.42	0.07	25.35	25.49
69 (106,118,139,149)	25.52	0.07	25.45	25.59
70 (140)*	25.63	0.07	25.56	25.70
71 (114,134,143)	25.93	0.07	25.86	26.00
72 (122,131,133,142)	26.13	0.07	26.06	26.20
73 (146,165,188)	26.41	0.07	26.34	26.48
74 (105,132,161)	26.54	0.07	26.47	26.61
75 (153)	26.70	0.07	26.63	26.77
76 (127,168,184)*	26.81	0.07	26.74	26.88
77 (141)	27.23	0.07	27.16	27.30
78 (179)	27.30	0.07	27.23	27.37
79 (137)	27.51	0.07	27.44	27.58
80 (130,176)	27.66	0.07	27.59	27.73
81 **				
82 (138,163,164)	27.89	0.07	27.82	27.96
83 (158,160,186)	28.07	0.07	28.00	28.14
84 (126,129)	28.27	0.07	28.20	28.34
85 (166,178)	28.62	0.07	28.55	28.69
86 **				
87 (175,159)	28.92	0.07	28.85	28.99
88 (182,187)	29.07	0.07	29.00	29.14
89 (128,162)	29.19	0.07	29.12	29.26
90 (183)	29.38	0.07	29.31	29.45
91 (167)	29.64	0.07	29.57	29.71
92 (185)	29.99	0.07	29.92	30.06
93 (174,181)	30.36	0.07	30.29	30.43

PCB RETENTION TIME SUMMARY
INITIAL 72-HOUR RETENTION TIME WINDOW MEASUREMENT

DB-1 PEAK NUMBER (IUPAC Congener Number)	MEAN R.T.	+/- 3SD	R.T. WINDOW FROM	TO
94 (177)	30.63	0.07	30.56	30.70
95 (156,171)	30.93	0.07	30.86	31.00
96 (157,202)	31.19	0.07	31.12	31.26
97 **				
98 (173)	31.36	0.07	31.29	31.43
99 (201)	31.75	0.07	31.68	31.82
100 (172,204)	31.98	0.07	31.91	32.05
101 (192,197)	32.29	0.07	32.22	32.36
102 (180)	32.47	0.07	32.40	32.54
103 (193)	32.71	0.07	32.64	32.78
104 (191)	33.02	0.07	32.95	33.09
105 (200,169)	33.37	0.07	33.30	33.44
106 (170)	34.53	0.07	34.46	34.60
107 (190)	34.80	0.07	34.73	34.87
108 (198)	35.67	0.07	35.60	35.74
109 (199)	35.91	0.07	35.84	35.98
110 (196,203)	36.45	0.07	36.38	36.52
111 (189)	37.60	0.07	37.53	37.67
112 (195)	39.18	0.07	39.11	39.25
113 (208)	39.71	0.07	39.64	39.78
114 (207)	40.65	0.07	40.58	40.72
115 (194)	42.07	0.07	42.00	42.14
116 (205)	42.96	0.08	42.89	43.04
117 (206)	48.13	0.07	48.06	48.20
118 (209)	54.18	0.07	54.11	54.25

* - A separate PCB congener calibration standard is analyzed for these PCB congeners that do not exist at measurable levels in the Green Bay multi-Aroclor calibration. These so-called non-Aroclor PCB congeners (with the exception of peak 3(2)) are analyzed to provide accurate retention time information and relative response factors in the event they need to be quantified.

* *- Refinements in the elution position of several congeners has occurred due to the availability of individual congener standards. The following low level congeners that were designated as separately eluting peaks have been determined to co-elute with another congener. The DB-1 peak numbers are no longer required for these congeners, but the original DB-1 numbering system has remained intact for all other peaks.

PK 18(23) now elutes in PK 19(23,34,54)
PK 40(68) now elutes in PK 41(68,96)
PK 81(176) now elutes in PK 80(130,176)
PK 86(166) now elutes in PK 85(166,178)
PK 97(157) now elutes in PK 96(157,202)

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Appendix E

Method Detection Limit Study

TABLE 1

Northeast Analytical Inc.
Quality Assurance/Quality Control

March 16, 2006
Revised:

Method Detection Limit Study

Method(s): Congener Specific Green Bay Method SOP: NE013_07.sop
Compound: Green Bay PCB Standard at various levels: 0.0784 ug/g, 0.784 ug/g
Matrix: Solid Sodium Sulfate - 10grams
Extraction: ASE (EPA 3545) SOP: NE143_03.sop
Date Extracted: 01/16/2006 & 01/18/2006
Date Analyzed: 02/17/2006 - 02/18/2006

Analysis: Internal Standard by Area
Instrument: GC-17 Agilent 6890
Column: DB-1; 30 meter x 0.25 mm x 0.25 µm
Detector: mirco-ECD

Peak Number (IUPAC Number)	MDL Concentration (ng/g)	MDL Recovery Sample #1 (ng/g)	MDL Recovery Sample #2 (ng/g)	MDL Recovery Sample #3 (ng/g)	MDL Recovery Sample #4 (ng/g)	MDL Recovery Sample #5 (ng/g)	MDL Recovery Sample #6 (ng/g)	MDL Recovery Sample #7 (ng/g)	MDL Recovery Sample #8 (ng/g)	Average MDL Recovery (ng/g)	Standard Deviation (ng/g)	%RSD (%)	Method Detection Limit (ng/g)	Method Detection Limit (mg/Kg)
2 (1)	5.48	4.64	5.42	5.55	5.44	5.13	5.39	5.38	5.00	5.25	0.302	5.75	0.905	0.000905
3 (2)	Supp. Congener													
4 (3)	3.20	3.05	3.09	3.12	2.99	2.97	3.11	3.14	3.38	3.11	0.127	4.09	0.381	0.000381
5 (4,10)	1.55	1.50	1.53	1.53	1.55	1.52	1.51	1.71	1.71	1.57	0.0867	5.52	0.260	0.000260
6 (7,9)	0.548	0.584	0.516	0.513	0.538	0.528	0.514	0.464	0.491	0.519	0.0350	6.76	0.105	0.000105
7 (6)	0.868	0.859	0.832	0.757	0.879	0.854	0.844	0.830	0.847	0.838	0.0360	4.30	0.108	0.000108
8 (5,8)	6.40	6.45	6.29	6.43	6.26	6.28	6.28	6.32	5.57	6.23	0.279	4.47	0.836	0.000836
9 (14)	Supp. Congener													
10 (19)	1.28	1.30	1.22	1.22	1.23	1.35	1.21	1.35	1.13	1.25	0.0743	5.94	0.223	0.000223
11 (30)	Supp. Congener													
12 (11)	Supp. Congener													
13 (12,13)	1.22	1.21	1.14	1.14	1.18	1.21	1.18	1.29	1.21	1.20	0.0483	4.04	0.145	0.000145
14 (15,18)	1.69	1.65	1.82	1.65	1.64	1.67	1.41	1.65	1.66	1.64	0.111	6.75	0.333	0.000333
15 (17)	1.69	1.59	1.67	1.62	1.65	1.66	1.47	1.63	1.58	1.61	0.0640	3.98	0.192	0.000192
16 (24,27)	0.119	0.118	0.114	0.107	0.107	0.111	0.126	0.106	0.121	0.114	0.00721	6.34	0.0216	0.0000216
17 (16,32)	1.78	1.75	1.75	1.72	1.88	1.73	1.63	1.69	1.70	1.73	0.0719	4.16	0.216	0.000216
19 (23,34,54)	Supp. Congener													
20 (29)	0.243	0.213	0.247	0.244	0.246	0.245	0.231	0.248	0.266	0.243	0.0153	6.29	0.0458	0.0000458
21 (26)	0.329	0.303	0.353	0.349	0.303	0.339	0.383	0.332	0.329	0.336	0.0263	7.82	0.0789	0.0000789
22 (25)	0.146	0.143	0.139	0.147	0.160	0.137	0.149	0.139	0.151	0.146	0.00763	5.24	0.0229	0.0000229
23 (31)	1.88	1.75	1.95	1.80	1.84	1.95	1.64	1.84	1.86	1.83	0.102	5.59	0.307	0.000307
24 (28,50)	2.41	2.59	2.42	2.40	2.31	2.72	2.22	2.37	2.45	2.43	0.156	6.39	0.467	0.000467
25 (20,21,33,53)	1.81	1.87	1.61	1.87	1.83	1.85	1.81	2.01	1.87	1.84	0.111	6.03	0.332	0.000332
26 (22,51)	1.32	1.33	1.51	1.34	1.27	1.33	1.37	1.38	1.41	1.37	0.0718	5.25	0.215	0.000215
27 (45)	0.407	0.432	0.401	0.410	0.442	0.425	0.453	0.415	0.466	0.430	0.0223	5.18	0.0668	0.0000668
28 (36)	Supp. Congener													
29 (46)	1.83	1.74	1.77	1.84	1.84	1.72	1.91	1.85	1.76	1.80	0.065	3.59	0.194	0.000194
30 (39)	Supp. Congener													
31 (52,69,73)	2.18	2.42	2.36	2.48	2.38	2.20	2.19	2.12	2.50	2.33	0.144	6.20	0.433	0.000433
32 (43,49)	1.05	1.07	0.940	0.993	0.999	1.05	1.16	1.06	1.10	1.05	0.0690	6.59	0.207	0.000207
33 (38,47)	0.457	0.511	0.463	0.465	0.441	0.503	0.498	0.458	0.482	0.477	0.0248	5.19	0.0743	0.0000743
34 (48,75)	0.457	0.486	0.481	0.447	0.432	0.473	0.436	0.473	0.452	0.460	0.0208	4.51	0.0622	0.0000622
35 (62,65)	Supp. Congener													
36 (35)	Supp. Congener													
37 (104,44)	1.96	2.00	1.71	1.89	1.83	1.89	1.83	1.88	1.89	1.87	0.0799	4.28	0.240	0.000240
38 (37,42,59)	1.19	1.03	1.15	1.13	0.972	1.16	1.13	1.15	1.00	1.09	0.0765	7.02	0.229	0.000229
39 (41,64,71,72)	1.87	1.91	1.76	1.96	1.90	1.92	1.82	1.91	1.96	1.89	0.0695	3.67	0.208	0.000208
41 (68,96)	Supp. Congener													
42 (40)	0.429	0.396	0.460	0.452	0.435	0.458	0.482	0.459	0.419	0.445	0.0271	6.09	0.0813	0.0000813
43 (57,103)	Supp. Congener													
44 (58,67,100)	0.502	0.516	0.545	0.540	0.529	0.525	0.516	0.511	0.465	0.518	0.0244	4.71	0.0733	0.0000733
45 (63)	0.959	0.946	0.875	0.955	0.951	0.940	0.922	0.962	0.877	0.93	0.0346	3.72	0.104	0.000104
46 (74,94,61)	0.868	0.901	0.851	0.897	0.848	0.822	0.795	0.870	0.866	0.856	0.0358	4.18	0.107	0.000107
47 (70)	1.55	1.55	1.54	1.45	1.51	1.38	1.43	1.58	1.56	1.50	0.0731	4.87	0.219	0.000219
48 (66,76,98,80,93,95,102,88)	3.29	3.16	3.26	3.35	3.20	3.36	3.28	3.53	3.17	3.29	0.124	3.76	0.371	0.000371
49 (55,91,121)	0.233	0.213	0.235	0.206	0.238	0.216	0.217	0.218	0.234	0.222	0.0121	5.43	0.0362	0.0000362
50 (56,60)	1.60	1.45	1.57	1.54	1.64	1.56	1.58	1.52	1.62	1.56	0.0604	3.87	0.181	0.000181
51 (84,92,155)	0.822	0.865	0.866	0.824	0.882	0.859	0.859	0.867	0.930	0.869	0.0295	3.40	0.0886	0.0000886
52 (89)	0.457	0.425	0.429	0.450	0.471	0.448	0.455	0.474	0.454	0.451	0.0174	3.87	0.0522	0.0000522

53 (90,101)	0.822	0.880	0.896	0.821	0.837	0.866	0.808	0.836	0.829	0.847	0.0306	3.61	0.0916	0.0000916
54 (79,99,113)	0.338	0.322	0.312	0.328	0.308	0.345	0.287	0.350	0.322	0.322	0.0203	6.31	0.0609	0.0000609
55 (119,150)	0.128	0.120	0.126	0.127	0.129	0.136	0.131	0.136	0.135	0.130	0.00562	4.33	0.0169	0.0000169
56 (78,83,112,108)	0.685	0.665	0.661	0.628	0.654	0.638	0.701	0.650	0.693	0.661	0.0253	3.82	0.076	0.0000757
57 (97,152,86)	0.256	0.259	0.254	0.254	0.247	0.255	0.255	0.261	0.223	0.251	0.0119	4.75	0.0357	0.0000357
58 (81,87,117,125,115,145)	0.530	0.523	0.552	0.565	0.602	0.535	0.535	0.526	0.530	0.546	0.0265	4.85	0.0794	0.0000794
59 (111,116,85)	0.320	0.324	0.313	0.320	0.306	0.348	0.337	0.330	0.332	0.326	0.0133	4.08	0.0399	0.0000399
60 (120,136)	0.343	0.322	0.341	0.345	0.381	0.321	0.323	0.376	0.329	0.342	0.0239	6.99	0.0717	0.0000717
61 (77,110,148)	0.973	0.927	1.00	0.921	0.965	0.963	0.934	1.09	0.932	0.967	0.0565	5.85	0.169	0.000169
62 (154)	Supp. Congener													
63 (82)	0.201	0.205	0.229	0.206	0.228	0.200	0.215	0.201	0.197	0.210	0.0127	6.06	0.0382	0.0000382
64 (151)	0.777	0.729	0.773	0.735	0.821	0.773	0.780	0.772	0.772	0.769	0.0285	3.70	0.0853	0.0000853
65 (124,135)	0.133	0.127	0.130	0.149	0.127	0.133	0.148	0.126	0.124	0.133	0.00992	7.46	0.0297	0.0000297
66 (144)	0.274	0.272	0.273	0.259	0.290	0.292	0.264	0.267	0.273	0.274	0.0117	4.27	0.0351	0.0000351
67 (107,109,147)	0.0594	0.0578	0.0579	0.0551	0.0571	0.0606	0.0489	0.0545	0.0548	0.0558	0.00347	6.22	0.01041	0.00001041
68 (123)	Supp. Congener													
69 (106,118,139,149)	1.83	1.70	1.90	1.97	1.88	1.89	1.81	1.79	1.86	1.85	0.0825	4.46	0.247	0.000247
70 (140)	Supp. Congener													
71 (114,134,143)	0.922	0.963	0.973	0.945	0.913	0.937	0.998	0.899	0.985	0.952	0.0348	3.65	0.104	0.000104
72 (122,131,133,142)	0.133	0.140	0.133	0.147	0.136	0.149	0.144	0.136	0.133	0.140	0.00630	4.51	0.0189	0.0000189
73 (146,165,188)	0.178	0.172	0.183	0.178	0.178	0.169	0.165	0.190	0.171	0.176	0.00818	4.65	0.0245	0.0000245
74 (105,132,161)	0.619	0.658	0.617	0.599	0.624	0.647	0.684	0.616	0.640	0.636	0.0272	4.28	0.0815	0.0000815
75 (153)	1.35	1.31	1.35	1.37	1.34	1.40	1.30	1.26	1.32	1.332	0.0460	3.45	0.138	0.000138
76 (127,168,184)	Supp. Congener													
77 (141)	0.777	0.721	0.791	0.796	0.776	0.778	0.738	0.732	0.747	0.760	0.0288	3.79	0.0864	0.0000864
78 (179)	0.667	0.666	0.634	0.691	0.671	0.690	0.694	0.657	0.702	0.676	0.0228	3.38	0.0685	0.0000685
79 (137)	0.342	0.381	0.331	0.339	0.336	0.331	0.342	0.372	0.384	0.352	0.0229	6.51	0.0686	0.0000686
80 (130,176)	0.119	0.122	#REF!	0.116	0.117	0.111	0.129	0.124	0.105	0.118	0.00751	6.36	0.0225	0.0000225
82 (138,163,164)	1.23	1.27	0.119	1.22	1.29	1.23	1.15	1.42	1.24	1.26	0.0755	5.99	0.226	0.000226
83 (158,160,186)	0.114	0.115	1.26	0.121	0.111	0.122	0.124	0.121	0.114	0.121	0.00867	7.18	0.0260	0.0000260
84 (126,129)	0.0591	0.0568	0.0592	0.0517	0.0558	0.0539	0.0550	0.0511	0.0560	0.0549	0.00267	4.86	0.00801	0.00000801
85 (166,178)	0.502	0.498	0.553	0.502	0.544	0.517	0.491	0.531	0.509	0.518	0.0225	4.34	0.0675	0.0000675
87 (175,159)	0.914	0.858	0.986	0.938	0.913	0.963	0.849	0.954	0.982	0.930	0.0530	5.69	0.159	0.000159
88 (182,187)	1.64	1.62	1.70	1.68	1.69	1.50	1.66	1.66	1.68	1.65	0.0644	3.90	0.193	0.000193
89 (128,162)	0.0457	0.0472	0.0467	0.0451	0.0462	0.0470	0.0474	0.0461	0.0505	0.0470	0.00159	3.39	0.00478	0.00000478
90 (183)	0.777	0.769	0.775	0.846	0.782	0.784	0.750	0.761	0.785	0.782	0.0287	3.67	0.0859	0.0000859
91 (167)	0.224	0.232	0.215	0.232	0.243	0.234	0.244	0.252	0.224	0.234	0.0119	5.07	0.0356	0.0000356
92 (185)	0.215	0.263	0.233	0.206	0.207	0.220	0.229	0.220	0.217	0.224	0.0180	8.02	0.0540	0.0000540
93 (174,181)	1.46	1.43	1.49	1.45	1.45	1.59	1.49	1.51	1.45	1.48	0.0515	3.47	0.154	0.000154
94 (177)	0.777	0.788	0.769	0.773	0.653	0.767	0.776	0.772	0.756	0.757	0.0429	5.67	0.129	0.000129
95 (156,171)	0.361	0.359	0.390	0.339	0.363	0.357	0.360	0.383	0.355	0.363	0.0163	4.49	0.0489	0.0000489
96 (157,202)	0.0302	0.0314	0.0304	0.0290	0.0314	0.0321	0.0285	0.0271	0.0317	0.0302	0.00181	6.00	0.00543	0.00000543
98 (173)	0.174	0.197	0.197	0.169	0.176	0.170	0.169	0.180	0.182	0.180	0.0116	6.47	0.0349	0.0000349
99 (201)	0.178	0.160	0.172	0.183	0.180	0.186	0.179	0.177	0.186	0.178	0.00869	4.88	0.0261	0.0000261
100 (172,204)	0.256	0.253	0.285	0.260	0.233	0.259	0.256	0.262	0.250	0.257	0.0143	5.55	0.0428	0.0000428
101 (192,197)	0.502	0.583	0.599	0.533	0.586	0.545	0.591	0.563	0.582	0.573	0.0232	4.06	0.0697	0.0000697
102 (180)	2.79	3.03	2.79	2.71	2.82	2.77	2.79	2.75	2.77	2.80	0.097	3.45	0.290	0.000290
103 (193)	0.192	0.194	0.198	0.181	0.203	0.190	0.200	0.188	0.189	0.193	0.00708	3.67	0.0212	0.0000212
104 (191)	0.548	0.531	0.526	0.535	0.593	0.511	0.533	0.526	0.544	0.537	0.0244	4.54	0.0732	0.0000732
105 (200,169)	0.196	0.207	0.198	0.190	0.197	0.190	0.191	0.195	0.209	0.197	0.00740	3.76	0.0222	0.0000222
106 (170)	0.585	0.661	0.578	0.599	0.577	0.568	0.595	0.594	0.586	0.595	0.0286	4.82	0.0859	0.0000859
107 (190)	0.192	0.197	0.204	0.195	0.193	0.213	0.187	0.193	0.192	0.197	0.00812	4.12	0.0243	0.0000243
108 (198)	0.548	0.535	0.547	0.578	0.563	0.594	0.546	0.540	0.559	0.558	0.0200	3.59	0.0600	0.0000600
109 (199)	1.92	1.92	1.98	2.00	2.02	1.84	1.88	2.08	1.90	1.95	0.0818	4.19	0.245	0.000245
110 (196,203)	1.96	1.77	1.98	1.92	1.87	1.99	1.92	1.93	1.91	1.91	0.0678	3.55	0.203	0.000203
111 (189)	0.182	0.162	0.188	0.183	0.164	0.171	0.190	0.182	0.188	0.178	0.0112	6.27	0.0336	0.0000336
112 (195)	0.253	0.268	0.259	0.274	0.241	0.240	0.257	0.243	0.263	0.256	0.0131	5.11	0.0392	0.0000392
113 (208)	1.13	1.17	1.02	1.09	1.12	1.22	1.23	1.09	1.16	1.14	0.0721	6.34	0.216	0.000216
114 (207)	0.425	0.362	0.372	0.350	0.353	0.381	0.356	0.390	0.360	0.365	0.0142	3.89	0.0426	0.0000426
115 (194)	0.822	0.750	0.851	0.823	0.828	0.850	0.824	0.841	0.858	0.828	0.0341	4.12	0.102	0.000102
116 (205)	0.502	0.514	0.586	0.507	0.545	0.511	0.555	0.571	0.497	0.536	0.0332	6.20	0.100	0.000100
I.S. (OCN)	internal standard													
117 (206)	0.311	0.346	0.317	0.322	0.304	0.323	0.305	0.305	0.306	0.316	0.0143	4.54	0.0430	0.0000430
118 (209)	0.0554	0.0568	0.0548	0.0574	0.0526	0.0541	0.0505	0.0476	0.0549	0.0536	0.00326	6.08	0.0098	0.0000098
												Total MDL =	12.90	0.0129

- Data from 0.0784 ug/g MDL Study

- Data from 0.784 ug/g MDL Study

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TABLE 2

Northeast Analytical Inc.

Quality Assurance/Quality Control

March 16, 2006

Revised:

Method Detection Limit Study

Method(s): Congener Specific Green Bay Method SOP: NE013_07.sop

Compound: Supplemental Congener Standard at various levels

Matrix: Solid - Sodium Sulfate 10 grams

Extraction: ASE (EPA 3545) SOP: NE143_03.sop

Date Extracted: 01/16/2006 & 01/18/2006

Date Analyzed: 02/17/2006 - 02/18/2006

Analysis: Internal Standard by Area

Instrument: GC-17 Agilent 6890

Column: DB-1; 30 meter x 0.25 mm x 0.25 µm

Detector: mirco-ECD

Peak Number (IUPAC Number)	MDL Concentration (ng/g)	MDL Recovery Sample #1 (ng/g)	MDL Recovery Sample #2 (ng/g)	MDL Recovery Sample #3 (ng/g)	MDL Recovery Sample #4 (ng/g)	MDL Recovery Sample #5 (ng/g)	MDL Recovery Sample #6 (ng/g)	MDL Recovery Sample #7 (ng/g)	MDL Recovery Sample #8 (ng/g)	Average MDL Recovery (ng/g)	Standard Deviation (ng/g)	%RSD (%)	Method Detection Limit (ng/g)	Method Detection Limit (mg/Kg)
3 (2)	200	211	204	202	199	217	210	220	208	209	7.19	3.44	21.6	0.0216
9 (14)	1.25	1.11	1.21	1.30	1.33	1.16	1.19	1.19	1.21	1.21	0.0717	5.92	0.215	0.000215
11 (30)	1.25	1.18	1.18	1.22	1.25	1.21	1.01	1.21	1.26	1.19	0.0760	6.39	0.228	0.000228
12 (11)	5.00	5.19	4.76	5.46	5.07	5.03	5.10	5.04	5.07	5.09	0.195	3.83	0.584	0.000584
19 (23,34,54)	1.25	1.24	1.21	1.28	1.28	1.20	1.13	1.26	1.29	1.24	0.0519	4.19	0.156	0.000156
28 (36)	1.25	1.20	1.18	1.25	1.16	1.18	1.19	1.31	1.16	1.20	0.0510	4.24	0.153	0.000153
30 (39)	1.25	1.14	1.22	1.16	1.23	1.28	1.19	1.24	1.14	1.20	0.0523	4.35	0.157	0.000157
35 (62,65)	1.25	1.26	1.23	1.42	1.31	1.33	1.27	1.32	1.24	1.30	0.0619	4.76	0.186	0.000186
36 (35)	1.25	1.23	1.26	1.13	1.27	1.20	1.25	1.22	1.26	1.23	0.0468	3.82	0.140	0.000140
41 (68,96)	1.25	1.37	1.23	1.34	1.10	1.27	1.26	1.28	1.30	1.27	0.0805	6.35	0.241	0.000241
43 (57,103)	1.25	1.30	1.22	1.23	1.26	1.37	1.25	1.33	1.21	1.27	0.0561	4.41	0.168	0.000168
62 (154)	5.00	4.80	4.90	5.13	5.04	4.97	4.84	4.65	5.16	4.94	0.174	3.52	0.52	0.00052
68 (123)	1.25	1.30	1.26	1.19	1.24	1.25	1.25	1.14	1.18	1.23	0.0520	4.23	0.156	0.000156
70 (140)	1.25	1.20	1.21	1.25	1.36	1.25	1.22	1.23	1.15	1.23	0.0611	4.95	0.183	0.000183
76 (127,168,184)	1.25	1.26	1.15	1.18	1.25	1.27	1.21	1.26	1.26	1.23	0.0445	3.61	0.133	0.000133

Q:\MDL\PCB\2006\GC17_2006_CSGB_ASE\[CSGB_MDL_ASE_SOLID_060217A.XLS]Low_Level

STANDARD OPERATING PROCEDURE REVIEW

SOP Name	Review Number	Reviewers	Title	QAO Approval	Effective Date
NE133_02	01	Inga Hotaling Christina L. Braidwood Robert E. Wagner	GC Supervisor QAO Lab Director	Christina Braidwood	02/20/09

APPENDIX 47
SOP FOR THE EXTRACTION OF LIPIDS FROM FISH AND BIOTA MATERIAL (NE158_05)

STANDARD OPERATING PROCEDURE

NORTHEAST ANALYTICAL, INC.

NE158_05.DOC
REVISION NUMBER: 05

THE EXTRACTION OF LIPIDS FROM FISH AND BIOTA MATERIAL

COPY #___

NORTHEASTANALYTICAL, INC
2190 TECHNOLOGY DRIVE
SCHENECTADY, NY 12308

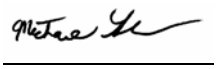
(518) 346-4592

STANDARD OPERATIONG PROCEDURE

LABORATORY PROCEDURE NE158_05.DOC

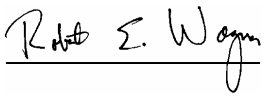
REVISION 5 (06/17/08)

Author:



Mike Glenn
Operations Manager

Reviewed by:



Robert E. Wagner
Laboratory Director

Approved by:

Christina L. Braidwood
Quality Assurance Officer

1.0 IDENTIFICATION OF TEST METHOD

1.1 This is the Standard Operating Procedure for the extraction and analysis of % lipids from fish and biota material.

1.2 The purpose of this SOP is to provide a method for extraction of lipids from fish tissue and other biota samples.

2.0 APPLICABLE MATRIX AND MATRICES

2.1 This test method is appropriate for fish and biota tissue. This method may be restricted to use by or under the supervision of a technician knowledgeable in the area of sample extraction and clean-up.

2.2 The technician should further be aware of the proper care and handling of Polychlorinated Biphenyls (PCBs) as well. The technician must have an understanding of the methods and requirements of USEPA-SW-846A "Test Methods for Solid Wastes" Volume 1B: Lab Manual, 3rd edition and SW-846 EPA Methods 3540, 3500, 2500A.

2.3 The extraction technician must also be certified to perform the procedure by an approved instructor by performing precision and accuracy requirement.

3.0 DETECTION LIMIT

3.1 The detection limit is defined by the precision of the balance used while weighing the sample. The detection limit for the Mettler Toledo PL303 balance is 0.001g. If there is a limited amount of oil to detect it may be necessary to utilize the Mettler Toledo AG204 balance, which has a detection limit of 0.0001g.

4.0 SCOPE AND APPLICATION

4.1 The following procedure is used by NEA for the extraction of fish tissue for lipid analysis, though it may in part be adapted for other biota extractions.

5.0 SUMMARY OF TEST METHOD

5.1 This method outlines the procedures used for the extraction of lipids from fish and biota material. Biota samples are extracted by a Soxhlet extractor apparatus over a defined length of time.

5.2 Once the extraction is complete, the solvent is exchanged with pure hexane utilizing a LV evaporation system.

5.3 After solvent exchange, the solvent extract is set to 25ml using a 25ml volumetric flask. Once set to volume, 10ml are withdrawn and placed in a properly labeled, pre-weighed aluminum dish.

5.4 The extracted solvent in the tin is evaporated utilizing a micro blowdown apparatus. Using the initial weight and the final weight of the aluminum dish, the % lipid concentration in the sample material can be calculated (see **Section 15.0**).

6.0 DEFINITIONS

6.1 **Laboratory Reagent Blank (B):** A sample consisting of laboratory grade water run in parallel with the sample set to evaluate any cross contamination**.**

6.2 **Lab Control Standard (LCS)**: A non site sample created in the laboratory to which a known amount of target analyte is added for assessment of analyte recovery efficiency.

6.3 **Lab Control Standard Duplicate (LCSD)**: A replicate of the Lab Control Standard to further assess analyte recovery efficiency**.**

6.4 **Matrix Spike (MS)**: A site sample to which a known amount of target analyte is added for assessment of analyte recovery efficiency.

6.5 **Matrix Spike Duplicate (MSD)**: A replicate of the Matrix Spike utilizing the same site sample and known amount of target analyte for assessment of analyte recovery efficiency**.**

6.6 **Relative Percent Difference (RPD**): A quality control measure designed to quantitate the difference in percentages for lipids/total solids, etc. of two identical samples.

7.0 INTERFERENCES

7.1 Laboratory technicians should exercise caution when completing percent lipid analysis. Technicians should be careful not to introduce laboratory contamination with extract when transferring sample to aluminum dish. For example, glass particles from pipettes may Give an incorrect value and compromise the integrity of the percent lipid analysis.

8.0 SAFETY

8.1 Polychlorinated biphenyls should be treated with extreme caution; as a class of chemical compounds they possess both toxic and carcinogenic properties. Refer to MSDS for further details.

8.2 The technician should have received in-house safety training and should know the location of first aid equipment and the emergency spill/clean-up equipment, before handling any apparatus or equipment.

8.3 Safety glasses and gloves must be worn when handling glassware and samples.

9.0 EQUIPMENT AND SUPPLIES

9.1 Water Cooled Condenser: Pyrex 45/50 #3840-MCO. (or equivalent)

9.2 250mL Round Bottom Flask: Pyrex #4100 (Or equivalent)

9.3 Soxhlet Repetitive Flushing (reflux) Unit: 45/50 Pyrex #3740-M. (or equivalent)

9.4 Heating Mantle: Type "VF" laboratory heating mantle #HM0250VF1. (or equivalent)

9.5 Heating Mantle Controller: Glass-Col #PL3122 Minitwin (or equivalent) regulates temperature control of the mantle.

9.6 Analytical Balance: Mettler PL-303 used to determine sample mass. (or equivalent)

9.7 Chiller: Pump driven water circulating cooling system cool flow #75 NESLABS Instruments, Inc. (or equivalent)

9.8 Turbo Vap Evaporator: Zymark #ZW640-3. (Or equivalent)

9.9 Turbo Vap Evaporator concentrator tubes: Zymark 250mL, 0.5mL endpoint. (or equivalent)

9.10 Beakers: Assorted Pyrex: 250mL, 600mL, and 1000mL, used for liquid containment and pipet storage.

9.11 Vials: glass, 40mL vial & 15 mL (with Polyseal sealed cap) (20 mL & 10 mL) capacity, for sample extracts.

9.12 Vial Rack: Plastic rack used to hold vials, during all phases of the extract processing.

9.13 Pipettes: S/P Disposable Serological Borosilicate Pipettes.

1. 1mL X 1/10
2. 5mL X 1/10
3. 10mL X 1/10
4. Fisher Pasteur Borosilicate glass pipette 9" (or equivalent)

9.14 Beakers: Assorted Pyrex: 250mL, 600mL, and 1000mL.

9.15 Weighing Boats: Aluminum weighing boats (dish) for percent lipid weight determination.

9.16 Metal spatula.

9.17 4 oz Jars: Industrial Glassware

10.0 REAGENTS AND STANDARDS

10.1 Cellulose Extraction Thimble: Contains sample during Soxhlet extraction.

10.2 Sodium Sulfate: J.T. Baker #3375-05 Anhydrous, Granular (12-60 Mesh). Used for the laboratory method blank and laboratory control spike.

10.3 Boiling Chips: Chemware PTFE Boiling Stones P#0919120 (or equivalent)

10.4 Hexane: High Purity Solvent Baxter (Burdick/Jackson) #UN1208. (Or equivalent)

10.5 Acetone: High Purity Solvent Baxter (Burdick/Jackson) #UN1090. (Or equivalent)

10.6 1:1 Hexane/Acetone: 50%/50% by volume solvent mixture prepared in the lab.

11.0 SAMPLE COLLECTION, PRESERVATION, SHIPMENT and STORAGE

11.1 All samples should remain frozen at all times unless being tested. Fish usually arrive whole-bodied or already filleted.

11.2 Once received, the sample must be ground and homogenized so that it may be analyzed. The homogenized fish tissue should be held for 6 to 12 months.

11.3 The fish solvent extracts should be held for 3 months. Some clients may request that the body and/or head of fish be saved once the fillets are cut out. Other biota material may have other specifications stated specifically for that project.

12.0 QUALITY CONTROL

12.1 The Method Reagent Blank (B) is used as a measure to ensure that there is no cross contamination across the sample set.

12.2 The Matrix Spike (MS) and Matrix Spike Duplicate (MSD) are further controls which test the method to ensure proper lipid recovery is performed by calculating the RPD (see **Section 18.0**).

13.0 CALIBRATION AND STANDARDIZATION

13.1 The PL303 and the AG201 analytical balances should be calibrated daily to ensure proper measurements are maintained.

14.0 PROCEDURES

14.1 Sample Preparation

14.1.1 Throughout the entire process it should be noted that if the technician encounters any problems or difficulties with any samples or steps involved, all work should **STOP**! Any problems should be brought to the attention of the supervisor and documented in the LIMS extraction logbook.

14.1.2 The technician should first review the sample job folder and fill in the appropriate spaces on the internal sample tracking form and initial.

14.1.3 The fish samples are usually received as fillets and must be processed to produce a homogenous material prior to extraction. Once the sample has been processed, the sample is cut up into small enough pieces to fit into a standard manual meat grinder. An acetone rinsed Pyrex tray should be placed under the grinder exit to catch the minced tissue. After the fish has been ground once, it should be ground again to ensure complete homogenization of the sample.

14.1.4 The ground fish is placed into an appropriate-sized jar and labeled. The sample is then placed in the freezer for storage until the extraction process is begun.

14.2 Procedure: Sample Extraction

14.2.3 Rinse the cellulose extraction thimbles with hexane; and allow to dry out in a 4 oz. jar in a fume hood.

14.2.4 Fill a Pyrex pan with ice cubes and cold water about 1/2 inch deep. As the samples are weighed out; place the jars in the Pyrex pan to chill for at least 15 minutes prior to the drying step.

14.2.5 Into a tarred 4oz. jar, accurately weigh to the nearest 0.001g using an analytical balance about 9.5 grams of tissue. Record this weight in the laboratory extraction logbook of the LIMS system. Place the jar containing the sample into the Pyrex pan to chill. Repeat for remaining samples.

Note: All sample containers are to be returned to the appropriate refrigerator. For all empty sample containers, see the Chemical Hygiene Plan for proper disposal.

14.2.6 After the sample has been sufficiently chilled, add approximately 10 g of a 1:1 mix of magnesium sulfate/sodium sulfate to the sample, and mix well with a clean metal spatula. If the sample has not dried after a few minutes, another 10 g may be added. Once the sample is well dried and free flowing, transfer the sample to an extraction thimble. Repeat with remaining samples. Set empty mixing jar in a glass disposal bin and stir utensil aside for cleaning.

Note: Be careful not to add too much drying agent to the sample; if too much is added, the sample may not fit completely in the thimble. In this case the sample will have to be split into two different Soxhlet units.

14.2.7 Add 200 mL of a 1:1 mixture of hexane/acetone to a 250 mL round bottom flask. Add several boiling chips. Place a Soxhlet extractor on top of the round bottom flask. Label the round bottom flask with a sample number and use a pair of long-handled tweezers to place the corresponding thimble into the Soxhlet extractor. After all samples have been processed add the specified surrogate and matrix spikes required directly into thimble.

14.2.8 Rinse the inside and the outside connecting joints of the condenser units that will be used to condense the extraction solvent during the Soxhlet extraction

of the sample with hexane. Turn on chiller to cool the condensers.

14.2.9 Place the round bottom flask with attached Soxhlet extractor onto a heating mantle and attach condenser unit. Turn corresponding thermostats on to setting 5.5. Double check Soxhlets at this time for any cracks or chips which may leak solvent. Once the solvent begins to boil, a flushing action of once every two to three minutes should be achieved.

14.2.10 The samples should be extracted overnight for a minimum of **18** hours. Once the sample has finished extracting (usually in the morning), turn the heating mantle off and allow samples to cool to room temperature. Once cool, rinse the inside of the condenser with several pipette volumes of hexane. Disengage the Soxhlet and condenser unit and rinse the joint off as well into the Soxhlet.

14.2.11 Move Soxhlet units into a chemical fume hood, and flush the remaining solvent from the Soxhlet extractor by tipping the Soxhlet. Using a pair of long-handled tweezers, pull the thimbles out of the Soxhlets one at a time and allow them to drip dry by balancing the thimbles on the tops of the Soxhlets. Once dry, remove the thimbles to a sheet of aluminum foil for total solvent evaporation and disposal.

14.2.12 Rinse the Soxhlet with several pipette volumes of hexane and tip again to drain into the round bottom. Set aside the Soxhlet at this time. Procure the same number of Turbo tubes as there are samples. Using an individual Turbotube stand, label a Turbotube with the corresponding sample ID number and place in the holder. Pour the contents of the round bottom into the Turbotube, using a pipette and hexane to rinse the last drop out of the mouth of the round bottom flask. Rinse the round bottom flask with several pipette volumes of hexane, swirl gently, and decant into same turbo tube. Repeat this step twice for same sample, and then repeat all preceding steps for all other samples.

14.2.13 All glassware must be rinsed with technical grade acetone or a "for rinsing-only" labeled solvent, and dried in the hood before other cleaning steps.

14.3 Solvent Reduction: TurboVap Evaporator System

14.3.3 The Turbovap evaporator system is used in place of the Kuderna Danish (KD) concentrator apparatus.

14.3.4 The turbovap uses a heated water bath and positive pressure nitrogen flow/vortex action. The unit maintains a slight equilibrium imbalance between the liquid and gaseous phase of the solvent extract, which allows fractional reduction of the solvents without loss of higher boiling point analytes.

14.3.5 Turn the unit on (switch is located on the backside of the unit) and allow to heat up to the specified temperature for individual solvent use. This is indicated by the "Heating" display light, located above the temperate control knob on the right side of the unit. The system is at the proper temperature when the "At Temperature" light is lit. This is located above the "Heating" display light. The temperature of the unit should be set at 40 ± 2ºC.

14.3.6 As a precaution the TurboVap system regulators should be checked to assure that no residual gas pressure remains within the system and that the gas cylinder valve and gas pressure regulators are both off before placing samples in the apparatus. Residual gas pressure may cause splashing and cross contamination of samples. To bleed the system of residual gas pressure place an empty turbo tube into the water bath and close the lid. Make sure that the nitrogen gas cylinder valve is turned off and slowly turn on the gas pressure regulator. Bleed any residual gas until the regulator output pressure gauge reads "0" psi. Proceed to 8.3.4.

14.3.7 Place the Turbo tube containing the samples into the Turbovap and close the lid. Turn on the gas cylinder valve first and then begin slowly turning the pressure regulator on. Keep the gas pressure very low, until the solvent level is decreased, to avoid splashing. Increase the gas pressure as the sample reduces maintaining uniform flow throughout the reduction.

14.3.8 The process for solvent (hexane/acetone) reduction takes approximately 20-30 minutes. Do not leave the unit unattended as extracts may be blown to dryness.

14.3.9 Concentrate the solvent to approximately 10.0 mL. Remove the samples from the Turbovap and place in the rack. The remaining solvent will consist largely of hexane since the acetone component is fractionally removed at a faster rate than hexane; however, a solvent exchange with hexane should be completed by filling the Turbo tube up with approximately 50 mls of hexane and concentrating back down to 10.0 mls to ensure the acetone has been entirely removed.

NOTE: Not all samples will evaporate at the same rate; sample extracts containing large amounts of lipids or other non-volatile liquids may stop reducing before the 10.0 mL point is achieved. Samples that stop reducing should be removed as soon as possible.

14.3.10 Quantitatively transfer the sample extract with a disposable transfer pipette into an appropriate volumetric flask (25mL for biota extracts) with three 2mL hexane rinses. After the sample has been transferred, rinse the disposable transfer pipette with 0.5 mL of hexane into the volumetric flask. Add hexane to the volumetric meniscus mark. Invert the volumetric flask at least three times to mix completely. Decant the contents into a pre-labeled 40mL vial.

14.3.11 All dirty glassware must be rinsed with tech-acetone or a "For Rinsing-Only"

labeled solvent and dried in the fume hood before being washed.

14.4 Sample Extract concentration

NOTE: NO CLEAN-UP STEPS ARE PERFORMED FOR PERCENT LIPID DETERMINATION.

14.4.1 Weigh a pre-labeled aluminum dish for each sample extract. Record the weight in the percent lipid log book of the LIMS system.

14.4.2 Shake samples for a few seconds then using a 10 mL pipette, transfer 10 mL of the extract into the corresponding dish.

14.4.3 Concentrate the extract in the dish using the nitrogen micro-blowdown. Place a maximum of 3 dishes at one time on the nitrogen blow down. Set the temperature at 40C and the pressure at 40 PSI.

14.4.4 After concentration has been completed, place the dishes into the desiccators for at least 4 hours.

14.4.5 Weigh sample dishes and record the weight in the percent lipid logbook of the LIMS system. Calculate percent lipids as seen in **Section 15.0**.

15.0 CALCULATIONS

15.1 Calculate percent lipids as follows:

$$\textbf{PERCENT LIPIDS} = \frac{\textbf{Vf} - \textbf{Ve} \times 2.5 \times 100}{\textbf{Sample weight (g)}}$$

Vf = weight of tin tray with sample (g)
Ve = weight of empty tin tray (g)

15.2 Calculate the Practical Quantitation Limit (PQL):

$$\textbf{PQL} = \frac{\textbf{0.001(or 0.0001)*}}{\textbf{sample weight}} \times \textbf{100}$$

****Note: Depending on which balance was used to weigh the sample. The PL303 analytical balance would use 0.001 while the AG204 would use 0.0001.***

16.0 METHOD PERFORMANCE

16.1 Method Performance is measured through the use of laboratory duplicates (Matrix Spike/Matrix Spike Duplicates and Duplicate sample). The Laboratory Information Management System (LIMS) maintains records of laboratory duplicate analysis.

17.0 POLLUTION PREVENTION

17.1 Refer to NEA168.SOP for details about pollution prevention.

18.0 DATA ASSESSMENT AND ACCEPTANCE CRITERIA FOR QUALITY CONTROL MEASURES

18.1 Laboratory Duplicate % RPD $\leq$ 20

18.2 Method Blank % lipid $\leq$ PQL

19.0 CORRECTIVE ACTIONS FOR OUT OF CONTROL DATA

19.1 Ensure that analytical balances have been calibrated prior to use on each working day.

19.2 If data is still out of control, re-homogenize the sample and re-extract and re-calculate.

20.0 CONTINGINCIES FOR HANDLING OUT-OF-CONTROL OR UNACCEPTABLE DATA

20.1 After all corrective actions are followed, with no change in the data or there is not enough sample material to perform corrective actions, report to client the data that is available, detailing how it is out of control.

21.0 WASTE MANAGEMENT

21.1 Refer to NE054.SOP, NE083.SOP, and NE089.SOP for waste management procedures.

22.0 REFERENCES

22.1 SW-846 methods 3500A & 3600A; United States Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Vol.1B, Cincinnati, OH 45268.

22.2 Guide to Environmental Analytical Methods, Genium Publishing Corporation, Schenectady, NY 12304.

23.0 TABLES, DIAGRAMS, FLOWCHARTS and VALIDATION DATA

23.0 No attachments.

APPENDIX 48
SOP FOR THE TISSUE REDUCTION/GRINDING FOR WHOLE BODY AND FILLETED FISH (NE132_06)

STANDARD OPERATING PROCEDURE

NORTHEAST ANALYTICAL, INC.

NE132_06.DOC
REVISION NUMBER: 06

TISSUE PREPARATION/ HOMOGENIZATION FOR BIOTA AND PLANT MATRIXES

COPY #___

NORTHEAST ANALYTICAL, INC
2190 TECHNOLOGY DRIVE
SCHENECTADY, NY 12308

(518) 346-4592

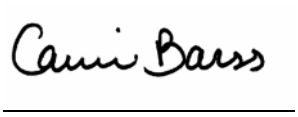
STANDARD OPERATING PROCEDURE

LABORATORY PROCEDURE NE132_06.DOC

REVISION 6 (02/20/09)

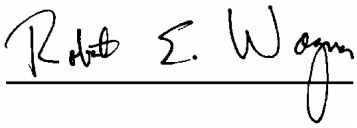
Author: Carrie Barss

Reviewed by:



Carrie Barss
Operations Manager

Reviewed by:



Robert E. Wagner
Laboratory Director

Approved by:

Christina L. Braidwood
Quality Assurance Officer

1.0 IDENTIFICATION OF TEST METHOD

1.1 Tissue Preparation/ Homogenization for Biota and Plant Matrixes.

1.2 This method describes the tissue processing and homogenization procedures used prior to the extraction/digestion and analysis of the sample. The methods in this procedure are utilized by Northeast Analytical for whole body and filleted fish and other biota samples.

2.0 APPLICABLE MATRIX OR MATRICES

2.1 This method is applicable to the preparation and homogenization of animal and plant matrixes; including but not limited to: fish (whole body and fillets), mollusks (mussels, clams, etc.), crustaceans (lobster or shrimp, etc.), mammals (mice, mink, muskrat, shrew etc.), reptiles and amphibians (frogs or turtles, etc.) macro invertebrates (benthic worms, eels, insects and other biota), and vegetation (coastal and wetland grasses/plants).

2.2 The preparation and homogenization of the biota samples is done prior to the extraction or digestion of the matrices.

3.0 DETECTION LIMIT

3.1 *Not applicable.*

4.0 SCOPE AND APPLICATION

4.1 This method is intended to describe the preparation and homogenization procedures prior to the extraction, digestion and/or clean up of sample extracts. This procedure uses a variety of cutting, grinding and scaling equipment for size reduction, composting, and homogenization.

5.0 SUMMARY OF TEST METHOD

5.1 This method describes the tissue processing and homogenization procedures used prior to extraction/digestion and analysis of the sample. Client and/or project may dictate additional specific requirements than stated below. Samples are best processed when partially frozen. Samples may be re-frozen after processing pending extraction or digestion.

5.2 Fish tissue samples (whole bodies or fillets) are weighed and the weights are recorded. Measurements may be taken as needed depending upon the project specifications. Gender determination of the fish may be done at this time depending upon the project specifications. This is done prior to any processing and recorded. The fish may be processed with the skin on or off, depending upon the project specifications. If fillets are to be removed and processed separately, this is generally done after the removal of the skin, however fillets can be processed with the skin on if requested. If compositing is required, the identified samples for composite are filleted or skinned prior to compositing homogenization. The carcass of the fish (after removal of the fillet) may be maintained for separate homogenization and analysis if requested.

5.3 Mollusks, crustaceans and other like invertebrates are measured and weighed prior to

processing. Mollusks must be removed from their shells before processing. Due to the low weight of a single mollusk, crustacean, or invertebrate, these sample types are generally composited with others of the same species and/or sampling area prior to homogenization. Gender determination may need to be performed, i.e. lobsters. This is done prior to any processing and recorded. Additionally, lobsters are usually dissected, and the edible meat (tail and claw) is removed for homogenization. Certain internal organs such as the hepatopancreas may need to be processed separately. If crabs are being processed, the legs, claws and body cavity are generally homogenized together.

5.4 Mammals such as mink, mice, shrew or other rodents, must be prepared in a glove box or bio-hazard hood due to the potential health hazards associated with mammal tissue. All project specific sample preparation (weighing, skinning, compositing and homogenization) is performed in the glove box. Waste from the process must be treated with bleach before disposal. The outside surfaces of the sample containers must be processing must be containerized and treated disinfected before removal from the glove box.

5.5 Reptiles and amphibians are generally processed as whole body samples. Depending upon the size, the specimen may need to be cut into small pieces and processed in part, then re-combined as a single sample. Due to the thickness of the skin of most reptiles, such as frogs, it is recommended that these be processed without the skin. If the skin must be processed, ensure that the grinder or processor blades are sharpened before use. The blades may need to be re-sharpened between every few samples as needed. Turtles must be removed from the shell prior to processing by digging out the head and legs, and as much of the body as feasible.

5.6 Macro invertebrates such as worms, eels, insects or benthic biota are generally processed as whole body samples. Depending upon the size, the specimen may need to be cut into small pieces and processed in part, then recombined as a single sample. Due to the low weight of a single invertebrate, these sample types are generally composited with others of the same species and/or sampling area prior to homogenization.

5.7 Plants are rinsed prior to processing to remove soil, silt, small insects or other debris. Depending upon the size of the plant and the leaves, the sample may be processed mechanically, or may have to be cut into small pieces by hand. Plants can be processed either wet or dry, depending upon project specifications.

5.8 After tissue processing, organic samples will be extracted and the extracts cleaned if needed, then analyzed by the determinative analytical procedure. Inorganic digestates do not require further clean up and will only undergo analysis by the determinative analytical procedure.

6.0 DEFINITIONS

6.1 Abdomen- the posterior section of the body behind the thorax in an arthropod.

6.2 Abductor- to draw or spread away (as a limb or the fingers) from a position near or parallel the median axis of the body or from the axis of a limb.

6.3 Arthropod- any of a phylum (Arthropoda) of invertebrate animals (as insects, arachnids, and crustaceans) that have a segmented body and jointed appendages, a usually chitinous exoskeleton molted at intervals, and a dorsal anterior brain connected to a ventral chain of ganglia.

6.4 Biota- the flora or fauna of a region.

6.5 Bivalve- being or having a shell composed of two valves (shells).

6.6 Caudal- directed toward or situated in or near the tail or posterior part of the body.

6.7 Carapace- bony or chitinous case or shield covering the back or part of the back of an animal (as a turtle or crab).

6.8 Composite- combining the typical or essential characteristics of individuals making up a group.

6.9 Crustacean- any of a large class (Crustacea) of mostly aquatic mandibulate arthropods that have a chitinous or calcareous and chitinous exoskeleton, a pair of often much modified appendages on each segment, and two pairs of antennae and that include the lobsters, shrimps, crabs, wood lice, water fleas, and barnacles.

6.10 Digestate- the action, process, or power of digesting.

6.11 Fillet- to cut.

6.12 Head- the upper or anterior division of the animal body that contains the brain, the chief sense organs, and the mouth.

6.13 Hepatopancreas- a glandular structure (as of a crustacean) that combines the digestive functions of the vertebrate liver and pancreas

6.14 Homogenize- to reduce the particles of so that they are uniformly small and evenly distributed.

6.15 Mantle- a fold or lobe or pair of lobes of the body wall of a mollusk or brachiopod that in shell-bearing forms, lines the shell and bears shell-secreting glands.

6.16 Pectoral muscle- any of the muscles which connect the ventral walls of the chest with the bones of the upper arm and shoulder and of which there are two on each side of the human body.

6.17 Swimmerets- one of a series of small unspecialized appendages under the abdomen of many crustaceans that are best developed in some decapods (as a lobster) and usually function in locomotion or reproduction

6.18 Telson- the terminal segment of the body of an arthropod or segmented worm.

6.19 Thorax- 1) the middle of the three chief divisions of the body of an insect; *also* **:** the corresponding part of a crustacean or an arachnid. **2)** the part of the mammalian body between the neck and the abdomen; *also* **:** its cavity in which the heart and lungs lie.

7.0 INTERFERENCES

7.1 Samples being tested for metals must be cut with a ceramic knife and/or ground with a plastic blade to prevent steel or tin getting into the samples.

7.2 Samples being tested for organics must processed with metal, Teflon, PTFE and or glass utensils to prevent plastic interference getting into the samples.

8.0 SAFETY

8.1 The use of laboratory equipment and chemicals exposes the analyst to several potential hazards. Good laboratory techniques and safety practices shall be followed at all times. Eating, drinking, smoking, or the application of cosmetics is not permitted in the laboratory area. Horseplay of any kind is prohibited. All Personal Protective Equipment (PPE) must be removed before leaving the laboratory area and before entering the employee lounge or eating area. Always wash your hands before leaving the laboratory. All relevant Material Safety Data Sheets (MSDSs) are kept alphabetically in the conference room.

8.2 Approved PPE, which includes Safety Glasses, Gloves and Lab Coats, must be worn at all times when handling samples, reagents, chemicals, or when in the vicinity of others, so that dermal contact is avoided. All standards, reagents and solvents shall be handled under a hood using the proper PPE. All flammable solvents must be kept in the flammable storage cabinet, and returned to the cabinet immediately after use. When transporting chemicals, make sure to use a secure transporting devise and/or secondary outer container.

8.3 The chemist should have received in-house safety training and should know the location of first aid equipment and the emergency spill/clean-up equipment before handling any apparatus or equipment.

8.4 Extreme caution must be taken when using or handling knives, scalers, and grinders to homogenize the biota samples.

8.5 Re-useable cotton mesh glove liners may be worn under latex or PVC gloves as an additional measure when using sharp tools or knives, or when dealing with samples that have sharp teeth, spines, fins, or thorns. The mesh lining can help prevent piercing the skin, in case a tool or sample slips, during dissection or other preparation steps.

8.6 Polychlorinated biphenyls should be treated with extreme caution; as a class of chemical compounds they possess both toxic and suspected carcinogenic properties.

8.7 All additional company safety practices shall be followed at all times as written in the NEA Chemical Hygiene Plan.

9.0 EQUIPMENT AND SUPPLIES

9.1 Cutting board-made of either glass or polyethylene.

9.2 Food processor with titanium cutting blade (small), or blender with stainless steel blades (large).

9.2.1 2- Restsch Grindomix (model GM200) with glass and or plastic mixing bowls

9.2.2 1-Kitchen Aid Little Ultra Power

9.2.3 1-Tor Rey (model M22) Large Food Processor

9.3 Knives: Ceramic stainless steel, or titanium. (See Section 7.0 for interferences and/or contamination associated with different material knives and blades).

9.3.1 Gerber Stainless Steel Boning knives

9.3.2 Dexter Russel Chopping knives

9.3.3 Oneida Stainless Steel fillet knives

9.3.4 URI Eagle Ceramic Knife

9.4 Necropsy dissection kits

9.5 Analytical balance with precision to 0.01g.

9.6 Labconco multi-hazard glove box.

9.7 Bench liner material (Lab Mat) and scissors.

9.8 Aluminum foil.

9.9 Plastic wrap or wax paper.

9.10 Titanium fork.

9.11 Teflon-coated spatula.

9.12 Teflon or stainless steel tweezers and dissection scissors.

9.13 PVC or Latex gloves.

9.14 Ruler.

9.15 Mallet.

9.16 Stainless steel or plastic strainer.
9.17 Salad spinner.

9.18 Pre-cleaned glass sample jars with Teflon or PTFE-lined caps.

9.19 Kim wipes.

9.20 Nylon bristled brushes for cleaning.

10.0 REAGENTS AND STANDARDS

10.1 *Note:* Use reagent grade or trace metals grade chemicals for all reagents.

10.2 **Deionized (DI) water**- Deionized (DI) water or reagent water is ASTM Type II laboratory reagent grade water or better (Type I).The Millpore NANO-pure system provides Type I water used in the metals laboratory for rinsing lab glass and plastic ware. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination. If the purity of a reagent is in question, analyze for contamination.

10.3 **Hexane** - (ACS approved), Pesticide grade.

10.4 **Acetone** - (ACS approved), HPLC grade.

10.5 **Nitric acid 25%** - Add 250mL concentrated HNO3 to 400mL of reagent water and dilute to 1L in an appropriate flask. (See metals lab for this prepared solution).

10.6 **10% Bleach solution** - Add 100mL of commercial bleach to 500mL of reagent water and dilute to 1 liter in an appropriate beaker or flask.

10.7 **Alconox** - cleaning solution.

11.0 SAMPLE COLLECTION, PRESERVATION, SHIPMENT and STORAGE

11.1 Sample collection is not applicable to the NEA laboratory operation.

11.2 Please see the NEA SOP (NE227) that describes the responsibilities of sample custody including all proper documentation, verification, and tracking procedures following Chain of Custody (COC) protocols, sample receipt procedures, and Internal COC procedures for sample tracking include the use of sample tracking logbooks.

11.3 All samples should remain frozen at all times unless being tested. Fish usually arrive whole bodied or already filleted. Once received the sample must be ground and homogenized so that it may be analyzed. The homogenized fish tissue can be held for 6 to 12 months. The fish solvent extracts can be held for 3 months. Some clients may request that the body

and/or head of fish be saved once the fillets are cut out. Other biota material may have other specifications stated specifically for that project.

11.3 If samples are not shipped frozen, they will be stored in freezers at NEA upon arrival, and until processing. The samples must remain frozen and maintained at < -20˚C. Sample processing and extraction/digestion hold times are suspended by freezing the sample. Hold time monitoring is resumed when samples are removed from freezers for processing and then returned to freezers pending extraction or digestion. The organic hold time is 14 days from sample collection to extraction, and 40 days from extraction to analysis. The metals hold time is six months from sample collection to digestion and analysis. If mercury is to be determined, the hold time is 28 days from sample collection to digestion and analysis.

11.4 Tissue samples: As guidance, a minimum of 50 grams of sample must be collected for organic analyses, and 5 grams for metals analyses, in a glass jar with a Teflon or PTFE lined screw cap. The amount of sample needed, will depend upon the project management plan such as reporting limits and the need for MS/MSD and/or duplicate analyses. Extra sample must be collected, if possible, to allow the laboratory adequate sample volume in case of re-extract and reanalysis is needed. Large whole individual fillets, or vegetation may be wrapped in plastic or aluminum foil depending upon the requested analyses. Large crustaceans, reptiles or amphibians may be individually packed in well-labeled Styrofoam coolers.

12.0 QUALITY CONTROL

12.1 *Prevention of Contamination:*

12.1.1 If the purity of a reagent is in question, analyze for contamination.

12.1.2 Blades for dissection may need to be re-sharpened between every few samples as needed.

12.1.3 All project specific sample preparation (weighing, skinning, compositing and homogenization) is performed in the glove box. Waste from the process must be treated with bleach before disposal. The outside surfaces of the sample containers must be processing must be containerized and treated disinfected before removal from the glove box.

12.2 The procedures described below are general cleaning and pre-processing procedures that are to be followed regardless of the type of tissue being processed. Samples are prioritized by the Laboratory Supervisor or Lab Manager based on hold time and client due date. All weights, measurements and other project required observations are recorded on the Processing Record bench sheets. Example bench sheets can be found in
section 23.1.

12.2.1 Wash all utensils, sample processors (blades, blade post, cup and lid) and cutting boards with an Alconox solution and a sponge. Rinse thoroughly with tap water, then with

DI water.

12.2.2 If the samples are going to be processed for organic analyses only rinse all wet utensils, processor parts and surfaces with hexane followed by rinsing with acetone.

12.2.3 If samples are going to be processed for metal analyses only rinse all plastic and ceramic utensils with DI water and then Nitric acid 25% solution and then DI water again.

12.2.4 If requested by the client, the equipment or processing blank should be collected at this time by pouring DI water into and out of the processor, over the surfaces of the utensils and over the cutting board. The blank is collected in the appropriate container, at the project specification frequency, for the determinative analysis.

12.2.5 Gloves must be worn when handling tissue samples. Latex gloves may be worn. All gloves must be talc or dust free.

12.2.6 Tissue samples should be partially thawed before starting, to the point where it becomes possible to make an incision in, or cut through, the flesh. When samples are completely thawed they become soft and difficult to cut or fillet. NOTE: If whole bodies are not being processed, and the tissue is partially frozen during dissection, there is less of a chance of puncturing the gut cavity and any internal organs. Inadvertent puncture of the internal organs may contaminate the part(s) of the animal that have been selected for analysis. Also, internal organs may rupture during freezing. If this is observed during dissection, it must be noted in the processing records. Note any morphological abnormalities on the processing records.

12.3 *Hold times:* The homogenized fish tissue can be held for 6 to 12 months. The fish solvent extracts can be held for 3 months.

13.0 CALIBRATION AND STANDARDIZATION

13.1 *Not Applicable.*

14.0 PROCEDURES

14.1 The below procedures are processing procedures that follow for each type of species.

14.2 **Fish Tissue Preparation:**

14.2.1 Determine the wet weight for each individual fish using a calibrated balance and record. The balance should be covered with aluminum foil if aluminum is not a metal of concern. If aluminum is a metal of concern and the sample will not be analyzed for organic compounds the balance should be covered with plastic wrap. If the sample is for both metal and organic compounds, wax paper may be used. Catch any excess fluid coming from the thawing specimen into the wax paper, foil or plastic wrap. All liquid from thawed whole fish must be kept as part of the sample. The technician must remember to zero the balance with the

aluminum foil, plastic wrap, or wax paper on it before weighing the specimen. The foil, plastic wrap, or wax paper must be changed after each weighing.

14.2.2 Determine the length of each fish using a ruler, and record with the weight. Some measurements may, or may not be, a part of the project specifications.

14.2.3 If gender identification is needed this must be done prior to the scaling and filleting processes.

14.2.4 Removal of Scales or Skin: If required by project specifications, the scales and/or skin of the fish will be removed prior to filleting.

14.2.5 Lay the fish on the cleaned, and/or lined, cutting board.

14.2.6 Scrape the fish from tail to head using the blade edge of a cleaned stainless steel, ceramic or titanium knife, to remove the scales. Note: If performing metals analysis, titanium or ceramic must be used.

14.2.7 Rinse the cutting board between fish. If plastic, wax paper, or foil is used, change between fish.

14.2.8 Rinse the outside of the fish with DI water and pat dry with paper towel Place the fish on its side, on a clean cutting board, for filleting or skinning.

14.2.9 To skin the fish loosen the skin behind the gill cover and pull the skin off toward the tail with a knife blade, or other cleaned utensil, cutting lightly along the inside of the skin, Slowly separate the skin from the muscle tissue of the body or the fillet.

14.3 Filleting the Fish:

14.3.1 Using fresh gloves and the specified knife, make a cut behind the entire length of the gill cover, making sure to cut through the skin, if still attached, flesh, and as close to the bone as possible. Note: If the fish samples are small, and it appears difficult to fillet, or if the amount of the fillet appears to be insufficient for the analysis, consult the Project Manager prior to filleting. In some cases it may be necessary to homogenize the whole body (Spot tailed shiners).

14.3.2 Make a cut across the base of the tail fin keeping as close to the caudal (tail) fin as possible. Continue cutting along the underbelly of the fish moving from the head to the tail.

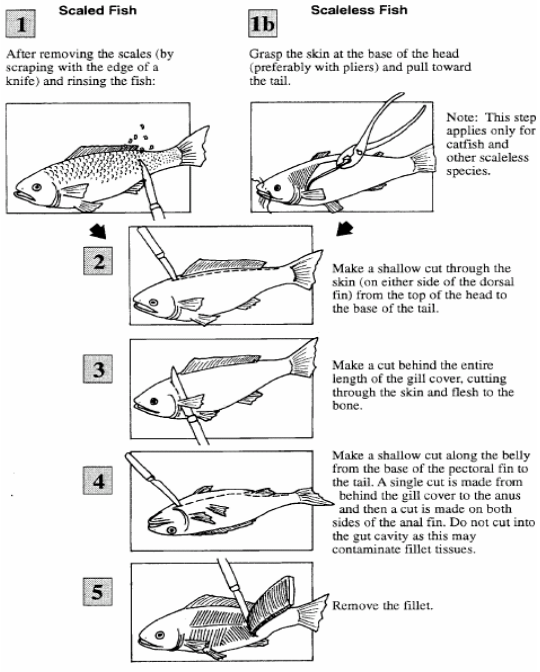
14.3.3 Go back to the cut made at the beginning at the gill cover and slice down the entire length of the fish following along the backbone until reaching the cut previously made across the tail.

14.3.4 Remove the fillet from the fish. Be sure to include the belly flap in each fillet and do not remove the dark muscle tissue in the vicinity of the lateral line from

the light muscle tissue that makes up the rest of the muscle tissue mass.

14.3.5 Remove any bones that may be left attached to the fillet. Repeat the fillet steps for the second side of the specimen.

14.3.6 The general procedure recommended for filleting fish is illustrated below. Source: U.S. EPA, 1991d.



14.3.7 Note in the sample processing records if the internal organs were ruptured during freezing or if inadvertent puncture of the internal organs occurred during the filleting process, rinse the fillet(s) tissue with DI water.

14.3.8 Cover the balance with the appropriate clean lining, and weigh the fillet(s). Record the fillet(s) weight(s) in the processing records.

14.3.9 If the fillet(s) and/or the carcass are to be homogenized immediately, proceed to Section 14.4. If not, rinse all fish parts with DI water and store in the appropriate container; see Section 9.0 for allowable materials. Note that it may be necessary to chop the fillet(s) or carcass into smaller pieces, with the appropriately cleaned knife, before storage, and before homogenization, so the entire sample will fit into the storage container or the homogenization vessel. If the samples will not be homogenized immediately, the samples must be placed back into the freezer, until homogenization.

14.4 <u>Homogenization:</u>

14.4.1 Allow the fillet(s), carcass or whole body to partially thaw. Retain all fluids as

part of the sample.

14.4.2 Homogenize whole fish bodies, carcasses, or fish fillets by placing them into the small or large food processor fitted with the appropriate blades. The sample may need to be cut into smaller pieces for processing. Process the sample until it appears to be fully and consistently homogenous. Continue to grind the sample until there are no chunks present in the homogenate.

14.4.3 Individual homogenates may be processed further to prepare composite homogenates as required by project specifications. Composite homogenates must be prepared from equal weights of individual homogenates. All individual weights that make up one composite must be recorded, if required, or one composite weight may be recorded. If individual or composite homogenates were frozen prior to extraction/digestion, these homogenates must be thawed and re-homogenized by hand mixing prior to being extracted or digested.

14.4.4 Place the individual or composite homogenized samples into the appropriate glass jars to be frozen pending future extraction/digestion. If the samples will not be extracted/digested immediately, the samples must be returned to the freezer, until extraction/digestion.

14.4.5 All utensils and equipment must be washed in between samples according to the procedures described previously in Section 12.2.

14.5 <u>Mollusk (Bivalves) Preparation (Mussels, Clams):</u>

14.5.1 Wash all utensils, the cutting board, and surfaces as previously described in Section 12.2 . Obtain samples from freezer.

14.5.2 If required by the project specifications, measure and record the length of the sample shell. Cover the balance with the proper material as described in Section 9.0, and weigh and record the sample weight.

14.5.3 Wearing the proper gloves, place the sample on a clean, cutting board. Samples should be partially thawed. If the sample is frozen, it will be difficult to break open the shell. If the sample is excessively thawed, the internal tissue will become soupy and difficult to remove.

14.5.4 If preparing bivalve specimens, use the titanium knife to cut the abductor muscle by sliding the knife through the crevice where the two shells meet. Once the abductor muscle is cut the two shell pieces should come apart easily.

14.5.5 Carefully remove the top shell, and using the Teflon coated spatula, scoop out the internal tissue that is resting on the mantle.

14.5.6 Cover the balance with the proper material and weigh the amount of tissue obtained from the sample. Record the weight along with the information previously recorded on the processing records. The sample may now be

stored pending homogenization in the appropriate jar.

14.5.7 Since the amount of tissue obtained from one bivalve is generally small, several specimens are frequently combined to make one sample. Utensils do not need to be rinsed between the individual samples that comprise one composite, but utensils must always be rinsed in between each composite sample.

14.5.8 After the tissue has been removed from all of the specimen shells for one composite or individual sample, place the tissue in the clean small processor with the titanium blade to be homogenized. Grind the sample until it appears to be fully and consistently homogenized and there are no large chunks.

14.5.9 If tissue is being processed for volatile organic carbon (VOC) analysis the homogenization must be done by hand.

14.5.10 Individual homogenates may be processed further to prepare composite homogenates as required by project specifications. Composite homogenates must be prepared from equal weights of individual homogenates. All individual weights that make up one composite must be recorded, if required, or one composite weight may be recorded. If individual or composite homogenates were frozen prior to extraction/digestion, these homogenates must be thawed and re-homogenized by hand mixing prior to being extracted or digested.

14.5.11 Place the processed samples into the appropriate glass jars to be frozen for future extraction/digestion, and place back into the freezer.

14.5.12 All utensils and equipment must be washed in between samples according to the procedures described previously in Section 12.2.

14.6 <u>Crustaceans (Lobsters, Crabs, Shrimp):</u>

14.6.1 Wash all utensils, the cutting board, and surfaces as previously described in Section 12.2. Obtain samples from the freezer.

14.6.2 If project specifications require gender determination of lobsters, this must be done prior to dissecting. To determine the gender, hold the lobster by the thorax, and flip it over to examine the underneath abdomen, just below the legs and where the abdomen division begins, there is a first pair of swimmerets. The first pair of swimmerets is what is used to distinguish the lobster's gender. If the first pair is soft, has small hairs, and the swimmerets are crossed, it is female. On a male lobster, the first pair of swimmerets is hard and stiff, and generally do not touch.

14.6.3 If the hepatopancreas of the lobster samples is to be analyzed, the lobster samples must be received alive. If the samples are frozen prior to dissection, the hepatopancreas will burst upon thawing making it impossible to remove. To remove the hepatopancreas, the live lobster should be placed on a cleaned

cutting board. Wearing the proper gloves, one analyst holds claws out in front of the lobster, while also holding down the lower abdomen and tail. The second analyst takes a titanium-coated knife, and places it on the grove in the outer shell, just behind the head region. Keeping the knife at an angle, the second analyst must push down and forward, to remove the head. Once the head is removed, the hepatopancreas can be seen lying just under the carapace and running the length of the thorax. The hepatopancreas is generally a greenish-yellow color, but there may be some variation. Using the Teflon coated spoon, scoop the hepatopancreas out gently trying not to break it into pieces. Cover the tray of the balance with the proper material, and weigh and record the weight of the hepatopancreas in the processing record, and place it into an appropriate sample jar for freezing and future extraction/digestion.

14.6.4 To remove the edible meat, remove the two claws from the body of the lobster at the joint. Place a piece of lab mat or paper towel over the claw and pound with a mallet. Once the shell is crushed, remove the meat, using the appropriately cleaned tweezers or other tool, making sure to get all the meat in the joints and arms. Cover the balance tray with the appropriate material and record the total tissue weight arms. Record this weight with the previously recorded information from the two claws and sample processing record.

14.6.5 Remove the abdomen and telson from the rest of the outer shell by pulling the lobster apart. Using the titanium coated knife, cut through the center underside tissue of the lobster and laterally along the exoskeleton of the tail. Once the abdomen and tail have been cut open, separate the shell from the edible meat using cleaned utensils. Any eggs found in the female lobsters will have to be removed and discarded or sampled separately. Cover the balance tray with the appropriate material, and record the weight of the tissue obtained from the abdomen and telson on the processing record. The sample may now be stored pending homogenization in the appropriate jar.

14.6.6 If removing tissue from crabs, break off all legs and claws. Squeeze, pull, or pick all the tissue out of the legs and claws. Pull apart the outer shell. Scoop out the tissue using a Teflon coated spatula. Cover the balance tray with the appropriate material, and record the weight of the tissue obtained from the abdomen and telson on the processing record. The sample may now be stored pending homogenization in the appropriate jar.

14.7 <u>Mammals (Mice, Mink, Muskrat, Shrew):</u>

14.7.1 Wash all utensils, the cutting board, and surfaces as previously described in Section 12.2. Obtain samples from the freezer.

14.7.2 Place the first specimen partially thawed to be processed, and all equipment needed into the glove box/Bio-hood on a freshly laid out lab mat (Blue diaper).

14.7.3 Equipment needed includes:

14.7.3.1 Empty and pre-labeled glass sample containers for the processed homogenate.

14.7.3.2 10% Bleach solution, acetone, and hexane in squirt bottles.

14.7.3.3 Grinding unit.

14.7.3.4 Balance.

14.7.3.5 Ceramic, titanium, teflon-coated or stainless steel (organic compounds only) knives, spatulas.

14.7.3.6 Cutting board(s).

14.7.3.7 DI water in a squirt bottle.

14.7.3.8 Kim wipes.

14.7.3.9 Laboratory waste bottles with caps.

14.14.3 Once all materials are in the glove box and set up for use, seal the transfer box and ensure the motor blower is on. Over tightening of the outer or inner door knobs is not necessary to achieve a good seal. Place your hands into the gloves attached to the glove ports and place Latex gloves over the glove port gloves for use. The outer Latex gloves will need to be changed in between each sample.

14.14.4 If the gender of the mouse or shrew needs to be determined, turn the animal over and note the length of the anus and the distance of the anus from the tail. If the anus is elongated in shape and does not touch the base of the tail, testicles and a large genital papilla are visible, and there are no nipples, the animal is male. If the anus is round in shape and almost touches the base of the tail and/or there are nipples (up to five sets), the animal is female. If the animal is very small, young or immature and a gender determination cannot be made, note that the gender is non determinable. Record the gender observations on the processing records.

14.8 Organ Dissection/Processing:

14.8.1 If the mammal is being dissected for Brain, Liver, Kidney, Heart, Lung, or Adipose (Fat) tissue, each organ will need to be harvested.

14.8.2 Place the animal on its back with forceps. Pinch the skin at the base of anus and carefully make an incision at the tail end, and cut just below the skin along the abdomen and past the chest cavity. Cutting the skin flap at the abdomen cavity carefully separate the adipose tissue from the muscle tissue. Below it should be a white/yellow material. Take this material out.

14.8.3 Identify each organ and remove them from the abdomen cavity.

14.8.4 Weigh and record the weight of the mammal organs and place into the appropriate container.

14.8.5 The rib cage will need to be cut with scissors. Once chest cavity is open, remove the heart and lungs.

14.8.6 Weigh and record the weight of the mammal organs and place into the appropriate container.

14.8.7 Since the amount of tissue obtained from one animal may be small, manually grinding of the organs may need to be done at the time of extraction.

14.8.8 Place the processed samples into the appropriate glass jars to be frozen for future extraction/digestion into the freezer.

14.8.9 Before removing any equipment all utensils and equipment must be washed with DI water and 10% bleach solution.

14.8.10 All disposable materials must be double bagged for disposal.

14.9 Whole Animal Processing:

14.9.1 If skinning of the mammal is required, carefully make an incision at the tail end and cut just below the skin along the back, from one hind leg to the other. Make another cut from one hind leg to one front leg and repeat the cut on the other side of the animal. Starting from the tail, lift the skin flap, and carefully separate the skin from the muscle tissue below. Pull the skin forward from the tail to the head to expose the back tissue of the animal. Repeat the procedure on the stomach side of the animal. Note: it may be very difficult to remove the skin from the legs, head, and tail. If some skin cannot be removed, note this on the processing records.

14.9.2 Weigh and record the weight of the mammal on the processing records. Depending upon the size of the mammal, it may need to be chopped into small pieces before being ground. Generally, mice and shrew can be quartered before homogenization if needed.

14.9.3 Put the whole body or chopped sample into the cup of the grinding unit. Turn the grinding unit on low speed and gradually increase the speed to homogenize the sample being careful to minimize any splatter or outside contamination. Homogenize until a uniform consistency is achieved.

14.9.4 Transfer the homogenized sample from the cup to the pre-labeled sample jar using the appropriate utensil. Clean the outside of the sample jar with the 10% bleach soaked Kim wipe.

14.9.5 To clean the grinding unit in between samples, remove as much residual tissue on the blade as possible by operating the unit at low or medium speed, using DI water and 10% bleach. Rinse unit with DI water if metals are being done and/or hexane or acetone for organics.

14.9.6 Repeat steps 14.9.2 through 14.9.5 until the samples are complete.

14.9.7 Since the amount of tissue obtained from one mouse or shrew may be small, several specimens may be combined to make one sample, as required by project specifications. Utensils do not need to be rinsed between the individual samples that comprise one composite, but utensils must always be cleaned in between each composite sample.

14.9.8 If several specimens will be composited to make one sample, follow the applicable Sections of 14.9.2 through 14.9.5, for each of the specimens. The tissue obtained from each specimen may be weighed and recorded individually, then totaled for the composite weight. If only one composite weight is sufficient for the project specifications, weigh the entire composite and record that weight.

14.9.9 Place the processed samples into the appropriate glass jars to be frozen for future extraction/digestion, placed back into the freezer.

14.9.10 Before removing any equipment all utensils and equipment must be washed with DI water and 10% bleach.

14.9.11 All disposable materials must be double bagged for disposal.

14.10 <u>Reptiles and Amphibians (Frogs and Turtles):</u>

14.10.1 Wash all utensils, the cutting board, and surfaces as previously described in Section 12.2. Obtain samples log them out of the freezer for hold time tracking purposes. Note removal of samples in the Internal Tracking COC.

14.10.2 Wearing the proper gloves, place the turtle sample on the cleaned cutting board. The turtle should be partially thawed. If the turtle is frozen, it will be difficult to remove the muscle. If the sample is excessively thawed, the internal tissue will become soupy and difficult to remove.

14.10.3 Take all project required measurements. The distance between the anterior and posterior edge of a turtle carapace (top of shell) should be measured with a ruler and recorded on the processing records. If the entire mass of the turtle, including the shell, needs to be recorded, cover the balance with the proper material and weigh and record this weight on the processing records.

14.10.4 Since the bottom of shell and carapace are extremely dense and difficult to cut through with normal dissecting tools, the muscle tissue of the turtle must be removed by cutting the body of the turtle away from the shell. Insert a knife,

made of the proper material, into the skin of the turtle, close to the shell on the lower half of the body. Slowly, cut along the entire circumference of the shell. Repeat the procedure on the upper half of the body, on both sides of the shell.

14.10.5 With dissection scissors or a ceramic or titanium paring knife of the proper material, remove the skin from the hind limbs, tail, and fore limbs and neck. Remove any visible muscle tissue within the carapace. Most of this tissue will be found in the upper portion of the carapace around the pectoral area.

14.10.6 Using the appropriate utensils, remove the muscle tissue from the tail, neck, hind limbs, and fore limbs, including the feet, leaving bone and claws behind.

14.10.7 Cover the balance with the proper material and weigh the amount of tissue of the turtle sample. Record the weight along with the information previously recorded on the processing records. The sample may now be stored pending homogenization in the appropriate jar.

14.10.8 If processing frogs, allow the frogs to partially thaw, take the project specific measurements, and record them on the processing records. The number of frogs required to make up one sample, and the weight and length of the individual frogs, must be taken and recorded, if specified. In all cases, the skin must be removed from the frog prior to processing and chopped into smaller pieces, due to its thickness. It will then be added to the processor with the whole body of the frog, or it may be discarded depending upon the project specifications.

14.10.9 To skin the frog, make an incision, using the proper utensils, and cut into an area where there is an excess of skin, most likely around the neck. Slowly, pull the skin off of the frog using dissecting scissors, or a ceramic or titanium paring knife, as needed. Once skin is removed, chop it up into tiny pieces using the appropriate knife and set it aside to be processed with the whole frog body.

14.10.10 Cover the balance with the proper material and weigh the amount of tissue obtained from the frog samples if the tissue and the whole body will not be processed. Record the weight along with the information previously recorded on the processing records. The sample may now be stored pending homogenization in the appropriate jar.

14.10.11 Since the amount of tissue obtained from one small turtle or frog may be insignificant, several specimens may be combined to make up one sample. Utensils do not need to be rinsed between the individual samples that comprise one composite, but utensils must always be rinsed in between each composite sample.

14.10.12 If several specimens will be composited to make up one sample, the tissue obtained from each specimen may be weighed and recorded individually, then totaled for the composite weight. If only the composite weight is sufficient for the project specifications, weigh the entire composite and record that weight.

14.10.13 After the tissue has been removed from all of the specimens, homogenize the muscle tissue, and skin if required, by placing it into the small or large food processor fitted with the appropriate blades. The sample may need to be cut into smaller pieces for processing. Grind the sample until it appears to be fully and consistently homogenous. Continue to grind the sample until there are no chunks present in the homogenate.

14.10.14 Individual homogenates may be processed further to prepare composite homogenates as required by project specifications. Composite homogenates must be prepared from equal weights of individual homogenates. All individual weights that make up one composite must be recorded, if required, or one composite weight may be recorded. If individual or composite homogenates were frozen prior to extraction/digestion, these homogenates must be thawed and re-homogenized by hand mixing prior to being extracted or digested.

14.10.15 Place the processed samples into the freezer to be frozen for future extraction/digestion..

14.10.16 All utensils and equipment must be washed in between samples according to the procedures described previously in Section 12.2.

14.11 Macro Invertebrates (Benthic Worms, Eels, Insects and other Biota):

14.11.1 Wash all utensils, the cutting board, and surfaces as previously described in Section 12.2. Obtain samples from the freezer.

14.11.2 Cover the balance tray with the appropriate material and record the weight of the invertebrate sample. Since the weight obtained from one invertebrate (benthic worm, insect, biota) may be small, several invertebrates may be combined to make one sample. In many cases, several invertebrates of the same species and sample location are delivered to the laboratory in one sample jar. Each specimen from this jar must be weighed, if requested, and composited to form one homogenized and unique sample. If only one composite weight is sufficient for the project specifications, weigh the entire composite and record that weight. Utensils do not need to be rinsed between the individual samples or specimens that comprise one composite, but utensils must always be rinsed between each composite sample.

14.11.3 Invertebrates such as eels must be chopped into smaller pieces before homogenization. This is generally due to the length of the specimen and the thickness of the skin.

14.11.4 Place the weighed specimen into the clean small processor with the titanium blade to be homogenized. Process the sample until it appears to be fully and consistently homogenized and there are no large chunks.

14.11.5 Individual homogenates may be processed further to prepare composite

homogenates as required by project specifications. Composite homogenates must be prepared from equal weights of individual homogenates. All individual weights that make up one composite must be recorded, if required, or one composite weight may be recorded. If individual or composite homogenates were frozen prior to extraction/digestion, these homogenates must be thawed and re-homogenized by hand mixing prior to being extracted or digested.

14.11.6 Place the processed samples into the appropriate glass jars to be frozen for future extraction/digestion, into the freezer.

14.11.7 All utensils and equipment must be washed in between samples according to the procedures described previously in Section 12.2.

14.12 <u>Vegetation (Coastal and Wetland Grasses/Plants):</u>

14.12.1 Wash all utensils, the cutting board, and surfaces as previously described in Section 12.2. Obtain samples from the freezer.

14.12.2 Wearing the appropriate gloves, plants must be rinsed with DI water to remove soil, silt, small insects, and other debris. Place the plants in a stainless steel or plastic strainer, depending on the determinative sample analysis, and rinse thoroughly with DI water. If analyzing the sample for both metals and organic compounds, rinse the plants carefully over a sink, being sure not to touch the sides of the sink with the plant sample.

14.12.3 Depending on the size and texture of the plants, some may be homogenized in the small food processor with the titanium blade. Samples such as long grass will have to be chopped into small pieces (approximately ½ inch) using titanium or ceramic knives. Leaves can generally be homogenized in the small food processor without pre-cutting.

14.12.4 Cover the balance tray with the appropriate material and record the weight of the plant sample. Since the weight obtained from one plant may be small, several plants may be combined to make one sample. Utensils do not need to be rinsed between the individual samples that comprise one composite, but utensils must always be rinsed in between each composite sample.

14.12.5 If several plants will be composited to make one sample, the weight of each specimen may be recorded individually, and then totaled for the composite weight. If only one composite weight is sufficient for the project specifications, weigh the entire composite and record that weight on the processing records.

14.12.6 After the plant weight for one composite or individual sample has been recorded, place the plant(s) in the clean small processor with the titanium blade to be homogenized, or place them onto the cleaned cutting board to be chopped. Grind or chop the plants until they appear to be fully homogenized.

14.12.7 Individual homogenates may be processed further to prepare composite

homogenates as required by project specifications. Composite homogenates must be prepared from equal weights of individual homogenates. If required, all individual weights that make up one composite must be recorded, otherwise one weight may be recorded for the composite. If individual or composite homogenates were frozen prior to extraction/digestion, these homogenates must be thawed and re-homogenized by hand mixing prior to being extracted or digested.

14.12.8 Place the homogenized plants back into the freezer to be frozen for future extraction/digestion.

14.12.9 All utensils and equipment must be washed between samples according to the procedures described previously in section 12.2.

15.0 CALCULATIONS

15.1 *Not Applicable.*

16.0 METHOD PERFORMANCE

16.1 *Not Applicable.*

17.0 POLLUTION PREVENTION

17.1 Refer to SOP NEA054 and NEA089 for instructions on the disposal of waste generated during the procedures previously mentioned.

18.0 DATA ASSESSMENT AND ACCEPTANCE CRITERIA FOR QUALITY CONTROL MEASURES

18.1 *Not Applicable*.

19.0 CORRECTIVE ACTIONS FOR OUT OF CONTROL DATA

19.1 *Not Applicable.*

20.0 CONTINGINCIES FOR HANDLING OUT-OF-CONTROL OR UNACCEPTABLE DATA

20.1 *Not Applicable.*

21.0 WASTE MANAGEMENT

21.1 Refer to SOP NEA054 and NEA089 for instructions on the disposal of waste generated during the procedures previously mentioned.

22.0 REFERENCES

22.1 NELAP "Quality Systems" Manual, 2005.

22.2 U.S.EPA SW-846 "Test Methods for Evaluating Solid Waste; Volume 1B Laboratory Manual Physical/Chemical Methods", Office of Solid Waste and Emergency Response, Third Edition, Final Update III, December 1996.

22.2 EPA/6OOIR-961027, Guidance for the Preparation of Standard Operating Procedures (SOPS) for Quality Related Documents, 1996.

22.3 US EPA 823-R-95-007, "Guidance for Assessing Chemical Contaminated Data for Use in Fish Advisories", Volume 1: Fish Sampling and Analysis 2nd Edition, Office of Science and Technology, Office of Water, 1995.

23.0 TABLES, DIAGRAMS, FLOWCHARTS and VALIDATION DATA

23.1 Sample Bench Sheet.

NEA SAMPLE PROCESSING/ORGAN HARVESTING

SAMPLE INFORMATION:

Client ID: _____ Project: _____

NEA Lab ID: _____ LRF Number: _____

Species: _____

Whole Body Weight (g):_____ Length (inches):_____

Gender (Male/Female/Not visible):_____

ORGAN HARVEST:

1) Organ: _____ (Liver, Stomach, Gonads, etc.) Collected: Y N

Date of Harvest: _____ Time of Harvest: _____

Equipment Type: _____ (Stainless steel, Ceramic, etc.)

Organ Weight (g): _____ Organ Appearance: _____ Organ Preservation Y N

Formalin:____mLs used Lot #_____ Sample Storage: Freezer□ Cold Room □ Bench □

Jar Type: Glass Non Sterile□, Glass Sterile □, Plastic□

Client ID: _____NEA ID: _____

Personnel: _____, _____

2) Organ: _____ (Liver, Stomach, Gonads, etc.) Collected: Y N

Date of Harvest: _____ Time of Harvest: _____

Equipment Type: _____ (Stainless steel, Ceramic, etc.)

Organ Weight (g): _____ Organ Appearance: _____ Organ Preservation Y N

Formalin:____mLs used Lot #_____ Sample Storage: Freezer□ Cold Room □ Bench □

Jar Type: Glass Non Sterile□, Glass Sterile □, Plastic□

Client ID: _____NEA ID: _____

Personnel: _____, _____

APPENDIX 49
SOP FOR THE EXTRACTION AND CLEANUP OF PCBS FROM FISH AND BIOTA MATERIAL (NE17_07_R01)

STANDARD OPERATING PROCEDURE

NORTHEAST ANALYTICAL, INC.

NE017_07.DOC
REVISION NUMBER: 07

EXTRACTION AND CLEANUP OF FISH AND BIOTA MATERIALS BY EPA METHODS 3540 AND 8082 FOR POLYCHLORINATED BIPHENYL ANALYSIS

COPY #___

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NORTHEASTANALYTICAL, INC
2190 TECHNOLOGY DRIVE
SCHENECTADY, NY 12308

(518) 346-4592

STANDARD OPERATING PROCEDURE

LABORATORY PROCEDURE NE017_07.DOC

REVISION 7 (02/20/09)

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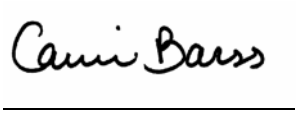
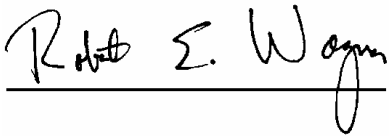


Carrie Barss
Extractions Supervisor

Reviewed by:



Robert E. Wagner
Laboratory Director

Approved by:

Christina L. Braidwood
Quality Assurance Officer

1.0 IDENTIFICATION OF TEST METHOD

1.1 This is a Standard Operating Procedure for the extraction and cleanup of polychlorinated biphenyls from fish and biota material by SW-846 Method 3540 (Soxhlet Extraction).

1.2 This SOP provides the method for extraction of polychlorinated biphenyls (PCB) from fish tissue for analysis by EPA Method 8082.

2.0 APPLICABLE MATRIX AND MATRICES

2.1 This test method is appropriate for all fish and biota material. The extraction technician must have an understanding of the methods and requirements of USEPA-SW- 846A "Test Methods for Solid Wastes" Volume 1B: Lab Manual, 3rd edition. Methods 3540, 3500, 2500A.

2.2 An approved instructor must also certify the extraction technician for performing the procedure. The extraction technician should have completed an acceptable demonstration of precision and accuracy before performing this method without supervision. This method may be restricted to use by or under the supervision of an extraction technician knowledgeable in the area of PCB extraction and clean-up. The extraction technician should further be aware of the proper care and handling of PCBs as well. Refer to MSDS for details.

3.0 DETECTION LIMIT

3.1 See determinative method (Lab SOP NE148) for details.

4.0 SCOPE AND APPLICATION

4.1 The following procedure is used by NEA for the extraction of fish tissue for PCB analysis, although it may be adapted for other biota extractions.

5.0 SUMMARY OF TEST METHOD

5.1 The extraction and cleanup of polychlorinated biphenyls from fish and biota material starts with sample prep such as sexing, de-scaling, filleting, and grinding fish or the grinding of any biota material to be tested. Once ready the sample material needs to be weighed and then dried using 1:1 (magnesium: sodium) sulfate. The material is then transferred to a pre-rinsed cellulose extraction thimble which is then placed into a Soxhlet extractor apparatus to be extracted for 18 ± 2 hours. Once the extraction is complete the solvent is then exchanged to pure hexane utilizing an evaporation system. After solvent exchange, the extract proceeds through several cleaning procedures including acid, florisil, TBA and mercury clean-up. Once cleaned, the solvent extract is ready to dilute for GC analysis.

6.0 DEFINITIONS

6.1 **Laboratory Reagent Blank (B)**: A sample consisting of laboratory grade water run in

parallel with the sample set to evaluate any cross contamination.

6.2 **Lab Control Standard (LCS)**: A non-site sample created in the laboratory in which a known amount of target analyte is added for assessment of analyte recovery efficiency.

6.3 **Lab Control Standard Duplicate (LCSD)**: A replicate of the Lab Control Standard to further assess analyte recovery efficiency.

6.4 **Matrix Spike (MS)**: A site sample to which a known amount of target analyte is added for assessment of analyte recovery efficiency.

6.5 **Matrix Spike Duplicate (MSD)**: A replicate of the Matrix Spike utilizing the same site sample and known amount of target analyte for assessment of analyte recovery efficiency.

7.0 INTERFERENCES

7.1 Laboratory contamination can occur by the introduction of plasticizers (phthalate esters) into the samples through the use of certain plastics. Phthalate esters respond on electron capture detectors, usually as late eluting peaks, and can interfere in PCB quantification. Samples and extracts should not be exposed to plastics such as gloves, tubing, coating on clamps, and pipette bulbs, etc.

8.0 SAFETY

8.1 Polychlorinated biphenyls should be treated with extreme caution; as a class of chemical compounds they possess both toxic and suspected carcinogenic properties. Refer to MSDS for further details.

8.2 The extraction technician should have received in-house safety training and should know the location of the first aid equipment and the emergency spill/clean-up equipment, before handling any apparatus or equipment.

8.3 Safety glasses and gloves must be worn when handling glassware and samples.

9.0 EQUIPMENT AND SUPPLIES

9.1 Water Cooled Condenser: Pyrex 45/50 #3840-MCO (or equivalent)

9.2 250mL Round Bottom Flask: Pyrex #4100 (or equivalent)

9.3 Soxhlet Repetitive Flushing (reflux) Unit: 45/50 Pyrex #3740-M (or equivalent)

9.4 Heating Mantle: Type "VF" laboratory heating mantle #HM0250VF1 (or equivalent)

9.5 Heating Mantle Controller: Glass-Col #PL3122 Minitwin (or equivalent) regulates temperature control of the mantle.

9.6 Analytical Balance: Mettler PL-303 (or equivalent) used to determine sample mass.

9.7 Cellulose Extraction Thimble: Contains sample during Soxhlet extraction.

9.8 Chiller: Pump driven water circulating cooling system cool flow #75 NESLABS Instruments, Inc. (or equivalent)

9.9 TurboVap Evaporator: Zymark #ZW640-3.

9.10 TurboVap Evaporator concentrator tubes: Zymark 250mL, 0.5mL endpoint.

9.11 Beakers: Assorted Pyrex: 250mL, 600mL, and 1000mL, used for liquid containment and pipette storage.

9.12 Vials: glass, 40mL & 4 dram (with polyseal sealed cap) (20 mL & 10 mL) capacity, for sample extracts.

9.13 Vial Rack: Plastic rack used to hold vials, during all phases of the extract processing.

9.14 Centrifuge: International Equipment Co., Model CL. (or equivalent)

9.15 Wrist Shaker: Burrell wrist action shaker, Model 75 and 88. (or equivalent)

9.16 Pipettes: S/P Disposable Serological Borosilicate Pipettes.

1. 1mL X 1/10
2. 5mL X 1/10
3. 10mL X 1/10
4. Fisher Pasteur Borosilicate glass pipette 9" #72050 (or equivalent)

9.17 Aluminum weigh dishes: Eagle Thermo Plastics, #64-D70-100-PK (or equivalent)

9.18 4oz. Jars: Industrial Glassware

9.19 Micro-blowdown Apparatus

10.0 REAGENTS AND STANDARDS

10.1 Sodium Sulfate: J.T.Baker, #3375-05 Anhydrous, Granular (12-60 Mesh) (or equivalent). Used for the laboratory method blank and laboratory control spike.

10.2 Boiling Chips: Chemware PTFE Boiling Stones, P#0919120 (or equivalent)

10.3 Hexane: High Purity Solvent Baxter (Burdick/Jackson) #UN1208. (or equivalent)

10.4 Acetone: High Purity Solvent Baxter (Burdick/Jackson) #UN1090. (or equivalent)

10.5 1:1 Hexane/Acetone: 50%/50% by volume solvent mixture prepared in the lab.

10.6 Florisil: deactivated, Tested and Approved, see NE095.SOP

10.7 TBA Reagent: Tetrabutylammonium Hydrogen-Sulfite Reagent (prepared in the laboratory)

10.8 Mercury: Triple distilled Mercury Waste Solutions, Inc. (or equivalent)

10.9 Sulfuric Acid: Na_2SO_4 (concentrated) Malinkrodt #2468 #UN1830. (or equivalent)

10.10 1:1 Magnesium Sulfate/Sodium Sulfate: 1:1 by volume, mixture prepared in the lab.

10.11 Sodium Sulfite: Sigma – Aldrich, #23932-1 (or equivalent)

10.12 Propanol: JT Baker, #11-9095-03 (or equivalent)

11.0 SAMPLE COLLECTION, PRESERVATION, SHIPMENT and STORAGE

11.1 All samples should remain frozen at all times unless being tested. Fish usually arrive whole bodied or already filleted. Once received, the sample must be ground and homogenized so that it may be analyzed. The homogenized fish tissue should be held for 6 to 12 months.

11.2 The fish solvent extracts should be held for 3 months. Some clients may request that the body and/or head of fish be saved once the fillets are cut out. Other biota material may have other specifications stated specifically for that project.

12.0 QUALITY CONTROL

12.1 A Method Blank and a Laboratory Control Sample is run with each sample batch. Every 20^{th} sample batch is run with a Matrix Spike and Matrix Spike Duplicate. Clients also have the option of requesting that a Matrix Spike and Lab Control Standard Duplicate be run with their specific sample set (see **Section 6.0** for nomenclature).

12.2 Please see determinative method (Lab SOP NE148) for details.

13.0 CALIBRATION AND STANDARDIZATION

13.1 The analytical balance should be calibrated daily to ensure accurate measurements are made when weighing out samples for extraction.

13.2 Please see determinative method (Lab SOP NE148) for details.

14.0 PROCEDURES

14.1 Sample Preparation

14.1.1 Throughout the entire process it should be noted that if the extraction technician encounters any problems or difficulties with any samples or steps involved, all work should STOP! Any problems should be brought to the attention of the supervisor and documented in LIMS.

14.1.2 The extraction technician should match each sample container label to the chain of custody identification number which is in the job folder.

14.1.3 The fish samples are usually received as fillets and must be processed to produce a homogenous material prior to extraction. Once the sample has been logged into LIMS, the sample is processed according to SOP NE132.SOP.

14.1.4 The sample is then placed into the freezer (R-4) for storage until the extraction process is started.

14.2 Procedure: Sample Extraction

14.2.1 Rinse enough cellulose extraction thimbles for one per sample and QC sample with Hexane. Allow them to dry out in a 4oz. jar in a fume hood.

14.2.2 Fill a Pyrex pan with ice cubes and cold water to about a 1/2 inch deep.

14.2.3 Into a pre-cleaned and tared 4oz. jar, accurately weigh to the nearest 0.001g, using an analytical balance, between 9-10 grams of homogenized tissue with a metal spatula. Record this weight in LIMS. Place the beaker containing the sample into the Pyrex pan to chill. Repeat for remaining samples.

Note: All sample containers are to be returned to the appropriate refrigerator / freezer. For all empty containers, see the Chemical Hygiene Plan for proper disposal.

14.2.4 After the sample has been sufficiently chilled, add approximately 10 g. of a 1:1 mix of magnesium sulfate/sodium sulfate to the sample and mix well with the metal spatula. If the sample has not dried after a few minutes, another 10 g may be added. Once the sample is well-dried and free flowing, transfer the sample to an extraction thimble using the same metal spatula.

Note: Be careful not to add too much drying agent to the sample, if too much is added, the sample may not fit completely into the thimble. In this case the sample will have to be split into two separate Soxhlet apparatus set-ups and re-combined following extraction.

14.2.5 Add several boiling chips to a 250 mL round bottom flask. Then add 200mL of a 1:1 Hexane/Acetone mixture. Place a Soxhlet extractor onto the round bottom flask, checking for cracks or chips that would cause solvent to leak out. Label the round bottom flask with the sample number and place the corresponding thimble into the Soxhlet extractor using long tweezers. Record the round bottom and soxhlet number in LIMS. Repeat for each sample, rinsing tweezers between samples.

14.2.6 Spike surrogate and spike compound solutions directly into the soxhlet into the thimble. The addition of spiking material to a sample, blank, or QC must be witnessed by another extraction technician. Record the names of the technicians

spiking and witnessing, surrogate and spike concentration, the amount spiked, and the spike solution reference code in LIMS.

14.2.7 Rinse the inside and the outside connecting joints of the condenser units that will be used with hexane. Then, turn on chiller to cool the condensers. Chiller should be set to approximately 12°C.

14.2.8 Place the round bottom flask with attached Soxhlet extractor into a heating mantle and attach condenser unit. Turn corresponding thermostats on to setting 5. Double check Soxhlets at this time for any cracks or chips, which may leak solvent. Once the solvent begins to boil, a flushing action of once every two to three minutes should be achieved.

14.2.9 The samples should be extracted for a minimum of 16 hours, usually overnight. Once the sample has finished extracting (usually in the morning), turn the heating mantle off and allow samples to cool to room temperature. Disengage the condenser from the Soxhlet and move the unit to a fume hood.

14.2.10 Move Soxhlet units into a chemical fume hood and flush the remaining solvent from the Soxhlet extractor by tipping the Soxhlet. Using a pair of long-handled tweezers, pull the thimbles out of the Soxhlets one at a time and allow them to drip dry by balancing the thimbles on the tops of the Soxhlets. Once dry, remove the thimbles to a sheet of aluminum foil for total solvent evaporation then dispose of them into solid PCB waste.

14.2.11 Rinse the Soxhlet with Hexane and tip again to drain into the round bottom flask. Disconnect the soxhlet from the round bottom and rinse the connecting joint of the soxhlet into the round bottom. Set aside the Soxhlet at this time.

14.2.12 Procure the same number of TurboTubes as there are samples. Rinse turbo tubes with hexane, and label with the corresponding sample ID number and place in a holder.

14.2.13 Add sodium sulfate to each round bottom, swirling contents. Add as much sodium sulfate as necessary until the drying agent is free flowing.

14.2.14 Decant the contents of the round bottom into the Turbo Tube, using a pipette and Hexane to rinse the last drops out of the mouth of the round bottom flask, making sure not to transfer any boiling chips or sodium sulfate. Rinse the round bottom with several pipettes full of Hexane, swirl gently, and decant into same Turbo Tube. Repeat the rinse twice more, then repeat all preceding steps for each sample.

14.2.15 All glassware must be rinsed with technical grade Acetone or a "for rinsing-only" labeled solvent, and dried in the hood before proceeding to other cleaning steps.

14.3 Solvent Reduction: TurboVap Evaporator System

14.3.1 The TurboVap evaporator system is used in place of the Kuderna Danish (KD)-

concentrator apparatus. The TurboVap evaporator system is used to reduce the sample volume. The TurboVap uses a heated water bath and positive pressure nitrogen flow / vortex action. The unit maintains a slight equilibrium imbalance between the liquid and gaseous phase of the solvent extract, which allows fractional reduction of the solvents without loss of higher boiling point analytes.

14.3.2 Turn the unit on and allow to heat up to 40°C $\pm$ 2°C.

14.3.3 As a precaution the TurboVap system regulators should be checked to assure that there is no residual gas pressure within the system and that the gas pressure regulator is off before placing samples in the apparatus. Residual gas pressure may cause splashing and cross contamination of samples. To bleed the system of residual gas pressure place an empty TurboTube into the water bath and close the lid. Make sure that the nitrogen gas pressure regulator is off. Bleed any residual gas until the regulator gauge reads "0" psi. Remove the empty TurboTube.

14.3.4 Wipe down inside of TurboVap with a Hexane wetted paper towel including top lid and pins. Place TurboTubes containing the sample extracts into the TurboVap and close lid. Slowly open the pressure regulator. Keep the gas pressure very low, until the solvent level is decreased, to avoid splashing. Increase the gas pressure as the sample reduces, maintaining uniform flow throughout the volume reduction.

14.3.5 The process for solvent (Hexane/Acetone) reduction takes approximately 20-30minutes. Do not leave the unit unattended as extracts may be blown to dryness and PCB loss may occur. Immediately notify a supervisor if an extract is blown to dryness.

14.3.6 Concentrate the solvent to approximately 10 mL. Remove the samples from the TurboVap and place in the rack. The remaining solvent will consist largely of Hexane since the Acetone component is fractionally removed at a faster rate than Hexane. However, a solvent exchange with Hexane should be completed to ensure the Acetone has been entirely removed.

14.3.7 Fill the turbo tube back up to approximately 200mls with hexane. Concentrate the solvent back to 10mls. Then remove the turbo tube and place in a rack.

NOTE: Not all samples will evaporate at the same rate; sample extracts containing large amounts of petroleum or other non-volatile liquids may stop reducing before the 10.0 mL point is achieved. Samples, which stop reducing, should be removed as soon as possible.

14.3.8 Quantitatively transfer the sample extract with a disposable transfer pipette into an appropriate volumetric flask (25mL for biota extracts) with three 2mL Hexane rinses.

14.3.9 Add Hexane to the volumetric meniscus mark. Invert the volumetric flask at least three times to mix completely. Decant the contents into a pre-labeled 40mL vial and cap.

14.3.10 All dirty glassware must be rinsed with Tech-grade Acetone or a "For Rinsing-Only" labeled solvent and dried in the fume hood before being washed.

14.4 % Lipid Analysis

14.4.1 Label one aluminum weigh dish for each sample. Using an analytical balance accurately weigh each aluminum dish to the nearest 0.0001g and record in LIMS.

14.4.2 Using a pipette, remove 10mLs of the 25x sample completed in step 14.3.9, and place in the aluminum dish.

14.4.3 Blow the sample to dryness using a micro blowdown apparatus.

14.4.4 Once dry, place the dish in a dessicator for a minimum of 4 hours.

14.4.5 After the four hours, weigh the dish a final time using the same analytical balance, and enter the weight into LIMS.

14.4.6 See Section 15.1 for instructions on calculating % lipids.

14.5 Sample Extract Cleanup

14.5.1 Most extracts of environmental samples that are to be analyzed for PCBs by gas chromatography with electron capture detection, contain co-extracted xenobiotics and other interfering substances which must be removed before accurate chromatographic analysis can be performed.

14.5.2 Not all clean-up procedures need to be performed on every sample and several are sample matrix specific. The experience of the analyst combined with the sampling site history should guide the selection of which clean-up procedures are necessary. The sample extraction technician records the cleanup step sequence and number of times performed into LIMS.

14.5.3 Sample extract cleanups are performed on set volume extracts. The default set volume is 25 mL for biota samples.

14.6 Sulfuric Acid Wash

14.6.1 The concentrated sulfuric acid treatment removes hydrocarbons and other organic compounds, which are co-extracted with the PCB residues.

14.6.2 Chill the sample in the freezer for 10-20 minutes. Add 5.0 mL concentrated H_2S0_4 and shake for 30 seconds by hand. Centrifuge for approximately 1 minute on a speed setting of ¾. Transfer the Hexane layer (upper layer) to a new, labeled 40mL vial.

14.6.3 Repeat **Section 14.5.2** if the sample extract appears to be heavily loaded (opaque) with colored material. Two to three acid washes may be required.

Note: it is entirely possible that all colored material will not be removed from

the extract.

14.7 Elemental Sulfur Clean-up

14.7.1 Elemental sulfur is soluble in the extract solvents used for biota samples. It is commonly found in many sediment/soil samples, decaying organic material, and some industrial wastes. Large amounts of sulfur can cause the electron capture detector (ECD) to signal saturate for long periods during the elution envelope of PCBs. Even small amounts of sulfur can interfere with PCB measurement as a co-eluting chromatographic peak.

14.7.2 Two techniques exist for the elimination of elemental sulfur in PCB extracts. Mercuric precipitation (Mercury Shake) and the Tetrabutylammonium (TBA) sulfite procedure. Tetrabutylammonium sulfite causes the least amount of degradation of a broad range of pesticides and organics compounds, while mercury may degrade organophosphorus and some organochlorine pesticides. The TBA procedure also has a higher capacity for samples containing high concentrations of elemental sulfur.

14.7.3 Removal of Sulfur Using Mercury

Note: Mercury is a highly toxic metal. All operations involving mercury should be performed within a hood. Prior to using mercury, the extraction technician should become acquainted with proper handling and emergency spill/clean-up procedures associated with this metal and must have reviewed the material safety data sheet MSDS.

14.7.3.1 Add 1-3 drops of mercury to the sample extracts, cap vial, and place on the wrist shaker for 30 min. The sulfur is converted to mercuric sulfide and precipitates out of the sample extract. A black precipitate may be seen in sample extracts containing elemental sulfur.

14.7.3.2 Transfer the sample extract to a clean and properly labeled 40mL vial.

14.7.3.3 The precipitated sulfur can be removed from the extract by performing a sulfuric acid clean-up or Florisil slurry (**Section 14.8**).

14.7.4 Removal of Sulfur using TBA Sulfite

14.7.4.1 The TBA procedure removes elemental sulfur by converting it to the thiosulfate ion, which is water soluble.

14.7.4.2 Add 2.0mL TBA Sulfite Reagent, 1.0 mL 2-propanol, and approximately 1 aliquot (using the dedicated scoop) of sodium sulfite crystals to the extract.

14.7.4.3 Place the samples on the wrist shaker for 45 minutes observing at 15 minute intervals to make sure that the sodium sulfite is not consumed.

14.7.4.4 After 45 minutes, add 5mL organic free water (DI water) and shake for ten additional minutes on the wrist shaker.

14.7.4.5 Place the samples into the centrifuge and spin for approximately 2 minutes on a speed setting of ¾.

14.7.4.6 Transfer the Hexane layer (top layer) to a new and properly labeled 40mL vial and cap.

14.8 Florisil Adsorption (Slurry)

14.8.4 The Florisil slurry removes co-extracted polar compounds, residual water, and residual acid and is recommended as the final cleanup step before the extract is submitted for GC analysis.

14.8.2 Add approximately 1.5 grams of tested and approved deactivated Florisil to each vial containing the sample extract.

SEE SUPERVISOR FOR THE APPROPRIATE FLORISIL DEACTIVATION CONCENTRATION TO BE USED.

14.8.3 Vigorously shake the vial for approximately 1 min by hand or on the wrist shaker.

14.8.4 Place the vial(s) into the centrifuge for 2 minutes on a speed setting of ¾.

14.8.5 Transfer the extract to a clean and properly labeled 40mL vial.

14.9 Extract Screening and Dilution:

14.9.1 PCB extracts are generally screened by GC initially to determine the approximate concentration before final analysis. Prior site history and client supplied estimates of sample concentration may be used to determine what, if any, extract dilution is necessary. Extracts of unknown concentration are generally screened at a 10 to 100 fold dilution.

14.9.2 The supervisor is responsible for determining initial screening dilutions. Extract dilutions are prepared by transferring an aliquot of the original sample extract into a vial containing the correct amount of "make up" volume of Hexane. For example, adding 1.0 mL of the extract to 9.0 mL Hexane performs a 1 to 10 dilution. The vial containing the diluted extract is labeled denoting the equivalent extract volume after the dilution; e.g. a 25mL extract diluted 1 to 10 is labeled "250X", an undiluted 25mL extract is labeled "25X". When high dilutions are prepared, secondary (serial) dilutions of the initial diluent are prepared; e.g. a 100 fold dilution is prepared by a 1 to 10 dilution of the initial extract, then a 1 to 10 dilution of the resulting diluent.

14.9.3 Perform the dilution using an appropriate disposable volumetric pipette to transfer the extract and the make-up volume of Hexane. Make sure that the vial is properly labeled. Cap and invert the vial at least three times to thoroughly mix the extract with

the solvent.

14.9.4 Transfer 1 mL of the extract to a labeled 1.5 mL GC autosampler vial. Record the screening dilution in LIMS along with the extract volume, and the sample mass. Submit the sample extracts to the GC analyst.

15.0 CALCULATIONS

15.1 All fish samples require a % lipid analysis, see section 14.4. The lipid content is calculated utilizing the below equation:

$$\% \text{ Lipids} = \frac{(\text{Final Wight} - \text{Initial Wight})}{\text{Sample Wight}} \times \frac{\text{Extracted Volume(10 ml)}}{\text{Whole Volume (25ml)}} \times 100$$

15.2 Please see determinative method (Lab SOP NE148) for details.

16.0 METHOD PERFORMANCE

16.1 Please see determinative method (Lab SOP NE148) for details.

17.0 POLLUTION PREVENTION

17.1 See NEA.168.SOP for proper pollution prevention procedures.

18.0 DATA ASSESSMENT AND ACCEPTANCE CRITERIA FOR QUALITY CONTROL MEASURES

18.1 Please see determinative method (Lab SOP NE148) for details.

19.0 CORRECTIVE ACTIONS FOR OUT OF CONTROL DATA

19.1 Please see determinative method (Lab SOP NE148) for details.

20.0 CONTINGINCIES FOR HANDLING OUT-OF-CONTROL OR UNACCEPTABLE DATA

20.1 Please see determinative method (Lab SOP NE148) for details.

21.0 WASTE MANAGEMENT

21.1 See NEA054.SOP, NEA083.SOP, and NEA089.SOP

22.0 REFERENCES

22.1 SW-846 methods 3500A & 3600A; United States Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Vol.1B, Cincinnati, OH 45268.

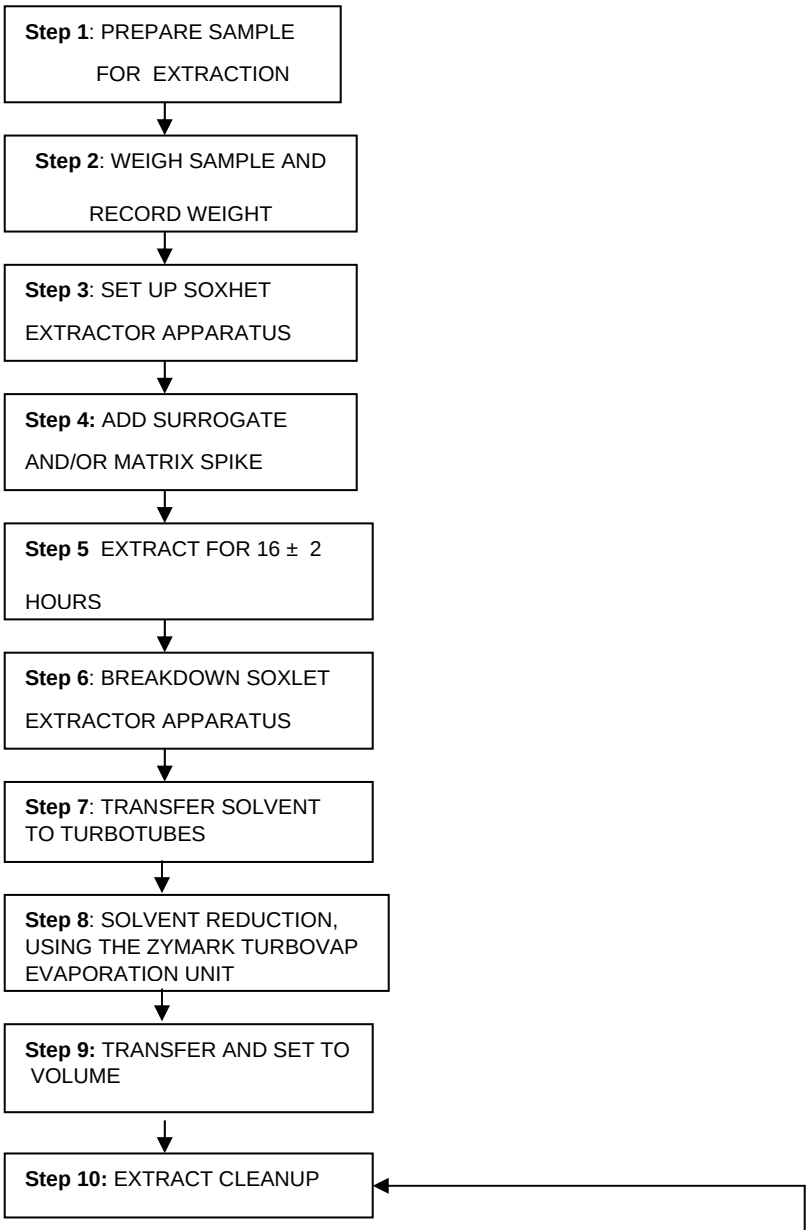
22.2 Guide to Environmental Analytical Methods, Genium Publishing Corporation,

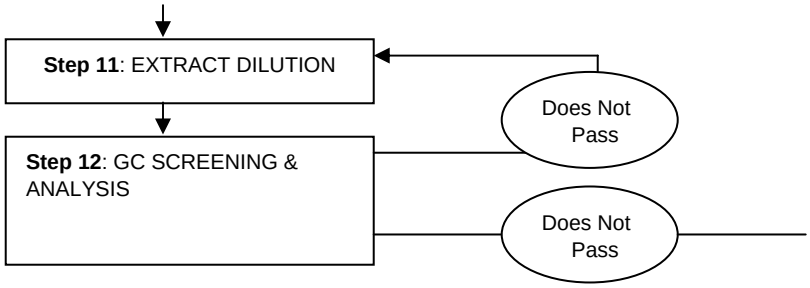
Schenectady, NY 12304.

23.0 TABLES, DIAGRAMS, FLOWCHARTS and VALIDATION DATA

23.1 **Attachment A**: Flowchart for the Extraction and Clean-up of Fish and Biota Materials for PCB Analysis

ATTACHMENT A: FLOWCHART FOR THE EXTRACTION AND CLEAN-UP OF FISH AND BIOTA MATERIALS FOR PCB ANALYSIS





STANDARD OPERATING PROCEDURE REVIEW

SOP Name	Review Number	Reviewers	Title	QAO Approval	Effective Date
NE017_07	01	Carrie Barss Christina L. Braidwood Robert E. Wagner	Extractions Sup. QAO Lab Director	Christina Braidwood	02/20/09

APPENDIX 50
SOP FOR THE ANALYSIS OF PCBS IN SEDIMENT BY SW-846 METHOD 8082 (GEHR8082)

STANDARD OPERATING PROCEDURE (SOP) GEHR8082

1.0 Title: General Electric (GE) Hudson River Remedial Action Monitoring Program (RAMP) Standard Operating Procedure for the analysis of Polychlorinated Biphenyls (PCBs) by SW-846 Method 8082

Capillary Column

Standard operating procedure for the analysis of Polychlorinated Biphenyls by Gas Chromatography with Electron Capture Detection and Total Aroclor Quantification.

(Acknowledgment: This SOP is based substantially on internal method SOPs provided by Northeast Analytical, Inc. of Schenectady, N.Y.)

2.0 Purpose

The purpose of this SOP is to provide a detailed written document for measurement of Polychlorinated Biphenyls (PCBs) according to SW-846 Method 8082 specifications.

3.0 Scope

3.1 This SOP is applicable to the determination and quantification of PCBs as outlined in EPA SW-846 Method 8082 for the GE Hudson River RAMP. It is applicable to the sediment/solid samples.

3.2 The following compounds can be determined by this method:

Compound	CAS Number
Aroclor-1016	12674-11-2
Aroclor-1221	11104-28-2
Aroclor-1232	11141-16-5
Aroclor-1242	53469-21-9
Aroclor-1248	12672-29-6
Aroclor-1254	11097-69-1
Aroclor-1260	11096-82-5

3.3 In general, samples are extracted, with a pesticide-grade solvent. The extracts are further processed by concentrating or diluting, depending on the PCB concentration, and carried through a series of clean-up techniques. The sample is then analyzed by injecting the extract onto a gas chromatographic system and detected by an electron capture detector.

3.4 This SOP provides detailed instructions for gas chromatographic conditions, calibration, and analysis of PCBs by gas chromatography. Sediment extraction procedures are covered in separate standard operating procedures.

4.0 Comments

4.1 One of the major sources of interference in the analysis of PCBs is that organochlorine pesticides are co-extracted from the samples. Several of the commonly found pesticides and associated degradation products (DDT, DDE, DDD) overlap the PCB profile envelope and co-elute with several PCB GC peaks and therefore cannot be accurately measured. The analyst must be careful in chromatographic pattern review and flag peaks that are suspected of being contaminated so that they are not included in the total PCB values generated.

4.2 Laboratory contamination can occur by introduction of plasticizers (phthalate esters) into the samples through the use of flexible tubing. Samples and extracts should not be exposed to plastic materials. Phthalate esters respond on electron capture detectors, usually as late eluting peaks, and can interfere in PCB quantification.

5.0 Safety

5.1 Safety glasses and disposable gloves must be worn when handling samples and extracts.

5.2 All manipulations of sample extracts should be conducted inside a chemical fume hood. The analyst should minimize manipulation of sample extracts outside of a fume hood.

5.3 Safe laboratory practices should be followed by the analyst at all times when conducting work in the lab. The analyst should refer to the reference file of material safety data sheets to familiarize themselves with the precautions of handling applicable solvents and chemicals used to process samples. The analyst should refer to the project laboratory's internal chemical hygiene plan for further safety information.

5.4 Samples remaining after analysis should be disposed of through the project laboratory's internal disposal plan. Refer to the project laboratory's internal standard operating procedures for disposal of laboratory waste.

6.0 Requirements

6.1 Extensive knowledge of this standard operating procedure and SW-846 Method 8082 is required.

6.2 The analysis portion of this method should be performed by a skilled chemist or by an analyst trained in the quantification of trace organics by gas chromatography.

7.0 Equipment

7.1 Instrumentation

7.1.1 Gas chromatograph: Varian Model 3400 or equivalent, equipped with Model 1077 split/splitless injector or equivalent, temperature programmable oven, electron capture detector, and Model 8100 autosampler or equivalent.

7.1.1.1 Column - A 30 meter, 0.25 mm ID, 0.25-micron phase DB-1 capillary column is used for analysis.

7.1.2 Chromatographic Data System: A data system for measuring peak height and peak area. A Millennium_32 computer network based workstation (Waters Associates) or equivalent, will be employed to capture detector response and digitally store the chromatographic information. This system will allow for chromatographic review of

data from the gas chromatograph, electronic peak integration for precise calculations, database structuring of the analytical information, and archival capabilities.

7.2 Glassware and Accessories

7.2.1 25-mL volumetric flasks, Class A, (Baxter Cat. No. F4635-25 or equivalent)

7.2.2 5-mL volumetric flasks, Class A, (Baxter Cat. No. F4635-5 or equivalent)

7.2.3 10-mL volumetric flasks, Class A, (Baxter Cat. No. F4635-10 or equivalent)

7.2.4 50-mL volumetric flasks, Class A, (Baxter Cat. No. F4635-50 or equivalent)

7.2.5 100-mL volumetric flasks, Class A, (Baxter Cat. No. F4635-100 or equivalent)

7.2.6 4-dram vials for sample extract storage
(Kimble Opticlear, part no. 60910, code no. 60910-4 or equivalent)

7.2.7 8-dram vials for sample extract storage (Kimble Opticlear, part no. 60910, code no. 60910-8 or equivalent)

7.2.8 Pasteur pipettes (Kimble, part no. 72050 or equivalent)

7.2.9 250-mL beakers, glass (Baxter Cat. No. B2650-250 or equivalent)

7.2.10 100-mL beakers, glass (Baxter Cat. No. B2650-100 or equivalent)

7.2.11 Disposable 10-mL pipettes (Baxter P4650-110 or equivalent)

7.2.12 Disposable 5-mL pipettes (Baxter P4650-15 or equivalent)

7.2.13 Disposable 1.0-mL pipette (Baxter P4650-11X or equivalent)

7.3 Chemicals

7.3.1 Pesticide-Grade Hexane, Burdick and Jackson, (Cat. No. 216-4) or equivalent

7.3.2 Pesticide-Grade Acetone, Burdick and Jackson, (Cat.No.010-4) or equivalent

7.3.3 Pesticide-Grade Toluene, Baker, (Cat. No. 9336-03) or equivalent

7.3.4 Pesticide-Grade Methylene Chloride, Burdick and Jackson, (Cat. No. 300-4) or equivalent

7.4 Analytical Standard Solutions

7.4.1 Aroclor Stock Standard Solutions

7.4.1.1 Polychlorinated Biphenyls - Neat commercial material for standard preparation. These materials are multi-component mixtures of PCB congeners and are the actual materials that were used in products such as electric power transformers and capacitors. Commercially-prepared stock standards can be used if they are certified by the manufacturer or by an independent source and traceable to National Standards of Measurement.

7.4.1.2 Stock standards are prepared from individual Aroclor formulations by weighing an exact amount of the neat material to the nearest 0.1 mg, and dissolving and diluting to volume in a 100 mL volumetric flask with hexane. See Attachment A, Table 1 for an example of exact weights of each compound. For decachlorobiphenyl (DCB), dissolve neat formulation in 10 mL of toluene and then transfer to a 100 mL volumetric flask bringing to volume with hexane. Alternatively, commercially-prepared stock standards may be used providing they are traceable to National Standards of Measurement.

7.4.1.3 The stock standards are transferred into Boston bottles and stored in a refrigerator at 0-6°C, protected from light.

7.4.1.4 Stock PCB standards must be replaced after one year, or sooner if comparison with certified check standards indicate a problem. See 8.5.3 for limits.

7.4.1.5 The labeling and tracking of standards should be in accordance with the project laboratory's internal standard operating procedures for preparation of standards. Labeling of standards should also be in accordance with NELAC standards, section 5.10.5.

7.4.2 Calibration Standards

7.4.2.1 Calibration standards are prepared at five concentration levels using a prepared working standard. See Attachment A, Table 2 for an example of the preparation and exact concentrations of the working standards. The following five standards make up the initial calibration curve standard set for each of Aroclor-1221, Aroclor-1242, and Aroclor-1254: 20 ng/mL, 100 ng/mL, 250 ng/mL, 500 ng/mL, and 1000 ng/mL. One calibration standard at 50 ng/mL, which is below the reporting limit (80 ng/mL) will be prepared for each of Aroclor-1016, Aroclor-1232, Aroclor-1248, and Aroclor-1260 (unless observed to be present in a project sample which would require recalibration for the detected

Aroclor at the five standard levels used for Aroclor-1221, Aroclor-1242, and Aroclor-1254).

7.4.2.2 The two surrogates tetrachloro-*meta*-xylene (TCMX) and DCB are included in the Aroclor-1254 calibration standards. The stock standard for TCMX is prepared by diluting 1 mL of TCMX solution (ULTRA, cat. #IST-440 or equivalent, at 2000 μg/mL) into a 100-mL volumetric flask resulting in a solution of TCMX at 20 ppm.

7.4.2.3 To prepare the working surrogate standard, pipet 5.0 mL of the 100ppm DCB stock standard and 2.5 mL of the 20 ppm TCMX stock standard into a 100 mL volumetric flask and bring to volume with hexane. The final concentration of this solution will be 5.0 ppm of DCB and 0.5 ppm of TCMX.

7.4.2.4 Refer to Attachment A, Table 4 for an example of the instructions on preparation of the calibration standards containing Aroclor-1254 and the surrogates. Refer to Attachment A, Table 3 for an example of the instructions on preparing the remaining calibration standards.

7.4.2.5 Transfer all calibration standards to 8-dram vials (or equivalent) and store in a refrigerator at 0-6°C, protected from light. Calibration standards must be replaced after six

months, or sooner, if comparison with check standards indicates a problem. See 8.5.3 for acceptance limits.

7.4.3 Continuing Calibration Check Standards

7.4.3.1 Continuing calibration check standards are prepared independently from calibration standards, by using an alternate source purchased from standard vendors. Continuing calibration check standards will be prepared for Aroclor-1221, Aroclor-1242, and Aroclor-1254 (and other Aroclors, if detected). All continuing calibration check standards will contain the surrogate compounds TCMX and DCB. Refer to Attachment B, Tables 1-3 for instructions on preparation of these standards.

8.0 Procedure

8.1 Gas Chromatographic Operating Conditions

8.1.1 Establish the gas chromatograph (GC) operating parameters as follows:

Autosampler parameters: Multi-vial mode, ECD Attenuation and range are 1. Refer to Attachment C for all other GC operating procedures.

Note: GC helium gas flow is optimized after instrument maintenance by adjusting nitrogen flow to elute a PCB calibration standard to a known retention time.

8.2 Data Acquisition

8.2.1 Chromatographic information will be collected and processed utilizing a computer based data acquisition workstation (Waters Associates, Millennium_32 computer network based workstation or equivalent). The GC workstation acquires the millivolt detector signal, performs an analog to digital conversion and stores the digital chromatogram on the computer network's disk. The chromatography software performs all data reduction including, long term data storage on magnetic media, chromatographic peak integration, all calculations, report generation, chromatogram plots, and calibration functions.

8.3 Initial GC Calibration

8.3.1 GC calibration will be performed by the external calibration procedure. Prior to running samples the system must be calibrated and system performance must be verified.

8.3.2 Establish the gas chromatographic operating parameters outlined in Section 8.1. Five calibration standard levels are to be prepared for each Aroclor-1221, Aroclor-1242, and Arclor-1254 and the surrogate compounds TCMX and DCB and one calibration standard level (at 50 ng/mL) is to be prepared initially for each Aroclor-1016, Aroclor-1232, Aroclor-1248 and Aroclor-1260 as discussed in section 7.4.2. If Aroclor-1016, Aroclor-1232, Aroclor-1248 or Aroclor-1260 is detected in any project sample based on the single-point calibration, the affected samples must be reanalyzed after a five-point calibration for the detected Aroclor.

8.3.3 Inject each calibration standard using the GC autosampler and the parameters outlined in section 8.1, which are those used for actual samples.

8.3.4 For each Aroclor, 5 peaks are selected to prepare calibration curves (or calibration factor for single-point calibrations). The peaks selected from the multi-component Aroclor formulations were based on maximizing the separation for each Aroclor (*i.e.*, minimizing peak overlap in retention time). Consideration was also given to selecting peaks that normally did not have problems with co-elution with interfering peaks or possible co-elution with organochlorine pesticides. The determined area of the five peaks selected for

calibration is processed by the data workstation as a group, combining the area for calculations of the calibration factors. The following table lists the Aroclors that are included in the initial calibration and group number that represents the group of peaks selected for that Aroclor for calibration purpose.

Aroclor	Group Number
A1221	1
A1232	2
A1016	3
A1242	4
A1248	5
A1254	6
A1260	7

8.3.5 Attachment D is an example of chromatograms of standards of each Aroclor for a DB-1 column with peaks selected for calibration labeled.

8.3.6 For the initial calibration curve to be considered valid, the percent relative standard deviation must be less than 20% over the working range. In addition, the correlation coefficient for the linear calibration curve must be greater than or equal to 0.99. The linear-fit calibration curve (not forced through zero) is used for quantification in every case and is not replaced with the average calibration factor.

8.4 Retention Time Windows

8.4.1 The GC system should be checked by the analyst to make sure it is functioning properly before establishing retention time windows. Make three injections of each Aroclor at a mid-level concentration throughout a minimum 72-hour time period.

8.4.2 For the 5 peaks selected for calibration of each Aroclor, calculate the standard deviation resulting from the variation in the three retention times for that peak.

8.4.3 The retention time window is defined as plus or minus three times the standard deviation of the three retention time determinations.

8.4.4 If the standard deviation of the selected peak is zero, the standard deviation of the peak eluting after it is used. If it is the last eluting peak that has zero for the standard deviation, then substitute the standard deviation of the peak eluting before the last peak.

8.4.5 Retention time (R.T.) windows established in section 8.4.3 to 8.4.4 may not be practical when samples containing matrix interferences are injected onto the GC column. The default R.T. window of ± 0.08 minutes is employed when the established windows are below ±0.08 minutes. Besides using retention time windows to assign peaks for quantification, the analyst should rely on their experience in pattern recognition of multi-response chromatographic response exhibited by PCB Aroclors.

8.4.6 Attachment E provides examples of calculated retention time windows generated by the above outlined procedures.

8.5 Gas Chromatographic Analysis

8.5.1 Prior to conducting any analyses on samples, calibrate the system as specified in Section 8.3

8.5.2 To start an analytical sequence, the 500 ppb calibration standard is injected and analyzed for the Aroclor-1221, Aroclor-1242, and Aroclor-1254 after the initial calibration and if more than 24-hours has elapsed since the last valid continuing calibration check standard. If less than 24-hours has elapsed since the last valid continuing calibration check standard, select one 500 ppb continuing calibration check standard (Aroclor-1221, Aroclor-1242, or Aroclor-1254, each containing the surrogate compounds TCMX and DCB). Selection of continuing calibration check standards other than Aroclor-1221, Aroclor-1242, or Aroclor-1254 should be based on anticipated Aroclor contamination that the samples may exhibit. Selection of the continuing calibration check standard after the start of a sequence should also be alternated among the three Aroclors.

8.5.3 The calculated value for each Aroclor and surrogate in the continuing calibration check standard must be $\pm$15% of the true value for it to be valid and analysis to proceed. If this criterion is exceeded, the analyst should inspect the system to determine the cause and perform maintenance as necessary. The system can then be recalibrated and sample analysis can

proceed. **Note:** If a failed continuing calibration check returns to acceptable calibration later in the sequence, samples following the acceptable continuing calibration check will be reported; and samples between the failed continuing calibration check and subsequent compliant continuing calibration check will be reanalyzed. All samples which are not bracketed by valid continuing calibration check standards must be reanalyzed when the system is in-control. The analytical sequence must end with the analysis of the CCCs for each Aroclors-1221, -1242, and -1254 (and/or other Aroclors if to be quantitated).

8.5.4 The daily retention time windows must be established. Use the retention time for the selected 5 peaks of the continuing calibration check standard as the midpoint of the window for that day. If all seven Aroclors were analyzed as the initial calibration or continuing calibration check standard, then establish retention time windows using the retention time plus or minus the windows established in Section 8.4. If not all Aroclors were analyzed as the initial calibration or continuing calibration check standard, use the retention time from these Aroclor standard(s) as the midpoint plus or minus the windows established in Section 8.4 to establish the daily retention time windows. For the remaining Aroclors, go back to the previous time the remaining Aroclors were analyzed as the initial or continuing calibration check standards in the past 24 hours and use those retention times plus or minus the windows established in Section 8.4 to develop daily retention time windows. If greater than 24 hours have elapsed since a particular Aroclor was analyzed as part of the initial or continuing calibration check, the daily

retention time window for that Aroclor will be updated by reference to the surrogate or Aroclor continuing calibration check shift(s).

8.5.6 Each Aroclor and surrogate in all succeeding continuing calibration check standards analyzed during an analysis sequence must also have a percent difference of 15% or less when compared to the initial calibration generated from the 5-point calibration curve.

8.5.7 All succeeding standards in an analysis sequence should exhibit retention times that fall within the daily retention time window established by the first continuing calibration check standard(s) of that analytical sequence. If the retention times are outside the established windows instrument maintenance must be performed and recalibration may be required.

8.5.8 The following is the order that initial calibration standards, continuing calibration check standards, method blanks, QC samples, and samples are placed in an analytical sequence. A continuing calibration check standard is run after every ten injections in the analytical sequence. All analytical sequences must end with a continuing calibration check standard regardless of the number of samples analyzed.

ANALYTICAL SEQUENCE

INJECTION	MATERIAL INJECTED
1	Hexane Blank
2-20	Initial Calibration Standards
21-23	Continuing Calibration Check Standards (Aroclor-1221, Aroclor-1242, and Aroclor-1254 and other Aroclors if reanalysis occurs if other Aroclors were observed in the samples)
24-33	Sample analyses, including method blanks, matrix spikes, matrix spike duplicates, and QC reference check standard (LCS). A maximum of 10 samples between continuing calibration check standards.
34	Continuing calibration check standard

ANALYTICAL SEQUENCE (CONTINUED)

INJECTION	MATERIAL INJECTED
45 and higher	Repeat inject. 24-34 sequence (Alternating continuing calibration check standards between Aroclor-1221, Aroclor-1242, and Aroclor-1254 and other Aroclors [reanalysis occurs if other Aroclors were observed in the samples])
Closing injections:	Continuing calibration check standards (Aroclor-1221, Aroclor-1242, and Aroclor-1254 and other Aroclors [reanalysis occurs if other Aroclors were observed in the samples])

8.6 Quality Control (Refer to Attachment F for a summary of the quality control requirements.)

8.6.1 This section outlines the necessary quality control samples that need to be instituted at the time of sample extraction. The data from these quality control samples is maintained to document the quality of the data generated.

8.6.2 Each analyst must demonstrate competence in accuracy and precision on quality control samples before beginning analysis on samples. This demonstration must be on-going and be repeated if there is any modification to the method.

8.6.3 With each batch of samples to be extracted a method blank is processed. The method blank is carried through all stages of sample preparation and measurement steps. For sediment/solid samples, a laboratory sodium sulfate blank is processed.

8.6.4 The method blank must exhibit PCB levels less than the matrix-defined reporting limit. If the method blank exhibits PCB contamination above the reporting limit, the samples associated with the contaminated blank should be re-extracted and analysis repeated. If there is no original sample available for re-extraction, then the results should be flagged with a "B" indicating blank contamination. The value measured in the blank is reported for those samples associated with the particular blank out of criteria.

8.6.5 At this time, the GE Hudson River RAMP does not require the preparation and analysis of matrix spike and/or matrix spike duplicate samples. If requested in the future, a matrix spike for Aroclor-1221 and Aroclor-1242 at a 3:1 ratio is to be analyzed at a rate of 1 matrix spike per every 20 samples at a Total PCB concentration of 400 ng/mL in the extract (300 ng/mL Aroclor-1221 and 100 ng/mL Aroclor-1242). Also a matrix spike duplicate sample is to be analyzed at a rate of 1 per every 20 samples.

8.6.6 If requested, analyze one unspiked and two spiked samples. Calculate the percent recovery based on Aroclor concentration of both samples as follows:

A = concentration of spiked sample
B = concentration of unspiked sample (background)
T = known true value of the spike

Percent Recovery (p) = 100 (A-B) %/T

Compare the percent recovery calculated with the project limits of 50-150%. If the concentrations of the matrix spikes are *greater* than four times the calculated sample amount then the quality control limits should be applied. If the concentrations of the matrix spikes are *less* than four times the sample than there are no established limits applicable. If the percent recovery falls outside the acceptance range for the given Aroclor used as the spiking analyte, then the matrix spike recovery failed the acceptance criteria. Check for documentable errors (*e.g.*, calculations and spike preparations) and then check the unspiked sample results and surrogate recoveries for indications of matrix effects. If no errors are found and the associated QC reference check standard (Laboratory Control Sample [LCS]) is within 50-150%, then sample matrix effects are the most likely cause. Note this in the Case Narrative.

A relative percent difference (RPD) must also be calculated on the matrix spike set recoveries. This is calculated as follows:

A = % recovery of matrix spike sample
B = % recovery of matrix spike duplicate sample

RPD = [(A-B)/{(A+B)/2}] x 100
where (A-B) *is taken as an absolute value*

If the concentrations of the matrix spike set are *greater* than four times the calculated sample amount, then an RPD of 40% or less is acceptable. If the concentrations of the matrix spike set are *less* than four times the calculated sample amount than there are no established limits applicable to the RPD. If the criterion is not met, check for documentable errors (*e.g.,* calculations and spike preparations) and then check the unspiked sample results and surrogate recoveries for indications of matrix effects. If no errors are found and the associated LCS is within 50-150%, then sample matrix effects are the most likely cause. Note this in the Case Narrative.

8.6.7 A QC reference check standard (LCS) is also prepared and analyzed for Aroclor-1221 and Aroclor-1242 at a 3:1 ratio and a Total PCB concentration of 400 ng/mL (300 ng/mL Aroclor-1221 and 100 ng/mL Aroclor-1242) in the extract. For sediment/solid samples, sodium sulfate is used for the QC reference check standard (LCS). Calculate the percent recovery for the Aroclor spike and compare to the project limits of 50-150%. If the percent recovery for either Aroclor in the QC reference check standard (LCS) is out of criteria, the analysis is out of the control for that analyte and the problem should be immediately corrected. The entire batch of samples will need to be re-extracted and re-run (Exception: If the LCS recovery is high and there were no associated positive results for any Aroclor, then address the issue in the Case Narrative and no further action is needed).

8.6.8 Surrogate compounds are added to each sample, matrix spike, matrix spike duplicate, method blank, and QC reference check standard (LCS) at time of extraction. The surrogate compounds TCMX and DCB are to be added prior to extraction for final extract concentrations of 10 ng/mL and 100 ng/mL, respectively (refer to extraction SOPs).

8.6.9 **Only one surrogate analyte needs to meet established control limits for the analysis to be valid. For samples analyzed at a five-fold dilution of the extract or less, the data is compared to the project limits of 60-140%. If percent surrogate recovery is not within limits for either surrogate, the following steps are required.**

8.6.9.1 Review calculations that were used to generate surrogate percent recovery values to make certain there are no errors.

8.6.9.2 Check by GC analysis surrogate solutions used during sample extraction steps to ensure that no problems exist with spiking solutions.

8.6.9.3 Re-analyze the extracts that did not meet control limits at the previously analyzed dilution to assess if the sample matrix interfered with surrogate measurement.

8.6.9.4 If the above steps do not give satisfactory results, re-extract and re-analyze the sample. Report this data if surrogate recovery is within limits. If surrogate percent recovery is out of limits for the re-extracted samples, low or high surrogate recovery is due to matrix affects and the data can be reported as estimated and the data user is notified in the form of a case narrative.

8.7 Qualitative/Quantitative Issues

8.7.1 Quantitation of Aroclors is complex. In each case, the Aroclor is made up of numerous compounds and, consequently, the chromatograms are multi-peak; also, in each case, the chromatogram of the residue may not match that of the standard. These residues are quantitated by comparison to one or more of the Aroclor mixtures, depending on the chromatographic pattern of the residue.

A choice must be made as to which Aroclor or mixture of Aroclors will produce a chromatogram most similar to that of the residue.

8.7.2 If Aroclors-1016, -1232, -1248, and/or -1260 are detected in a project sample, the instrument must be calibrated using 5 concentration levels (20 ng/mL, 100 ng/mL, 250 ng/mL, 500 ng/mL, and 1000 ng/mL) for the detected Aroclor(s) and the sample reanalyzed for quantitation by a 5-point linear fit calibration curve. The same acceptance criteria that applied to initial calibration and continuing calibration check standard analysis for Aroclors -1221, -1242, and -1254 will apply to Aroclors-1016, -1232, -1248, and/or -1260 when samples are reanalyzed for quantitation of any of these Aroclors.

8.7.3 All quantitations are to be based on 5-point initial calibrations (using external standard calibration techniques). The concentration of each Aroclor and surrogate in the sample will be determined by using the linear-fit calibration curve (see section 8.7.5) determined from the initial calibration standards. Refer to section 8.3 for initial calibration procedures. The final calculated sample concentration will take into account the sample-specific dilution factor, initial sample weight, final extract volume, and percent solids. All solids will be reported on a dry-weight basis.

8.7.4 If the instrument level of any Aroclor in a sample exceeds the instrument level of that Aroclor in the highest level standard, the sample must be diluted to approximately mid-level of the calibration range and reanalyzed for quantitation.

8.7.5 Calibration Curve by First Order Linear Regression External Standard Calibration.

Five selected Aroclor quantitation peaks are calibrated by first order linear regression with intercept. The surrogates TCMX and DCB are calibrated and quantified in the same manner using the individual peak areas for these analytes:

Equation of Line: $Y = aX + b$

where:

Y = summed total peak area of quantitation peaks used (uV-sec)
a = coefficient constant (slope)
X = calibration concentration (ng/mL)
b = first order coefficient (intercept)

8.7.6 Sample Concentration result calculation (solid samples)

$$C = \frac{(Y_i - b) * V_e * df}{a * M * \%TS * 1000}$$

where:

C = sample concentration (μg/g)
Y_i = summed total area of quantitation peaks in sample. (uV-sec)
b = intercept from (#1 above) (uV-sec)
V_e = concentrated extract volume (mL)
df = analytical dilution factor of extract
a = slope (from #1 above)
M = mass of sample in (g)
%TS = Percent Total Solid (in decimal format)
1000 = units conversion ng to μg

9.0 References

9.1 U.S. EPA SW-846 "Test Methods for Evaluating Solid Waste; Volume 1B Laboratory Manual Physical/Chemical Methods", Office of Solid Waste and Emergency Response, Third Edition, Final Update, December 1996.

9.2 U.S. EPA 40 CFR Part 136, "Guidelines Establishing Test Procedures for the Analysis of Pollutants", July 1988.

9.3 New York State Department of Health, "Environmental Laboratory Approval Program Certification Manual", Wadsworth Center for laboratories and Research, 1988, updated 1998.

9.4 "Guide to Environmental Analytical Methods", fourth edition, Genium Publishing Corporation, 1998.

10.0 Attachments (**Note:** Attachments are not paginated.)

10.1 Attachment A: Example PCB Standards Preparation Tables

10.2 Attachment B: PCB Continuing Calibration Tables

10.3 Attachment C: Gas Chromatograph Operating Procedures

10.4 Attachment D: Chromatograms of PCB standards.

10.5 Attachment E: Retention Time Windows

10.6 Attachment F: Quality Control Requirements Summary Table for SOP GEH8082

ATTACHMENT A

Table 1
Example PCB Stock Standard Preparation Table

PCB Formulation	Supplier	Catalog #	Std. weight (mg)	Conc.(PPM)
A1016	Neat Material Source	NA	93.2	932.0
A1221	Neat Material Source	NA	106.8	1068.0
A1232	Neat Material Source	NA	103.3	1033.0
A1242	Neat Material Source	NA	99.0	990.0
A1248	Neat Material Source	NA	101.9	1019.0
A1254	Neat Material Source	NA	99.6	996.0
A1260	Neat Material Source	NA	99.2	992.0
DCB	Chem Service	F2170	10	100.0

Unless otherwise noted hexane is the solution used to make all dilutions.

Table 2
Example PCB Working Standard Preparation Table

PCB Stock Standards	Init. Volume(mL)	Final Volume(mL)	Conc.(PPM)
A1016	1.0	100	9.32
A1221	1.0	100	10.68
A1232	1.0	100	10.33
A1242	1.0	100	9.90
A1248	1.0	100	10.19
A1254	1.0	100	9.96
A1260	1.0	100	9.92

ATTACHMENT A cont'd

Table 3
Example PCB Calibration Standard Preparation Table

Init. Volume (mL)	Final Volume (mL)	Final Concentration (PPM)					
		A1016	A1221	A1232	A1242	A1248	A1260
5.0	50	0.932	1.068	1.033	0.990	1.019	0.992
2.5	50	0.466	0.534	0.5165	0.495	0.5095	0.496
1.25	50	0.233	0.267	0.25825	0.2475	0.2548	0.248
1.00	50	0.1864	0.2136	0.2066	0.198	0.2038	0.1984
0.500	50	0.0932	0.1068	0.1033	0.0990	0.1019	0.0992
5.0*	50	0.01864	0.02136	0.02066	0.0198	0.02038	0.01984

*This initial volume is of the nominal 0.250 ppm standard. All others are from the nominal 10 ppm standard.

Table 4
Example PCB Aroclor-1254 Calibration Standard Preparation Table

Init. Volume (mL) A1254	Init. Volume (mL) Surrogate	Final Volume (mL)	Final Concentration(PPM)		
			A1254	TCMX	DCB
5.0	0	50	0.996	0	0
10.0	4.0	100	0.996	0.020	0.200
25.0*	0	50	0.498	0.010	0.100
1.25	0.800	50	0.249	0.008	0.080
0.500	0.500	50	0.0996	0.005	0.050
0.100**	0.200	50	0.01992	0.002	0.020

*This initial volume is of the A1254 0.996ppm solution with surrogates.
**This initial volume is of the A1254 0.996ppm solution without surrogates.
All others are from the A1254 9.96ppm working standard.

ATTACHMENT B

Table 1
PCB Continuing Calibration Stock Standards

PCB	Supplier*	Catalog #*	Conc. (μg/mL)
A1016	Chem Service	F107AS	1000
A1221	Chem Service	F108AS	1000
A1232	Chem Service	F113AS	1000
A1242	Chem Service	F109AS	1000
A1248	Chem Service	F110AS	1000
A1254	Chem Service	F111AS	1000
A1260	Chem Service	F112BS	1000

*Or Equivalent.

Table 2
PCB Continuing Calibration Working Standards

PCB	Initial Volume(mL)	Final Volume(mL)	Concentration(PPM)
A1016	1.0	100	10
A1221	1.0	100	10
A1232	1.0	100	10
A1242	1.0	100	10
A1248	1.0	100	10
A1254	1.0	100	10
A1260	1.0	100	10

ATTACHMENT B cont'd

Table 3
PCB Continuing Calibration Standards

PCB	Initial Volume(mL)	Final Volume(mL)	Concentration (PPM)
A1016	2.5	50	0.500
A1221	2.5	50	0.500
A1232	2.5	50	0.500
A1242	2.5	50	0.500
A1248	2.5	50	0.500
A1254	2.5	50	0.500
A1260	2.5	50	0.500

ATTACHMENT C

Gas Chromatograph Operating Procedures[1]

Column Type	Capillary
Column ID	DB-1
Vendor	J&W (or equivalent)
Part Number	122-1032
Column Length(m)	30
ID(mm)	0.25
Film Thick.(um)	0.25
1)Initial Col. Temp. (^{o}C)	140
1)Col. Hold Time (min.)	1.0
1)Col. Temp. Rate (^{o}C/min.)	10
1)Final Col. Temp. (^{o}C)	200
1)Col. Hold Time (min.)	NA
2)Col. Temp. Rate (^{o}C/min.)	5
2)Final Col. Temp. (^{o}C)	245
2)Col. Hold Time (min.)	14.50
GC Col. gas flow rate (mL/min.)	17-24
ECD autozero	Yes
Detector Temp.(^{o}C)	300
Init. Injector Temp. (^{o}C)	300
A/S Vial Needle Depth	85
A/S Solvent Select	3
A/S Upper Air Gap	Yes
A/S Lower Air Gap	Yes
A/S Viscosity Factor	1

ATTACHMENT C cont'd

Gas Chromatograph Operating Procedures[1]

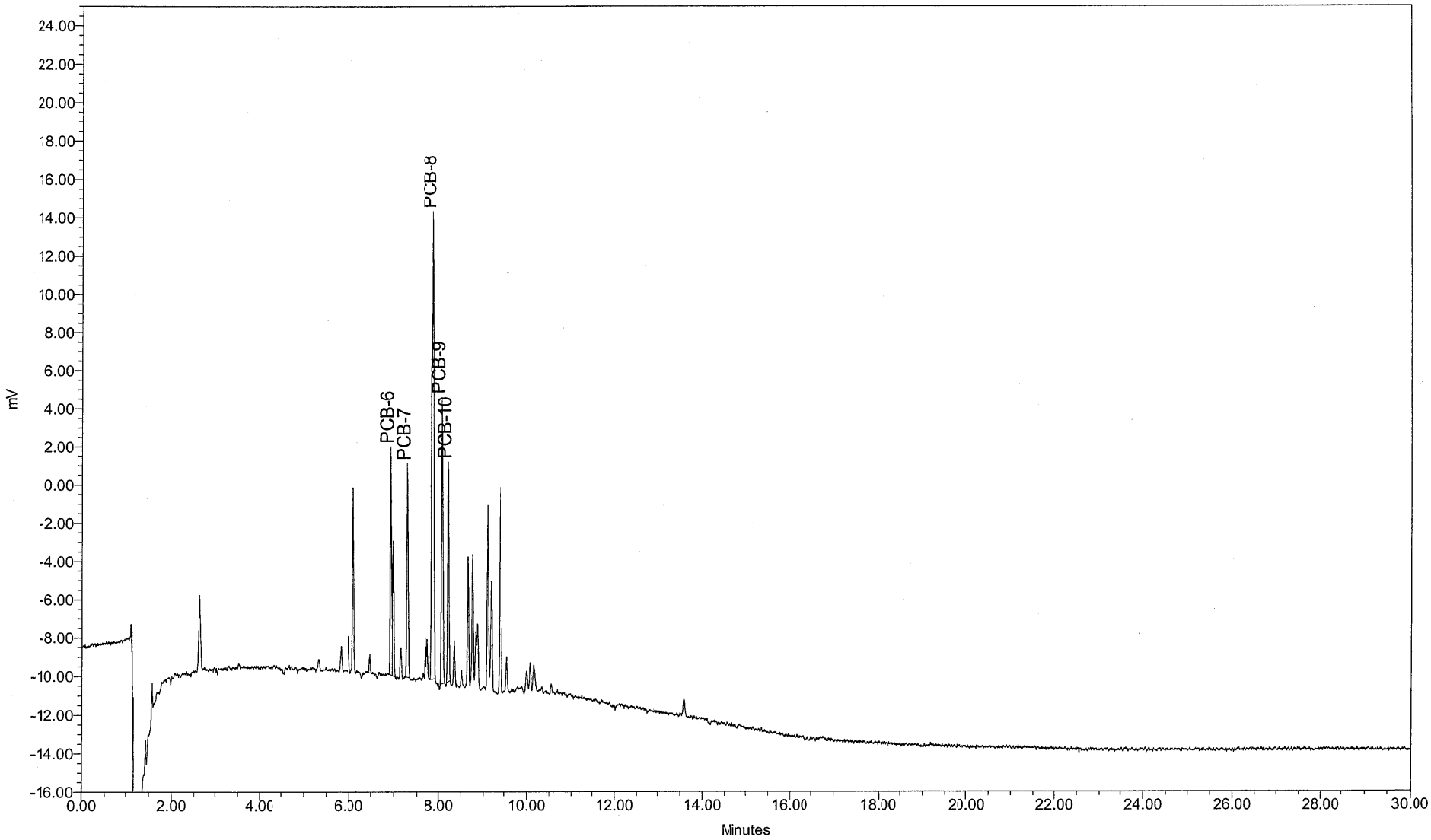
A/S Hot Needle Time (min.)	0.05
Autosampler (A/S) Model Number	8100 (or equivalent)
A/S Injection Volume (uL)	Lab-determined
A/S Injection Time (min.)	0.01
A/S Injection Rate (uL/sec.)	Fast 4.0
A/S Solvent Inj. plug size (uL)	0.2

Note:
1 – Parameters can be adjusted as necessary for the specific instrument used by the laboratory provided that chromatography for quantitation peaks is consistent with the examples in this SOP.

ATTACHMENT D
DB-1 CHROMATOGRAMS

Chromatogram Report, PCB by SW846 Method 8082

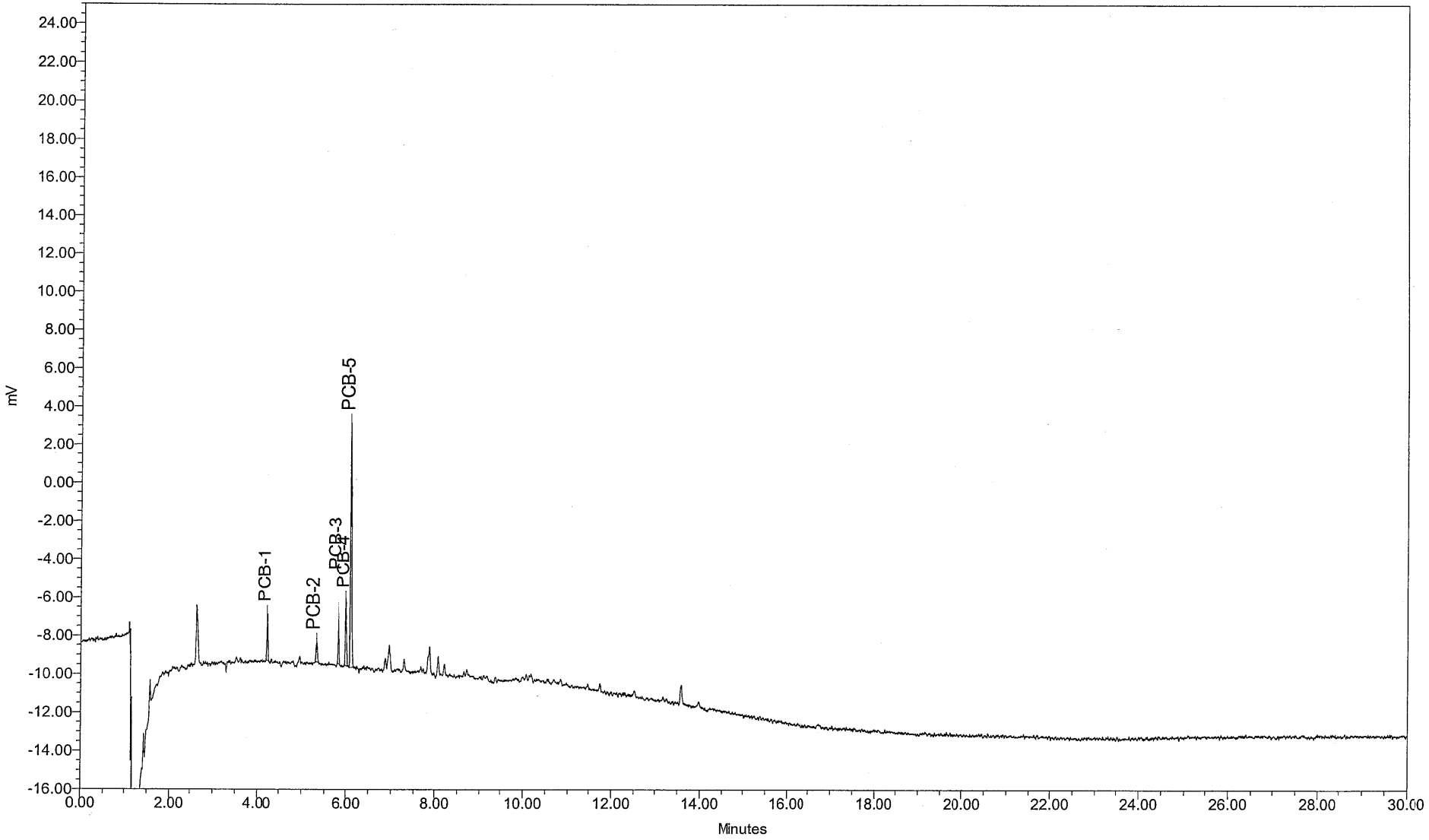
Northeast Analytical, Inc., 2190 Technology Drive, Schenectady, NY 12308
Phone: (518)-346-4592 Fax: (518)-381-6055 e-mail: nelab@aol.com



Sample Name:	CS160725	Sample Amount:	1
Sample ID:	A1016 500 PPB	Dilution:	1
Date Acquired:	07/26/1999 09:32:16	Processing Method:	GC7_8082_060899

Chromatogram Report, PCB by SW846 Method 8082

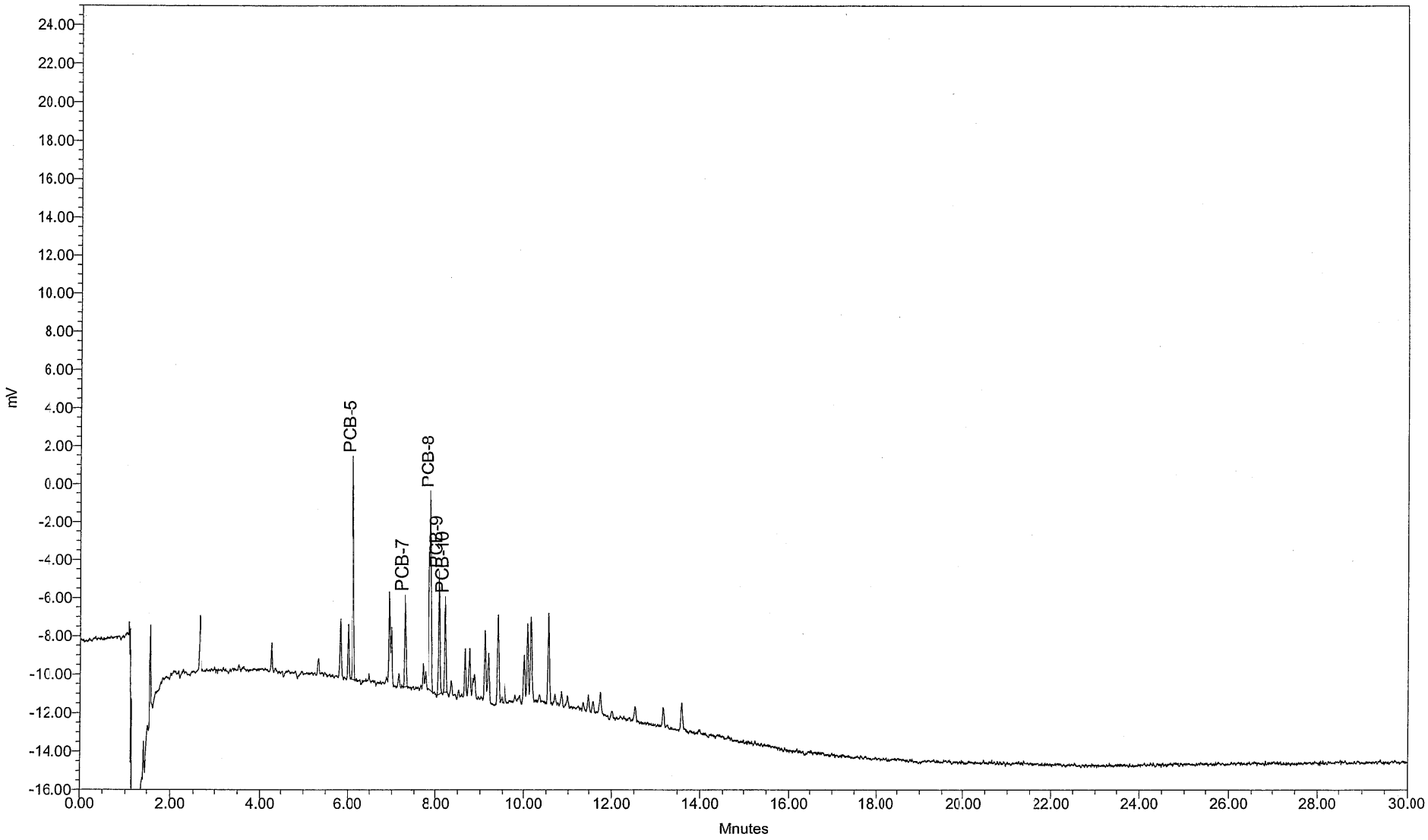
Northeast Analytical, Inc., 2190 Technology Drive, Schenectady, NY 12308
Phone: (518)-346-4592 Fax: (518)-381-6055 e-mail: nelab@aol.com



Sample Name:	CS210725	**Sample Amount:**	1
Sample ID:	A1221 500 PPB	**Dilution:**	1
Date Acquired:	07/26/1999 10:08:26	**Processing Method:**	GC7_8082_060899

Chromatogram Report, PCB by SW846 Method 8082

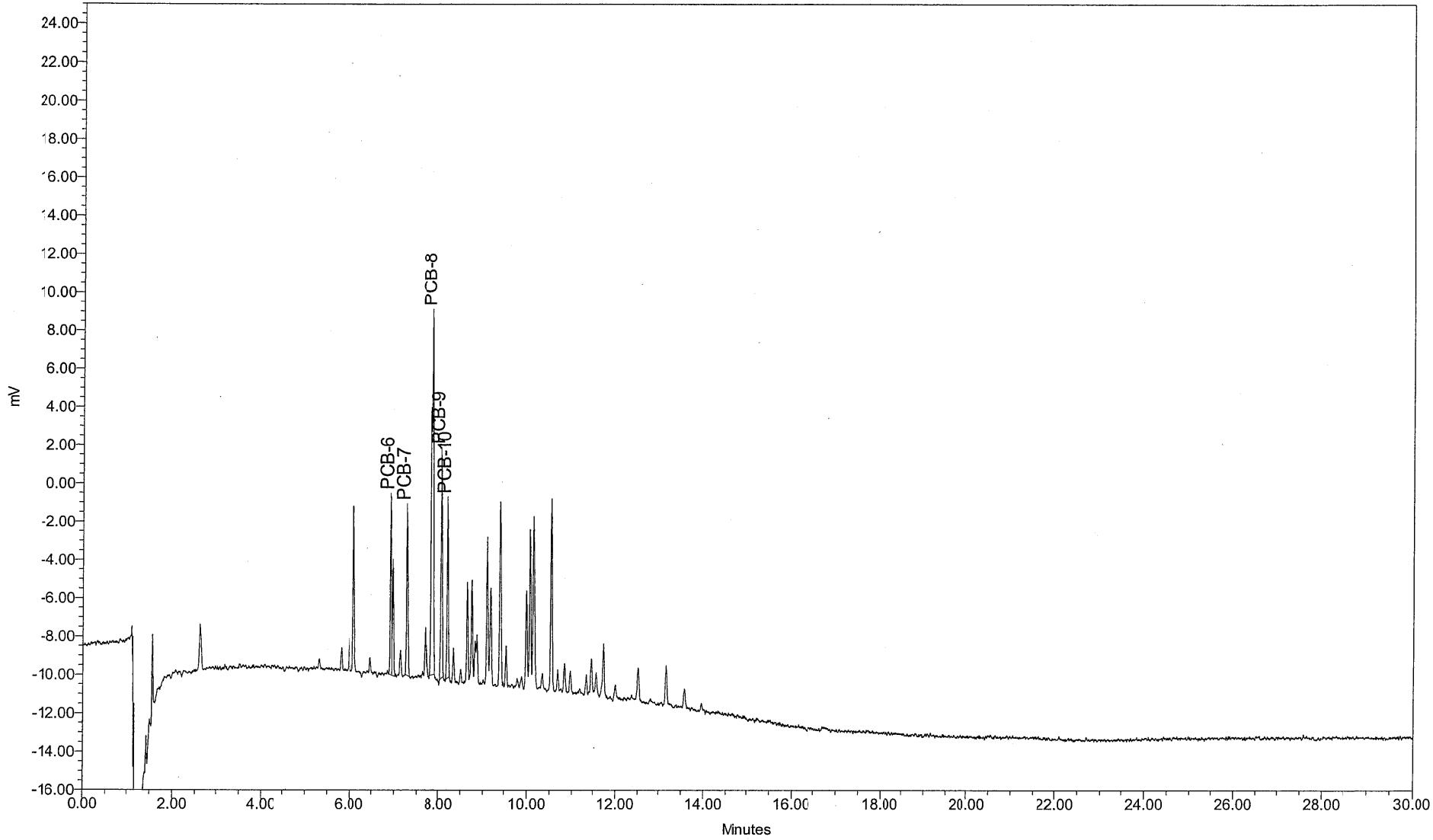
Northeast Analytical, Inc., 2190 Technology Drive, Schenectady, NY 12308
Phone: (518)-346-4592 Fax: (518)-381-6055 e-mail: nelab@aol.com



Sample Name:	CS320725	**Sample Amount:**	1
Sample ID:	A1232 500 PPB	**Dilution:**	1
Date Acquired:	07/26/1999 11:09:59	**Processing Method:**	GC7_8082_060899

Chromatogram Report, PCB by SW846 Method 8082

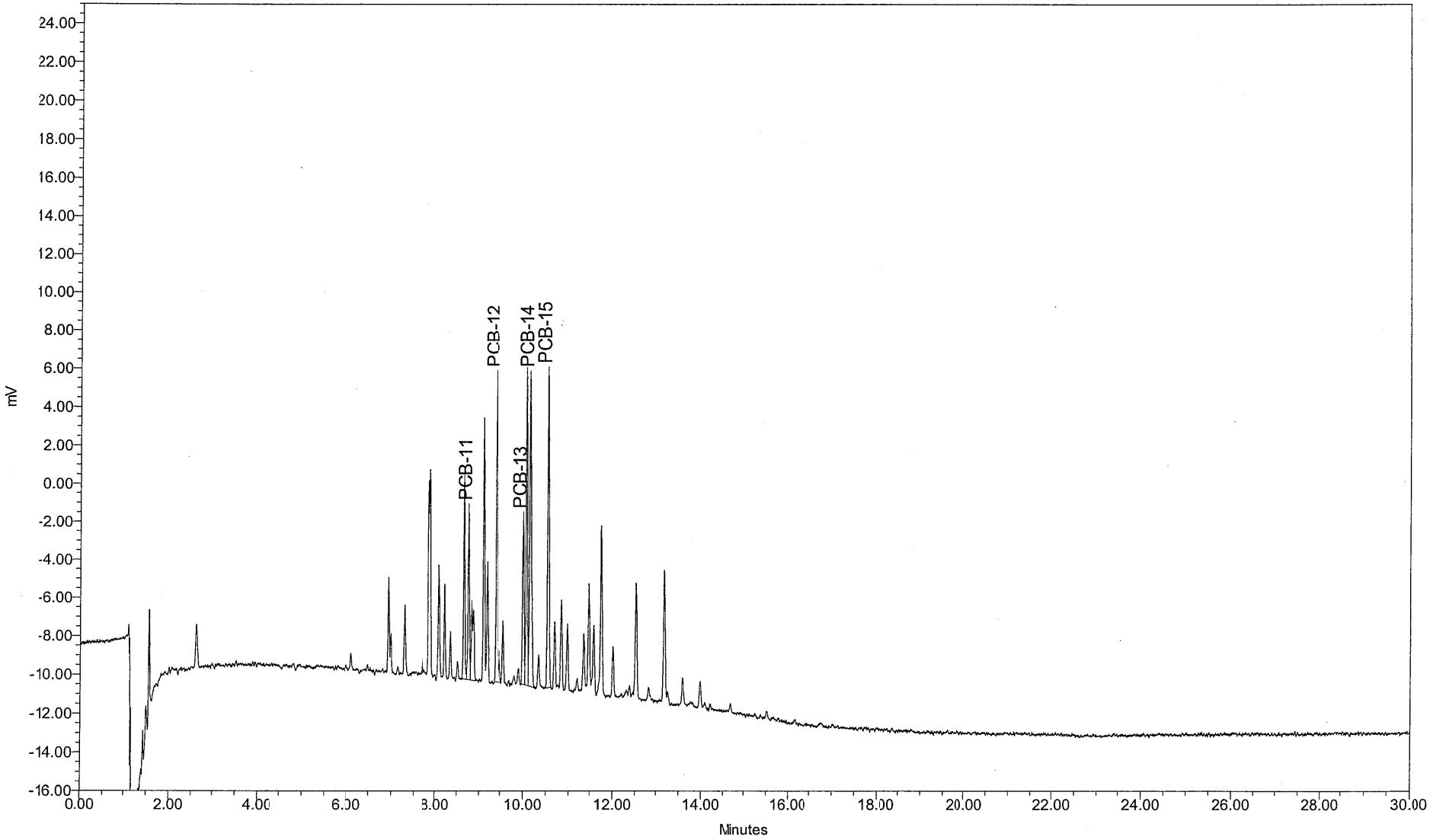
Northeast Analytical, Inc., 2190 Technology Drive, Schenectady, NY 12308
Phone: (518)-346-4592 Fax: (518)-381-6055 e-mail: nelab@aol.com



Sample Name:	CS420725	Sample Amount:	1
Sample ID:	A1242 500 PPB	Dilution:	1
Date Acquired:	07/26/1999 11:46:07	Processing Method:	GC7_8082_060899

Chromatogram Report, PCB by SW846 Method 8082

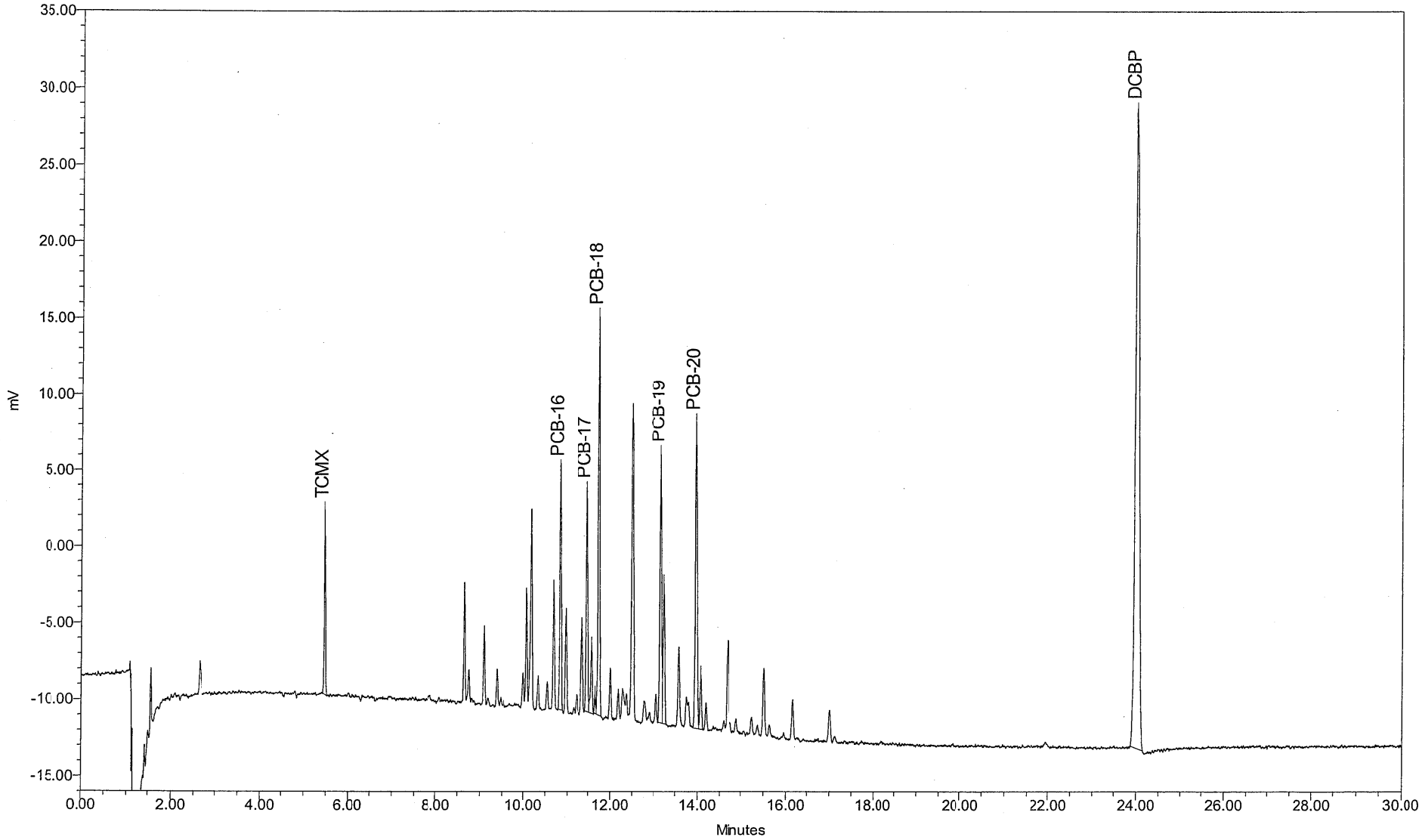
Northeast Analytical, Inc., 2190 Technology Drive, Schenectady, NY 12308
Phone: (518)-346-4592 Fax: (518)-381-6055 e-mail: nelab@aol.com



Sample Name:	CS480725	**Sample Amount:**	1
Sample ID:	A1248 500 PPB	**Dilution:**	1
Date Acquired:	07/26/1999 12:22:14	**Processing Method:**	GC7_8082_060899

Chromatogram Report, PCB by SW846 Method 8082

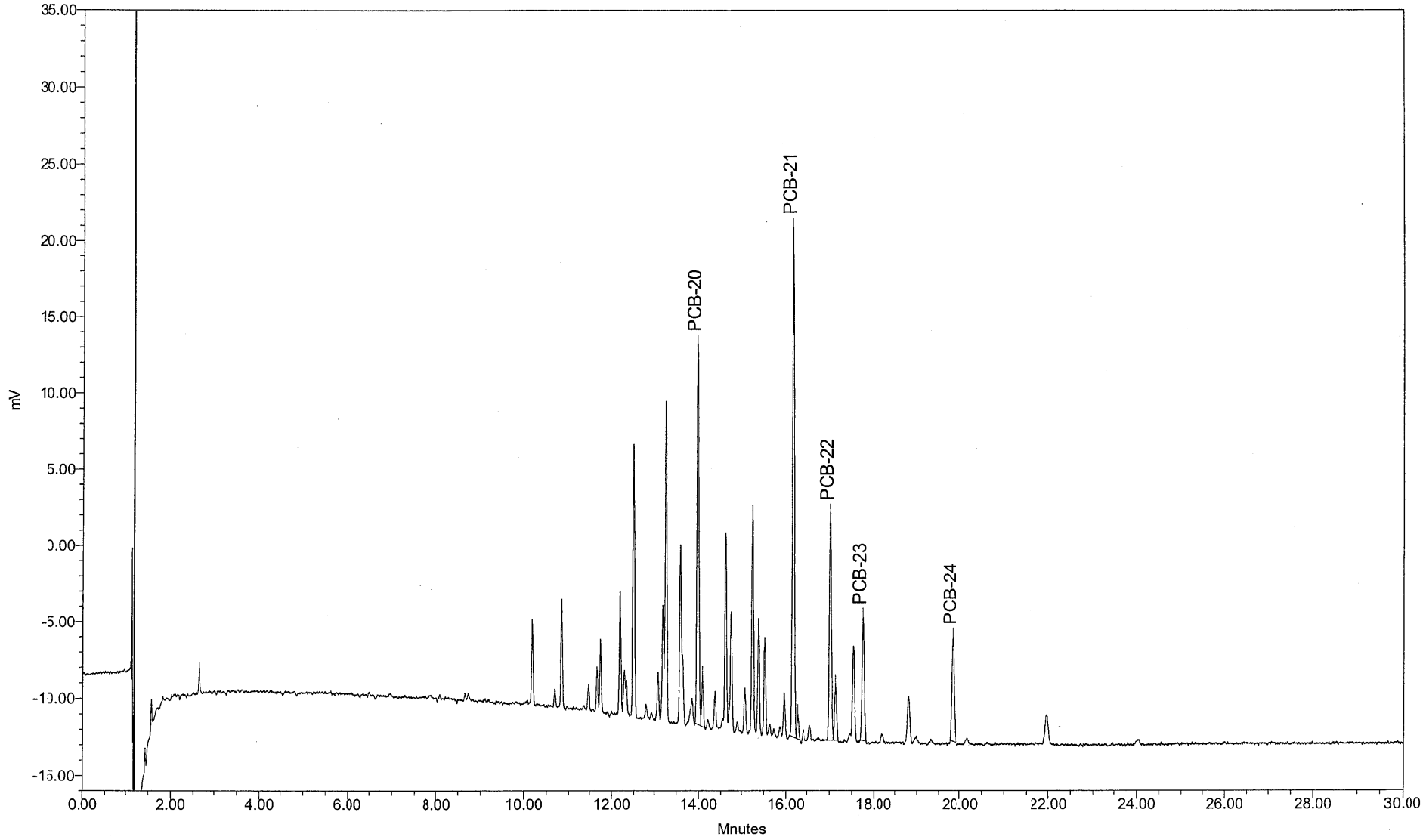
Northeast Analytical, Inc., 2190 Technology Drive, Schenectady, NY 12308
Phone: (518)-346-4592 Fax: (518)-381-6055 e-mail: nelab@aol.com



Sample Name:	CS540725	Sample Amount:	1
Sample ID:	A1254 500 PPB	Dilution:	1
Date Acquired:	07/26/1999 12:58:21	Processing Method:	GC7_8082_060899

Chromatogram Report, PCB by SW846 Method 8082

Northeast Analytical, Inc., 2190 Technology Drive, Schenectady, NY 12308
Phone: (518)-346-4592 Fax: (518)-381-6055 e-mail: nelab@aol.com



Sample Name:	CS500725	**Sample Amount:**	1
Sample ID:	A1260 500 PPB	**Dilution:**	1
Date Acquired:	07/26/1999 13:34:27	**Processing Method:**	GC7_8082_060899

ATTACHMENT E
RETENTION TIME WINDOWS

Northeast Analytical Inc 11/01/99

Retention Time Window Study
for Aroclors (PCB) by GC/ECD
EPA Method 8082

Instrument: GC 7
Column: DB-1

Analyte	PEAK	Standard 1 500 PPB R.T. Min	Standard 2 500 PPB R.T. Min	Standard 3 500 PPB R.T. Min	STD. DEV Min	%RSD	Window +/- Min.
		CS__0919	CS__1003	CS__1011			
Aroclor 1016	6	6.902	6.922	6.876	0.0231	0.33	0.069
	7	7.260	7.228	7.232	0.0174	0.24	0.052
	8	7.852	7.818	7.823	0.0184	0.23	0.055
	9	8.051	8.018	8.022	0.0180	0.22	0.054
	10	8.185	8.151	8.155	0.0186	0.23	0.056
Aroclor 1221	1	4.212	4.199	4.190	0.0111	0.26	0.033
	2	5.294	5.277	5.269	0.0128	0.24	0.038
	3	5.787	5.775	5.765	0.0110	0.19	0.033
	4	5.962	5.951	5.941	0.0105	0.18	0.032
	5	6.072	6.062	6.051	0.0105	0.17	0.032
Aroclor 1232	5	6.080	6.050	6.059	0.0154	0.25	0.046
	7	7.258	7.227	7.237	0.0158	0.22	0.047
	8	7.852	7.819	7.829	0.0169	0.22	0.051
	9	8.050	8.018	8.028	0.0164	0.20	0.049
	10	8.184	8.152	8.163	0.0163	0.20	0.049
Aroclor 1242	6	6.894	6.927	6.872	0.0277	0.40	0.083
	7	7.251	7.234	7.228	0.0119	0.16	0.036
	8	7.844	7.826	7.820	0.0125	0.16	0.037
	9	8.043	8.025	8.020	0.0121	0.15	0.036
	10	8.178	8.159	8.155	0.0123	0.15	0.037
Aroclor 1248	11	8.724	8.689	8.700	0.0179	0.21	0.054
	12	9.352	9.313	9.324	0.0201	0.22	0.060
	13	9.965	9.927	9.938	0.0196	0.20	0.059
	14	10.122	10.082	10.094	0.0205	0.20	0.062
	15	10.511	10.470	10.480	0.0214	0.20	0.064
Arolcor 1254	16	10.795	10.773	10.767	0.0147	0.14	0.044
	17	11.431	11.409	11.403	0.0147	0.13	0.044
	18	11.703	11.680	11.673	0.0157	0.13	0.047
	19	13.139	13.113	13.108	0.0166	0.13	0.050
	20	13.931	13.907	13.902	0.0155	0.11	0.047
Arolcor 1260	20	13.942	13.896	13.911	0.0235	0.17	0.070
	21	16.125	16.081	16.093	0.0227	0.14	0.068
	22	16.985	17.049	16.943	0.0534	0.31	0.160
	23	17.717	17.665	17.675	0.0276	0.16	0.083
	24	19.799	19.732	19.750	0.0347	0.18	0.104
TCMX (SURROGATE)	Surr.	5.445	5.429	5.425	0.0106	0.19	0.032
DCB (SURROGATE)	Surr.	23.984	23.91	23.91	0.0439	0.18	0.132

ATTACHMENT F
QUALITY CONTROL REQUIRMENTS
SUMMARY TABLE

Summary Table GEHR8082

Polychlorinated Biphenyls - SW-846 Method 8082
Quality Control Requirements

Quality Control Item	Frequency	Acceptance Criteria	Corrective Action
Sulfuric Acid Cleanup, Sulfur Cleanup, Florisil Cleanup	All samples for PCB only.	Not applicable.	Not applicable.
Initial Calibration	• Established initially and when CCC fails criteria. • At 5 concentration levels for Aroclors -1221, -1242, and -1254 and surrogate compounds (TCMX and DCBP). The 5 concentration levels are to be 20 ng/mL, 100 ng/mL, 250 ng/mL, 500 ng/mL, and 1000 ng/mL for each Aroclor. The surrogate compounds are to be combined with the Aroclor 1254 standards at concentrations of 2 ng/mL, 5 ng/mL, 8 ng/mL, 10 ng/mL and 20 ng/mL (TCMX) and 20 ng/mL, 50 ng/mL, 80 ng/mL, 100 ng/mL, and 200 ng/mL (DCB). • One standard calibration for each of the remaining Aroclor mixtures (1016, 1232, 1248, and 1260), at the reporting limit. If any one of these Aroclors is detected in a sample, the sample must be reanalyzed under a 5-point calibration for the detected Aroclor(s) for quantitation.	• %RSD≤20% among calibration factors (CFs) AND correlation coefficient ≥ 0.99 for each Aroclor mixture and surrogate (to be quantitated using linear-fit calibration curve not forced through zero). • Calibration factors are to be calculated using the total area for 5 peaks for each Aroclor. (Refer to SOP GEHR8082 Section 8.3.4 for selection of peaks.) • Each Aroclor must display distinctive pattern.	• Reanalyze the initial calibration curve and/or evaluate/correct instrument malfunction to obtain initial calibration which meets criteria. • Sample results above highest standard concentration require dilution and reanalysis. • If Aroclors-1016, -1232, -1248, and/or -1260 is detected in a project sample, the instrument must be calibrated using 5 concentration levels (20 ng/mL, 100 ng/mL, 250 ng/mL, 500 ng/mL, and 1000 ng/mL) for the detected Aroclor(s) and the sample reanalyzed. Same acceptance criteria that applied to 5-point calibration for Aroclors -1221, -1242, and -1254 will apply to these Aroclors.

Summary Table GEHR8082

Polychlorinated Biphenyls - SW-846 Method 8082
Quality Control Requirements

Quality Control Item	Frequency	Acceptance Criteria	Corrective Action
Continuing Calibration Check (CCC) Standard	• CCC for each Aroclors -1221, -1242, and -1254 at the beginning of the daily sequence (when >24-hour break in continuous analysis), unless initial calibration is performed. • If <24 hours break, CCCs will be alternated among Aroclors -1221, -1242, and -1254 after each analysis of 10 samples. • All CCCs must contain TCMX and DCB. • If analytical run is being performed for quantitation of Aroclors-1016, -1232, -1248, and/or -1260 (refer to initial calibration), CCCs for Aroclor(s) to be quantitated must be analyzed at the same frequency required for Aroclors -1221, -1242, and -1254. • Analytical sequence must end with analysis of CCCs for each Aroclors-1221, -1242, and -1254 (and/or other Aroclors if to be quantitated).	• ≤15% Drift based on "true" concentration for each Aroclor and surrogate when quantitated as a sample. • RT of each peak used for identification of the Aroclor must be within RT window (reset daily at the beginning of the sequence for the 24-hour day). • All samples must be bracketed by CCCs for Aroclors -1221, -1242, and -1254 (and/or other Aroclors if to be quantitated) that meet all criteria stated above.	• Correct system, if necessary, and recalibrate. Criteria must be met before sample analysis may begin. Samples that are not bracketed by compliant CCCs must be reanalyzed. • If a failed CCC returns to acceptable calibration later in the sequence, samples following the acceptable CCC will be reported; and samples between the failed CCC and subsequent compliant CCC will be reanalyzed.
Retention Time (RT) Windows	1. Established at ± 3 × std. dev. of RT of three standard analyses over 72-hour period. Must establish whenever a new column is installed. (Default RT window is ±0.08 minutes - Refer to SOP GEHR8082 Section 8.4 for additional guidance.) 2. RT windows are recentered daily based on RT of each of the peaks used for Aroclor identification in the first CCC of the day. (Refer to SOP GEHR8082 Section 8.5.4 for guidance on setting daily RT windows for Aroclors not analyzed as part of initial CCC.)	• RT of CCC peaks must be within established windows in the CCCs analyzed throughout day. • Recentering windows is permitted only once per 24 hours.	Adjust system, reestablish RT windows, and recalibrate.
Retention Time (RT) Shift	Each CCC analysis: RT of the peaks chosen for the identification of the Aroclors in the CCC are evaluated against the first CCC of the day.	Each quantitation peak for each Aroclor and each surrogate peak should be within window established.	Inspect chromatographic system for malfunction; correct identified malfunctions, if appropriate.

Summary Table GEHR8082

Polychlorinated Biphenyls - SW-846 Method 8082
Quality Control Requirements

Quality Control Item	Frequency	Acceptance Criteria	Corrective Action
Method Blank	• One per extraction batch of ≤20 samples of the same matrix per day. • Must be analyzed on each instrument used to analyze associated samples. • Must undergo all sample preparative procedures.	• Concentration does not exceed the reporting limit of any Aroclor. Not applicable if positive results were not reported for any associated samples. • Must meet surrogate criteria.	1. Reanalyze blank to determine if instrument contamination was the cause. If the method blank is still non-compliant, then follow 2 below. 2. Reextract and reanalyze all associated samples.
QC Reference Standard - Laboratory Control Sample (LCS)	One per extraction batch of ≤20 samples per matrix per day. The LCS must be from a second source and contain Aroclor 1221 and Aroclor 1242 at a 3:1 ratio at a Total PCB concentration of 400 ng/mL in the extract (300 ng/mL Aroclor 1221 and 100 ng/mL of Aroclor 1242)..	• % Recovery of Aroclor 1221 and Aroclor 1242 within project limits of 50-150%. • Must meet surrogate criteria.	Reanalyze LCS. If still out, reextract and reanalyze all associated samples. (Exception: If LCS recovery is high and no associated positives, then address in Case Narrative and no further action needed.)
Matrix Spike/Matrix Spike Duplicate (MS/MSD)	At this time, the GE Hudson River Remedial Action Monitoring Program does not require the preparation and analysis of matrix spike and/or matrix spike duplicate samples. If requested in the future, one MS/MSD pair per extraction batch of ≤20 samples per matrix per day. The MS/MSD samples must be spiked with Aroclor 1221 and Aroclor 1242 at a 3:1 ratio at a Total PCB concentration of 400 ng/mL in the extract (300 ng/mL Aroclor 1221 and 100 ng/mL of Aroclor 1242).	• Aroclor 1221 and Aroclor 1242 % Recoveries within 50-150% (when MS/MSD spike concentration is greater than 4× the unspiked sample amount). • RPD within 40% (when MS/MSD spike concentration is greater than 4× the unspiked sample amount). • Must meet surrogate criteria (unless also outside of criteria in unspiked sample).	1. If recoveries for the spiked Aroclors are not within 50-150% or the RPD is >40%, check for documentable errors (*e.g.*, calculations and spike preparation). 2. Check unspiked sample results and surrogate recoveries for indications of matrix effects. 3. If no errors are found, and the associated LCS is within 50-150%, then sample matrix effects are the most likely cause. Note in Case Narrative.

Summary Table GEHR8082

Polychlorinated Biphenyls - SW-846 Method 8082
Quality Control Requirements

Quality Control Item	Frequency	Acceptance Criteria	Corrective Action
Surrogates	• TCMX and DCB are added to all standards, blanks, samples, and QC samples at a concentration of 10 ng/mL TCMX and 100 ng/mL DCB at instrument level. • Calibrated as a target compound in the Aroclor 1254 initial calibration standards.	% Recovery of at least one surrogate within 60-140% for samples analyzed at an extract dilution factor of 5 or less.	If both recoveries are not within limits: 1. Check to be sure that there are no errors in calculations and surrogate solutions. Also, check instrument performance. 2. If no problem is found, reextract and reanalyze the sample. 3. If the reanalysis is within limits and holding time, then report only the reanalysis. 4. If the reanalysis is within limits, but out of holding time, then report both sets of data. 5. If the reanalysis is still out of limits, then report both sets of data. 6. No reanalysis is required if the sample was chosen for the MS/MSD analysis and the MS and/or MSD are also outside limits.
Qualitative/Quantitative Issues	If Aroclors-1016, -1232, -1248, and/or -1260 are detected in a project sample analyzed under a single-point calibration for the detected Aroclor, the sample must be reanalyzed under a 5-point calibration for the detected Aroclor(s).	All positive results for Aroclors must be quantitated using a 5-point linear-fit calibration curve and must be bracketed by compliant CCCs containing the detected Aroclor.	If Aroclors-1016, -1232, -1248, and/or -1260 are detected in a project sample, the instrument must be calibrated using 5 concentration levels for the detected Aroclor(s) and the sample reanalyzed. Same acceptance criteria that applied to initial calibration and CCC analysis for Aroclors -1221, -1242, and -1254 will apply to these Aroclors.
	If instrument level of any Aroclor in a sample exceeds the instrument level of that Aroclor in the highest level standard, the sample must be diluted to approximately mid-level of the calibration range and reanalyzed.	The instrument level of all Aroclors must be within the calibration range for all samples.	Dilute the sample to bring the level of the highest concentration of Aroclors within the calibration range.

APPENDIX 51
TRI+ PCB REGRESSION - TECHNICAL MEMO

Quantitative Environmental Analysis, LLC
$\partial c/\partial t$

TECHNICAL MEMORANDUM

TO:	Michael Elder	**DATE:**	March 7, 2006
FROM:	John Connolly, Ph.D., P.E., D.E.E.	**RE:**	Tri+ PCB Regression Model
CC:	John Haggard Bob Gibson Angus MacBeth Jim Bieke	**JOB#:**	GENrem:213

Assessment of the Correlation of Tri+ PCB and Aroclor PCB Measurements

Background

The delineation of dredge areas reported in the Phase 1 Dredge Area Delineation (DAD) Report (QEA, 2005) and being conducting for Phase 2 areas of the Upper Hudson River relies on the following regression model to convert measured Aroclor PCB concentrations to PCBs with three or more chlorine atoms (PCB_{3+}) concentrations (USEPA 2004, Appendix E):

$$PCB_{3+} = 0.03[A1221] + 1.16[A1242 + a1254]$$

where:

[Aroclor1221] = the reported Aroclor 1221 PCB concentration (mg/kg); and
[Aroclor1242 + Aroclor1254] = the sum of the reported Aroclor 1242 and Aroclor 1254 PCB concentrations (mg/kg).

This equation was developed from paired homolog and Aroclor measurements from a subset of the SSAP sample extracts. The United States Environmental Protection Agency (USEPA) calculated PCB_{3+} concentrations for each pair of homolog and Aroclor measurements by multiplying the Aroclor Total PCB concentration by the PCB_{3+} fraction of the homolog Total PCB concentration. This method of calculating PCB_{3+} concentrations assumed that GEHR680 produced accurate measurements of the PCB_{3+} fraction and that GEHR8082 produced accurate measurements of Total PCBs. The regression equation was developed using the calculated PCB_{3+} concentrations. It should be noted that this procedure to calculate PCB_{3+} concentrations

inflated the correlation between PCB_{3+} and Aroclor concentrations because the calculation resulted in both being functions of the Aroclor Total PCB concentration.

GE conducted a laboratory methods comparison study to compare the relative accuracy and precision of GEHR680, GEHR8082 and the modified Green Bay method (mGBM). That study found that the mGBM has superior accuracy and precision to GEHR680 and GEHR8082 in measuring Total PCBs and PCB_{3+} (ESI and QEA, 2005). Moreover, that study found a strong correlation between PCB_{3+} concentrations measured by the mGBM and the Aroclor concentrations measured by GEHR8082. Using paired analyses on 150 sample extracts and 30 archived sediment samples, the following regression equation was developed:

$$PCB_{3+} = 0.13[A1221] + 0.94[A1242 + a1254]$$

After reviewing the results of the methods comparison study, USEPA requested that General Electric (GE) analyze additional samples to provide more data at low concentrations to support using an mGBM-based regression to calculate PCB_{3+} concentrations from GEHR8082 Aroclor concentrations that will be measured on residual sediments post-dredging, which are expected to have relatively low PCB concentrations. This memo describes the additional sample analysis and the regression model obtained by regression using the full database of paired mGBM and GEHR8082 analyses.

Samples Selected for Analysis

Samples with PCB concentration in the desired range and sufficient time for analysis before extract expiration were selected to be representative of the overall population of data with regard to spatial distribution and analytical laboratory responsible for the GEHR8082 analysis. To provide a robust data set at low concentration, 71 samples were selected from those having a GEHR8082 Total PCB concentration less than 7 ppm. To fill in gaps at higher concentrations, 29 samples were selected from those having a GEHR8082 Total PCB concentration greater than 57 ppm. The IDs of the selected samples are provided in Table 1.

Table 1. Samples selected for analysis

RS1-9089-TT246-000002	RS2-8685-GR240-002006	RS3-6160-TT216-006012	RS3-6968-AR215-002012
RS1-9190-TT231-006012	RS2-8685-GR240-006012	RS3-6463-PR053-024030	RS3-6968-AR216-006012
RS1-9190-TT231-012018	RS2-8685-GR240-018020	RS3-6463-PR056-002006	RS3-6968-AR216-012018
RS1-9190-TT233-006012	RS2-8685-PR049-002006	RS3-6665-PR048-002012	RS3-7069-VT212-000002
RS1-9190-TT233-012018	RS2-8685-PR049-006012	RS3-6665-PR061-000002	RS3-7069-VT212-002012
RS1-9291-TT219-018024	RS2-8786-AR211-002012	RS3-6766-AR211-030036	RS3-7170-AR219-000002
RS1-9291-TT249-012018	RS2-8786-PR045-002012	RS3-6766-AR212-012018	RS3-7170-AR219-002012
RS1-9291-TT249-018024	RS2-8887-AR214-002012	RS3-6766-AR212-018024	RS3-7170-IN212-002012
RS1-9291-TT303-012018	RS2-8887-AR253-012024	RS3-6766-AR212-024030	RS3-7170-IN212-012024
RS1-9392-TT221-012018	RS2-8887-AR261-012024	RS3-6766-AR214-006012	RS3-7170-IN212-024030

305 West Grand Avenue
Suite 300
Montvale, NJ 07645
(201) 930-9890
(201) 930-9805 *fax*

290 Elwood Davis Road
Suite 230
Liverpool, NY 13088
(315) 453-9009
(315) 453-9010 *fax*

80 Glen Street
Suite 2
Glens Falls, NY 12801
(518) 792-3709
(518) 792-3719 *fax*

800 Brazos Street
Suite 1040
Austin, TX 78701
(512) 707-0090
(512) 275-0915 *fax*

RS1-9392-TT231-006012	RS2-8887-TT221-018024	RS3-6766-AR216-012018	RS3-7170-VT216-002012
RS1-9392-TT231-012018	RS2-8887-TT251-012018	RS3-6766-AR216-018020	RS3-7170-VT216-030036
RS1-9392-TT244-012018	RS2-8887-TT255-012018	RS3-6766-AR217-012024	RS3-7170-VT224-000006
RS1-9392-TT248-012018	RS2-8988-AR248-012018	RS3-6766-AR218-012018	RS3-7170-VT224-012018
RS1-9493-AR318-002012	RS2-8988-ID249-018024	RS3-6766-AR220-012024	RS3-7170-VT224-024030
RS1-9493-TT215-000002	RS3-5857-AR211-000002	RS3-6766-AR220-024030	RS3-7271-PR059-000002
RS1-9493-TT221-018024	RS3-5857-PR060-002012	RS3-6766-IN213-012024	RS3-7271-PR059-002012
RS1-9493-TT225-012018	RS3-5857-PR060-012024	RS3-6766-IN213-054060	RS3-7372-AR221-006012
RS1-9594-TT214-002006	RS3-5857-PR060-024030	RS3-6968-AR211-002012	RS3-7574-AR211-002012
RS2-8584-AR216-000002	RS3-5958-PR059-000002	RS3-6968-AR211-012024	RS3-7574-PR048-002012
RS2-8584-TT230-006012	RS3-5958-PR059-002012	RS3-6968-AR211-024030	RS3-7675-PR048-000002
RS2-8584-TT230-012018	RS3-5958-PR059-012024	RS3-6968-AR212-000006	RS3-7675-PR048-002012
RS2-8584-TT230-018024	RS3-5958-PR059-024030	RS3-6968-AR212-006009	RS3-7675-PR048-030036
RS2-8685-AR225-012024	RS3-6059-PR060-002006	RS3-6968-AR213-002012	RS3-7675-PR050-002012
RS2-8685-AR239-006012	RS3-6160-TT215-006012	RS3-6968-AR213-012018	RS3-8281-PR060-002006

Regression Results

The data for the original 180 paired samples and 98 of the 100 supplemental paired samples (two samples were excluded because they did not have results for Aroclor 1221 in the March 6, 2006 edition of QeaExport) were used to develop a refined regression model. Regression analysis was performed using the statistical software package R (http://www.R-project.org). The basic regression methodology consisted of applying a weighted least squares (i.e., "damped-leveraged) algorithm to calculate the coefficients, summary statistics and goodness of fit measures.

The regression equation is:

$$PCB_{3+} = 0.14[A1221] + 0.91[A1242 + a1254]$$

It is nearly identical to the equation developed from the original subset of 180 samples. The additional data result in tighter bounds on the coefficients (i.e., lower standard errors) and approximately the same goodness of fit statistics (see Table 2 and summary at top of Figure 1). Figure 1 presents comparisons of predicted and measured PCB_{3+} concentrations for the entire data set (top left panel) and for measured concentrations in the range of 0-5 mg/kg (top right panel), 5-80 mg/kg (bottom left panel) and greater than 80 mg/kg (bottom right panel). The model shows little decay in predictive ability at low concentrations and no significant bias. Residuals and relative residuals for the three concentration ranges are shown in Figure 2. The relative residuals are largely between ± 50% of the measured PCB_{3+} concentration. Even at concentrations less than 0.5 mg/kg, the relative residuals remain below ± 100%.

Table 2. Statistics of the regression models

Statistic	Model using original 180	Model using full data set
A1221 Coefficient	0.126	0.140
Std. Error of A1221 Coefficient	0.0114	0.0105
A1242+A1254 Coefficient	0.944	0.913
Std. Error of A1242+A1254 Coefficient	0.0293	0.0253
Multiple R^2	0.970	0.961

References

Environmental Standards, Inc., and Quantitative Environmental Analysis, LLC, 2005. *Data Summary Report: PCB Methods Comparison Study Congener Analytical Standards Analysis*. Prepared for the General Electric Company, May 20, 2005.

Quantitative Environmental Analysis, LLC, 2005. *Hudson River PCBs Site Phase 1 Dredge Area Delineation Report*. Prepared for the General Electric Company, February 28, 2005.

[USEPA] U.S. Environmental Protection Agency, 2004. *Resolution of GE Disputed Issues since GE's May 21, 2004 Presentation to the Regional Administrator*. July 22, 2004.

RESULTS FOR DATA WITH Tri+>0, A1221>0, and A1242+A1254>0 mg/kg. - ALL LABS COMBINED
Coefficients:

	Estimate	Std. Error	t value	Pr(>|t|)	
A1	0.1404	0.0105	13.4	<2e-16	***
A2	0.9126	0.0253	36.0	<2e-16	***

Signif. codes: 0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1

Residual standard error: 298 on 276 degrees of freedom
Multiple R-Squared: 0.961, Adjusted R-squared: 0.961
F-statistic: 3.4e+03 on 2 and 276 DF, p-value: <2e-16

Best Model PRESS = 66530

Reported residual quantiles and standard error are scaled by the square root of the leverage weight of the observation.
The unscaled residual summary statistics are:

Min.	1st Qu.	Median	Mean	3rd Qu.	Max.
-109.0000	-1.2300	-0.0128	-1.3800	0.9300	105.0000

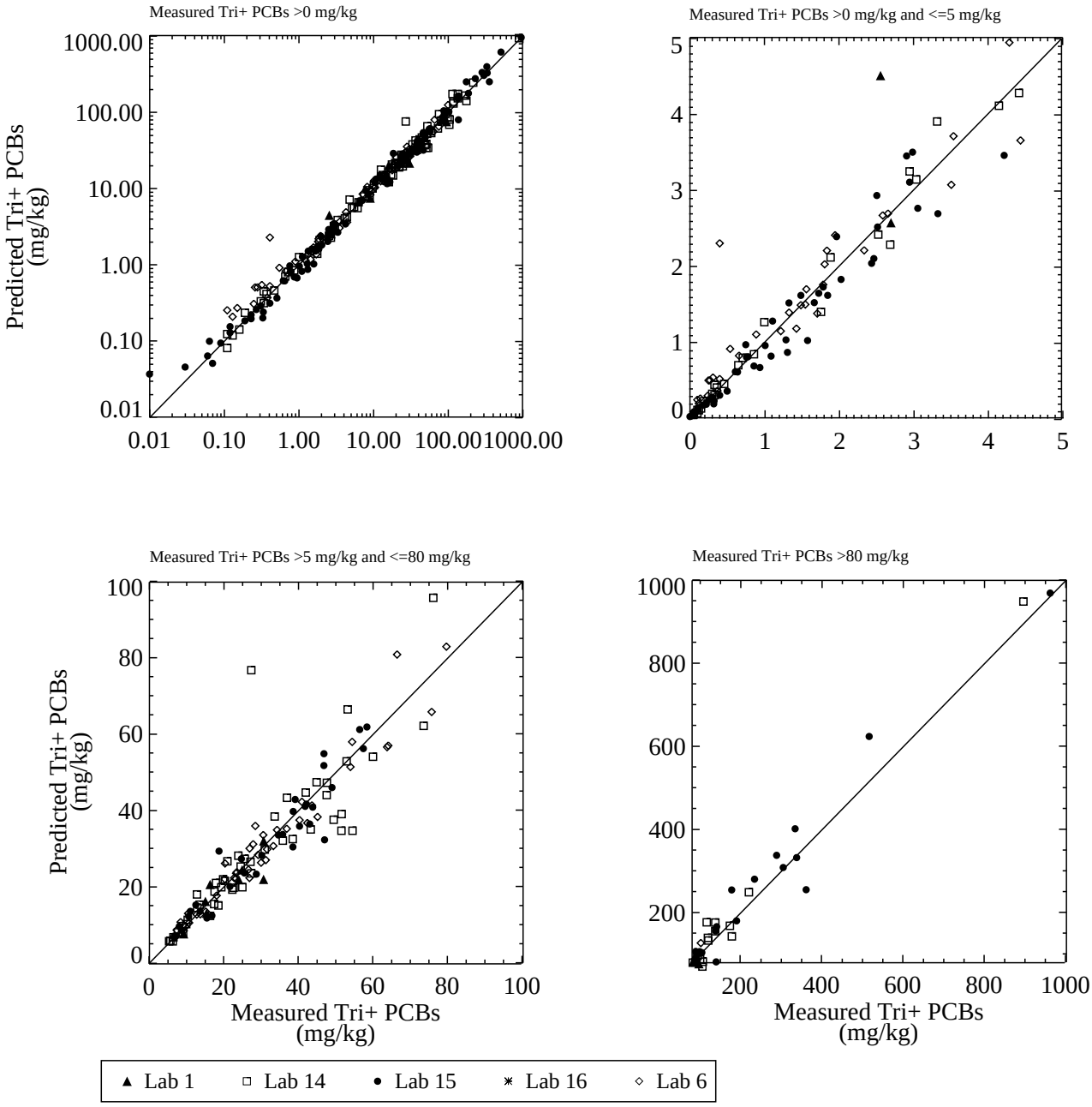


Figure 1. Comparison of predicted and measured tri+ PCBs. Tri+>0, A1221>0, and A1242+A1254>0 mg/kg.

Model 2: Predicted Tri+ PCBs = 0.14[A1221] + 0.91[A1242 + A1254]

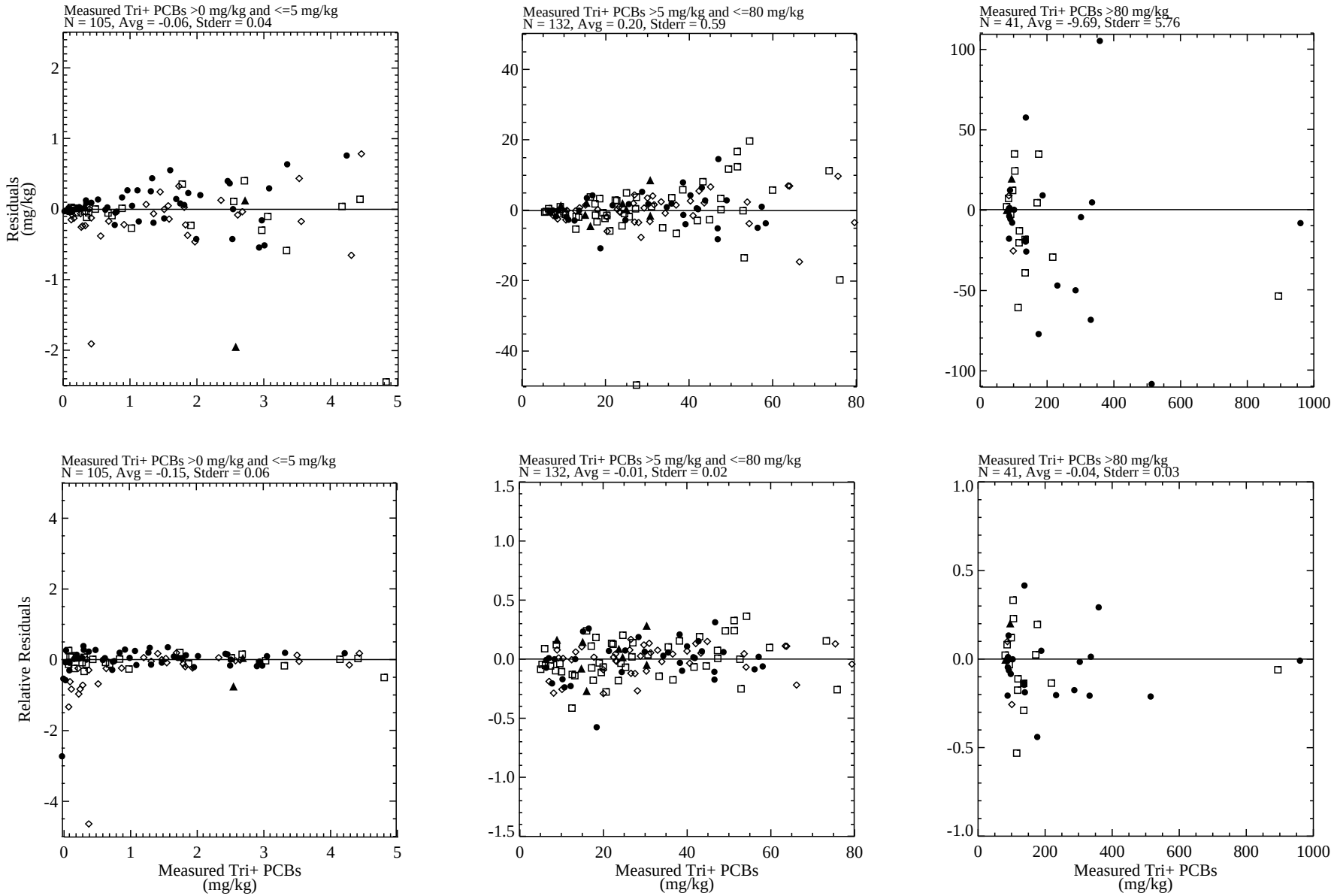


Figure 2. Regression residuals and relative residuals. Tri+>0, A1221>0, and A1242+A1254>0 mg/kg.

Model 2: Predicted Tri+ PCBs = 0.14[A1221] + 0.91[A1242 + A1254]

Residuals = Measured Tri+ PCBs - Predicted Tri+ PCBs
Relative Residuals = (Measured Tri+ PCBs - Predicted Tri+ PCBs) / Measured Tri+ PCBs

EC - \\Hendrix\V_Drive\Genrem\Working\Chen\Analysis\Sediment\Methods_analysis\Triplus_regression_GBM\plot_regression_models_resid.pro
Mon Mar 06 16:34:20 2006

APPENDIX 52
SOP FOR THE EXTRACTION AND CLEANUP OF SEDIMENT/SOLID SAMPLES FOR PCB ANALYSIS USING THE PRESSURIZED FLUID EXTRACTION BY SW-846 METHOD 3545 (GEHR3545)

STANDARD OPERATING PROCEDURE (SOP) GEHR3545

1.0 TITLE

General Electric (GE) Hudson River Remedial Action Monitoring Program (RAMP) Standard Operating Procedure for the extraction and cleanup of sediment/solid samples for Polychlorinated Biphenyl (PCB) analysis using the pressurized fluid extraction technique as per SW-846 Method 3545 for subsequent analysis by SW-846 Method 8082.

(Acknowledgement: This SOP is based substantially on internal method SOPs provided by Northeast Analytical, Inc. of Schenectady, N.Y.)

2.0 PURPOSE

The purpose of this SOP is to provide to the chemist the procedures required to perform extractions of PCBs, in sediment/solid samples, using the pressurized fluid extraction technique and to perform the subsequent extract volume reduction and cleanup for the GE Hudson River RAMP.

3.0 SCOPE

The following procedure is utilized by the project laboratories for the extraction and cleanup of PCBs from sediment/solid samples using the pressurized fluid extraction method for subsequent analysis by SW-846 Method 8082.

4.0 COMMENTS

The soxhlet technique may be used in place of the pressurized fluid extraction at the discretion of the supervising chemist.

5.0 SAFETY

The chemist should have received in-house safety training and should know the location of first aid equipment and the emergency spill/clean-up equipment, before handling any apparatus or equipment. Safety glasses and protective exam

gloves must be worn when handling glassware and samples. Polychlorinated biphenyls have been tentatively classified as known or suspected carcinogens. The chemist must review the Material Safety Data Sheets (MSDS) for PCBs and all reagents used in the procedure before handling them. All solvents should be handled within a lab fume hood.

6.0 REQUIREMENTS

The chemist must have an understanding of the methods and requirements of USEPA-SW- 846A "Test Methods for Solid Wastes" Volume 1B: Lab Manual, 3rd edition. Methods 3545, 3500B, 3620B, 3660B, 3665A. An approved instructor must also certify the chemist to perform the procedure.

7.0 EQUIPMENT

7.1 Extraction Vessel (cell):

- 7.1.1 ASE 200™ (Accelerated Solvent Extractor) Dionex, 33mL #048822 (or equivalent) with caps: Dionex #049450 (or equivalent).
- 7.1.2 *fast* PSE (Pressurized Solvent Extractor) Applied Separations. 33mL #10627

7.2 Syringes:

- 7.2.1 500µL Syringe, gas-tight, Hamilton #81217
- 7.2.2 1000µL Syringe, gas-tight, Hamilton #81317
- 7.2.3 250µL Syringe, gas-tight, Hamilton #81100

7.3 Teflon Rod: Used to press cellulose filter/sample into the cell

7.4 Hydromatrix (Pre-cleaned and suitable for use): Varian #0019-8004 (or equivalent).

7.5 Metal spatula.

7.6 Mixing Tray: Used to mix sample prior to weighing sample.

7.7 Analytical Balance: Mettler AG-204 (or equivalent) used to determine sample mass.

7.8 Cellulose Filter: Prevents the frits of the cell end pieces from being clogged during ASE extraction.

7.9 Sodium Sulfate: Anhydrous (12-60 Mesh), used for the laboratory method blank and laboratory control sample.

7.10 Hexane: High Purity Solvent Baxter (Burdick/Jackson) #UN1208 (or equivalent).

7.11 Acetone: High Purity Solvent Baxter (Burdick/Jackson) #UN1090 (or equivalent).

7.12 ASE 200: extractor, Dionex

7.13 *fast* PSE: extractor, Applied Separations

7.14 1:1 Hexane/Acetone: 50%/50% by volume solvent mixture prepared in the lab.

7.15 Zymark Turbo Vap LV: (or equivalent).

7.16 60mL VOA vials.

7.17 Vials: glass, 40mL & 4 dram (with Polyseal sealed cap), for sample extracts.

7.18 Vial Rack: Plastic rack used to hold vials, during all phases of the extract processing.

7.19 Centrifuge: International Equipment Co., Model CL (or equivalent).

7.20 Wrist Shaker: Burrell wrist action shaker, Model 75 and 88 (or equivalent).

7.21 Florisil: solvent washed and deactivated (10%), EM Science #FX0282-1 (or equivalent).

7.22 TBA Reagent: Tetrabutylammonium Hydrogen-Sulfite Reagent (prepared in the laboratory).

7.23 Mercury: Triple distilled Mercury Refining Co, Albany, NY #328502 (or equivalent).

7.24 Sulfuric Acid: H_2SO_4 (concentrated) Mallinkrodt #2468 #UN1830 (or equivalent).

7.25 Pipettes: S/P Disposable Serological Borosilicate Pipettes.
1. 1mL × 1/10 #P4650-11X (or equivalent)
2. 5mL × 1/10 #P4650-15 (or equivalent)
3. 10mL × 1/10 #P4650-110 (or equivalent)
Kimble Pasteur Borosilicate glass pipette 9" #72050 (or equivalent)

7.26 Beakers: Assorted Pyrex, used for liquid containment and pipette storage: 250mL, 600mL, and 1000mL.

7.27 Jars: for sampling, weighing, and mixing: 4oz & 8oz

8.0 PROCEDURES

8.1 Sample Preparation

8.1.1 Throughout the entire process it should be noted that if the chemist encounters any problems or difficulties with any samples or steps involved, these problems should be brought to the attention of the supervisor and/or quality assurance manager for guidance and then documented.

8.1.2 If the sample is a sediment and contains a water layer, decant and discard the layer as aqueous PCB waste. Mix the sample thoroughly and discard

any foreign objects such as sticks, rocks, leaves, twigs, or pebbles. **Note:** the sample may be composed entirely of rock, concrete or some other solid material in which case the entire sample is treated as the solid.

8.2 Sample Extraction

8.2.1 Set up one 4oz. jar for each sample. Pick the first sample, label a jar with the sample number, and tare the jar. Using a metal spatula, add 20g to 21g of the wet sample to the beaker. Samples that are observed to be very wet will require additional mass of sample such that the project sensitivity requirements are met. **The moisture content of the sample as determined in Section 8.2.2 should be evaluated so that a larger wet-weight sample can be obtained to provide a dry amount of solids to meet the project sensitivity requirements. The amount taken must consider the size limitations of the extraction vessel. The laboratory should target a wet-weight amount of 25g for very wet samples.** Use sodium sulfate as the sample for the method blank and Laboratory Control Sample (LCS). Record the weight.

NOTE: ALL SAMPLE CONTAINERS ARE TO BE RETURNED TO THE APPROPRIATE REFRIGERATOR. FOR ALL EMPTY SAMPLE CONTAINERS, SEE THE LABORATORY'S INTERNAL CHEMICAL HYGIENE PLAN FOR PROPER DISPOSAL.

8.2.2 The PCB concentration is to be determined on a dry-weight basis and therefore, the percent total solids must be determined. Weigh approximately 5 grams of the previously homogenized sample in a previously weighed, tarred aluminum-weighing pan. Record the weight of the sample and the tare weight of the pan. Place the sample in a drying oven at 100 to 110 degrees Celsius for at least 8 hours. Record the time placed in the oven and the oven temperature. Remove the samples from the drying oven and allow to cool in a desiccator. Weigh the pan and sample.

Calculate the percent solids by:

$$\frac{\{(\text{wt. of pan + dried sample}) - (\text{wt.of pan})\}}{(\text{wt. of wet sample})} \times 100\%$$

8.2.3 Before the sample is added to the extraction cell, the sample must be dried. The sample is dried by adding Hydromatrix. The amount of this drying agent being used depends on how much water is in the sample. The more water present in the sample, the more drying agent will be needed to dry the sample. Mix the sample and drying agent thoroughly with a metal spatula.

8.2.4 The cell size to be used during the extraction will be determined by the final volume of the sample after the drying agent has been added. **Note:** sometimes the sample will have to be separated into two cells for the extraction if too much drying agent has been added.

8.2.5 Select the appropriate cell body size for each sample and the extractor to be used. Assemble one cell. If using an ASE cell, place 2 cellulose filters into the open end of the cell and push it down to the cell end cap using the black ASE push rod. If using a PSE cell, place 1 cellulose filter into the open end of the cell and push it down to the frit using a Teflon rod.

8.2.6 Label cells with the sample number. Label the corresponding 60mL VOA vials with a label. **Note**: If using the PSE label placement has no effect on the extraction, but if using the ASE labels must be placed an inch down from the cap but no lower than three inches down from the cap.

8.2.7 Place the cell into a clean mixing pan. Add the dried extract to the cell using the metal spatula to guide the sample into the cell. Any sample that fell outside of the cell will be collected in the mixing tray. Remove the cell from the mixing tray and add the sample that is in the mixing tray to the cell. Compact the sample in the cell, using the Teflon rod, while the sample is being added. **Note**: Do not overly compress the

sample. Rinse the rod with acetone and dichloromethane before using on a different sample or placing it in the storage drawer.

8.2.8 Add surrogate and matrix spike solution at this point. The final extract volume concentration of the surrogate compounds tetrachloro-*meta*-xylene (TCMX) and decachlorobiphenyl (DCB) should be 10ng/mL and 100ng/mL, respectively. At this time, the GE Hudson River RAMP does not require the preparation and analysis of matrix spike and/or matrix spike duplicate samples. If requested in the future, the final extract volume concentration for the spiked Aroclors (Aroclor-1221 and Aroclor –1242 in a 3:1 ratio) in the matrix spike and matrix spike duplicate sample should be 400ng/mL Total PCBs (300ng/mL Aroclor-1221 and 100ng/mL Aroclor-1242). The final extract volume concentration of the LCS should be 400ng/mL Total PCBs (300ng/mL Aroclor-1221 and 100ng/mL Aroclor-1242).

8.2.9 ASE: Assemble the top end cap to the cell (if using an ASE cell) and hand tighten. Place the first cell to be extracted in position 1 on the cell tray (top tray) and the 60mL VOA vial in position 1 on the vial tray (bottom tray). PSE: Place 1 cellulose filter into the top of the cell and push it down to the sample using a Teflon rod. Again, rinse the rod with acetone and dichloromethane before next use. Place the first cell in the oven in position 1. Place the 60mL VOA vial into the collection vial rack in position 1 and load the rack. Each cell and its 60mL vial must be in the same numerical position for both the ASE and PSE.

8.2.10 The solvent used for PCB extraction is 1:1 hexane/acetone

8.2.11 Select the appropriate method for PCB extraction (see Attachment 3) and start the extractor. **NOTE**: all 6 positions on the PSE must be full to start.

8.2.12 When the extraction program is complete, use a 10mL pipette to transfer the hexane layer (top layer) into a new 60mL VOA vial. Leave only the water layer in the original 60mL VOA vial.

8.2.13 Rinse the water layer in the 60mL VOA vial using 5 Pasteur pipette volumes of hexane. Hand shake for 30 seconds. Allow the two layers to separate, and pipette the hexane layer (using the same 10mL pipette) into the new 60mL VOA vial. Repeat this step 1 more time for a total of 2 hexane extractions on the water layer.

8.2.14 Rinse the 10mL pipette with two Pasture pipette volumes of hexane on the outside of the 10mL pipette that was in contact with the sample extract and two Pasture pipette volumes of hexane through the 10mL pipette and collect into the new vial.

8.3 Solvent Reduction: TurboVap LV Evaporator System

8.3.1 The Turbo Vap LV evaporator system is used in place of the Kuderna Danish (KD)-concentrator apparatus. The Turbo Vap LV uses a heated water bath and positive pressure nitrogen flow/vortex action. The unit maintains a slight equilibrium imbalance between the liquid and gaseous phase of the solvent extract that allows fractional reduction of the solvents without loss of higher boiling point analytes.

8.3.2 Turn the unit on and allow to heat up to 40°C ± 2°C.

8.3.3 As a precaution the TurboVap LV system regulators should be checked to assure that no residual gas pressure remains within the system and that the gas cylinder valve and gas pressure regulators are both off before placing samples in the apparatus. Residual gas pressure may cause splashing and cross contamination of samples. To bleed the system of residual gas pressure place an empty vial into the water bath and close the lid. Make sure that the nitrogen gas cylinder valve is turned off and slowly turn on the gas pressure regulator. Bleed any residual gas until the regulator output pressure gauge reads "0" psi. Proceed to 8.3.4. Make sure to wipe down all surfaces with hexane before concentrating samples.

8.3.4 Place the vials containing the samples into the TurboVap LV and close the lid. Press the button to turn on the appropriate row of stations that are being used. The press the start button and adjust the regulator until the

samples begin to swirl. Turn on the gas cylinder valve first and then begin slowly turning the pressure regulator on.

8.3.5 Keep the gas pressure very low, until the solvent level is decreased, to avoid splashing. Increase the gas pressure as the sample reduces maintaining uniform flow throughout the reduction. Check the sample every few minutes to keep the samples swirling.

8.3.6 The process for solvent (hexane/acetone) reduction takes approximately 20-30 minutes. Do not leave the unit unattended as extracts may be blown to dryness and PCB loss may occur. Immediately notify a supervisor if an extract is blown to dryness.

8.3.7 Concentrate the solvent to approximately 10mL. Remove the samples from the TurboVap LV and place in the rack. The remaining solvent will consist largely of hexane since the acetone component is fractionally removed at a faster rate than hexane; however, a solvent exchange with hexane should be completed an additional time to ensure the acetone has been entirely removed. Fill the vials with hexane and concentrate an additional time as in section 8.3.4 and 8.3.5. Concentrate to approximately 5mL. **Note**: Not all samples will evaporate at the same rate; sample extracts containing large amounts of petroleum or other non-volatile liquids may stop reducing before the desired volume is achieved. Samples that stop reducing should be removed as soon as possible.

8.3.8 Quantitatively transfer the sample extract with a Pasteur pipette into an appropriate volumetric flask (10mL for sediment/solid extracts). Rinse the vial with 3 Pasteur pipette volumes of hexane, then transfer the hexane rinse to the volumetric. Repeat the hexane rinse two more times for a total of three hexane rinses. After the sample has been transferred, rinse the Pasteur pipette with 0.5mL of hexane into the volumetric flask. Add hexane up to the volumetric meniscus mark. Stopper and invert the volumetric flask at least three times to mix completely. Decant the contents into a pre-labeled 4dram vial.

8.3.9 All dirty glassware must be rinsed with technical grade acetone or a "For Rinsing-Only" labeled solvent and dried in the fume hood before being washed.

8.4 Sample Extract Cleanup

8.4.1 Most extracts of environmental samples that are to be analyzed for PCBs by gas chromatography with electron capture detection contain co-extracted xenobiotics and other interfering substances that must be removed before accurate chromatographic analysis can be performed.

8.4.2 Sulfuric acid, sulfur removal and Florisil® clean-ups should be performed on every sample. The sequence and number of replicates of cleanup steps performed are recorded by the sample preparation chemist. Sample extract cleanups are performed on set volume extracts. The set volume is 10mL for sediment/solid samples.

8.4.3 Sulfuric Acid Wash

8.4.3.1 The concentrated sulfuric acid treatment removes hydrocarbons and other organic compounds, which are co-extracted with the PCB residues.

8.4.3.2 Add 3.0mL of concentrated H_2SO_4 and shake for 30 seconds by hand, centrifuge for approximately 2 minutes, transfer the hexane upper layer to a new 4 dram or 40mL vial depending on choice of sulfur cleanup.

8.4.3.3 Repeat 8.4.3.2 if the sample extract appears to be heavily loaded (opaque) with colored material. Two to three acid washes may be required. **Note**: it is entirely possible that all colored material will not be removed from the extract.

8.4.4 Elemental Sulfur Clean-up

8.4.4.1 Elemental sulfur is soluble in the extract solvents used for sediment and soil samples. It is commonly found in many sediment/soil samples,

decaying organic material, and some industrial wastes. Large amounts of sulfur can cause the electron capture detector (ECD) to signal saturate for long periods during the elution envelope of PCBs. Even small amounts of sulfur can interfere with PCB measurement as a co-eluting chromatographic peak.

8.4.4.2 Two techniques exist for the elimination of elemental sulfur in PCB extracts. Mercuric precipitation (Mercury Shake) and the Tetrabutylammonium (TBA) sulfite procedure. Tetrabutylammonium sulfite causes the least amount of degradation to a broad range of pesticides and organics compounds, while mercury may degrade organophosphorus and some organochlorine pesticides. The TBA procedure also has a higher capacity for samples containing high concentrations of elemental sulfur.

8.4.5 Removal of Sulfur Using Mercury

8.4.5.1 Mercury is a highly toxic metal. All operations involving mercury should be performed within a hood. Prior to using mercury, the chemist should become acquainted with proper handling and emergency spill/clean-up procedures associated with this metal and must have reviewed the material safety data sheet for mercury.

8.4.5.2 Add 1-3 drops of mercury to the sample extracts (4dram vial used), cap, and place on the wrist shaker for 30 minutes. The sulfur is converted to mercuric sulfide and precipitates out of the sample extract. A black precipitate may be seen in sample extracts containing elemental sulfur.

8.4.5.3 Transfer the sample extract to a clean 4dram vial.

8.4.5.4 Any precipitated sulfur can be removed from the extract by performing a sulfuric acid clean-up or a Florisil® slurry.

8.4.6 Removal of Sulfur using TBA Sulfite

8.4.6.1 The TBA procedure removes elemental sulfur by conversion to the thiosulfate ion, which is water-soluble.

8.4.6.2 Add 2.0mL TBA Sulfite Reagent, 1.0mL 2-propanol, and approximately 0.65 g of sodium sulfite crystals to the extract (40mL vial used) and shake for at least 5 minutes on the wrist shaker and observe. An excess of sodium sulfite must remain in the sample extract during the procedure. If the sodium sulfite crystals are entirely consumed add one or two more aliquots (approximately 0.65 g) to the extract and observe.

8.4.6.3 Place the samples on the wrist shaker for 45 minutes observing at 15-minute intervals to make sure that the sodium sulfite is not consumed. Add 5mL organic free water and shake for an additional 10-15 minutes.

8.4.6.4 Place the samples into the centrifuge and spin at a setting and duration appropriate to spin down the solids.

8.4.6.5 Transfer the hexane layer to a new 4dram vial and cap.

8.4.7 Florisil® Adsorption (Slurry)

8.4.7.1 The Florisil® slurry removes co-extracted polar compounds, residual water, and residual acid and is recommended as the final cleanup step before the extract is submitted for GC analysis.

8.4.7.2 Add approximately 3 grams of tested and approved 10% deactivated Florisil® to each vial containing the sample extract.

8.4.7.3 Vigorously shake the vial for approximately 1 minute by hand or on the wrist shaker.

8.4.7.4 Place the vial(s) into the centrifuge at a setting and duration appropriate to spin down the solids.

8.4.7.5 Transfer the extract to a clean 4dram vial.

8.5 Extract Screening and Dilution

8.5.1 Screening of PCB extracts by GC to determine the approximate concentration before final analysis is highly recommended. If possible, prior site history and estimates of sample concentration will be provided by field personnel and may be used to determine what, if any, extract dilution is necessary.

8.5.2 The supervising chemist is responsible for determining initial screening dilutions. Extract dilutions are prepared by transferring an aliquot of the original sample extract into a vial containing the correct amount of "make up" volume of hexane. Dilutions must be recorded in the instrument logbook or in the data system.

8.5.3 Perform the dilution using an appropriate disposable volumetric pipette to transfer the extract and for the make-up volume of hexane. Make sure that the vial is properly labeled. Cap and invert the vial at least three times to thoroughly mix the extract with the solvent.

8.5.4 Transfer 1mL of the extract to a labeled GC autosampler vial. Record the sample data and submit with the sample extracts to the GC analyst.

9.0 QUALITY CONTROL

9.1 This section outlines the necessary quality control samples that need to be instituted at the time of sample extraction. The data from these quality control samples is maintained to document the quality of the data generated.

9.2 With each batch of samples to be extracted a method blank is processed. The method blank is carried through all stages of sample preparation steps (including clean-up steps). For sediment/solid samples, a laboratory sodium sulfate blank is processed.

9.3 At this time, the GE Hudson River RAMP does not require the preparation and analysis of matrix spike and/or matrix spike duplicate samples. If requested in the future, a matrix spike for Aroclor-1221 and Aroclor-1242 at a 3:1 ratio is to be analyzed at a rate of 1 matrix spike per every 20 samples at a Total PCB concentration of 400ng/mL in the extract (300ng/mL Aroclor-1221 and 100ng/mL Aroclor-1242). Also a matrix spike duplicate sample is to be analyzed at a rate of 1 per every 20 samples.

9.4 A QC reference check standard (LCS) is also prepared and analyzed for Aroclor-1221 and Aroclor-1242 at a 3:1 ratio and a Total PCB concentration of 400ng/mL (300ng/mL Aroclor-1221 and 100ng/mL Aroclor-1242) in the extract. For sediment/solid samples, sodium sulfate is used for the QC reference check standard (LCS). Calculate the percent recovery for the Aroclor spike and compare to the project limits of 50-150%. If the percent recovery for either Aroclor in the QC reference check standard (LCS) is out of criteria, the analysis is out of the control for that analyte and the problem should be immediately corrected. The entire batch of samples will need to be re-extracted and re-run (Exception: If the LCS recovery is high and there were no associated positive results for any Aroclor, then address the issue in the Case Narrative and no further action is needed).

9.5 Surrogate compounds are added to each sample, matrix spike, matrix spike duplicates, method blank, and QC reference check standard (LCS) at time of extraction. The surrogate compounds TCMX and DCB are to be added for final extract concentrations of 10ng/mL and 100ng/mL, respectively.

10.0 POLLUTION PREVENTION AND WASTE MANAGEMENT

10.1 Pollution Prevention: see laboratory's internal SOPs

10.2 Waste Management: see laboratory's internal SOPs

11.0 REFERENCES

11.1 U.S. EPA SW-846 "Test Methods for Evaluating Solid Waste; Volume 1B Laboratory Manual Physical/Chemical Methods", Office of Solid Waste and Emergency Response, Third Edition, Final Update III, December 1996.

11.2 "Guide to Environmental Analytical Methods", Third Edition, Genium Publishing Corporation, 1996.

11.3 “ASE 200 Accelerated Solvent Extractor Operator’s Manual”, Dionex Corporation, December 1999.

11.4 “*fast* PSE Users Manual”, Applied Separations, Version 5, May 2005.

12.0 ATTACHMENTS

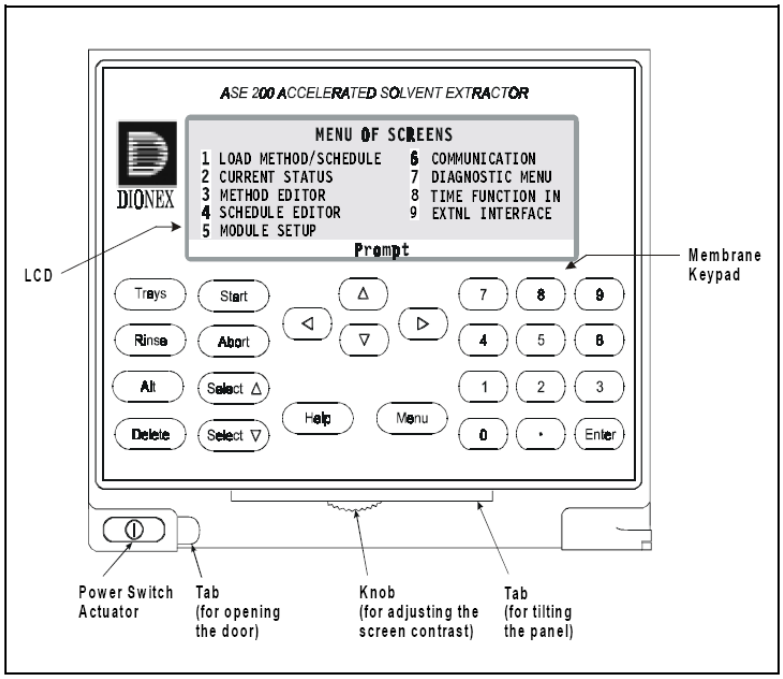
12.1 Extractor Control Panel Keypad.

12.2 Extractor Vessel (Cell) Cleanup Procedure.

12.3 Extraction Conditions for PCB in Sediment

ATTACHMENT 1: CONTROL PANEL KEYPAD

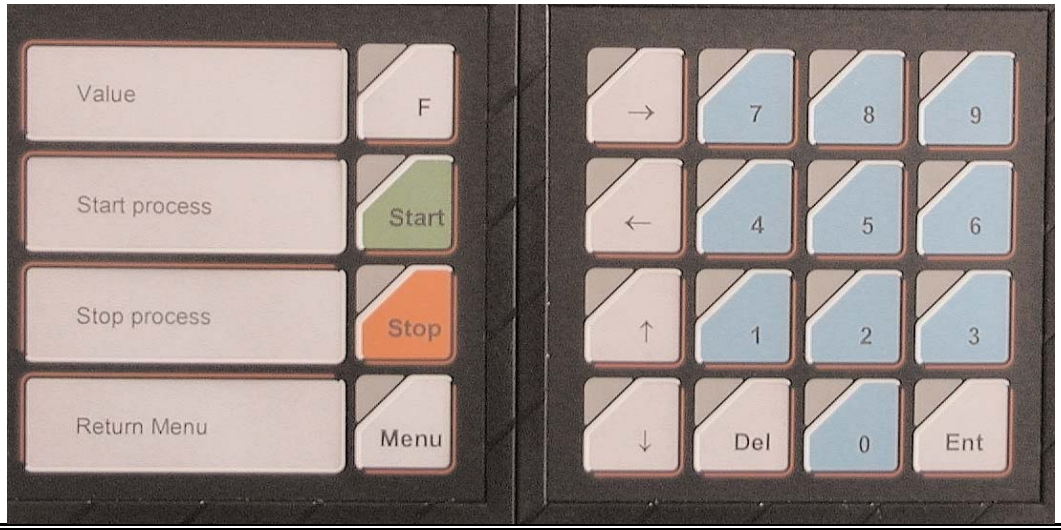
ASE



* TRAY	Tray is in free spin for manual turning.
TRAY *	Tray drive mechanisms are engaged and cannot be moved manually.
RINSE	Starts a manual rinse cycle.
* START	System is idle.
START *	System is currently running a method or schedule.
ABORT	Interrupts current run. Continue with abort function to terminate ASE run.
MENU	Displays a list of available screens.

* - LIGHT IS ON

PSE



F	Switches between the programmed values and the current values.
Start	Begins selected option.
Stop	Pauses and aborts current run.
Menu	Brings up the main menu. Returns to the previous menu.
Arrows	Moves the cursor to options on the screen in the appropriate direction
Del	Deletes the number in a field when editing
Enter	Selects the option. Moves to the next option.

ATTACHMENT 2
Extraction Vessel (Cell) Cleaning Procedure

ASE:

Remove the end caps of ASE cells. Using a metal spatula designated for cell clean up, push the extracted sample out of the cell into a garbage can. Wash the interior and exterior of the cell and cell end caps with soap and water (use the brush designated for ASE use only). Dry the cell parts with a paper towel and reassemble the cell.

Run the washed cells on the ASE (use a new 60mL VOA vial for each cell) using method 5 for 33 mL cells.

ASE Method 5

Temperature °C	150
Pressure	2000 psi
Number of Cycles	1
Static Time (minutes)	8
Purge	150seconds
Flush	20% of volume
Solvent	1:1 Acetone/Dichloromethane

Note: After the cells has been used 20 times or if the frits become clogged, the cell end caps should be taken apart and sonicated for 10 minutes in acetone and 10 minutes in dichloromethane.

PSE:

Remove the retaining nut and frit from the bottom of the cell. Using a Teflon rod designated for cell clean up, push the extracted sample out of the cell and into the garbage can. Wash the interior and exterior of the cell, retaining nut, and frit with soap and water. Dry the cell parts with a paper towel and reassemble the cell.

Run the washed cells on the PSE (use a new 60mL VOA vial for each cell) using method 1 for 33mL cells.

PSE Method 1

Temperature °C	125
Pressure	125 bar
Number of Cycles	1
Static Time (minutes)	8
Purge/Rinse	Yes
Flush/Nitrogen	Yes
Solvent	1:1 Acetone/Dichloromethane

ATTACHMENT 3
Recommended Extraction Conditions for PCB in Sediment

The following instrument conditions will be utilized for extraction of sediment samples by accelerated solvent extraction for PCB. These conditions may need to be optimized, as needed, according to the instrument manufacturer's recommendations. Once conditions are established, the same procedures should be performed on all samples.

Extractor / Method	**Dionex ASE 200 / 3**	**Applied Separations *fast* PSE / 3**
Temperature °C	150	125
Pressure	1750 psi	125 bar
Number of Cycles	3	2
Static Time (minutes)	5	4
Purge/Rinse	30 seconds	Yes
Flush/Nitrogen	60% of volume	Yes
Solvent	1:1 Hexane/Acetone	1:1 Hexane/Acetone

APPENDIX 53
SOP FOR THE PREPARATION, PURIFICATION, STORAGE, AND HANDLING OF POLYURETHANE FOAM (PUF) AIR SAMPLES FOR PCBS ANALYSES (NE153_04)

STANDARD OPERATING PROCEDURE

NORTHEAST ANALYTICAL, INC.

NE153_04.SOP
REVISION NUMBER: 04

STANDARD OPERATING PROCEDURE FOR THE PREPARATION, PURIFICATION, STORAGE, AND HANDLING OF POLYEURETHANE FOAM AIR SAMPLES

JULY 17, 2002

COPY

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Northeast Analytical, Inc.
Issuing Section: Organics
SOP Name: NE153_04.DOC
Date: 7/17/2002
Revision: 04

1.0 TITLE Standard Operating Procedure for the preparation, purification, storage and handling of Poly Urethane Foam (PUF) cartridge for the Polychlorinated Biphenyl (PCB) Air Monitoring sampling technique EPA Method TO-4.

2.0 PURPOSE The purpose of this SOP is to provide to the chemist with the procedures required to prepare and package PUF cartridges and Quartz Microfiber Filters(QMF) to be shipped to clients for sampling.

3.0 SCOPE The following procedure is utilized by Northeast Analytical, Inc. for the preparation and packaging of PUF cartridges and Quartz Microfiber Filters.

4.0 COMMENTS

Interferences: Puf samples are known to be extremely low level. Laboratory contaminents including pthatate esters may be introduced during extraction and subsequent cleanup procedures. The extractiontechnician should scrupulously clean glassware that is used and ensure plastic tubing and other plastic materials do not contact samples fume hoods must be decontaminated and PCB waste buckets should be removed from the fumehood.

PUF samples are known to be extremely low level. Fume hoods must be decontaminated and PCB waste buckets should be removed from the fume hood. All glassware must be pre-rinsed with hexane.

Refer to the PUF Extraction Technique SOP(NE151_01) for extraction and cleanup procedures for the verification sample in this SOP.

5.0 SAFETY The chemist should have received in-house safety training and should know the location of first aid equipment and the emergency spill/clean-up equipment, before handling any apparatus or equipment. Safety glasses, gloves, and a lab coat must be worn when handling glassware and samples.

Polychlorinated biphenyls have been tentatively classified as known or suspected carcinogens. The chemist must review the Material Safety Data Sheets (MSDS) for PCBs and all reagents used in the procedure before handling them. All equipment and solvents should be handled within a lab fume hood.

6.0 REQUIREMENTS

The chemist must have an understanding of the methods and requirements of EPA method TO-4, Determination of Organochlorine Pesticides and PCBs in Ambient Air.

7.0 EQUIPMENT

7.0.1 Water Cooled Condenser: Pyrex 45/50 #3840-MCO.

7.0.2 250ml Round Bottom Flask: Pyrex #4100.

7.0.3 Soxhlet Repetitive Flushing (reflux) Unit: 45/50 Pyrex #3740-M.

7.0.4 Heating Mantle: Type "VF" laboratory heating mantle #HM0250VF1. (or equivalent)

7.0.5 Heating Mantle Controller: Glass-Col #PL3122 Minitwin (or equivalent) regulates temperature control of the mantle.

7.0.6 Boiling Chips: Chemware PTFE Boiling Stones P#0919120 (or equivalent)

7.0.7 Chiller: Pump driven water circulating cooling system cool flow #75 NESLABS Instruments, Inc. (or equivalent)

7.0.8 Hexane: High Purity Solvent Baxter (Burdick/Jackson) #UN1208. (or equivalent)

7.0.9 Beakers: Assorted Pyrex: 250ml, 600mL, and 1000mL, used for liquid containment and pipet storage.

7.0.10 Replacement PUFs: High Volume Polyurethane Foam filters, 75mm, Density: 0.0225 g/cm^3

7.0.11 PUF Tubes: High Volume, 75mm.(SKC P226-131)

7.0.12 Pipets: S/P Disposable Serological Borosilicate Pipets.
1. 1mL X 1/10
2. 5mL X 1/10
3. 10mL X 1/10

Fisher Pasteur Borosilicate glass pipet 9" #72050 (or equivalent)

7.0.13 Quartz Microfiber Filters(QMF): 10.16 cm Dia.,100 circles(Whatman Cat# 1851-101) Baked at 450 C for 3 hours

7.0.14 Acetone: High Purity Solvent Baxter (Burdick/Jackson) #UN1090

7.0.16 Petrie Dishes: width 150mm/height 20mm. (VWR 25353-340)

7.0.17 Ice chest: Coleman Cooler. (or equivalent)

7.0.18 Clear Tape: Scotch Tape. (or equivalent)

7.0.19 Zip Lock Bags: To enclose individual PUF Cartridges and Petri dishes

7.0.20 Bubble Wrap: To protect samples from breaking during.

8.0 PUF PREPARATION PROCEDURES:

8.1 Preparation

8.1.1 Throughout the entire process it should be noted that if the chemist encounters any problems or difficulties with any samples or steps involved, all work should STOP! Any problems should be brought to the attention of the supervisor and documented in the extraction logbook.

8.1.2 Prior to extraction all surfaces and fume hoods used must be cleaned and wiped down with hexane three times. It is also advised to remove any PCB solid or liquid waste containers from the fume hood.

8.1.3 PUF preparation and purification require all glassware to be pre-rinsed with acetone.

8.1.4 One Verification PUF in each batch must be analyzed and pass with a level of less than 10 ng/PUF. Batch sizes should be approximately 20. The verification PUF must be logged in and have a valid sample ID.

8.2 Procedure for PUF Purification

8.2.1 Rinse enough 250 mL round bottoms and soxhlets for each PUF in the batch. Place in fume hood and let dry.

8.2.2 After the glassware dries, add a few boiling chips to each round bottom and add approximately 200 mL of Acetone to each round bottom. Label one with the verification sample ID.

8.2.3 Using a pipet or tongue depressor push clean PUFs to the bottom of the soxhlet, just below the top of the capillary tube. Don't compress PUF completely to the bottom of the soxhlet, because they need to be taken out of the soxhlet without tearing after purification. Then attach soxhlet to round bottoms.

8.2.4 Rinse the inside and the outside connecting joints of the condenser units that will be used to condense the extraction solvent during the soxhlet extraction of the sample. Turn on chiller to cool the condensers.

8.2.5 Place the round bottom flask with attached soxhlet extractor onto a heating mantle and attach condenser unit. Turn corresponding thermostats on to setting 5. Double check soxhlets at this time for any cracks or chips which may leak solvent. Once the solvent begins to boil, a flushing action of once every two to three minutes should be achieved.

8.2.6 The batch should be extracted overnight for a 14 to 24 hours. Once the batch has finished extracting (usually in the morning), turn the heating mantle off and allow samples to cool to room temperature. Once cool, rinse the inside of the condenser with several pipet volumes of hexane. Disengage the soxhlet and condenser unit and rinse the joint off as well into the soxhlet.

8.2.7 Layout enough aluminum foil in the fume hood to wrap around the entire batch. Using a paper towel, wipe down the aluminum foil with hexane and let dry. Procure designated PUF tweezers and rinse with hexane.

8.2.8 Set labeled Verification PUF unit aside at this time or leave it on heating mantle temporarily.

8.2.9 If hood space is available move all the round bottom flasks and soxhlet units to a fume hood. If not use a decontaminated cart to temporarily hold disassembled units. Do not put assembled units on the cart because it is not a stable surface. Using 10 mL pipets, lightly push the PUF down to release solvent from the PUF and allow the unit to drain into the round bottom.

8.2.10 Unattach soxhlets from the roundbottoms and discard the acetone into a non-PCB liquid waste container.

8.2.11 Using pre-rinsed, puf only tweezers, pull each PUF out of it's soxhlet and place on pre-rinsed aluminum foil. Let air dry until the acetone has evaporated.

8.2.12 Allow all glassware to dry then rinse with tap water and put in muffle buckets.

8.3 Procedure for Quartz Fiber Filter Preparation

8.3.1 Procure a clean glass tray and rinse it with hexane. Set aside and let air dry.

8.3.2 Set filters in glass dish in an a overlapping fashion. Place in muffle oven at a temperature of 450 C for at least 3 hours. During this time, layout a piece of aluminum foil large enough to wrap the quartz filters.

Using a paper towel, wipe down the aluminum foil with hexane and allow to air dry.

8.3.3 After 3 hours, cool filters enough to handle and wrap in pre-rinsed aluminum foil.

8.4 Procedure for Packaging PUFs For Shipping.

8.4.1 Rinse enough PUF tubes and petri dishes for the number of PUFs being shipped with acetone. Leave in hood to dry.

8.4.2 Load dry PUFs into PUF tubes and load Quartz Filters into petri dishes. Tape the petri dishes closed. Neatly wrap each PUF tube with a pre-rinsed piece of aluminum foil. Seal individual PUF tubes in a zip lock bag.

8.4.3 Wrap loaded PUF tubes in groups of three with bubble wrap between each PUF tube then tape closed. Repeat for the loaded petri dishes.

8.4.4 Put completed cartridges and petri dishes into coolers for shipment.

8.5 Verification PUF Extraction and Analysis

8.5.1 The verification PUF needs to be extracted and cleaned following the PUF Extraction Technique (NE151_02).

8.5.2 If the verification PUF does not pass you must go back and repeat this SOP from the beginning with all the PUFs

8.6 PUF Glassware Cleaning Procedures

8.6.1 After receiving samples from clients and extracted, all glassware must be cleaned following these Procedures. PUF tubes and Petri dishes can not be muffled. After removing samples from glassware, all labels and tape should be removed.

8.6.2 Then rinse all glassware three times using acetone, hexane, and acetone again into a PCB liquid waste container. Then let air dry.

8.6.3 Wash all glassware with soap and tap water. Then dry in drying oven. Let cool and put in storage.

8.7 Storage of Clean Glassware, Pre-cleaned PUFs, and QMF Filters

8.7.1 All glassware, must be cleaned according to section 8.6. Store all PUF glassware in hexane cleaned and aluminum foil lined drawers or cabinets.

8.7.2 Wrap extra PUFs and QMF filters with hexane rinsed aluminum foil, and store in a hexane cleaned and aluminum foil lined drawer or cabinet.

9.0 Pollution Prevention and Waste Management

9.1 Pollution Prevention: see NEA168.SOP

9.2 Waste Management: see NEA054.SOP, NEA083.SOP, and NEA089.SOP

10.0 References

1. EPA Method TO-4, Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air. pp TO4-1 to TO-20

11.0 Attachments

A. Method Outline

ATTACHMENT A: METHOD OUTLINE

METHOD OUTLINE FOR PUF EXTRACTION
USING SOXHLET TECHNIQUE

PUF PURIFICATION

1. **PREPARE FUME HOOD**
2. **RINSE GLASSWARE WITH HEXANE AND LET DRY**
3. **SET UP SOXHLET EXTRACTOR APPARATUS**
5. **EXTRACT BATCH FOR 14-24 HOURS**
6. **BREAKDOWN SOXHLET EXTRACTOR APPARATUS**
7. **DISCARD ACETONE AND DRY PUFS**
8. **SETUP VERIFICATION PUF**
9. **IF VERIFICATION IS GOOD PACKAGE SAMPLES FOR SHIPPING**
10. **IF VERIFICATION IS DIRTY THE BATCH MUST BE RE-EXTRACTED UNTIL VERIFICATION IS CLEAN.**

QUARTZ FILTER PREPARATION

1. **RINSE GLASS TRAY WITH HEXANE, LET DRY**
2. **PUT QUARTZ FILTERS IN GLASS TRY**
3. **BAKE AT 450^{0}C FOR 3 HOURS**
4. **WRAP IN HEXANE CLEANED ALUMINUM FOIL**

PACKAGING PUFS FOR SHIPPING

1. **PUSH PUFS INTO PUF TUBES**
2. **WRAP PUF TUBES WITH HEXANE CLEANED ALUMINUM FOIL**
3. **PUT PUF TUBES INTO ZIP LOCK BAGS**
4. **WRAP PETRI DISHES AND PUF TUBES IN GROUPS OF THREE WITH BUBBLE WRAP**
5. **LOAD COOLERS AND SEAL**
6. **WRAP LEFT OVER CLEAN PUFS AND QMF FILTERS IN ALUMINUM FOIL.**
7. **STORE LEFT OVER GLASSWARE, PUFS AND QMF FILTERS IN AN ALUMINUM FOIL LINED DRAWER**

APPENDIX 54
SOP FOR THE EXTRACTION AND CLEAN-UP OF POLYURETHANE FOAM AIR CARTRIDGES (PUFS) FOR EPA METHOD TO-4A POLYCHLORINATED BIPHENYLS IN AIR CASSETTE MEDIA (NE151_06)

STANDARD OPERATING PROCEDURE

NORTHEAST ANALYTICAL, INC.

NE151_06.DOC
REVISION NUMBER: 06

STANDARD OPERATING PROCEDURE FOR THE EXTRACTION AND CLEAN-UP OF POLYURETHANE FOAM AIR CARTRIDGES (PUFS) FOR EPA METHOD TO-4A POLYCHLORINATED BIPHENYLS IN AIR CASSETTE MEDIA

COPY #___

Property of Northeast Analytical, Inc.

NORTHEAST ANALYTICAL, INC.
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STANDARD OPERATING PROCEDURE

LABORATORY PROCEDURE NE151_06.DOC

REVISION 6 (06/18/2008)

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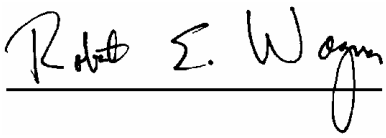
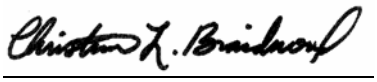


Robert E. Wagner
Laboratory Director

Approved by:



Christina L. Braidwood
Quality Assurance Officer

1.0 IDENTIFICATION OF TEST METHOD

1.1 Standard Operating Procedure for the extraction and cleanup of High Volume Polyurethane Foam (PUF) air cassette samples for Polychlorinated Biphenyl (PCB) analysis using the Soxhlet extraction technique (Modified SW-846 Method 3540C/EPA Method TO-4A for subsequent analysis by SW-846 Method 8082. Note: The Determinative Method (EPA Method 8082) requires secondary GC column analysis on dissimilar column for PUF samples.

1.2 The purpose of this SOP is to provide to the chemist the procedures required to perform extractions of PCBs in PUF (air cassette) samples, using the soxhlet extraction technique and to perform the subsequent extract volume reduction and cleanup.

2.0 APPLICABLE MATRICES

2.1 This test method is appropriate for polyurethane foam air cartridges (Pufs) & air filters (TO-4A).

3.0 DETECTION LIMIT

3.1 Please see determinative method (Lab SOP NE148) for details.

4.0 SCOPE AND APPLICATION

4.1 The following procedure is utilized by Northeast Analytical, Inc. for the extraction and cleanup of PCBs from PUF (air) samples using the soxhlet extraction method of Method TO-4A for subsequent analysis by SW-846 Method 8082.

5.0 SUMMARY OF TEST METHOD

5.1 The extraction and preparation of polyurethane foam air cartridges (PUFS) for EPA method TO-4A Polychlorinated Biphenyls in air cassette media: prepare fume hood and samples for extraction. Rinse the glassware you are going to use and allow it to dry. Set up a soxhlet extractor apparatus for each sample. This includes the loading of the polyurethane cartridge into the soxhlet. Add the necessary surrogates and/or matrix spike. Load the extraction apparatus into its heating mantle and condenser and allow it to extract for approx. 18 hours +- 2hrs. After the extraction is complete unload the extraction apparatus and break it down. Transfer the extracted solvent into a designated turbo tube. Load the turbo tube into the Zymark Turbovap evaporation system and concentrate the sample. Transfer the solvent to an eight dram vial and cleanup the sample utilizing acid, florisil and mercury cleaning methods, performing a backwash for each step. Then concentrate again using the Zymark Turbovap evaporation system to about 4 ml. Once concentrated, set the solvent to 5.0ml and hand in for GC analysis.

6.0 DEFINITIONS

6.1 **Method Blank**: With each batch of samples to be extracted a method blank is processed. The method blank is carried through all stages of sample preparation and measurement steps. For water samples an organic-free reagent water blank is processed.

6.2 **Lab Control Standard:** A non site sample created in the laboratory to which a known amount of target analyte is added for assessment of analyte recovery efficiency.

6.3 **Lab Control Standard Duplicate**: An exact copy of the Lab Control Standard to further assess analyte recovery efficiency.

6.4 **Matrix Spike**: A site sample to which a known amount of target analyte is added for assessment of analyte recovery efficiency.

6.5 **Matrix Spike Duplicate**: An exact copy of the Matrix Spike utilizing the same site sample and known amount of target analyte for assessment of analyte recovery efficiency.

6.6 **Surrogate Compound Spike**: In chemical composition and chromatography similar to the analytes of interest. Usually not found in environmental samples. These compounds are spiked into all samples, standards, blanks, and matrix spike samples prior to analysis. Percent recoveries are calculated for each surrogate.

6.7 **QC-Quality Control**: A set of measures for each sample within an analysis methodology to assure that the process is in control.

7.0 INTERFERENCES

7.1 Laboratory contaminants including phthalate esters may be introduced during extraction and subsequent cleanup procedures. The extraction technician should exercise caution that scrupulously cleaned glassware is used and that plastic tubing and other plastic materials do not contact samples or extracts. Please see determinative method (Lab SOP NE148) for details. Please see determinative method (Lab SOP NE148) for details

8.0 SAFETY

8.1 The chemist should have received in-house safety training and should know the location of first aid equipment and the emergency spill/clean-up equipment, before handling any apparatus or equipment. Safety glasses and gloves must be worn when handling glassware and samples.

8.2 Polychlorinated biphenyls have been tentatively classified as known or suspected carcinogens. The chemist must review the Material Safety Data Sheets (MSDS) for PCBs and all reagents used in the procedure before handling them. All equipment and solvents should be handled within a lab fume hood.

9.0 EQUIPMENT AND SUPPLIES

9.1 Water Cooled Condenser: Pyrex 45/50 #3840-MCO.

9.2 250ml Round Bottom Flask: Pyrex #4100.

9.3 Soxhlet Repetitive Flushing (reflux) Unit: 45/50 Pyrex #3740-M.

9.4 Heating Mantle: Type "VF" laboratory heating mantle #HM0250VF1. (or equivalent)

9.5 Heating Mantle Controller: Glass-Col #PL3122 Minitwin (or equivalent) regulates temperature control of the mantle.

9.6 Chiller: Pump driven water circulating cooling system cool flow #75 NESLABS Instruments, Inc. (or equivalent)

9.7 Turbo Vap Evaporator: Zymark #ZW640-3.

9.8 Turbo Vap Evaporator concentrator tubes: Zymark 250ml, 0.5ml 1ndpoint.

9.9 Beakers: Assorted Pyrex: 250ml, 600mL, and 1000mL, used for liquid containment and pipette storage.

9.10 Vials: glass, 4 dram & 40mL (with Polyseal sealed cap) (20 ml & 10 ml) capacity, for sample extracts.

9.11 Vial Rack: Plastic rack used to hold vials, during all phases of the extract processing.

9.12 Centrifuge: International Equipment Co., Model CL. (or equivalent)

9.13 Wrist Shaker: Burrell wrist action shaker, Model 75 and 88. (or equivalent)

9.14 Pipettes: S/P Disposable Serological Borosilicate Pipits.

1. 1mL X 1/10 #P4650-11X
2. 5mL X 1/10 #P4650-15
3. 10mL X 1/10 #P4650-110

Kimble Pasteur Borosilicate glass pipette 9" #72050 (or equivalent)

9.15 Quartz Microfiber Filters(QMF): 10.16 cm Dia., 100 circles(Whatman Cat# 1851-101) or equivalent Baked at 450 degrees Celsius for 4 hours. **(Only use with TO-4A)**

9.16 Tweezers: Laboratory stainless steel tweezers used to place PUFs into soxhlet and to squeeze extracted solvent out of PUFs into soxhlet.

9.17 Replacement PUFs: 75mm, pre-cleaned and tested. CAT# P226131

10.0 REAGENTS AND STANDARDS

10.1 Boiling Chips: Hengar #5785 Alltech Associates, Inc. (or equivalent)

10.2 Hexane: High Purity Solvent Baxter (Burdick/Jackson) #UN1208. (or equivalent)

10.3 Diethyl Ether: Nanograde Mallinckrodt #3434-08

10.4 Hexane/Ether: 90% Hexane/10% Ether for TO-4A by volume solvent mixture prepared in the lab.

10.5 Florisil: deactivated (10% Florisil), Deactivated with D.I. water. EM Science #FX0282-1.

10.6 Mercury: Triple distilled Mercury Refining Co, Albany, NY #328502. (or equivalent)

10.7 Sulfuric Acid: Na_2SO_4 (concentrated) Mallinkrodt #2468 #UN1830. (or equivalent)

10.8 Surrogate Spike Solution: Laboratory prepared from primary stock solution Tetra-Chloro-meta-Xylene and Decachlorobiphenyl at 0.500 ug/mL.

10.9 Laboratory Control Spike Solution: Laboratory prepared from primary stock solution of PCB Aroclor at 1.00 ug/mL

11.0 SAMPLE COLLECTION, PRESERVATION, SHIPMENT and STORAGE

11.1 Samples are collected as per EPA method TO-4A and the client's Field Sampling and Analysis Plan. Northeast Analytical does not provide field sample collection services for air monitoring projects. Samples should be stored at < 4 degrees Celsius until shipping to laboratory.

11.2 Field samples are shipped to the laboratory in a cooler chilled with Ice (<4 Degrees Celsius).

11.3 Upon receipt samples are stored in laboratory under refrigeration at < 4 degrees Celsius until extraction.

11.4 Samples must be extracted within 7 days of collection and analysis must be performed within 40 days of extraction.

12.0 QUALITY CONTROL

12.1 Verification PUF sample:

NOTE: A verification (a.k.a. certification) PUF sample is a cartridge and filter assembly that has been pre-cleaned as described in SOP NE_153 before delivery to field personnel or laboratory client

12.1.1 Extract and prepare one pre-cleaned PUF cartridge/filter assembly at a batch frequency described in the client's sampling/analytical plan. Note: Method TO-4A requires one verification PUF/Filter per extraction batch (or of 10 % of batch whichever greater).

12.1.2 Submit extract for analysis by GC-ECD (EPA Method 8082) as described in

8.6.4.

12.1.3 GC analysis of verification PUF must exhibit chromatogram free of PCB Aroclors (< Practical Quantitation Limit) and also be free of interfering non-target co-eluting contaminants. If PUF exhibits either contamination, re-prepare batch according to SOP NE_153. The default Practical Quantitation Limit for Method TO-4A is 0.100 ug total PCB.

12.2 Laboratory Method Blank

12.2.1 A Laboratory method blank sample is prepared and extracted with each site sample extraction batch of up to 20 samples. A pre-cleaned PUF and filter is spiked with surrogate solution and extracted and prepared identically to project samples. The analyte concentration must be less than the Practical Quantitation Limit. If the blank concentration exceeds the PQL the laboratory client is notified and data is qualified (B-flagged) and a case narrative is generated. All analysis must cease until the source of contamination is isolated and the problem is resolved. The default Practical Quantitation Limit for Method TO-4A is 0.100 ug total PCB.

12.3 Laboratory Control Spike/ Laboratory Control Spike Duplicate Sample

12.3.1 A laboratory control spike(LCS)/ laboratory control spike duplicate (LCSD) sample is prepared by spiking a pre-cleaned PUF cassette and filter with an Aroclor of interest applicable to the project. If the aroclor of interest is unknown rotate the spike between the 7 common Aroclors: Aroclor 1016, 1221, 1232, 1242, 1248 1254 and 1260. See table 8.2.4 for spike information. The percent recovery must meet project specified or laboratory established limits. The default Recovery Limit is 60-120 %.

12.3.2 Prepare LCS and LCSD samples at frequency specified in the clients sampling and analysis plan. The laboratory default is one LCS, LCSD per batch or 20 site samples whichever is greater.

12.3.3 IF the LCS/LCSD does not meet recovery limits the extraction of samples must stop until the problem is identified and corrected. The client is notified and a case narrative is issued to the client along with the affected data describing the LCS failure. Re-extraction of PUF samples is not possible.

12.4 Field Spike Sample

12.4.1 A field spike sample is prepared for each 20 PUF cartridges supplied to field personnel or as the client's field sampling analysis plan requires. The spike is prepared in the same fashion as an LCS sample and is shipped to the field and then returned to the laboratory unopened. The Field Spike sample is extracted and analyzed with the sample batch. The percent recovery criteria and corrective action are the same as the LCS/LCSD sample described in section 9.3.

12.5 Surrogate Spike

12.5.1 Every site sample and QC sample is spiked with the TCMX/DCBP surrogate solution described in table 8.4.2. The Surrogate recovery must meet project specified limits or default limits (60-120%). If the surrogate recovery does not meet specified limits then identify the problem, re-analyze extract by GC if necessary and provide case narrative describing the problem along with associated sample concentration results.

12.6 Field Blank Sample

12.6.1 A Field blank sample consists of a pre-cleaned cartridge assembly that as packaged and shipped to field personnel un-opened. The un-opened PUF is returned to the laboratory and analyzed with the sample batch. The PCB concentration should be less than the Practical Quantitation Limit. If PCBs are observed greater than the PQL compare results with laboratory method blank. Notify the client/field personnel of the problem and generate a case narrative that is issued with the analytical results.

13.0 CALIBRATION AND STANDARDIZATION

13.1 Please see determinative method (Lab SOP NE148) for details.

14.0 PROCEDURES

14.1 Sample Preparation

14.1.1 Throughout the entire process it should be noted that if the chemist encounters any problems or difficulties with any samples or steps involved, all work should STOP! Any problems should be brought to the attention of the supervisor and documented in the extraction logbook.

14.1.2 Before any steps are taken, the chemist should first review the sample job folder. The chemist should also verify the sample IDs on the bottle against the chain of custody. If there is a discrepancy on either the sample label or the chain of custody, this should brought to the attention of a supervisor.

14.1.3 Prior to extraction all surfaces and fume hoods used must be cleaned and wiped down with hexane nad then lined with aluminum foil. It is also advisable to remove any PCB solid or liquid waste containers from the fume hood

14.1.4 PUF samples require all glassware to be pre-rinsed with hexane. PUF samples are for extremely low level PCB concentrations and require clean; hexane rinsed glassware.

14.1.5 Use extreme caution using Ether during this extraction. Ether and its vapors are extremely flammable and must be used in a fume hood.

14.1.6 Prior to being used in the field all TO-4A PUFs are pre-cleaned in the lab utilizing soxhlet extraction apparatuses with pure acetone for 18 +- 2 hours.

14.1.7 All quartz micro fiber filters are baked in a drying oven for four hours at 450 degrees Celsius.

14.2 Procedure: Sample Extraction

14.2.1 Rinse enough 250 mL round bottoms and soxhlets for each sample, blank, and QC sample. Place in fume hood and let dry.

14.2.2 After the glassware dries, add a few boiling chips to each round bottom and add approximately 200 mL of Hexane/Ether mixture to each round bottom. Use 10% Hexane/Ether for the TO-4A extraction. Label them with a sample ID.

14.2.3 Blank, QC PUFs, and baked QMF filters (filters only for TO-4A) should be prepared prior to extraction using the PUF preparation SOP (NE153). Each sample must be handled using a clean pair of tweezers. Use the pre-cleaned replacement PUFs and pre-baked QMF filters for the Blank and QC samples.

14.2.3.1 For each sample, use a pair of tweezers to pull the PUF out of its PUF tube and push it into the appropriate soxhlet. Try to handle as PUF as little as possible. Using pair of tweezers depress both sides of the PUF and push the PUF to the bottom of the soxhlet.

14.2.3.2 Using tweezers, fold the glass fiber filter that came with the sample and push it into the soxhlet. Use the tweezers to push the filter down to the PUF. Be sure that both the PUF and the filter are below the capillary tube on the soxhlet to ensure proper drainage of the soxhlet.

14.2.3.2.1 Some Clients ask for QMF filters and T0-4A to be extracted and analyzed seperatly

14.2.3.3 Place the soxhlet onto the appropriate round bottom. Put clean gloves on and repeat with each sample.

14.2.4 Add Spike and Surrogate mixture to appropriate samples. All PUFS are surrogated the same, TO-4A PUFs rotate spikes. See table below.

Table 11

14.2.5 Rinse the inside and the outside connecting joints of the condenser units that will be used to condense the extraction solvent during the soxhlet extraction of the sample. Turn on chiller to cool the condensers.

14.2.6 Place the round bottom flask with attached soxhlet extractor onto a heating mantle and attach condenser unit. Turn corresponding thermostats on to setting 3.5. Double check soxhlets at this time for any cracks or chips which may leak solvent. Once the solvent begins to boil, a flushing action of three or more flushes per hour should be achieved.

14.2.7 The samples should be extracted overnight for a minimum of 18 hours. Once the sample has finished extracting (usually in the morning), turn the heating mantle off and allow samples to cool to room temperature. Once cool, rinse the inside of the condenser with several pipette volumes of hexane. Disengage the soxhlet and condenser unit and rinse the joint off as well into the soxhlet

14.2.8 Move all round bottom and soxhlet units to the fume hood. The diethyl-ether in the samples will continue to release vapors. Using tweezers, squeeze the PUF extracted solvent into the soxhlet. Rinse soxhlet with hexane and then allow the unit to drain into the round bottom.

14.2.9 Rinse the connecting joint into the round bottom. Set the soxhlet aside at this time and leave it in the hood to evaporate the remaining diethyl -ether. Procure the same number of turbo tubes as there are samples. Rinse all the turbo tubes with hexane and let dry. Using an individual turbo tube stand, label a turbo tube with the corresponding sample ID number and place in the holder. Add a layer of sodium sulfate into the round bottom and swirl content. Then pour the contents of the round bottom into the turbo tube, using a pipette and hexane to rinse the last drop out of the mouth of the round bottom. Rinse the round bottom with several pipettfuls of hexane, swirl gently, and decant into same turbo tube. Repeat this step twice for same sample, then repeat all preceding steps for all other samples.

Fortification Mixture	**Concentration**	**Volume added to Samples**
TCMX/DCBP Surrogate mix in hexane	0.05 ug/mL TCMX/ 0.5 ug/mL DCBP	0.500 mL
Aroclor 1016 Spike mix in hexane	1.000 ug/mL	1.000 mL
Aroclor 1221 Spike mix in hexane	1.000 ug/mL	1.000mL
Aroclor 1232 Spike mix in hexane	1.000 ug/mL	1.000 mL
Aroclor 1242 Spike mix in hexane	1.000 ug/mL	1.000 mL
Aroclor 1248 Spike mix in hexane	1.000 ug/mL	1.000 mL
Aroclor 1254 Spike mix in hexane	1.000 ug/mL	1.000 mL
Aroclor 1260 Spike mix in hexane	1.000 ug/mL	1.000 mL

14.2.10 All glassware must be rinsed with technical grade (tech)-acetone or a "for

rinsing-only" labeled solvent, and dried in the hood before other cleaning steps.

14.3 Solvent Reduction: TurboVap Evaporator System

14.3.1 The TurboVap evaporator system is used in place of the Kuderna Danish (KD)-concentrator apparatus. The turbovap uses a heated water bath and positive pressure nitrogen flow/vortex action. The unit maintains a slight equilibrium imbalance between the liquid and gaseous phase of the solvent extract which allows fractional reduction of the solvents without loss of higher boiling point analytes.

14.3.2 Turn the unit on (switch is located on the back side of the unit) and allow to heat up to the specified temperature for individual solvent use. This is indicated by the "Heating" display light, located above the temperate control knob on the right side of the unit. The system is at the proper temperature when the "At Temperature" light is lit. This is located above the "Heating" display light.

14.3.3 As a precaution the TurboVap system regulators should be checked to assure that no residual gas pressure remains within the system and that the gas cylinder valve and gas pressure regulators are both off before placing samples in the apparatus. Residual gas pressure may cause splashing and cross contamination of samples. To bleed the system of residual gas pressure place an empty turbo tube into the water bath and close the lid. Make sure that the nitrogen gas cylinder valve is turned off and slowly turn on the gas pressure regulator. Bleed any residual gas until the regulator output pressure gauge reads "0" psi. Proceed to 14.3.4. Make sure to wipe down all surfaces with hexane before concentration samples.

14.3.4 Place the turbo tube containing the samples into the Turbovap and close the lid. Turn on the gas cylinder valve first and then begin slowly turning the pressure regulator on. Keep the gas pressure very low, until the solvent level is decreased, to avoid splashing. Increase the gas pressure as the sample reduces maintaining uniform flow throughout the reduction.

14.3.5 The process for solvent (hexane/ether) reduction takes approximately 20-30 minutes. Do not leave the unit unattended as extracts may be blown to dryness and PCB loss may occur. Immediately notify a supervisor if an extract is blown to dryness.

14.3.6 Concentrate the solvent to approximately 25.0 mL. Remove the samples from the turbovap and place in the rack. The remaining solvent will consist largely of hexane since the ether component is fractionally removed at a faster rate than hexane; however, a solvent exchange with hexane should be completed 2x to ensure the ether has been entirely removed. NOTE:

Not all samples will evaporate at the same rate; sample extracts containing large amounts of petroleum or other non-volatile liquids may stop reducing before the 5.0 mL point is achieved. Samples which stop reducing should be removed as soon as possible.

14.3.7 Quantitatively transfer the sample extract with a disposable transfer pipette into a pre-labeled 40ml vial. Rinse Turbo tube with 2 Pasteur pipettes of hexane, then transfer the rinse to the vial. After the sample has been transferred, rinse the disposable transfer pipette with 0.5mL of hexane into the vial . **(Samples are not set to volume until after clean-up process).**

14.3.8 All dirty glassware must be rinsed with tech-acetone or a "For Rinsing-Only" labeled solvent and dried in the fume hood before being washed.

14.4 Sample Extract Cleanup

NOTE: Most extracts of environmental samples that are to be analyzed for PCBs by gas chromatography with electron capture detection contain co-extracted xenobiotics and other interfering substances which must be removed before accurate chromatographic analysis can be performed.

Not all clean-up procedures need to be performed on every sample and several are sample matrix specific. The experience of the analyst combined with the sampling site history should guide the selection of which clean-up procedures are necessary. The sequence and number of repeats of cleanup steps performed are recorded by the sample preparation chemist in the extraction logbook.

14.4.1 Sulfuric Acid Wash

14.4.1.1 The concentrated sulfuric acid treatment removes hydrocarbons and other organic compounds which are co-extracted with the PCB residues.

14.4.1.2 Add 3.0 mL concentrated H_2S0_4 and shake for 30 seconds by hand, centrifuge for approximately 1 minute on a setting of #4,
transfer the hexane upper layer to new 40 mL vial. Add a pipetteful of hexane to acid, swirl and transfer the hexane upper layer into vial with the sample, repeat 3x.

14.4.1.3 Repeat 8.4.2 if the sample extract appears to be heavily loaded (opaque) with colored material. Two to three acid washes may be required. Note: it is entirely possible that all

colored material will not be removed from the extract.

14.4.2 Florisil Adsorption (Slurry)

14.4.2.1 The florisil slurry removes co-extracted polar compounds, residual water, and residual acid and is recommended as the final cleanup step before the extract is submitted for GC analysis.

14.4.2.2 Add approximately 0.5 grams of tested and approved deactivated florisil to each vial containing the sample extract. **SEE EXTRACTION SUPERVISOR FOR THE APPROPRIATE DEACTIVATION CONCENTRATION TO BE USED.**

14.4.2.3 Vigorously shake the vial for approximately 1 min by hand or on the wrist shaker.

14.4.2.4 Place the vial(s) into the centrifuge for 2 minutes on setting #4.

14.4.2.4 Transfer the extract to a clean pre-labeled turbo tube. Add a pipetteful of hexane to florisil, swirl and transfer the hexane upper layer into the turbo tube with the sample, repeat 3x.

14.4.3 Elemental Sulfur Clean-up

14.4.3.1 Elemental sulfur is soluble in the extract solvents used for sediment and soil samples. It is commonly found in many PUF/sediment/soil samples, decaying organic material, and some industrial wastes. Large amounts of sulfur can cause the electron capture detector (ECD) to signal saturate for long periods during the elution envelope of PCBs. Even small amounts of sulfur can interfere with PCB measurement as a co-eluting chromatographic peak. PUF samples normally have less sulfur than sediment/soil samples.

14.4.3.2 Two techniques exist for the elimination of elemental sulfur in PCB extracts. Mercuric precipitation (Mercury Shake) and the Tetrabutylammonium (TBA) sulfite procedure. Tetrabutylammonium sulfite causes the least amount of degradation of a broad range of pesticides and organics compounds, while mercury may degrade organophosphorus and some organochlorine pesticides. The TBA procedure also has a higher capacity for samples containing high concentrations of elemental sulfur.

14.4.4 Removal of Sulfur Using Mercury

Note: Mercury is a highly toxic metal. All operations involving mercury should be performed within a hood. Prior to using mercury, the chemist should become acquainted with proper handling and emergency spill/clean-up procedures associated with this metal and must have reviewed the material safety data sheet MSDS.

14.4.4.1 Add 1-3 drops of mercury to the sample extracts, cap, and place on the wrist shaker for 30 mins. The sulfur is converted to mercuric sulfide and precipitates out of the sample extract. A black precipitate may be seen in sample extracts containing elemental sulfur.

14.4.4.2 Remove the sample extracts from the wrist shaker and place in the centrifuge for 2 minutes on speed setting on #4.

14.4.4.3 Transfer the sample extract to a clean 40 mL vial. Add a pipetteful of hexane to mercury, swirl and transfer the hexane upper layer into vial with the sample, repeat 3x.

14.4.4.4 The precipitated sulfur can be removed from the extract by performing a sulfuric acid clean-up or a Florisil slurry.

14.5 Setting to Volume:

14.5.1 There will be approximately 20-30 ml of sample in the turbo tube, using the Turbo Vap evaporator system concentrate the solvent to approximately 4.0ml.

14.5.2 Transfer the sample extract with a disposable pipette into a clean volumetric flask (5ml for PUF extracts). Rinse turbo tube with a pipetteful of hexane, transfer the rinse into the flask. Add hexane to the volumetric meniscus mark. Decant the contents into a pre-labeled 4 dram vial.

14.6 Extract Screening and Dilution:

14.6.1 PCB extracts are ordinarily screened by GC initially to determine the approximate concentration before final analysis. Prior site history and client supplied estimates of sample concentration may be used to determine what, if any, extract dilution is necessary. Extracts of unknown concentration are generally screened at a 10 to 100 fold dilution.

14.6.2 The supervising chemist is responsible for determining initial screening dilutions. Extract dilutions are prepared by transferring an aliquot of the

original sample extract into a vial containing the correct amount of "make up" volume of hexane. For example, a 1 to 10 dilution is performed by adding 1.0 mL of the extract to 9.0 mL hexane. The vial containing the diluted extract is labeled denoting the equivalent extract volume after the dilution; e.g. a 5mL extract diluted 1 to 10 is labeled "50X", an undiluted 5mL extract is labeled "5X".
When high dilutions are prepared, secondary (serial) dilutions of the initial diluent are prepared; e.g. a 100 fold dilution is prepared by a 1 to 10 dilution of the initial extract, then a 1 to 10 dilution of the resulting diluent.

14.6.3 Perform the dilution using an appropriate class A disposable volumetric pipette to transfer the extract and a calibrated volumetric autodispensette to dispense the make-up volume of hexane. Make sure that the vial is properly labeled. Cap and invert the vial at least three times to thoroughly mix the extract with the solvent.

14.6.4 Transfer 1 mL of the extract to a labeled 1.5 mL GC autosampler vial. Record the screening dilution and Set Volume in the Log Book, enter data into the LIMS. Create a Access Report Sheet prepared in LIMS. Submit the Access Report Sheet, a photocopy of the logbook, and completed internal chain of custody tracking form with the sample extracts to the GC analyst.

15.0 CALCULATIONS

15.1 Please see determinative method (Lab SOP NE148) for details.

16.0 METHOD PERFORMANCE

16.1 Please see determinative method (Lab SOP NE148) for details.

17.0 POLLUTION PREVENTION

17.1 See NEA168.SOP.

18.0 DATA ASSESSMENT AND ACCEPTANCE CRITERIA FOR QUALITY CONTROL MEASURES

18.1 Please see determinative method (Lab SOP NE148) for details.

19.0 CORRECTIVE ACTIONS FOR OUT OF CONTROL DATA

19.1 Please see determinative method (Lab SOP NE148) for details.

20.0 CONTINGINCIES FOR HANDLING OUT-OF-CONTROL OR UNACCEPTABLE DATA

20.1 Please see determinative method (Lab SOP NE148) for details

21.0 WASTE MANAGEMENT

21.1 See NEA054.SOP, NEA083.SOP, NEA089.SOP

22.0 REFERENCES

22.1 US-EPA SW-846 Test Methods for Solid Waste; Soxhlet Extraction Method 3540C; United States Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Vol.1B, Cincinnati, OH 45268. December 1996.

22.2 US-EPA Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air Second Edition Compendium Method TO-4A Determination of Pesticides and Polychlorinated Biphenyls in Ambient Air Using High Volume Polyurethane Foam (PUF) Sampling Followed by Gas Chromatographic/Multi-Detector Detection (GC/MS) 3/18/99

22.3 Guide to Environmental Analytical Methods, Genium Publishing Corporation, Schenectady, NY 12304. 1997

23.0 TABLES, DIAGRAMS, FLOWCHARTS and VALIDATION DATA

23.1 Method Outline Summary

ATTACHMENT A: METHOD OUTLINE

METHOD OUTLINE FOR PUF EXTRACTION USING SOXHLET TECHNIQUE

1. PREPARE FUME HOOD AND SAMPLES FOR EXTRACTION
2. RINSE GLASSWARE AND LET DRY
3. SET UP SOXHLET EXTRACTOR APPARATUS
4. ADD SURROGATES AND/OR MATRIX SPIKE
5. EXTRACT SAMPLE FOR APPROXIMATELY 18 HOURS +/- 2hours
6. BREAKDOWN SOXHLET EXTRACTOR APPARATUS
7. TRANSFER SOLVENT TO TURBO TUBE
8. SOLVENT REDUCTION, USING THE TURBOVAP EVAPORATION SYSTEM
9. TRANSFER TO 40mL VIAL
10. EXTRACT CLEANUP (ACID, MERCURY OR TBA, FLORISIL) W/ BACKWASHES

11. SOLVENT REDUCTION, USING THE TURBOVAP EVAPORATOION SYSTEM

12. SET TO VOLUME

13. EXTRACT DILUTION

14. GC SCREENING/ ANALYSIS

APPENDIX 55
SOP FOR THE EXTRACTION AND EXTRACT PREPARATION OF POLYURETHANE FOAM AIR CARTRIDGES (PUFS) FOR EPA METHOD TO-10A POLYCHLORINATED BIPHENYLS IN AIR CASSETTE MEDIA (NE241_02_R01)

STANDARD OPERATING PROCEDURE

NORTHEAST ANALYTICAL, INC.

NE241_02.DOC
REVISION NUMBER: 02

THE EXTRACTION AND EXTRACT PREPARATION OF POLYURETHANE FOAM AIR CARTRIDGES (PUFS) FOR EPA METHOD TO-10A POLYCHLORINATED BIPHENYLS IN AIR CASSETTE MEDIA

COPY #: _____

NORTHEAST ANALYTICAL, INC.
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STANDARD OPERATING PROCEDURE

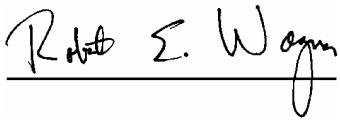
LABORATORY PROCEDURE NE241_02.DOC

REVISION 2 (02/20/09)

Author: Carrie Barss

Carrie Barss
Extractions Manager

Reviewed by:



Robert E. Wagner
Laboratory Director

Approved by:

Christina Braidwood
Quality Assurance Manager

Table of Contents

1.0 IDENTIFICATION OF TEST METHOD

1.1 This is a Standard Operating Procedure for the Extraction and Cleanup procedures of Low Volume Polyurethane Foam (PUF) air cassette samples for Polychlorinated Biphenyl (PCB) analysis using the Soxhlet extraction technique (Modified SW-846 Method 3540C/EPA Method TO-10A for subsequent analysis by SW-846 Method 8082 or EPA Method 680 (PCB Homologs by GC/MS).

Note: The Determinative Method for PCB Aroclors (EPA Method 8082) requires secondary GC column analysis on dissimilar column for PUF samples.

2.0 APPLICABLE MATRICES

2.1 This test method is appropriate for air.

3.0 DETECTION LIMIT

3.1 Please see determinative method (Lab SOP NE148, EPA Method 8082 or Lab SOP NE 040, EPA Method 680) for details.

4.0 SCOPE AND APPLICATION

4.1 The following procedure is utilized by Northeast Analytical, Inc. for the extraction and cleanup of PCBs from PUF (air) samples using the soxhlet extraction method of TO-10A PUFS for subsequent analysis by SW-846 Method 8082 or EPA Method 680.

5.0 SUMMARY OF TEST METHOD

5.1 Set up a soxhlet extractor apparatus for each sample.

5.2 Load the PUF into the soxhlet. Add the necessary surrogates and/or matrix spikes.

5.3 Load the extraction apparatus into its heating mantle and condenser and allow it to extract for 18 $\pm$ 2 hours.

5.4 Solvent exchange and cleanup the sample utilizing acid, florisil and mercury; performing a backwash for each step.

5.5 Concentrate and set to 5.0ml. Submit for GC analysis.

6.0 DEFINITIONS

6.1 **Method Blank:** With each batch of samples to be extracted a method blank is processed. The method blank is carried through all stages of sample preparation and measurement steps.

6.2 **Lab Control Standard:** A non-site sample created in the laboratory to which a known amount of target analyte is added for assessment of analyte recovery efficiency

6.3 **Lab Control Standard Duplicate:** An exact copy of the Lab Control Standard to further assess analyte recovery efficiency.

6.4 **Matrix Spike:** A site sample to which a known amount of target analyte is added for assessment of analyte recovery efficiency.

6.5 **Matrix Spike Duplicate:** An exact copy of the Matrix Spike utilizing the same site sample and known amount of target analyte for assessment of analyte recovery efficiency.

6.6 **Surrogate Compound Spike:** In chemical composition and chromatography similar to the analytes of interest. Usually not found in environmental samples. These compounds are spiked into all samples, standards, blanks, and matrix spike samples prior to analysis. Percent recoveries are calculated for each surrogate.

6.7 **QC-Quality Control:** A set of measures for each sample within an analysis methodology to assure that the process is in control.

7.0 INTERFERENCES

7.1 Laboratory contaminants including phthalate esters may be introduced during extraction and subsequent cleanup procedures. The extraction technician should exercise caution that scrupulously cleaned glassware is used and that plastic tubing and other plastic materials do not contact samples or extracts.

8.0 SAFETY

8.1 The chemist should have received in-house safety training and should know the location of first aid equipment and the emergency spill/clean-up equipment, before handling any apparatus or equipment. Safety glasses and gloves must be worn when handling glassware and samples.

8.2 Polychlorinated biphenyls have been tentatively classified as known or suspected carcinogens. The chemist must review the Material Safety Data Sheets (MSDS) for PCBs and all reagents used in the procedure before handling them. All equipment and solvents should be handled within a lab fume hood.

9.0 EQUIPMENT AND SUPPLIES

9.1 Water Cooled Condenser: Pyrex 45/50 #3840-MCO.

9.2 250ml Round Bottom Flask: Pyrex #4100.

9.3 Soxhlet Repetitive Flushing (reflux) Unit: 45/50 Pyrex #3740-M.

9.4 Heating Mantle: Type "VF" laboratory heating mantle #HM0250VF1. (or equivalent)

9.5 Heating Mantle Controller: Glass-Col #PL3122 Minitwin (or equivalent) regulates temperature control of the mantle.

9.6 Chiller: Pump driven water circulating cooling system cool flow #75 NESLABS

Instruments, Inc. (or equivalent)

9.7 Turbo Vap Evaporator: Zymark #ZW640-3.

9.8 Turbo Vap Evaporator concentrator tubes: Zymark 250ml, 0.5ml 1ndpoint.

9.9 Beakers: Assorted Pyrex: 250ml, 600mL, and 1000mL, used for liquid containment and pipette storage.

9.10 Vials: glass, 4 dram & 40mL(with Polyseal sealed cap) (20 ml & 10 ml) capacity, for sample extracts.

9.11 Vial Rack: Plastic rack used to hold vials, during all phases of the extract processing.

9.12 Centrifuge: International Equipment Co., Model CL. (or equivalent)

9.13 Wrist Shaker: Burrell wrist action shaker, Model 75 and 88. (or equivalent)

9.14 Pipettes: S/P Disposable Serological Borosilicate Pipettes.

1. 1mL X 1/10 #P4650-11X
2. 5mL X 1/10 #P4650-15
3. 10mL X 1/10 #P4650-110

Kimble Pasteur Borosilicate glass pipette 9" #72050 (or equivalent)

9.15 Tweezers: Laboratory stainless steel tweezers used to place PUFs into soxhlet and to squeeze extracted solvent out of PUFs into soxhlet.

9.16 Replacement PUFs: ORBO-1000 or equivalent 22mm O.D. X 7.6 cm length, pre-cleaned and pre-tested certified by Vendor. Supelco CAT# 20600-U

10.0 REAGENTS AND STANDARDS

10.1 Boiling Chips: Hengar #5785 Alltech Associates, Inc. (or equivalent)

10.2 Hexane: High Purity Solvent Baxter (Burdick/Jackson) #UN1208. (or equivalent)

10.3 Diethyl Ether: Nanograde Mallinckrodt #3434-08

10.4 Hexane/Ether: 95%Hexane/5%Ether for TO-10A by volume solvent mixture prepared in the lab.

10.5 Florisil: solvent washed with 1:1 hexane/ether, baked at 130°C for 16 hours. Deactivated with D.I. water. EM Science #FX0282-1.

10.7 Mercury: Triple distilled Mercury Refining Co, Albany, NY #328502. (or equivalent)

10.8 Sulfuric Acid: Na_2SO_4 (concentrated) Mallinkrodt #2468 #UN1830. (or equivalent)

10.9 Surrogate Spike Solution: Laboratory prepared from primary stock solution Tetra-Chloro-meta-Xylene and Decachlorobiphenyl at 0.500 ug/mL.

10.10 Laboratory Control Spike Solution: Laboratory prepared from primary stock solution of PCB Aroclor at 1.00 ug/mL

11.0 SAMPLE COLLECTION, PRESERVATION, SHIPMENT and STORAGE

11.1 Samples are collected as per EPA method TO-10A, the client's Field Sampling, and Analysis Plan. Northeast Analytical does not provide field sample collection services for air monitoring projects. Samples should be stored at < 4 degrees Celsius until shipping to laboratory.

11.2 Field samples are shipped to the laboratory in a cooler chilled with ice (< 4 °C).

11.3 Upon receipt samples are stored in laboratory under refrigeration at < 4 °C until extraction.

11.4 Samples must be extracted within 7 days of collection and analysis must be performed within 40 days of extraction.

12.0 QUALITY CONTROL

12.1 Verification PUF sample:

A verification (a.k.a. certification) PUF sample is a cartridge assembly that is tested at the laboratory prior to delivery to field personnel. In general each vendor lot # is pre tested by the laboratory.

12.1.1 Extract and prepare one pre-cleaned PUF cartridge assembly at a batch frequency described in the client's sampling/analytical plan (1 per 50 PUFs.)

12.1.2 Submit extract for analysis by GC-ECD or GC/MS (EPA Method 8082 or EPA Method 680) as described in 14.7.4 8.6.4.

12.1.3 GC analysis of verification PUF must exhibit chromatogram free of PCB Aroclors (< Practical Quantitation Limit) and also be free of interfering non-target co-eluting contaminants.

12.2 Laboratory Method Blank

12.2.1 A Laboratory method blank sample is prepared and extracted with each site sample extraction batch of up to 20 samples. A pre-cleaned PUF is spiked with surrogate solution and extracted and prepared identically to project samples. The analyte concentration must be less than the Practical Quantitation Limit. If the blank concentration exceeds the PQL the laboratory client is notified and data is qualified (B-flagged) and a case narrative is generated. All analysis must cease until the source of contamination is isolated and the problem is resolved. The default Practical Quantitation Limit for Method TO-10A is 0.100 ug total PCB. Due to the nature of sample collection PUF samples cannot be re-extracted.

12.3 Laboratory Control Spike/ Laboratory Control Spike Duplicate Sample

12.3.1 A laboratory control spike (LCS)/ laboratory control spike duplicate (LCSD) sample is prepared by spiking a pre-cleaned PUF cassette with an Aroclor of interest applicable to the project. The percent recovery must meet project specified or laboratory established limits. The default Recovery Limit is 70-130%.

12.3.2 Prepare LCS and LCSD samples at frequency specified in the clients sampling and analysis plan. The laboratory default is one LCS, LCSD per batch or 20 site samples whichever is greater. TO-10A PUFS are spiked at default with Aroclor mix in hexane at a concentration of 1.000 ug/ml. Please see Table 23.1

12.3.3 IF the LCS/LCSD does not meet recovery limits the extraction of samples must stop until the problem is identified and corrected. The client is notified and a case narrative is issued to the client along with the affected data describing the LCS failure. Re-extraction of PUF samples is not possible.

12.4 Field Spike Sample

12.4.1 A field spike sample is prepared for each 20 PUF cartridges supplied to field personnel or as the client's field sampling analysis plan requires. The spike is prepared in the same fashion as an LCS sample and is shipped to the field and then returned to the laboratory unopened. The Field Spike sample is extracted and analyzed with the sample batch. The percent recovery criteria and corrective action are the same as the LCS/LCSD sample described in section 12.3. Please see Table 23.1 for spike amounts added to sample.

12.5 Surrogate Spike

12.5.1 Every site sample and QC sample is spiked with the TCMX/DCBP surrogate solution described in Table 23.1. The Surrogate recovery must meet project specified limits or default limits (60-120%). If the surrogate recovery does not meet specified limits then identify the problem, re-analyze extract by GC if necessary and provide case narrative describing the problem along with associated sample concentration results. Please see Table 23.1 for surrogate spike amounts added to sample.

12.6 Field Blank Sample

12.6.1 A Field blank sample consists of a pre-cleaned cartridge assembly that as packaged and shipped to field personnel un-opened. The un-opened PUF is returned to the laboratory and analyzed with the sample batch. The PCB concentration should be less than the Practical Quantitation Limit. If PCBs are observed greater than the PQL compare results with laboratory method blank. Notify the client/field personnel of the problem and generate a case narrative that is issued with the analytical results. Due to the nature of sample collection PUF samples cannot be re-extracted.

13.0 CALIBRATION AND STANDARDIZATION

Please see determinative method (Lab SOP NE148, EPA Method 8082 or NE 040, EPA Method 680) for details.

14.0 PROCEDURES

14.1 Sample Preparation

14.1.1 Throughout the entire process it should be noted that if the chemist encounters any problems or difficulties with any samples or steps involved, all work should STOP! Any problems should be brought to the attention of the supervisor and documented in the extraction logbook.

14.1.2 Before any steps are taken, the chemist should first review the sample job folder. The chemist should also verify the sample IDs on the bottle against the chain of custody. If there is a discrepancy on either the sample label or the chain of custody, this should be brought to the attention of a supervisor.

14.1.3 Prior to extraction all surfaces and fume hoods used must be cleaned and wiped down with hexane and then lined with aluminum foil. It is also advisable to remove any PCB solid or liquid waste containers from the fume hood

14.1.4 PUF samples require all glassware to be pre-rinsed with hexane. PUF samples are for extremely low level PCB concentrations and require clean; hexane rinsed glassware.

14.1.5 Use extreme caution while using Ether during this extraction. Ether and its vapors are extremely flammable and must be used in a fume hood.

14.2 Procedure: Sample Extraction

14.2.1 Rinse enough 250 mL round bottoms and soxhlets for each sample, blank, and QC sample. Place in fume hood and allow to dry.

14.2.2 After the glassware dries label them with a sample ID. To each round bottom add a few boiling chips and approximately 200 mL of 5% Hexane/Ether mixture.

14.2.3 Place a soxhlet onto each round bottom, checking for cracks or chips that would cause solvent to leak out. Record the ID number of each soxhlet and round bottom in LIMS.

14.2.4 Blank and QC PUFs are prepared using pre-cleaned replacement PUFs. For each sample, use a pair of tweezers to pull the PUF out of its PUF tube and push it into the appropriate soxhlet. Depress both sides of the PUF and push the PUF to the bottom of the soxhlet. Try to handle as PUF as little as possible. **Rinse tweezers in between handling each sample.**

14.2.5 Spike surrogate and spike compound solutions directly into the soxhlet onto the PUF. The addition of spiking material to a sample, blank, or QC must be witnessed by another extraction technician. Record the names of the technicians

spiking and witnessing, surrogate and spike concentration, the amount spiked, and the spike solution reference code in LIMS.

14.2.5 Rinse the inside and the outside connecting joints of the condenser units that will be used with hexane. Turn on chiller to cool the condensers.

14.2.6 Place the round bottom flask with attached soxhlet extractor onto a heating mantle and attach condenser unit. Turn corresponding thermostats on to setting 3.5. Double check soxhlets at this time for any cracks or chips. Once the solvent begins to boil, a flushing action of three or more flushes per hour should be achieved.

14.2.7 The samples should be extracted for 18 hours $\pm$ 2 hours, usually overnight. Once the sample has finished extracting (usually in the morning), turn the heating mantle off and allow samples to cool to room temperature.

14.2.8 Once cool, disengage the soxhlet from the condenser and move all round bottom/ soxhlet units to a fume hood. The diethyl-ether in the samples will continue to release vapors. Using hexane pre-rinsed tweezers squeeze the extracted solvent from the PUF and into the soxhlet. Tip the soxhlet/round bottom unit to get the solvent in the soxhlet to drain into the round bottom.

14.2.9 Rinse soxhlet with hexane and again tip to allow the unit to drain into the round bottom. Disconnect the soxhlet from the round bottom and rinse the connecting joint of the soxhlet into the round bottom. Set the soxhlet aside at this time and leave it in the hood to dry.

14.2.10 Label turbo tubes with sample ID, one per sample, and record the ID of each Turbo Tube in LIMS. Rinse turbo tubes with hexane and allow to dry in the hood.

14.2.11 Add sodium sulfate to each round bottom, swirling contents. Add as much sodium sulfate as necessary until the drying agent is free flowing.

14.2.12 Pour the contents of the round bottom into the turbo tube, decanting off the sodium sulfate. Using a pipette and hexane, rinse the last drop out of the mouth of the round bottom.

14.2.13 Add 3-4 Pasteur pipettes full of hexane to the round bottom. Swirl gently, and decant into same turbo tube. Repeat twice more for each sample.

14.2.14 All glassware must be rinsed with acetone, and dried in the hood before being washed.

14.3 Solvent Reduction: TurboVap Evaporator System

14.3.1 The TurboVap evaporator system is used in place of the Kuderna Danish (KD)-concentrator apparatus. The TurboVap evaporator system is used to reduce the sample volume. The TurboVap uses a heated water bath and positive pressure nitrogen flow / vortex action. The unit maintains a slight equilibrium imbalance

between the liquid and gaseous phase of the solvent extract, which allows fractional reduction of the solvents without loss of higher boiling point analytes.

14.3.2 Turn the unit on and allow to heat up to 40°C ± 2°C.

14.3.3 As a precaution the TurboVap system regulators should be checked to assure that there is no residual gas pressure within the system and that the gas pressure regulator is off before placing samples in the apparatus. Residual gas pressure may cause splashing and cross contamination of samples. To bleed the system of residual gas pressure place an empty TurboTube into the water bath and close the lid. Make sure that the nitrogen gas pressure regulator is off. Bleed any residual gas until the regulator gauge reads "0" psi. Remove the empty TurboTube.

14.3.4 Wipe down inside of TurboVap with a Hexane wetted paper towel including top lid and pins. Place TurboTubes containing the sample extracts into the TurboVap and close lid. Slowly open the pressure regulator. Keep the gas pressure very low, until the solvent level is decreased, to avoid splashing. Increase the gas pressure as the sample reduces, maintaining uniform flow throughout the volume reduction.

14.3.5 The process for solvent (hexane/ether) reduction takes approximately 20-30 minutes. Do not leave the unit unattended as extracts may be blown to dryness and PCB loss may occur. Immediately notify a supervisor if an extract is blown to dryness.

14.3.6 Concentrate the solvent to approximately 25.0 mL. Remove the samples from the turbovap and place in a rack.

NOTE: Not all samples will evaporate at the same rate; sample extracts containing large amounts of petroleum or other non-volatile liquids may stop reducing before the 5.0 mL point is achieved. Samples which stop reducing should be removed as soon as possible.

14.3.7 Using a disposable Pasteur pipette, quantitatively transfer the sample extract into a pre-labeled 40mL vial. Rinse Turbo tube with 2 Pasteur pipette volumes of hexane, and transfer the rinse to the vial. After the sample has been transferred, rinse the pipette into the vial with approximately 0.5mL of hexane.

14.3.8 Set turbo tubes aside for use in step 14.5.

14.4 Sample Extract Cleanup

14.4.1 Most extracts of environmental samples that are to be analyzed for PCBs by gas chromatography with electron capture detection contain co-extracted xenobiotics and other interfering substances which must be removed before accurate chromatographic analysis can be performed.

14.4.2 Not all clean-up procedures need to be performed on every sample and several are sample matrix specific. The experience of the analyst combined with the

sampling site history should guide the selection of which clean-up procedures are necessary. The sequence and number of repeats of cleanup steps performed are recorded by the sample preparation chemist in LIMS.

14.4.3 Sulfuric Acid Wash

14.4.3.1 Sulfuric acid removes hydrocarbons and other organic compounds which are co-extracted with the PCB residues.

14.4.3.2 Add 3.0 mL concentrated H_2S0_4 to vial and shake for 30 seconds by hand. Centrifuge for approximately 1 minute on a speed setting of ¾.

14.4.3.3 Transfer the hexane layer (top layer) to a new properly labeled 40mL vial. Add one pipette of hexane to the acid, swirl and transfer the hexane rinse into the vial containing sample. Repeat 3 times.

14.4.3.4 Repeat 14.4.1 if the sample extract appears to be heavily loaded (opaque) with colored material. Two to three acid washes may be required. Note: it is entirely possible that all colored material will not be removed from the extract.

14.4.4 Florisil Absorption (Slurry)

14.4.4.1 The florisil slurry removes co-extracted polar compounds, residual water, and residual acid.

14.4.4.2 Add one spatula (approximately 0.5g) of tested and approved Florisil to each extract vial. **SEE EXTRACTION SUPERVISOR FOR THE APPROPRIATE DEACTIVATION CONCENTRATION TO BE USED.**

14.4.4.3 Vigorously shake the vial for approximately 30 seconds by hand.

14.4.4.4 Place the vial(s) into the centrifuge for 2 minutes on speed setting ¾.

14.4.4.5 Transfer the hexane layer to a new properly labeled 40mL vial. Add one pipette of hexane to the florisil, swirl, and transfer the hexane rinse into the vial containing sample. Repeat 3 times.

14.4.5 Elemental Sulfur Clean-up

14.4.5.1 Elemental sulfur is soluble in the extract solvents used for sediment and soil samples. It is commonly found in many PUF/sediment/soil samples, decaying organic material, and some industrial wastes. Large amounts of sulfur can cause the electron capture detector (ECD) to signal saturate for long periods during the elution envelope of PCBs. Even small amounts of sulfur can interfere with PCB measurement as a co-eluting chromatographic peak. PUF samples normally have less sulfur than sediment/soil samples.

14.4.5.2 Two techniques exist for the elimination of elemental sulfur in PCB

extracts: Mercuric precipitation (Mercury Shake) and the Tetrabutylammonium (TBA) sulfite procedure. Tetrabutylammonium sulfite causes the least amount of degradation of a broad range of pesticides and organics compounds, while mercury may degrade organophosphorus and some organochlorine pesticides. The TBA procedure also has a higher capacity for samples containing high concentrations of elemental sulfur.

14.4.5.3 Removal of Sulfur Using Mercury

Note: Mercury is a highly toxic metal. All operations involving mercury should be performed within a hood. Prior to using mercury, the chemist should become acquainted with proper handling and emergency spill/clean-up procedures associated with this metal and must have reviewed the material safety data sheet MSDS.

14.4.5.3.1 Add 1-3 drops of mercury to the sample extracts, cap, and place on the wrist shaker for 30 minutes. The sulfur is converted to mercuric sulfide and precipitates out of the sample extract. A black precipitate may be seen in sample extracts containing elemental sulfur.

14.4.5.3.2 Transfer the extract back to it's original turbo tube. Add a pipette of hexane to the mercury, swirl, and transfer the hexane rinse into the turbo tube with the sample. Repeat 3 times.

14.5 Setting to Final Extract ConcentrateVolume:

14.5.1 There will be approximately 20-30 ml of sample in each turbo tube. Using the Turbo Vap evaporator system concentrate the solvent to approximately ½ the set volume. Default set volume is 5mL, so extract will be concentrated to 2.5mL.

14.5.2 Transfer the sample extract with a disposable pipette into a clean volumetric flask (5ml for PUF extracts). Rinse turbo tube with a pipetteful of hexane, transfer the rinse into the flask. Repeat until the level in the volumetric reaches the meniscus mark. Stopper and invert to mix. Pour the contents into a pre-rinsed and properly labeled 4 dram vial.

15.0 CALCULATIONS

15.1 Please see determinative (Lab SOP NE148, EPA Method 8082 or NE 040, EPA Method 680) for details

16.0 METHOD PERFORMANCE

16.1 Please see determinative method (Lab SOP NE148, EPA Method 8082 or NE 040, EPA Method 680) for details

17.0 POLLUTION PREVENTION

17.1 See SOP NE168.

18.0 DATA ASSESSMENT AND ACCEPTANCE CRITERIA FOR QUALITY CONTROL MEASURES

18.1 Please see determinative method (Lab SOP NE148, EPA Method 8082 or NE 040, EPA Method 680) for details

19.0 CORRECTIVE ACTIONS FOR OUT OF CONTROL DATA

19.1 Please see determinative method (Lab SOP NE148, EPA Method 8082 or NE 040, EPA Method 680) for details

20.0 CONTINGINCIES FOR HANDLING OUT-OF-CONTROL OR UNACCEPTABLE DATA

20.1 Please see determinative method (Lab SOP NE148, EPA Method 8082 or NE 040, EPA Method 680) for details

21.0 WASTE MANAGEMENT

21.1 See SOP NE054.

22.0 REFERENCES

22.1 US-EPA SW-846 Test Methods for Solid Waste; Soxhlet Extraction Method 3540C; United States Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Vol.1B, Cincinnati, OH 45268. December 1996

22.2 US-EPA Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air Second Edition Compendium Method TO-10A. Determination of Pesticides and Polychlorinated Biphenyls in Ambient Air Using High Volume Polyurethane Foam (PUF) Sampling Followed by Gas Chromatographic/Multi-Detector Detection (GC/MS), 3/18/99.

22.3 Guide to Environmental Analytical Methods, Genium Publishing Corporation, Schenectady, NY 12304, 1997.

23.0 TABLES, DIAGRAMS, FLOWCHARTS and VALIDATION DATA

23.1 Surrogate and Spike Additions

23.2 Method Outline Summary

23.1 Table 1. Surrogate and Spike Additions

Fortification Mixture	Concentration	Volume added to Samples
TCMX/DCBP Surrogate mix in hexane	0.05 ug/mL TCMX/ 0.5 ug/mL DCBP	0.500 mL
Aroclor 1016 Spike mix in hexane	1.000 ug/mL	1.000 mL
Aroclor 1221 Spike mix in hexane	1.000 ug/mL	1.000mL
Aroclor 1232 Spike mix in hexane	1.000 ug/mL	1.000 mL
Aroclor 1242 Spike mix in hexane	1.000 ug/mL	1.000 mL
Aroclor 1248 Spike mix in hexane	1.000 ug/mL	1.000 mL
Aroclor 1254 Spike mix in hexane	1.000 ug/mL	1.000 mL
Aroclor 1260 Spike mix in hexane	1.000 ug/mL	1.000 mL

23.2 Method Outline Summary: PUF Extraction Using Soxhlet Technique

Step 1: PREPARE FUME HOOD AND SAMPLES FOR EXTRACTION

Step 2: RINSE GLASSWARE AND LET DRY

Step 3: SET UP SOXHLET EXTRACTOR APPARATUS

Step 4: ADD SURROGATES AND/OR MATRIX SPIKE

Step 5: EXTRACT SAMPLE FOR APPROXIMATELY 18 HOURS +/- 2hours

Step 6: BREAKDOWN SOXHLET EXTRACTOR APPARATUS

Step 7: TRANSFER SOLVENT TO TURBO TUBE

Step 8: SOLVENT REDUCTION, USING THE TURBOVAP EVAPORATION SYSTEM

Step 9: TRANSFER TO 40mL VIAL

Step 10: EXTRACT CLEANUP (ACID, MERCURY OR TBA, FLORISIL) W/ BACKWASHES

Step 11: SOLVENT REDUCTION, USING THE TURBOVAP EVAPORATOION SYSTEM

Step 12: SET TO VOLUME

Step 13: EXTRACT DILUTION

Step 14: GC SCREENING/ ANALYSIS

STANDARD OPERATING PROCEDURE REVIEW

SOP Name	Review Number	Reviewers	Title	QAO Approval	Effective Date
NE241_02	01	Carrie Barss Christina L. Braidwood Robert E. Wagner	Extraction Sup. QAO Lab Director	Christina Braidwood	02/20/09

APPENDIX 56
SOP FOR NOISE METER CALIBRATION AND MAINTENANCE

Standard Operating Procedure: Noise Meter Calibration and Maintenance

I. Scope and Application

This Standard Operating Procedure (SOP) describes the procedures for sound level meter calibration and maintenance during Phase 1 of the Hudson River remedial action.

The methods for performing sound monitoring are described in Appendices 6 and 7.

II. Personnel Qualifications

Field sampling personnel will have current health and safety training, including 40-hour Occupational Safety and Health Administration (OSHA) Hazardous Waste Operations (HAZWOPER) training and an annual refresher course, site supervisor training, and site-specific training, as needed. In addition, personnel performing sound monitoring and sound level meter calibration and maintenance will be trained in the use of the sound level meter.

III. Equipment List

The following materials, as required, will be available while performing sound level meter calibration and maintenance:

- Personal protective equipment (PPE), as required by the Health and Safety Plan (HASP; Parsons 2008)
- Sound level meter (both CEL Instrument Model 593 and Larson Davis Model 820 or equivalents)
- Sound level meter calibrator
- Sound level meter manual
- Sound level meter calibration notebook
- Field notebook

IV. Cautions

Sound level meters will be kept dry and within recommended operating temperatures. Sound level meters may be exposed to inclement weather (such as rain or snow) or temperatures (such as temperatures below recommended operating temperatures) for short periods of time during measurements. Once a measurement is taken, the sound level meter will be brought to the field vehicle (or trailer), where it will be dried off and kept within recommended operating temperatures. Failure to keep the sound level meter dry and at optimal operating temperature may result in malfunction of the meter.

Keep the wind screen over the microphone at all times when calibrating. Keep the microphone clean. Dirt on the microphone may result in inaccurate measurements.

V. Health and Safety Considerations

The HASP will be followed when performing calibration and maintenance.

VI. Procedures

The sound level meter will be operated according to the procedures contained in the operating manual. Calibration and maintenance procedures are summarized below.

Field Calibration

1. Insert the calibrator onto the sound level meter.

2. Turn on the sound level meter.

3. With the calibrator securely in place, follow the operating manual for adjusting the sound level meter.

4. Record results of adjustment of the sound level meter in the sound level meter calibration notebook.

Factory Calibration

1. Calibration will be performed at the manufacturer's recommended frequency. Send the sound level meter to the manufacturer for calibration.

2. Record calibration activity in the sound level meter calibration notebook.

3. Maintain files received from the manufacturer on calibration in the sound level meter files.

Maintenance

Replace the battery when the low battery icon is displayed on the sound level meter. Follow the operating manual for battery replacement. Record battery replacement activities in the sound level meter calibration notebook.

VII. Waste Management

Paper towels or other items used to maintain the sound level meter in clean and dry condition will be disposed of at the end of each maintenance event as municipal solid waste.

VIII. Data Recording and Management

Calibration results will be recorded in the sound level meter calibration notebook. Files received from the manufacturer on calibration will be maintained in the sound level meter files. For each calibration, identification of sampling personnel, date, time, model of sound level meter, serial number of sound level meter, and calibration results will be recorded. Battery replacement will be recorded in the sound level meter calibration notebook. Maintenance activities will be recorded in the field notebook.

IX. Quality Assurance

The sound level meter will be maintained in accordance with this SOP and the operating manual.

X. References

Parsons, 2008. Phase 1 Remedial Action Health and Safety Plan, Hudson River PCBs Superfund Site. Prepared for General Electric Company, Albany, NY. August 2008.

APPENDIX 57
SOP FOR LIGHT METER CALIBRATION AND MAINTENANCE

Standard Operating Procedure: Light Meter Calibration and Maintenance

I. Scope and Application

This Standard Operating Procedure (SOP) describes the procedures for light meter calibration and maintenance during Phase 1 of the Hudson River remedial action. The method for performing light monitoring is described in Appendix 8.

II. Personnel Qualifications

Field sampling personnel will have current health and safety training, including 40-hour Occupational Safety and Health Administration (OSHA) Hazardous Waste Operations (HAZWOPER) training and an annual refresher course, site supervisor training, and site-specific training, as needed. In addition, personnel performing light monitoring and light meter calibration and maintenance will be trained in the use of the light meter.

III. Equipment List

The following materials, as required, will be available while performing light meter calibration and maintenance:

- Personal protective equipment (PPE), as required by the Health and Safety Plan (HASP; Parsons 2008)
- Light meter (Sper Scientific 840020 or equivalent)
- Light meter manual
- Light meter calibration notebook
- Field notebook

IV. Cautions

Light meters will be kept dry and within recommended operating temperatures. Light meters may be exposed to inclement weather (such as rain or snow) or temperatures (such as temperatures below recommended operating temperatures) for short periods of time during measurements. Once a measurement is taken, the light meter will be brought to the cab of the field vehicle (or trailer), where it will be dried off and kept within

recommended operating temperatures. Failure to keep light meter dry and at optimal operating temperature may result in malfunction of the meter.

Keep the lens cap on the photo sensor at all times except when calibrating. Keep the photo sensor clean. Dirt on the photo sensor may result in inaccurate measurements.

V. Health and Safety Considerations

The HASP (Parsons 2008) will be followed when performing calibration and maintenance.

VI. Procedures

The light meter will be operated according to the procedures contained in the operating manual. Zeroing, calibration, and maintenance procedures are summarized below.

Zeroing

1. Insert the photo sensor into the light meter.

2. Turn on the light meter.

3. With the lens cap securely in place, follow the operating manual for zeroing the light meter.

4. Record results of zeroing in the light meter calibration notebook.

Calibration

1. Calibration will be performed at the manufacturer's recommended frequency. Send the light meter to the manufacturer for calibration.

2. Record calibration activity in the light meter calibration notebook.

3. Maintain files received from the manufacturer on calibration in the light meter files.

Maintenance

Replace the battery when the low battery icon is displayed on the light meter. Follow the operating manual for battery replacement. Record battery replacement activities in the light meter calibration notebook.

VII. Waste Management

Paper towels or other items used to maintain the light meter in clean and dry condition will be disposed of at the end of each maintenance event as municipal solid waste.

VIII. Data Recording and Management

Zeroing and calibration results will be recorded in the light meter calibration notebook. Files received from the manufacturer on calibration will be maintained in the light meter files. For each zeroing and calibration event, sampling personnel, date, time, model of light meter, serial number of light meter, and zeroing or calibration results will be recorded. Battery replacement will be recorded in the light meter calibration notebook. Maintenance activities will be recorded in the field notebook.

IX. Quality Assurance

The light meter will be maintained in accordance with this SOP and the operating manual. No quality assurance activities, such as collection of a duplicate measurement, are scheduled.

X. References

Parsons, 2008. Phase 1 Remedial Action Health and Safety Plan, Hudson River PCBs Superfund Site. Prepared for General Electric Company, Albany, NY. August 2008.

APPENDIX 58
SOP FOR THE EXTRACTION AND CLEANUP OF SOIL, SEDIMENT, AND SOLIDS BY SOXHLET (NE143_05)

STANDARD OPERATING PROCEDURE

NORTHEAST ANALYTICAL, INC.

NE143_05.DOC
REVISION NUMBER: 05

THE EXTRACTION AND CLEANUP OF SOIL, SEDIMENT, AND SOLID SAMPLES FOR POLYCHLORINATED BIPHENYLS (PCB) ANALYSIS USING THE ASE EXTRACTION TECHNIQUE (SW-846 METHOD 3545) AND SUBSEQUENT ANALYSIS by SW-846 METHOD 8082

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STANDARD OPERATING PROCEDURE

LABORATORY PROCEDURE NE143_05.DOC

REVISION 5 (06/18/2008)

Author:

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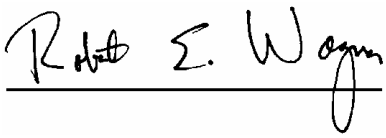

Robert E. Wagner
Laboratory Director

Approved by:

Christina L. Braidwood
Quality Assurance Officer

1.0 IDENTIFICATION OF TEST METHOD

1.1 Standard Operating Procedure for the extraction and cleanup of soil, sediment, and solid samples for Polychlorinated Biphenyl (PCB) analysis using the ASE extraction technique by SW-846 Method 3545 and subsequent Analysis by SW-846 Method 8082.

1.2 The purpose of this SOP is to provide to the chemist the procedures required to perform extractions of PCBs, in soil/sediment/solid sample, using the ASE extraction technique and to perform the subsequent extract volume reduction and cleanup.

2.0 APPLICABLE MATRICES

2.1 This test method is appropriate for Soil, sediment, and solid samples. Other extraction methods such as the soxhlet or sonication technique may be used in place of the ASE extraction at the discretion of the supervising chemist. Extract cleanup steps employed may vary from sample to sample, matrix to matrix. The chemist must have an understanding of the methods and requirements of USEPA-SW- 846A "Test Methods for Solid Wastes" Volume 1B: Lab Manual, 3rd edition. Methods 3545, 3500, 2500A. An approved instructor must also certify the chemist to perform the procedure. In general, samples designated as high level may have expected concentrations > 10 ug/L (10 PPB).

3.0 DETECTION LIMIT

3.1 *Please see determinative method (Lab SOP NE148) for details.*

4.0 SCOPE AND APPLICATION

4.1 The following procedure is utilized by Northeast Analytical, Inc. for the extraction and cleanup of PCBs from soil/sediment/solid samples using the ASE extraction method for subsequent analysis by SW-846 Method 8082.

5.0 SUMMARY OF TEST METHOD

5.1 The extraction and cleanup of soil, sediment, and solid samples for Polychlorinated Biphenyl (PCB) analysis using the ASE extraction technique SW-846 method 3545 begins with the weighing out of 10-11 grams of the sample. Next the sample is dried using hydromatrix and loaded into individual ASE cells where they are spiked and surrogated. Then utilizing the proper method and 1:1 Hexane and Acetone the sample is extracted via the Accelerated Solvent Extractor. The extracted solvent then undergoes several cleaning steps including the removal of water and exposure to acid, TBA, florisil, and mercury. Then the cleaned extract is properly diluted and sent for GC analysis.

6.0 DEFINITIONS

6.1 **Blank**: A non site sample created in the laboratory to evaluate cross contamination of the

sample set.

6.2 **Lab Control Standard**: A non site sample created in the laboratory to which a known amount of target analyte is added for assessment of analyte recovery efficiency.

6.3 **Lab Control Standard Duplicate**: An exact copy of the Lab Control Standard to further assess analyte recovery efficiency.

6.4 **Matrix Spike**: A site sample to which a known amount of target analyte is added for assessment of analyte recovery efficiency.

6.5 **Matrix Spike Duplicate**: An exact copy of the Matrix Spike utilizing the same site sample and known amount of target analyte for assessment of analyte recovery efficiency.

6.6 **ASE (Accelerated Solvent Extractor)**: A machine that utilizes solvents at high temperature and pressure to extract soil/sediment/ solid samples for PCB analysis.

6.7 **Surrogate Compound Spike**: In chemical composition and chromatography similar to the analytes of interest. Usually not found in environmental samples. These compounds are spiked into all samples, standards, blanks, and matrix spike samples prior to analysis. Percent recoveries are calculated for each surrogate.

6.8 **QC-Quality Control**: A set of measures for each sample within an analysis methodology to assure that the process is in control.

7.0 INTERFERENCES

7.1 Laboratory contamination can occur by the introduction of plasticizers (phthalate esters) into the samples through the use of certain plastics. Phthalate esters respond on electron capture detectors, usually as late eluting peaks, and can interfere in PCB quantification. Samples and extracts should not be exposed to plastics such as gloves, tubing, coating on clamps, and pipette bulbs, etc.

7.2 Also please see determinative method (Lab SOP NE148) for details.

8.0 SAFETY

8.1 The chemist should have received in-house safety training and should know the location of first aid equipment and the emergency spill/clean-up equipment, before handling any apparatus or equipment. Safety glasses and protective exam gloves must be worn when handling glassware and samples. Polychlorinated biphenyls have been tentatively classified as known or suspected carcinogens. The chemist must review the Material Safety Data Sheets (MSDS) for PCBs and all reagents used in the procedure before handling them. All solvents should be handled within a lab fume hood.

8.2 All ASE collection vessels should be examined for any small defects in the glass before pressurizing. A small crack or fissure in the collection vessel when under pressure will cause

the glass to shatter.

9.0 EQUIPMENT AND SUPPLIES

9.1 Cell Body: ASE 200 (Accelerated Solvent Extractor) Dionex, 22ML #048821, 33ML #048822. (or equivalent)

9.2 Cell caps: Dionex #049450. (or equivalent)

9.3 Steel Rod: Used to compresses sample in the cell.

9.4 Metal spatula.

9.5 Mixing Tray: Used to mix sample prior to weighing sample.

9.6 Analytical Balance: Mettler PL-303 used to determine sample mass. (or equivalent)

9.7 Cellulose Filter: Prevents the frits of the cell end pieces from being clogged during ASE extraction. (or equivalent)

9.8 Turbo Vap Evaporator: Zymark #ZW640-3.(or equivalent)

9.9 Turbo Vap Evaporator concentrator tubes: Zymark 250ML, 0.5ML endpoint. (or equivalent)

9.10 Turbo Vap LV. (or equivalent)

9.11 60 ml ASE vials. (or equivalent)

9.12 Vials: glass, 40mL & 4 dram (with Polyseal sealed cap) (20 ML & 10 ML) capacity, for sample extracts. (or equivalent)

9.13 Vial Rack: Plastic rack used to hold vials, during all phases of the extract processing.

9.14 Centrifuge: International Equipment Co., Model CL. (or equivalent)

9.15 Wrist Shaker: Burrell wrist action shaker, Model 75 and 88. (or equivalent)

9.16 Pipettes: S/P Disposable Serological Borosilicate Pipettes. (or equivalent)

1. 1ML X 1/10 #P4650-11X
2. 5ML X 1/10 #P4650-15
3. 10ML X 1/10 #P4650-110

Kimble Pasteur Borosilicate glass pipette 9" #72050 (or equivalent)

9.17 Beakers: Assorted Pyrex: 250ML, 600mL, and 1000mL.

10.0 REAGENTS AND STANDARDS

10.1 Hydromatrix: Varian #0019-8004.

10.2 Sodium Sulfate: Anhydrous (12-60 Mesh) Used for the laboratory method blank and laboratory control spike.

10.3 Hexane: High Purity Solvent Baxter (Burdick/Jackson) #UN1208. (or equivalent)

10.4 Acetone: High Purity Solvent Baxter (Burdick/Jackson) #UN1090. (or equivalent)

10.5 1:1 Hexane/Acetone: 50%/50% by volume solvent mixture prepared in the lab.

10.6 Florisil: deactivated, Deactivated with D.I. water. EM Science #FX0282-1.

10.7 TBA Reagent: Tetrabulylammonium Hydrogen-Sulfite Reagent. (prepared in the laboratory)

10.8 Mercury: Triple distilled Mercury Refining Co, Albany, NY #328502. (or equivalent)

10.9 Sulfuric Acid: Na_2SO_4 (concentrated) Mallinkrodt #2468 #UN1830. (or equivalent)

11.0 SAMPLE COLLECTION, PRESERVATION, SHIPMENT and STORAGE

11.1 All soil samples should be collected in 4 oz or 8 oz jars with Teflon lined lids.

11.2 All soil samples should be stored in the walk in refrigerator at 4 + or – 2 degrees C before extraction.

11.2 Soil samples have a hold time of 14 days before they need to be extracted.

11.3 The extracted solvents must be analyzed within 40 days of their extraction date.

12.0 QUALITY CONTROL

Note: Every sample set is run with two control samples: the blank standard and the lab control standard

12.1 The extraction chemist should have completed an acceptable demonstration of precision and accuracy before performing the method without supervision. The addition of spiking material to a sample or blank must be witnessed by another extraction chemist and signed in the extraction logbook. All surrogates and matrix spikes must meet acceptable QC limits.

12.2 A method blank sample and lab control spike must be prepared per each extraction batch or 1 per 20 site samples whichever is more frequent. A matrix spike/matrix spike duplicate (or lab duplicate) should be prepared for every 20 site samples or as per client specified quality assurance project plan (QAPP). Spike default for LCS, MS, MSD is 1.0mL of A1242 @ 0.5ppm. Client and/or project specifications may dictate alternate amount or Aroclor.

12.3 PCB Surrogates TCMX and DCBP are added to each sample prior to extraction to measure extraction/cleanup efficiency. Default surrogate is: 1.0mL of 0.05ppm TCMX / 0.5ppm DCBP. Client and/or project specifications may dictate alternate amount.

12.4 Also please see determinative method (Lab SOP NE148) for details.

13.0 CALIBRATION AND STANDARDIZATION

13.1 *Please see determinative method (Lab SOP NE148) for details.*

14.0 PROCEDURES

14.1 Sample Preparation

14.1.1 Throughout the entire process it should be noted that if the chemist encounters any problems or difficulties with any samples or steps involved, all work should STOP! Any problems should be brought to the attention of the supervisor and documented in the extraction logbook.

14.1.2 Before any steps are taken, the chemist should first review the sample job folder and COC to ensure sample ids and tests are correct.

14.1.3 If the sample is sediment and contains a water layer, decant and discard the layer as aqueous PCB waste. Mix sample thoroughly in the sample container. If there is not enough room to mix sample in the container then remove sample from container, using a metal spatula, into a mixing tray. Mix the sample thoroughly and discard any foreign objects such as sticks, rocks or leaves. Note however that the sample may be composed entirely of rock, concrete or some other solid material in which case the entire sample is treated as the solid.

14.2 Sample Extraction

14.2.1 Setup one 4 oz. jar for each sample. Pick the first sample, label a beaker with the sample number, and tare the beaker. Using a metal spatula, add 10 g to 11 g of the wet sample to the beaker. Use the sodium sulfate as the sample for the Blank and Laboratory Control Sample. Record the weight in the sample mass book.

NOTE: ALL SAMPLE CONTAINERS ARE TO BE RETURNED TO THE APPROPRIATE REFRIGERATOR. FOR ALL EMPTY SAMPLE CONTAINERS, SEE THE CHEMICAL HYGIENE PLAN FOR PROPER DISPOSAL.

14.2.2 If the PCB concentration is to be determined on a dry weight basis the percent total solid must be determined. Weigh approximately 5 grams of the

previously homogenized sample in a previously weighed, tarred aluminum-weighing pan. Record the weight of the sample and the tare weight of the pan in the percent total solids log. Place the sample in a drying oven at 100 to 110 degrees Celsius for at least 4 hours. Record the time placed in the oven and the oven temperature in the LIMS system. Remove the samples from the drying oven and allow to cool. Weigh the pan and sample (see calculations on how to calculate percent solids).

14.2.3 Before the sample is added to the cell, the sample must be dried. The sample is dried by adding Hydromatrix. The amount of this drying agent being used depends on how much water is in the sample. The more water present in the sample, the more drying agent will be needed to dry the sample. Mix the sample and drying agent thoroughly with a metal spatula.

14.2.4 The cell size to be used during the extraction will be determined by the final volume of the sample after the drying agent has been added. **NOTE: sometimes the sample will have to be separated into two cells for the extraction if too much drying agent has been added.**

14.2.5 Select the appropriate cell body size for each sample. Assemble one cell end cap to the cell body. Place 2 cellulose filters into the open end of the cell and push it down to the cell end cap using the black ASE push rod.

14.2.6 Label cells with the sample number. Label the corresponding 60mL VOA vials on the base of the vial.

14.2.7 Place the cell into a clean mixing pan. Add the dried extract to the cell using the metal spatula to guide the sample into the cell. Any sample that fell outside of the cell will be collected in the mixing tray. Remove the cell from the mixing tray and added the sample that is in the mixing tray to the cell. You may need to compact the sample in the cell, using the steel rod, while the sample is being added. **NOTE: rinse the steel rod with acetone and Dichloromethane before using on a different sample or placing it in the storage drawer.**

14.2.8 Add the appropriate amounts of surrogate and matrix spiking compounds at this point.

14.2.9 Assemble the top cell end cap to the cell, hand tighten. Place the first cell to be extracted in the 1 position on the cell tray (top tray) and the 60mL vial in the 1 position on the vial tray (bottom tray). The cells and 60mL vials for each sample must be in the same number position on the two trays.

14.2.10 Solvent used for PCB extraction is 1:1 Hexane/Acetone

14.2.11 Select the appropriate method or schedule and start the ASE.

14.2.12 When the extraction program is complete, transfer the hexane layer (top layer) using a 10mL pipette into a prerinsed turbo tube. Leaving only the water layer in the 60mL vial. Leave the 10ML pipette in the turbo tube.

14.2.13 Rinse the 60mL vial using 5 pipettes of hexane. Hand shake for 30 seconds. Allow the two layers to separate, and pipette the hexane layer, using the same 10ML pipette, into the turbo tube. Repeat this step 1 more time for a total of 2 hexane extractions on the water layer.

14.2.14 Rinse the 10ML pipette with two pipettes of hexane on the outside of the 10ML pipette that was in contact with the sample extract and two pipettes of hexane through the 10ML pipette and collect into the turbo tube.

14.2.15 All glassware must be rinsed with technical grade (tech)-acetone or a "for rinsing-only" labeled solvent, and dried in the hood before other cleaning steps.

14.3 Solvent Reduction: TurboVap Evaporator System

14.3.1 The Turbovap evaporator system is used in place of the Kuderna Danish (KD)-concentrator apparatus. The turbovap uses a heated water bath and positive pressure nitrogen flow/vortex action. The unit maintains a slight equilibrium imbalance between the liquid and gaseous phase of the solvent extract which allows fractional reduction of the solvents without loss of higher boiling point analytes.

14.3.2 Turn the unit on (switch is located on the backside of the unit) and allow it to heat up to the specified temperature for individual solvent use.This is indicated by the "Heating" display light, located above the temperate control knob on the right side of the unit. The system is at the proper temperature when the "At Temperature" light is lit. This is located above the "Heating" display light.

14.3.3 As a precaution the TurboVap system regulators should be checked to assure that no residual gas pressure remains within the system and that the gas cylinder valve and gas pressure regulators are both off before placing samples in the apparatus. Residual gas pressure may cause splashing and cross contamination of samples. To bleed the system of residual gas pressure place an empty turbo tube into the water bath and close the lid. Make sure that the nitrogen gas cylinder valve is turned off and slowly turn on the gas pressure regulator. Bleed any residual gas until the regulator output pressure gauge reads "0" psi. Make sure to wipe down all surfaces with hexane before concentration samples.

14.3.4 Place the turbo tube containing the samples into the TurboVap and close the lid. Turn on the gas cylinder valve first and then begin slowly turning the pressure regulator on.Keep the gas pressure very low, until the solvent level is decreased, to avoid splashing. Increase the gas pressure as the sample reduces maintaining uniform flow throughout the reduction.

14.3.5 Turbo Vap – LV low volume unit:
Turn the unit on (switch is located on the left side of the unit) and allow it to heat up to 40 degrees Celsius. This is indicated by the "Concentrating with Turbo Vap LV" blinking number under the temperature control button. When the system is at the proper temperature the number will no longer blink. As a precaution the Turbo Vap LV regulator should be checked to assure no residual gas remains in the system. Residual gas may cause splashing and cross contamination of the samples. To resolve this place a vial into the vial in to the turbo vap and close the lid. Press the start button and proceed to turn the gas regulator knob counter-clockwise until the regular reads zero. Place the 60 ml vials into the turbo vap. Press the button to turn on the appropriate row of stations that are being used. The press the start button and adjust the regulator until the samples begin to swirl. Check the sample every few minutes and adjust the gas to keep the samples swirling.

14.3.6 The process for solvent (hexane/acetone) reduction takes approximately 20-30 minutes. Do not leave the unit unattended as extracts may be blown to dryness and PCB loss may occur. Immediately notify a supervisor if an extract is blown to dryness. Concentrate the solvent to approximately 10.0mLs and fill back up with hexane and restart the solvent reduction (this step is done to make sure there is no acetone left over in the samples).

14.3.7 Concentrate the solvent to approximately 10.0mL. Remove the samples from the TurboVap and place in the rack. The remaining solvent will consist largely of hexane since the acetone component is fractionally removed at a faster rate than hexane. NOTE: Not all samples will evaporate at the same rate; sample extracts containing large amounts of petroleum or other non-volatile liquids may stop reducing before the 10.0mL point is achieved. Samples that stop reducing should be removed as soon as possible.

14.3.8 Quantitatively transfer the sample extract with a pasteur pipette into an appropriate volumetric flask (25mL for soil extracts). Rinse the turbo tube or vial with 3 pasteur pipettes of hexane, then transfer the hexane rinse to the volumetric. Repeat the hexane rinse two more times for a total of three hexane rinses of the turbo tube. After the sample has been transferred, rinse the pasteur pipette with 0.5mL of hexane into the volumetric flask. Add hexane to the volumetric meniscus mark. Invert the volumetric flask at least three times to mix completely. Decant the contents into a pre-labeled 40mL vial.

14.3.9 All dirty glassware must be rinsed with tech-acetone or a "For Rinsing-Only" labeled solvent and dried in the fume hood before being washed.

14.4 Sample Extract Cleanup

14.4.1 Most extracts of environmental samples that are to be analyzed for PCBs by gas chromatography with electron capture detection contain co-extracted xenobiotics and other interfering substances which must be removed before accurate chromatographic analysis can be performed.

14.4.2 Not all clean-up procedures need to be performed on every sample and several are sample matrix specific. The experience of the analyst combined with the sampling site history should guide the selection of which clean-up procedures are necessary. The sample preparation chemist in the extraction logbook records the sequence and number of repeats of cleanup steps performed. Sample extract cleanups are performed on set volume extracts. The default set volume is 25 mL for soil/sediment/solid samples.

14.4.3 Cleanup procedure will be done in the following order unless otherwise noted, Sulfuric Acid Wash, Florisil Slurry then TBA/Hg Shake.

14.4.3 Sulfuric Acid Wash

14.4.3.1 The concentrated sulfuric acid treatment removes hydrocarbons and other organic compounds that are co-extracted with the PCB residues.

14.4.3.2 Add 5.0 mL concentrated H_2S0_4 and shake for 30 seconds by hand, centrifuge for approximately 2 minutes, transfer approximately 20mLs of the Hexane upper layer to an 8 dram vial.

14.4.3.3 Repeat 8.4.2 if the sample extract appears to be heavily loaded (opaque) with colored material. Two to three acid washes may be required. **Note:** it is entirely possible that all colored material will not be removed from the extract.

14.4.4 Florisil Adsorption (Slurry)

14.4.4.1 The Florisil slurry removes co-extracted polar compounds, residual water, and residual acid and is recommended as the final cleanup step before the extract is submitted for GC analysis.

14.4.4.2 Add approximately 3 grams of tested and approved deactivated Florisil to each vial containing the sample extract. **SEE SUPERVISOR FOR THE APPROPRIATE FLORISIL DEACTIVATION CONCENTRATION TO BE USED.**

14.4.4.3 Vigorously shake the vial for approximately 1 min by hand or on the wrist shaker.

14.4.4.4 Place the vial(s) into the centrifuge for 2 minutes on setting (½).

14.4.4.5 Transfer the extract to a clean 40mL vial.

14.4.5 Elemental Sulfur Clean-up

14.4.5.1 Elemental sulfur is soluble in the extract solvents used for sediment and soil samples. It is commonly found sediment/soil samples,

decaying organic material and some industrial wastes. Large amounts of sulfur can cause the electron capture detector (ECD) to signal saturate for long periods during the elution envelope of PCBs. Even small amounts of sulfur can interfere with PCB measurement as a co-eluting chromatographic peak.

14.4.5.2 Two techniques exist for the elimination of elemental sulfur in PCB extracts. Mercuric precipitation (Mercury Shake) and the Tetrabutylammonium (TBA) sulfite procedure. Tetrabutylammonium sulfite causes the least amount of degradation of a broad range of pesticides and organics compounds, while mercury may degrade organophosphorus and some organochlorine pesticides. The TBA procedure also has a higher capacity for samples containing high concentrations of elemental sulfur.

14.4.6 Removal of Sulfur Using Mercury

Note: ***Mercury is a highly toxic metal. All operations involving mercury should be performed within a hood. Prior to using mercury, the chemist should become acquainted with proper handling and emergency spill/clean-up procedures associated with this metal and must have reviewed the material safety data sheet MSDS.***

14.4.7.1 Add 1-3 drops of mercury to the sample extracts, cap, and place on the wrist shaker for 30 minutes. The sulfur is converted to mercuric sulfide and precipitates out of the sample extract. A black precipitate may be seen in sample extracts containing elemental sulfur.

14.4.6.2 Transfer the sample extract to a new 8 dram vial.

14.4.6.3 The precipitated sulfur can be removed from the extract by performing a sulfuric acid clean-up or Florisil slurry (discussed in 8.8.0).

14.4.7 Removal of Sulfur using TBA Sulfite

14.4.7.1 The TBA procedure removes elemental sulfur by conversion to the thiosulfate ion, which is water soluble.

14.4.7.2 Add 2.0mL TBA Sulfite Reagent, 1.0 mL 2-propanol, and approximately 1 scoop (using the dedicated dispenser) of sodium sulfite crystals to the extract and shake for at least 45 minutes on the wrist shaker and observe. An excess of sodium sulfite must remain in the sample extract during the procedure. If the sodium sulfite crystals are entirely consumed add one or two more scoops to the extract and observe.

14.4.7.3 Place the samples on the wrist shaker for 45 minutes observing at 15

minute intervals to make sure that the sodium sulfite is not consumed. After the 45 minutes add 5mL's of organic free water and shake for 15 minutes.

14.4.7.4 Place the samples into the centrifuge and spin for approximately 2 minutes on setting #4.

14.4.7.5 Transfer the Hexane layer to a new 40mL vial and cap.

14.5 Extract Screening and Dilution:

14.5.1 PCB extracts are generally screened by GC to determine the approximate concentration before final analysis. Prior site history and client supplied estimates of sample concentration may be used to determine what, if any, extract dilution is necessary. Extracts of unknown concentration are generally screened at a 10 to 100-fold dilution.

14.5.2 The supervising chemist is responsible for determining initial screening dilutions. Extract dilutions are prepared by transferring an aliquot of the original sample extract into a vial containing the correct amount of "make up" volume of hexane. For example, a 1 to 10 dilution is performed by adding 1.0mL of the extract to 9.0mL hexane. The vial containing the diluted extract is labeled denoting the equivalent extract volume after the dilution; e.g. a 25ML extract diluted 1 to 10 is labeled "250X", an undiluted 25ML extract is labeled "25X". When high dilutions are prepared, secondary (serial) dilutions of the initial diluent are prepared; e.g. a 100-fold dilution is prepared by a 1 to 10 dilution of the initial extract, then a 1 to 10 dilution of the resulting diluent.

14.5.3 Perform the dilution using an appropriate class A disposable volumetric pipette to transfer the extract and for the make-up volume of hexane. Make sure that the vial is properly labeled. Cap and invert the vial at least three times to thoroughly mix the extract with the solvent.

14.5.4 Transfer 1mL of the extract to a labeled 1.5mL GC autosampler vial. Record the sample data on the LIMS GC Queue Lab Sheet. Submit the GC Queue Lab Sheet with the sample extracts to the GC analyst.

15.0 CALCULATIONS

15.1 Calculate the percent solids by:

$$\frac{\{(\text{wt. of pan + dried sample}) - (\text{wt.of pan})\} \times 100}{(\text{wt. of wet sample})}$$

15.2 Also please see determinative method (Lab SOP NE148) for details.

16.0 METHOD PERFORMANCE

16.1 *Please see determinative method (Lab SOP* NE148.SOP*) for details.*

17.0 POLLUTION PREVENTION

17.1 *Please see determinative method (Lab SOP* NE168.SOP*) for details.*

18.0 DATA ASSESSMENT AND ACCEPTANCE CRITERIA FOR QUALITY CONTROL MEASURES

18.1 *Please see determinative method (Lab SOP NE148) for details.*

19.0 CORRECTIVE ACTIONS FOR OUT OF CONTROL DATA

19.1 *Please see determinative method (Lab SOP NE148) for details.*

20.0 CONTINGINCIES FOR HANDLING OUT-OF-CONTROL OR UNACCEPTABLE DATA

20.1 *Please see determinative method (Lab SOP NE148) for details.*

21.0 WASTE MANAGEMENT

21.1 See NEA054.SOP, NEA083.SOP, NEA089.SOP

22.0 REFERENCES

22.1 U.S. EPA SW-846 "Test Methods for Evaluating Solid Waste; Volume 1B Laboratory Manual Physical/Chemical Methods", Office of Solid Waste and Emergency Response, Third Edition, Final Update III, December 1996.

22.2 "Guide to Environmental Analytical Methods", Third Edition, Genium Publishing Corporation, 1996.

23.0 TABLES, DIAGRAMS, FLOWCHARTS and VALIDATION DATA

23.1 ASE Methods

23.2 ASE control panel keypad

23.3 ASE cell cleanup procedure

23.1 ASE METHODS

METHOD #	ANALYTE OF INTEREST	MATRIX	REQUIRED SOLVENT *	AMOUNT OF SAMPLE
1	PCB	WIPE	1	WIPE
2	PET I.D.	SOIL	1	10 g
2	8270	SOIL	3	30 g
3	**PCB**	**SOIL**	**2**	**10 g**
4	22mL Cell cleaning	NONE	3	NONE
5	33mL Cell cleaning	NONE	3	NONE
6	8081 Pest	Soil	2	10g

*REQUIRED SOLVENT CHART

1 - HEXANE
2 - 1:1 HEXANE / ACETONE
3 - 1:1 DICHLOROMETHANE / ACETONE

23.2 CONTROL PANEL KEYPAD

* TRAY	Tray is in free spin for manual turning.
TRAY *	Tray drive mechanisms are engaged and cannot be moved manually.
RINSE	Starts a manual rinse cycle.
* START	System is idle.
START *	system is currently running a method or schedule.
ABORT	Interrupts current run. Continue with abort function to terminate ASE run.
MENU	Displays a list of available screens.

* - LIGHT IS ON

23.3 ASE CELL CLEANUP PROCEDURE

1.0 Remove the end caps of ASE cells. Using a metal spatula designated for cell clean up, push the extracted sample out of the cell into a garbage can.

2.0 Wash the interior and exterior of the cell and cell end caps with soap and water (use the brush designated for ASE use only).

3.0 Dry the cell parts with a paper towel and reassemble the cell.

4.0 Run the washed cells on the ASE (use a new 60mL vial for each cell) using method 4 for 22ml cells, 5 for 33 ml cells and 1:1 dichloromethane/acetone as the solvent.

NOTE: After the cells has been used 20 times or if the frits become clogged, the cell end caps should be taken apart and sonicated for 10 minutes in acetone and 10 minutes in dichloromethane.

APPENDIX 59
SOP FOR POC BY LLOYD KAHN METHOD (NE205_03)

STANDARD OPERATING PROCEDURE

NORTHEAST ANALYTICAL, INC.

NE205_03.DOC

REVISION NUMBER: 03

PREPARATION AND ANALYSIS OF SOLID SAMPLES FOR TOTAL ORGANIC CARBON BY US-EPA LLOYD KAHN METHOD

COPY #____

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STANDARD OPERATING PROCEDURE

LABORATORY METHOD NE205_03.DOC

REVISION 3 (03/31/09)

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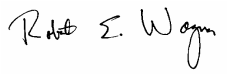


Robert E. Wagner
Laboratory Director

Approved by:

Christina Braidwood
Quality Assurance Officer

Table of Contents

1.0 IDENTIFICATION OF TEST METHOD

1.1 This test method is to determine total organic carbon by high-temperature combustion.

2.0 APPLICABLE MATRIX AND MATRICES

2.1 This test method is applicable to soil, sludge, sand, and other solid samples.

3.0 DETECTION LIMITS

3.1 Detection Limits are to the lowest calibration standard level for each instrument. Refer to Calibration and Standardization section for details.

4.0 SCOPE AND APPLICATION

4.1 This SOP describes the procedures for the preparation and analysis of solid samples for Total Organic Carbon (TOC) according to the Determination of Total Organic Carbon in Sediment, Lloyd Kahn, U.S. EPA Region II Edison NJ 1988.

5.0 SUMMARY OF TEST METHOD

5.1 TOC in solid samples is measured by high temperature combustion, followed by infrared detection. Organic carbon is converted to carbon dioxide (CO_2) by catalytic combustion. The CO_2 formed can be measured directly by an infrared detector. The amount of CO_2 is directly proportional to the concentration of carbonaceous material in the sample.

5.2 The fractions of total carbon (TC) are defined as:

5.2.1 Inorganic carbon (IC) – the carbonate, bicarbonate, and dissolved CO_2

5.2.2 Total organic carbon (TOC) – all carbon atoms covalently bonded in organic molecules

5.3 TOC in solid and sludge can be measured by utilizing the combustion-infrared method. The sample is homogenized and treated with acid. Then, the sample is heated to remove IC. The treated sample is placed into a heated reaction chamber packed with an oxidative catalyst such as cobalt oxide. The organic carbon is oxidized to CO_2 and H_2O. The sludge and sediment reactor combusts samples at 800°C to 900°C in an oxygen atmosphere so that solids and liquids can be analyzed.

5.4 The reactor consists of either a magnetically coupled boat inlet system or a push rod and boat holder system, which delivers the sample to the high temperature furnace. The CO_2 from the oxidation of organic carbon is transported in the carrier-gas stream and is measured by means of a non-dispersive infrared analyzer (NDIR).

6.0 DEFINITIONS

6.1 **Analytical Batch** – The basic unit for analytical quality control is the analytical batch. The analytical batch is defined as samples that are analyzed together with the same method sequence and the same lot of reagents and with the manipulations common to each sample within the same time period or in continuous sequential time period.

6.2 **Calibration** – The establishment of an analytical curve based on the area counts of known standards. The calibration standards should be prepared using the same type of acid and reagents or concentration of acids as used in the sample preparation.

6.3 **Calibration Blank** - A volume of reagent water that acts as a zero standard, and is used to calibrate the instrument.

6.4 **Calibration Standard (CAL)** - A solution prepared from the dilution of stock standard solutions. The CAL solutions are used to calibrate the instrument response with respect to organic carbon concentrations.

6.5 **Calibration curve**: If the correlation coefficient is less than 0.995, or if the calculated recoveries for any of the calibration standards are not within 10% of the true value, repeat analysis. If the analysis of each standard in duplicate is greater than 10%, repeat analysis of the outlying standards until the calibration curve is within acceptance criteria.

6.6 **Correlation Coefficient** – The correlation coefficient for the calibration curve must be greater than or equal to 0.995 according to NYSDOH requirements.

6.7 **Continuing Check Blank (CCB)**: Carbon free water obtained from NEA's water system can be used as the CCB. Analyze the CCB solution after each CCV solution. If the absolute value of the CCB is greater than the first standard, stop the analysis, correct problem, recalibrate the instrument if necessary, and reanalyze all samples up to last compliant CCB**.**

6.8 **Continuing Calibration Verification (CCV)** – A solution of known organic carbon concentration that is from a different source than the CAL standards, which evaluates the performance of the instrument system.

6.9 **Matrix** – The predominant material of which the sample to be analyzed is composed.

6.10 **Matrix Spike (MS)** – An aliquot of the sample is spiked with a known concentration of organic carbon. The spiking occurs after sample preparation, but prior to analysis. A matrix spike is used to document the bias of a method in a given matrix.

6.11 **Method Detection Limit (MDL)** – The minimum concentration of organic carbon that can be identified, measured, and reported within 99% confidence that the organic carbon concentration is greater than zero.

6.12 **Material Safety Data Sheet (MSDS)** – OSHA has established guidelines for the descriptive data that should be concisely provided on a data sheet to serve as the basis for written hazard communication programs. The thrust of the law is to have those who make, distribute, and use hazardous materials responsible for effective communication.

6.13 **Quaduplicate Analysis (QUAD)** – The analysis of a single sample four times.

6.14 **Practical Quantitation Limit (PQL)** – The lowest level that can be reliably achieved within specified limits of precision and accuracy during routine laboratory operating conditions.

6.15 **Relative Standard Deviation (RSD)** – To compare two or more values, the relative standard deviation is based on the mean of the values and the standard deviation of the values. RSD is reported as an absolute value, therefore, always expressed as a positive number or zero.

6.16 Replicate – Repeated operation occurring within an analytical procedure. Two or more analyses of a single sample constitute replicate analyses**.**

6.17 Reagent Water – Water in which interference is not observed at or above the minimum quantitation limit of the parameters of interest.

6.18 Rounding Rules – If the figure following those to be retained is less than 5, the figure is dropped, and the retained figures are kept unchanged. If the figure following those to be retained is greater than 5, the figure is dropped, and the last retained figure is raised by one. If the figure following those to be retained is 5, and if there are no figures other than zeros beyond the five, the figure 5 is dropped, and the last-place figure retained is increased by one.

6.18.1 If a series of multiple operations is to be performed (add, subtract, divide, multiply), all figures are carried through the calculations. Then the final answer is rounded to the proper number of significant figures.

6.19 Sample Delivery Group (SDG) – A unit within a single case that is used to identify a group of samples for delivery. An SDG is a group of 20 or fewer field samples within a batch, received over a period of up to 14 calendar days (7 calendar days for 14-day data turnaround contracts). Data from all samples in an SDG are due concurrently.

6.20 Stock Standard solution- A concentrated solution containing organic carbon prepared in the laboratory or purchased from a reputable commercial source.

7.0 INTERFERENCE

7.1 Volatile organics in sediments may be lost in the decarbonation step, resulting in a low bias.

7.2 Bacterial decomposition and volatilization of the organic compounds are minimized by maintaining the sample at 4˚C and analyzing within the specified holding times.

8.0 SAFETY

8.1 Safety glasses, lab coat or lab apron, and disposable gloves must be worn when handling chemicals and samples.

8.2 Personnel should be familiar with the necessary safety precautions by reading MSDS information covering any chemicals used to perform this SOP.

8.3 Each chemical should be regarded as a potential health hazard, and exposure to these compounds should be as low as reasonably achievable. Specifically, concentrated nitric, sulfuric, and hydrochloric acids present various hazards and are moderately toxic and extremely irritating to skin and mucous membranes. Use these reagents in a fume hood and if skin contact occurs, flush with large volumes of water.

8.4 Combustions process at high temperatures, thus care should be taken to avoid direct contact with the furnace or parts near the furnace.

9.0 EQUIPMENT AND APPARATUS

9.1 Rosemont-Dohrmann DC-190 IR-I NDIR detector module and TOC Boat Sampler Model 183.
9.2 Shimadzu TOC-V Analyzer, Solid Sample Module SSM-5000A, and Autosampler ASI-V.
9.3 Quartz boats. Dohrmann (p/n 899-624).
9.4 Ceramic boats. Shimadzu (p/n 638-92099).
9.5 Quartz wool. Dohrmann (p/n 511-735).
9.6 VWR Model 1370FM drying oven set at 104 ^{o}C.
9.7 Muffle oven.
9.8 Tweezers: large and small.
9.9 Magnet.
9.10 Steel spatula or tongue depressors.
9.11 Mettler AG204 analytical balance.
9.12 Aluminum weigh dishes.
9.13 9" Pasteur glass pipets.
9.14 White bulb.
9.15 10, 25, 50, 100, 500 mL Class A volumetric flasks.
9.16 Oxygen tank (2.6 purity or higher) with regulator.
9.17 Gray septum. Dohrmann (p/n 517-807).
9.18 Red/White septum. Dohrmann (p/n 511-914).
9.19 Cobalt catalyst. Dohrmann (p/n 511-883).
9.20 20-mesh tin. Dohrmann (p/n 511-876).
9.21 Copper. Dohrmann (p/n 511-895).
9.22 Pyrex wool. Dohrmann (p/n 511-895).
9.23 Cobalt oxide catalyst. Shimadzu (p/n 630-00566).
9.24 Platinum catalyst. Shimadzu (p/n 017-42801-01)
9.25 Metal screen for catalyst. Shimadzu (p/n 638-58102).
9.26 Platinum mesh. Shimadzu (p/n 630-00105-01).
9.27 Pyrex baking dish.
9.28 Alconox soap.
9.29 Sonicator in biota room.

10.0 REAGENTS AND STANDARDS

10.1 LGR water: Carbon free water obtained from NEA's water system can be used as the CCB. Laboratory research grade water system from U.S. Filter Water Systems Corporation.

10.2 Concentrated Nitric acid, 68-70 %, ACS grade, from EMD (p/n A200SI-212) or different vendor.

10.3 1:1 Nitric Acid (7.9 N). Dilute 50mL of concentrated nitric acid to a final volume of 100 mL with LGR water.

10.4 Concentrated Hydrochloride acid, 36.5-38.0 %, from J.T.Baker (p/n A144SI-212) or different vendor.

10.5 1:5 Hydrochloric Acid (2.4 N). Dilute 20mL of concentrated hydrochloric acid to a final volume of 100mL with LGR water.

10.6 ERA Demand TOC stock standard (p/n 516)

10.7 High Purity Standards TOC stock standard (p/n CWW-TOC-G)

10.8 High purity solid Potassium Hydrogen Phthalate from Shimadzu (p/n 630-00635-01), VWR (BDH0260-500G) or other vendor.

10.9 40,000 ppm stock TOC standard solution: dry solid potassium hydrogen phthalate at 104 ^{o}C for at least an hour. Cool in the desiccators to room temperature. Weigh 2.125g in a 25 ml volumetric flask, and fill to the line with LGR water.

10.10 Spiking standard solution (5000 ppm TOC): diluted from stock standard solution.

10.11 Calibration Standards for DC-190: Prepare 6 standards of different concentrations ranging from approximately 70 ppm to 11430 ppm from stock standard solution. Add a drop of concentrated phosphoric acid to each 25 ml.

10.12 Calibration Standards for Shimadzu: Prepare 5 standards of different concentrations ranging from approximately 100 ppm to 400,000 ppm. Add a drop of concentrated phosphoric acid to each 25 ml.

10.13 1000 ppm TOC standards: purchased from VWR (p/n VW3880-2), High Purity or other NIST traceable vendors. Use as CCV check standard.

10.14 Phosphoric acid: 85 % ACS grade can be from different vendors.

10.15 Sparging Fluid (DC-190) – fill a volumetric flask most of the way with LGR H_2O and then add a drop of Phosphoric Acid and test pH until it shows a pH of 2.

11.0 SAMPLE COLLECTION, PRESERVATION, SHIPMENT, AND STORAGE

11.1 Solid samples require no preservation prior to analysis other than store at 4 ^{o}C and have a holding time of 28 days.

12.0 QUALITY CONTROL

12.1 This section outlines the necessary quality control samples that need to be generated at the time of sample preparation. The results of the quality control measurement samples document the quality of the data generated. The following table lists the Quality Control samples required for total organic carbon.

Quality Control Requirements

QC Sample	Frequency
Continuing Calibration Verification	Analyzed immediately after calibration of instrument. Analyzed with each sample batch (up to 20 samples). Analyze at the end of each batch.
Continuing Calibration Blank	Analyzed immediately after the CCV.
Quadruplicate Sample	A single sample is analyzed four times at the beginning of a sample batch (up to 20 samples).

Matrix Spike	Analyzed with each sample batch (up to 20 samples).

12.2 Continuing Calibration Verification: The CCV should come from a different source than the CAL standards. A standard of 1000 ppm TOC is normally purchased and used. Recovery of the CCV should be within 85-115% of the known value.

12.3 Continuing Calibration Blank: The CCB is a blank that is analyzed immediately after every CCV that is analyzed. The CCB value should be lower than the low-level standard.

12.4 Quadruplicate analysis: The QUAD is usually analyzed on the first sample of the batch. Three more replicates of the same sample are analyzed and the RSD is compared to the QUAD limit. The QUAD limit is previously determined for each instrument. It should be analyzed once every 20 samples.

12.5 Matrix Spike: The MS is run once every 20 samples, and is usually analyzed on the same sample as the QUAD. The solution used for the DC-190 is 250 ul of the CCV solution (1000 ppm) and for the Shimadzu is 100 ul of a 5000ppm spiking standard solution. The recovery should be $\pm$ 25% of the known value.

13.0 CALIBRATION AND STANARDIZATION

13.1 Calibration of the DC-190

13.1.1 A new calibration should be created every four months. It should be run sooner if CCV is repeatedly outside of limits or if the instrument has had major repairs done.

13.1.2 The calibration curve is based on ‘ug of carbon’ versus ‘area’.

13.1.3 A Calibration blank should be obtained as well as the ERA standard. The ERA standard is then diluted appropriately in volumetrics to concentrations of approximately 5, 10, 100, 250, 500, 800 ug of carbon after 70 ul are injected of the dilutions made. Please see Attachment 23.2 for details.

13.1.4 The calibration blank and each standard should be run in duplicate. Each standard should be repeated until they are reproducible within 10% of each other. The procedures for running each sample can be found in Section 14.

13.1.5 The blank area should be subtracted from the average area of each calibration standard.

13.1.6 Each calibration should begin with a quartz boat filled with new quartz wool and freshly burned in the furnace until the baseline has stabilized.

13.1.7 The area counts obtained for each replicate of each standard should be entered into the excel spreadsheet S:\LabData\Metals\TOC\Data(year)\tocDC190 calibration(date). The ‘Calculate Curve Click Here’ tab should then be pressed. Be sure the R square is >0.995, the recovery of each standard is 90-110%, and the RPD is < 10% for each standard (the low level standard can be within 80-120%).

13.1.8 The curve is then entered into LIMS by going to the Wetlab department and selecting TOC. In the Prep Book tab create a new batch for the day and select the

DC-190 as the instrument. Press the Blank button twice and then the ICx button, which adds the standards into the Prep Book. Enter the area counts into the system as well as Std Lot, Blank Area, Slope, Low Std Concentration, and Calibration Date. To finalize the calibration in LIMS select all injections and press the 'calculate and send' button on top (a hand with a paper in it).

13.2 Calibration of the Shimadzu

13.2.1 A new calibration should be run every four months, if CCV is repeatedly outside of limits, or if the instrument has had major repairs completed.

13.2.2 The calibration curve is based on 'ug of carbon' versus 'area'.

13.2.3 A Calibration blank should be obtained as well as preparing the Potassium Hydrogen Phthalate standard at 40,000 ppm. The standard is then diluted down appropriately in a volumetric flask to concentrations of 100 ppm, 400 ppm and 4,000 ppm. Clean boats are then injected with different volumes of the 100 ppm, 400 ppm, 4,000 ppm, and 40,000 ppm standards and analyzed. The final concentrations analyzed are 10, 40, 400, 4,000, and 40,000 ug of carbon. Please see further details in Attachment 23.2.

13.2.4 To run the curve on the Shimadzu create a new Sample Run and save it as (date) TOC. Then select Insert – Calibration Curve. Select new curve.cal and then run according to Section 14.

13.2.5 The program will automatically zero shift the curve.

13.2.6 Each calibration should begin with a ceramic boat filled with new ceramic fibers and freshly burned in the furnace until the baseline has stabilized.

13.2.7 The curve is then entered into LIMS by going to the Wetlab department and selecting TOC. In the Prep Book tab create a new batch for the day and select the TOC-V as the instrument. Press the Blank button twice and then the ICx button, which then adds the standards into the Prep Book. Enter the area counts into the system as well as Std Lot, Blank Area, Slope, Intercept, Low Std Concentration, and Calibration Date. To finalize the calibration in LIMS select all injections and press the 'calculate and send' button on top (a hand with a paper in it).

14.0 PROCEDURES

14.1 Procedures for the DC-190

14.1.1 Refer to the instrument manual for specific instructions and part numbers for all components.

14.1.2 In general a portion of a sample is weighed into a quartz boat where it is acidified and dried. The boat is then placed in the boat port of the sampler and it is moved into the combustion chamber. Gas from the combustion tube flows into the right flask in front of the power switch panel where it passes through the sparging fluid. It then travels to the left flask where excess water is removed before traveling through the tin and copper scrubber to the detector.

14.1.3 To prepare the tin/copper scrubber (yearly maintenance):

14.1.3.1 Insert a tuft of Pyrex wool at the bottom of one half of the U-shaped scrubber tube.

14.1.3.2 Weigh out 10g of tin and pour into the scrubber tube and secure with another tuft of Pyrex wool.

14.1.3.3 Insert a tuft of Pyrex wool at the bottom of the other half of the U-shaped scrubber tube.

14.1.3.4 Weigh out 10g of copper and pour into the scrubber tube and secure with another tuft of Pyrex wool.

14.1.3.5 Top both ends of the scrubber with a cored gray septum.

14.1.3.6 Check the scrubber periodically and change when about half of the tin has become discolored.

14.1.4 To prepare the combustion tube (quarterly maintenance):

14.1.4.1 Insert a tuft of quartz wool into the combustion tube and push it down to the dimple.

14.1.4.2 Insert about 3 inches of cobalt oxide catalyst and tap down to be sure it is uniformly packed.

14.1.4.3 Secure the cobalt oxide with another tuft of quartz wool. Be sure the cobalt oxide will not move when the tube is turned horizontally.

14.1.4.4 Insert combustion tube into the furnace and secure tightly in large bolt near boat port. Also recap the left end with the cored gray septum.

14.1.5 The main NDIR detector should be turned on by the switch in the rear of the instrument and allowed to stabilize for a few hours. This module is generally left running and only shut off to reboot the machine when necessary.

14.1.6 The Analysis Mode should be set to TC and the Inlet Mode should be set to Boat.

14.1.7 At the start of each day carefully check all components of both the main unit and boat sampler for wear. Check the level of acidified water in the right flask to be sure it is above the sparging finger. Empty any fluid in the left flask into acid waste. Turn the power on to the TOC Boat Sampler so the furnace begins to heat up and turn the oxygen tank on. Be sure the oxygen is set to 30 psi. Check the right flask to be sure a vigorous flow of gas is emitted from the sparging finger. If not bubbling check lines for gas leaks.

14.1.8 The boat sampler must warm up until the Furnace light is green, the Carrier Gas light is green, and the baseline is stabilized at a number less than 2, which is displayed in the lower right-hand side of the main unit's display screen.

14.1.9 Preparation of solid samples.

14.1.9.1 All sample weights are tracked in the TOC Weight Log (a paper logbook).

14.1.9.2 Place a quartz boat in a labeled aluminum weigh boat and place on the analytical scale. Tare the scale.

14.1.9.3 Open the sample jar and stir with a spatula to homogenize the sample.

14.1.9.4 Each sample is weighed into a quartz boat between 0.005g and 0.01g, (if sample is sandy, more weight can be used). The QUAD is prepared with four replicates and the fifth boat is used to perform MS analysis. Weigh out all samples in a batch at the same time.

14.1.9.5 Once all samples are weighed they are carefully moved near the drying oven where they are acidified with 2-3 drops of 1:1 HNO_3, being sure to moisten the entire sample.

14.1.9.6 The aluminum weigh dishes with boats in them are then placed in the drying oven until the samples have dried (approximately 5-10 mins).

14.1.9.7 Total solids should also be determined as per NE090.SOP.

14.1.10 When the instrument and samples are ready the run is started by opening LIMS and entering the Wetlab department. Selecting the TOC tab on the left.

14.1.11 Create a new batch and then select the DC-190 as the instrument. Add in your first sample by selecting it in the To Be Done tab, right-click and append to Prep Book. In the Prep Book be sure the sample is selected, add the SET (which consists of a CCV and CCB) and move the set to the top, and then add in the QUAD by selecting the sample and pressing the X4 button, which automatically attaches an MS to the sample. Place your cursor in the Area box of the sample you intend to run (when you start the first sample should be a CCV).

14.1.12 Shut the oxygen off using the black toggle switch and toggling it down on the boat sampler. Slide the boat under the red septum using the magnet, open the red septum, and pipette 70 ul of the CCV solution into the boat. Turn on the oxygen by moving the black toggle switch up. If the Start light is lit then press Yes; and if the Start light is not lit press Start, 1, Enter. Once the instrument makes the start noise, use the magnet and slide the boat into the furnace.

14.1.13 When the instrument makes the end noise, use the magnet to slide the boat out from the furnace. The area should now be in the LIMS Area box for CCV and has automatically moved down to the CCB Area box. If the data was not captured because of the wrong cursor position, data from the instrument control panel will be manually input into LIMS. To be sure the CCV has passed select the line and press the 'calculate and send' button and scroll over to check the % Recovery column.

14.1.14 Once the boat has cooled, the CCB liquid sample can be added to the boat and measured likewise. Be sure the cursor is in the Area box for CCB before starting.

14.1.15 To add a solid sample, first shut off oxygen using the black toggle, and then open the boat port by pushing the red handle upward. Remove the CCV boat using the small tweezers and attach the sample boat to the hook of the wire. Close the boat port and toggle on the oxygen. Start the instrument and continue running samples likewise. Be sure to wait for the baseline to settle back down to a value below 3.0 before starting a new sample.

14.1.16 For the QUAD run all four samples and then select them all (clicking while using the shift button) and press the 'calculate and send' button. Compare the %RSD QUAD to the QUAD limit that has been determined.

14.1.17 To run the MS place the solid boat into the boat port then pipette 250 ul of CCV solution into the boat. Close the boat port and toggle on the oxygen. Press start/yes and gently glide the boat into the furnace so you do not spill the spike solution on the way to the furnace.

14.1.18 If at any point the concentration of the sample is higher than our calibration range re-prep the sample as noted above but weigh out a smaller amount, which should not go below 0.001g.

14.1.19 When finished with analysis be sure all samples have been calculated and sent. Select each CCV/CCB set and the following 20 sample injections, right click and assign Blank ID. Then select each LRF and the CCV/CCB sets, QUAD and MS assigned to it; right click and save selected QC injections for: (LRF). Fill in the parameters directly above the run log with the pressure of the oxygen tank for oxygen flow, select the HIGH setting for range, and then the number the baseline stabilized at throughout the day as baseline.

14.1.20 By selecting the entire run of the day and then pressing the Print button a Logbook page can be printed to go into the job folder and data package.

14.1.21 Shut off the oxygen tank and power off the boat sampler at the end of a day. Leave the main unit running.

14.1.22 To clean quartz boats place them in a jar and fill with water and a small dash of Alconox. Shake vigorously to make water sudsy and mix with boats. Place the jar in the sonicator and turn on sonics for 20 minutes. Remove from sonicator and rinse with water multiple times until water is not soapy. Place boats in drying oven to dry. When they are dry, the boats can be burnt in the muffle oven at 900˚C for about 10 minutes.

14.2 Procedures for the Shimadzu:

14.2.1 Refer to the instrument manual for specific instructions and part numbers for all components. Also you can reference the online Virtual Advisor on the Shimadzu website to watch repair videos and troubleshoot problems. The website is http://www.ssi.shimadzu.com/toc_virtualadvisor/.

14.2.2 A portion of sample is weighed into a ceramic boat where it is acidified and dried. The boat is placed on the boat holder of the TC port and it is moved into the combustion chamber. Gas from the combustion tube flows through a condensation coil, dryer and cooling coil into the main unit to the detector.

14.2.3 To prepare the TC catalyst of the SSM:

14.2.3.1 Be sure the instrument is turned off and cooled down to room temperature. Then remove the cover and unscrew the boat port. Gently remove the small end of the catalyst tube from the nut and slowly remove the catalyst tube from the furnace.

14.2.3.2 In a separate container mix two containers of cobalt oxide catalyst (50g total) and one container of platinum catalyst (20g).

14.2.3.3 Fold the catalyst support screen and insert into tube with the folds facing towards the thin opening of the catalyst tube.

14.2.3.4 Place about 2 mm of quartz wool on top of the screen.

14.2.3.5 Pour in the mixed catalyst and tap gently to settle it down. Be sure the catalyst is about 75 mm in height and well settled.

14.2.3.6 Add another 2 mm of quartz wool on top of the catalyst.

14.2.3.7 Fold another catalyst support screen and place it on top of the quartz wool. Be sure the folds are facing towards the large opening of the catalyst tube.

14.2.3.8 Gently slide the catalyst tube into the furnace and slide the thin tube into the nut. Reattach the boat port by screwing on the adapter and the small knobs that hold it in place. Replace the cover and turn on the instrument.

14.2.3.9 Allow the instrument to heat up to temperature with oxygen running through the system for 2-3 hours to stabilize by burning off any particles on the catalyst.

14.2.4 To prepare the main unit TC catalyst:

14.2.4.1 Be sure the instrument is turned off and has cooled to room temperature. Open the door of the main unit and remove the small top panel.

14.2.4.2 Disconnect the carrier gas tubing on the right and loosen all the thumbscrews and remove the injector block.

14.2.4.3 Gently remove the bottom end of the combustion tube from the nut and slowly pull the tube up and out of the furnace.

14.2.4.4 Remove the catalyst and clean the tube if necessary.

14.2.4.5 Place two platinum mesh screens on the bottom of the tube and add 5 mm of quartz wool.

14.2.4.6 Add 100mm of the regular sensitivity catalyst, which is platinum catalyst only. Tap gently to be sure it is settled.

14.2.4.7 Replace the tube into the furnace and connect to bottom nut.

14.2.4.8 Reattach the injector block and check that it is centered over the catalyst tube. Reconnect the carrier gas tubing line.

14.2.4.9 Close the instrument top. Turn on the instrument and allow the catalyst to burn off particles for 2-3 hours.

14.2.5 Turn on the main unit press the button on the bottom right corner on the front of the main unit. The main unit has the NDIR Detector and should warm up for an hour or two. This unit is generally left on and only shut off to reboot the instrument.

14.2.6 Turn on the SSM using the switch on the right side towards the back. This unit is generally left on but can be shut off. Warm it up long enough for the temperature to rise to its set point and the baseline to settle.

14.2.7 At the start of each day check the moisturizer level to be sure it is within the fill range and the humidifier to be sure the water level is above the end of the outlet tube on the main unit. Turn on the oxygen tank. Be sure the oxygen is set to 60psi on the regulator. On the SSM check the drain separator on the right side of the system to be sure it is not bubbling; fill with water to stop bubbling. Check the waste container and empty if needed.

14.2.8 Open the TOC-Control V program. Select the Sample Table Editor. Press the New button (piece of white paper) and select Sample Run. Select the TOC-V+SSM as the instrument and name the file as the (date)toc. Press the connect button (lightning bolt) and select use settings on PC. The instrument will now connect with the computer and SSM. When it is fully initialized you can watch the baseline by going to Instrument and Background Monitor.

14.2.9 The instrument is ready to run when in the Background Monitor all lights are green in both the SSM and TOC tabs.

14.2.10 Preparation of solid samples:

14.2.10.1 All sample weights are tracked in the TOC Weight Log (a paper logbook) or the LIMS logbook.

14.2.10.2 Place a pre-numbered ceramic boat on the analytical scale and tare the scale.

14.2.10.3 The sample jar is then opened and stirred with a spatula to homogenize.

14.2.10.4 Each sample is weighed into a pre-numbered ceramic boat to weigh about 0.05g, and the QUAD is prepared with four replicates in four individual boats, and the fifth boat is used to perform the MS. Weigh out all samples in a batch at the same time.

14.2.10.5 The ceramic boats are then placed carefully into a pyrex dish. The dish is then carefully moved near the drying oven where each boat is acidified with 3-4 drops of 1:5 HCl being sure to moisten the entire sample.

14.2.10.6 The dish is then placed into the drying oven until the samples have dried (approximately 5-10 mins).

14.2.10.7 Total solids should also be determined as per NE090.SOP.

14.2.11 When the instrument and samples are ready the run is started by opening LIMS and entering the Wetlab department. Selecting the TOC tab on the left.

14.2.12 Create a new batch and then select the TOC-V as the instrument. Add in your first sample by selecting it in the To Be Done tab, right-click and append to Prep Book.

In the Prep Book be sure the sample is selected, add the SET (CCV and CCB) and move the set to the top, then select the sample and add in the QUAD by pressing the X4 button which automatically adds the MS. Continue appending samples and adding SETs as needed.

14.2.13 When the entire run is entered select all the samples in the run and press the Save button (a disk). Select the New Curve method and then press yes for using soil samples. Enter the file name as (date)toc.

14.2.14 Go back to the TOC Control-V program and go to Edit and select Import. Select the file that was just created. All the samples should then appear in the sample table as they did in LIMS.

14.2.15 To start running samples select the first sample and press the Run button (green stoplight). Place the boat in the boat holder and close the boat port. It will then ask you to enter the weight of the sample. If you are running CCV or CCB you enter the volume (should be 100 ul) by un-checking the By Weight box. If you are running solid samples enter the weight in mg (not g which is recorded in the TOC Weight Log). Slide the boat in when the instrument prompts you by pushing the blue push bar.

14.2.16 After the sample is measured a window will pop up that prompts you to move the boat back to the cooling position and then again to the stop point. Press next to continue running the next sample.

14.2.17 When it is time to run the MS, spike the sample with 100 ul of the 5000 ppm spiking solution and enter the weight of the sample into the By Weight box. It should be spiked prior to being placed in the boat sampler. Continue running as a normal sample.

14.2.18 If you want to check the % Recovery or RSD during a run, when the sample is measured press Stop and then go into LIMS. From LIMS highlight the sample you want to check and press the Read Shimadzu data button (an open book). After a few seconds the information will appear in LIMS and can be calculated and sent (using the hand and paper button) to see the calculations.

14.2.19 To continue your run after checking on data just select the next sample to be run and press the green stoplight button.

14.2.20 When the entire run is completed select File then Print then Table. Change settings to landscape and print. Then go into LIMS highlight all samples that have not previously been acquired into LIMS, acquire them in from the Shimadzu, and then press the ‘calculate and send’ button.

14.2.21 Select each CCV/CCB set and the following 20 samples and right click and assign blank ID. Then select all QC and right click and Save selected QC for each LRF. Set the parameters to 30 psi for oxygen flow, Low range, and ‘NA‘ for baseline and save parameters. Check that the calibration information is correct.

14.2.22 Select the run for the day in LIMS and print a logbook (printer button).

14.2.23 To clean the ceramic boats start by scraping all the ash from the boats. Then place the boats in a jar with 2M HCl and cap. Shake the jar gently and let it sit for at least a half hour. Carefully remove the boats from the jar with tweezers and rinse

thoroughly with tap water and then LGR water. Then place the boats in the drying oven to dry. Once dry they can be placed in the muffle at 900° C for about ten minutes.

15.0 CALCULTIONS

15.1 RSD Calculation: $\frac{\text{(Standard Deviation of 4 runs)}}{\text{(Average of 4 runs)}} *100$

15.2 Spike Added Calculation: $\frac{\text{(volume of spike)*(spike concentration)}}{\text{(total solids\%)*(weight of sample)}}$

15.3 % Recovery of Spike: $\frac{\text{(TOC concentration of MS) – (TOC concentration of first run)}}{\text{Spike Added}} *100$

15.4 TOC Concentration Calculation for DC-190: $\frac{\text{(Sample Area-Blank Area)* (Inverse Slope)}}{\text{(sample weight)*(total solids\%)}}$

15.5 TOC Concentration Calculation of Shimadzu: $\frac{\text{(Sample Area - Intercept)}}{\text{(Slope) * (sample weight)}}$

15.6 Final TOC Concentration Calculation for Shimadzu: $\frac{\text{(TOC Concentration)}}{\text{(total solids\%)}}$

15.7 % Recovery of CCV: $\frac{\text{(TOC Concentration of CCV)}}{\text{(True Value of CCV)}} *100$

15.8 PQL Calculation: $\frac{\text{(concentration of lowest standard in ug)}}{\text{(sample weight in g) * (total solids\%)}}$

15.9 % Total Solids: $\frac{\text{(Dry sample weight) – (dish weight)}}{\text{(Wet sample weight) – (dish weight)}} *100$

16.0 METHOD PERFORMANCE

16.1 Method Detection Limit:

16.1.1 Method Detection Limits should be determined annually or when a change in instrument hardware or operating conditions dictates they need to be re-determined as judged by the analyst. Analyze 8 replicates of the lowest standard in each instrument. Follow the MDL rules, refer to SOP NE021.

16.2 Quadruplicate Limit Test should be determined annually or when a change in instrument hardware or operating conditions dictates it needs to be re-determined as judged by the analyst. It is performed by running 15 replicates of an average sample on each instrument. The sample chosen should be representative of those being analyzed and should be considered homogenous. The RSD is then calculated and the QUAD limit is set at $\pm$3 times the RSD.

16.3 Precision and Accuracy tests should be performed annually by the analysts to demonstrate their ability to reproduce a known sample four times accurately while following the SOP for each applicable matrix. All recoveries should be within the manufacturer's performance

acceptance limits and the RSD should be less than 10%. Analyst can also obtain a P&A certificate by analyzing a PT sample within the accepted range limit set by the sample provider.

16.4 Initial Demonstration of Capability:

16.4.1 Initial demonstrations of capability must be performed on each instrument upon initial training, using various matrices.

17.0 POLLUTION PREVENTION

17.1 Pollution prevention is practiced in the laboratory by minimizing usage of solvents and chemicals, so that disposal of waste generated is held to the smallest amount possible. This is directly linked to the types of extraction procedures in place at the laboratory to reduce the volumes of solvents used for semi-volatile extraction procedures. Northeast Analytical employs extraction procedures such as continuous liquid/liquid and solid phase extraction methods to reduce solvent requirements for water extraction protocols and ASE and Soxhlet extractions for solid matrices.

17.2 Pollution prevention also relies on minimizing to the best extent the chemicals and solvents required to perform extraction and analysis procedures. The laboratory personnel strive to purchase chemicals and standards that will be consumed based on anticipated workload. For additional information about laboratory pollution prevention, please refer to laboratory SOP NE168.

18.0 DATA ASSESSMENT AND ACCEPTANCE CRITERIA FOR QC MEASURES

18.1 The analyst is responsible for generating the data and also is the initial individual to review the data. This would include inspection of the data, processing the raw data, producing all required data forms, inspection of calibration curves for compliance, calibration verification, calibration blank, matrix spike/matrix spike duplicate recovery, and continuing calibration compliance.

18.2 Once the initial review of the data is performed by the analyst, decisions are made at that time to accept the data if all criteria are met or to reject sample data if any of the quality control parameters or limits are out of control. Depending on the situation, samples requiring re-analysis will be notified to the appropriate analysis personnel. New calibrations may have to be performed, or samples will be re-analyzed due to failing continuing check standards.

18.3 The analyst may also consult with the quality control officer as to the best form of action to take or if the situation warrants corrective action beyond routine practices. If no recourse is available and the data is to be reported out of criteria, a Case Narrative Report is generated and the deviation is documented and reported to the client. The Case Narrative Report is filed with the data and is also useful for production of case narratives that are issued with the final data reports. If a problem exists that requires follow-up to rectify, a Corrective Action Report (CAR) is issued to document the problem found, steps taken to resolve the problem, and what samples were affected. This CAR form is filed by the quality control officer and reviewed by management to verify that appropriate actions have been taken to correct the problem.

18.4 Calibration Assessment

18.4.1 All standards are run in duplicate with RPD < 10%

18.4.2 Linear Regression should be $\geq$ 0.995

18.4.3 Recovery of the calculated concentration for each standard should be 90 – 110%. The lowest standard can have a recovery between 80 – 120%.

18.5 CCV recovery should be 85–115%

18.6 QUAD RSD for each instrument is different and should be updated annually.

18.7 MS recovery should be 75-125%

18.8 CCB should have an area count lower than the mean area count of the low level calibration standard.

18.9 All samples should have area counts lower than the mean area count of the highest calibration standard.

19.0 CORRECTIVE ACTIONS FOR OUT-OF-CONTROL DATA

19.1 Calibration must meet all requirements in Section 18, if it does not, the analyst can re-analyze a standard that is believed to be off the curve once and remake the solution and re-analyze as well. If requirements are still not met, begin troubleshooting for mechanical issues. Start with air flow check and catalyst performance.

19.2 If CCV does not pass, the boat should be burned in the furnace for 5 minutes and then cooled. Retry the CCV, and if it still does not pass, and there are no pipette issues (tip not on tightly, air bubble when solution drawn into tip) a new solution should be obtained and analyzed. If it still does not pass, then air flow should be checked. If the recovery is too high, then there is too little flow or there may be a catalyst issue. If the recovery is too low, then it may be a catalyst issue.

19.3 If the QUAD does not pass, check the matrix to verify if it is non-homogenous, and write up a case narrative, and continue on with the analysis. If the sample appears homogenous, then mix the sample well and re-prepare another QUAD set. If the second QUAD set does not pass, then write up a case narrative and continue on with the analysis.

19.4 If the MS does not pass, check that the amount being spiked with is at least 1/5 of the total carbon in the sample. If it is greater than 1/5, then re-prepare an MS sample and reanalyze. If the MS fails again, write up a case narrative. If the MS is less than 1/5, write up a case narrative, and continue on with the analysis.

19.5 If the CCB does not pass, the boat should be burned in the furnace for 5 minutes and then cooled. Retry the CCB, and if it still does not pass, then air flow should be checked as well as catalyst performance.

19.6 If a sample is found to be over the range of the calibration area count, then the sample should be re-prepared at a smaller weight that would proportionally bring it into the range of the curve. The sample should still weigh more than 0.001g.

19.7 Also see the flow chart provided in Attachment 23.1 for decisions on how to proceed with sample analysis and when data requires qualification.

20.0 CONTIGENCIES FOR HANDLING OUT-OF-CONTROL DATA

20.1 If the acceptance criteria for QC measures has been exceeded, or is under the limits and the data is to be reported, the following procedures must be implemented:

20.1.1 The Quality Assurance officer must be notified.

20.1.2 The data must be flagged with the appropriate qualifiers and a case narrative must be written.

20.1.3 The client must be notified about the data.

21.0 WASTE MANAGEMENT

21.1 All applicable federal and state rules and regulations governing hazardous waste will be followed when the disposal of laboratory waste is generated during the execution of this method.

21.2 Please refer to standard operating procedures NE089 and NE054 regarding how hazardous waste is handled and disposed of by the laboratory.

22.0 REFERENCES

22.1 "Determination of Total Organic Carbon in Sediment," Lloyd Kahn, U.S.E.P.A. Region II, Edison, NJ 1988.

22.2 "DC-190 High-Temperature TOC Analyzer Operation Manual," Rosemont, Inc. 1990,1991 Rev. C.

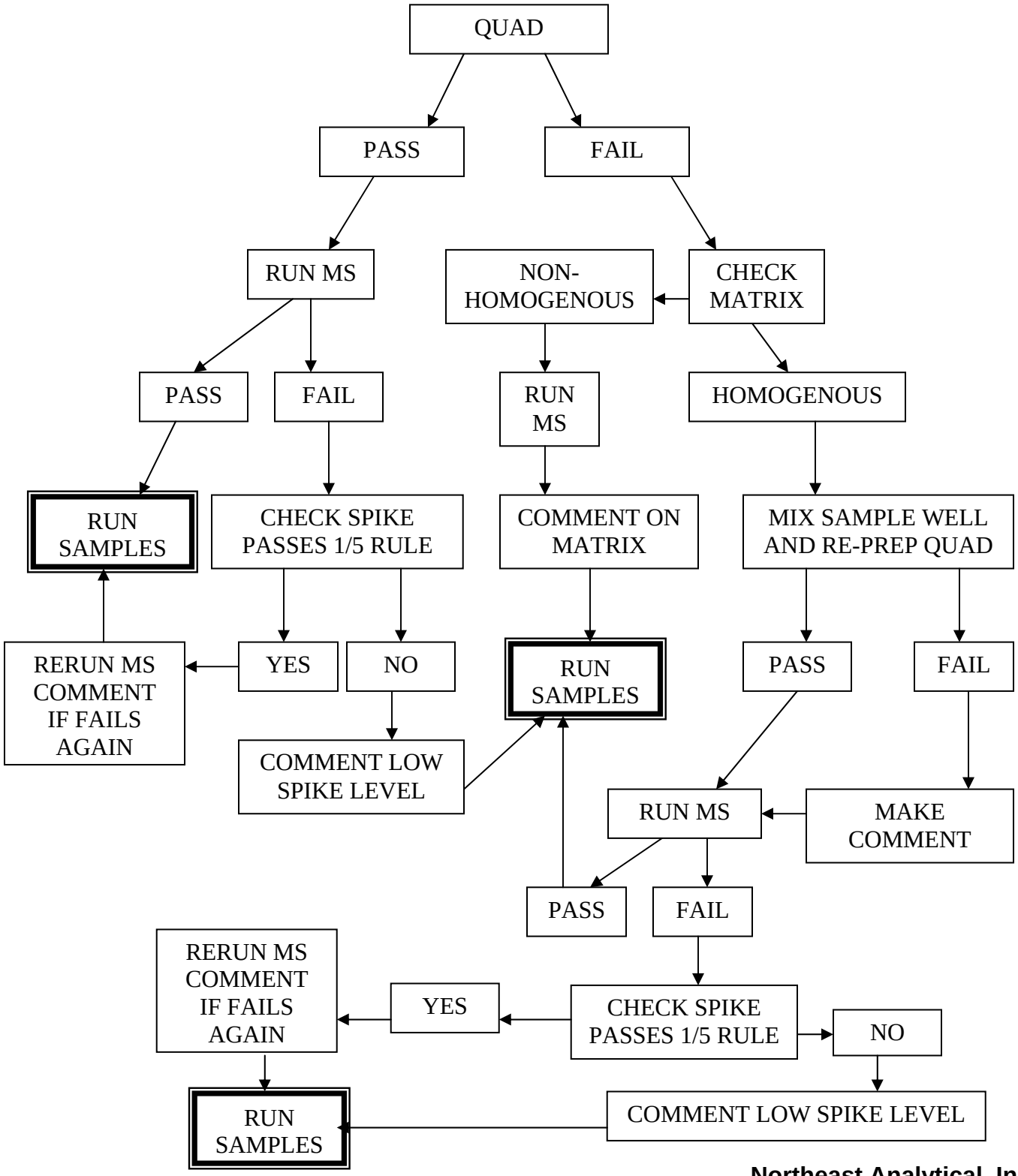
22.3 "TOC-V CPH/CPN & TOC-Control Software User Manual," Shimadzu Corporation 2004.

22.4 "SSM-5000A for TOC-V Series Total Organic Carbon Analyzers User Manual," Shimadzu Corporation 2001.

23.0 ATTACHMENTS

23.1 TOC Test Flow Chart
23.2 Curve Preparation and Information
23.3 Example of LIMS Logbook
23.4 Example of a Certificate of Analysis
23.5 MDL Results

Attachment 23.1
TOC FLOW CHART



Attachment 23.2
Curve Preparation and Information

DC-190 Curve

To calculate the standards to use for the DC-190 curve there is an excel file located at:
S:\Lab Data\Metals\TOC\DC190 std calc

Enter the certified TOC concentration of the ERA standard and then adjust the Amount used column numbers until they match or are near the desired values. These final concentrations should then be adjusted in the calibration curve page when calibrating.

Below is a sample of the dilutions done for one ERA standard stock solution.

ERA certified concentration: 90.2 ppm
Actual undiluted concentration: 18040 ppm

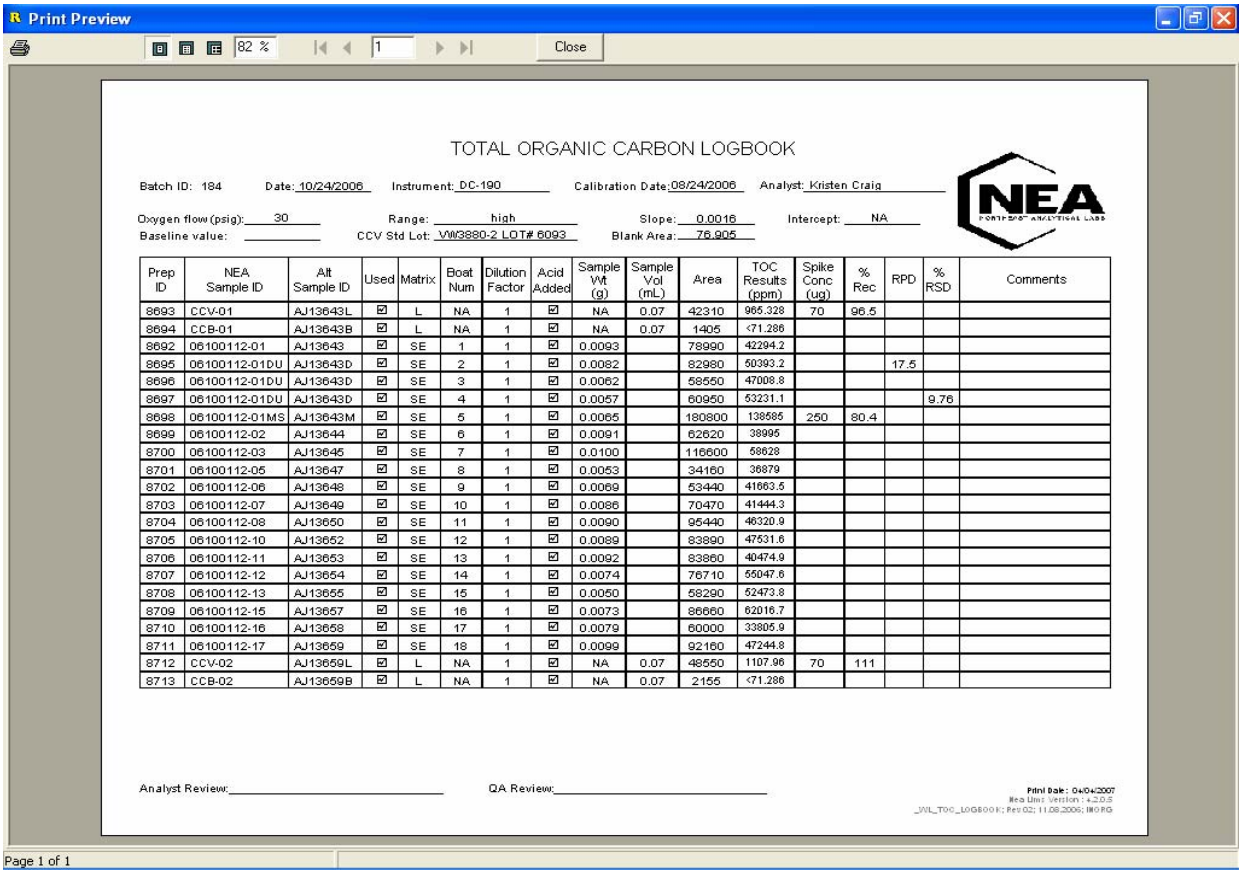
Standard Number	Amount used (ml)	Final Volume (ml)	Concentration (ppm)	Volume Used to calibrate (ml)	End Concentration (ug)	Desired Concentration (ug)
1	0.039	10	70.356	0.07	4.92	5
2	0.079	10	142.516	0.07	9.98	10
3	0.397	5	1432.376	0.07	100.27	100
4	0.99	5	3571.92	0.07	250.03	250
5	1.98	5	7143.84	0.07	500.07	500
6	3.167	5	11426.536	0.07	799.86	800

Shimadzu Curve

Begin by placing Potassium Hydrogen Phthalate in a clean jar and drying in the oven at 104°C for an hour. Once it is cooled in the dessicator, 2.125 g is weighed into a 25 mL volumetric. The volumetric is then filled with fresh DI H_2O. Shake the volumetric until completely dissolved; it can be warmed to help this process. This solution has a concentration of 40,000 ppm. It can then be diluted to appropriately 100 ppm, 400 ppm, and 4,000 ppm.

Standard 1 – 100 ppm – pipette 100 uL of the 100 ppm standard into a boat
Standard 2 – 400 ppm - pipette 100 uL of the 400 ppm standard into a boat
Standard 3 – 4,000 ppm - pipette 100 uL of the 4,000 ppm standard into a boat
Standard 4 – 40,000 ppm - pipette 100 uL of the 40,000 ppm standard into a boat
Standard 5 – 400,000 ppm - pipette 1 mL of the 40,000 ppm standard into a boat and place it in the drying oven until it is completely dry and then run in the Shimadzu.

Attachment 23.3
Example of LIMS Logbook


Print Preview

82 %

1

Close

TOTAL ORGANIC CARBON LOGBOOK

Batch ID: 184 Date: 10/24/2006 Instrument: DC-190 Calibration Date: 08/24/2006 Analyst: Kristen Craig

Oxygen flow (psig): 30 Range: high Slope: 0.0016 Intercept: NA

Baseline value: CCV Std Lot: VW3880-2 LOT# 6093 Blank Area: 76.905

Prep ID	NEA Sample ID	Alt Sample ID	Used	Matrix	Boat Num	Dilution Factor	Acid Added	Sample Wt (g)	Sample Vol (mL)	Area	TOC Results (ppm)	Spike Conc (ug)	% Rec	RPD	% RSD	Comments
8693	CCV-01	AJ13643L	☑	L	NA	1	☑	NA	0.07	42310	965.328	70	96.5			
8694	CCB-01	AJ13643B	☑	L	NA	1	☑	NA	0.07	1405	<71.286					
8692	06100112-01	AJ13643	☑	SE	1	1	☑	0.0093		78990	42294.2					
8695	06100112-01DU	AJ13643D	☑	SE	2	1	☑	0.0082		82980	50393.2			17.5		
8696	06100112-01DU	AJ13643D	☑	SE	3	1	☑	0.0062		58550	47008.8					
8697	06100112-01DU	AJ13643D	☑	SE	4	1	☑	0.0057		60950	53231.1				9.76	
8698	06100112-01MS	AJ13643M	☑	SE	5	1	☑	0.0065		180800	138585	250	80.4			
8699	06100112-02	AJ13644	☑	SE	6	1	☑	0.0091		62620	38995					
8700	06100112-03	AJ13645	☑	SE	7	1	☑	0.0100		116600	58628					
8701	06100112-05	AJ13647	☑	SE	8	1	☑	0.0053		34160	36879					
8702	06100112-06	AJ13648	☑	SE	9	1	☑	0.0069		53440	41663.5					
8703	06100112-07	AJ13649	☑	SE	10	1	☑	0.0086		70470	41444.3					
8704	06100112-08	AJ13650	☑	SE	11	1	☑	0.0090		95440	46320.9					
8705	06100112-10	AJ13652	☑	SE	12	1	☑	0.0089		83890	47531.6					
8706	06100112-11	AJ13653	☑	SE	13	1	☑	0.0092		83860	40474.9					
8707	06100112-12	AJ13654	☑	SE	14	1	☑	0.0074		76710	55047.6					
8708	06100112-13	AJ13655	☑	SE	15	1	☑	0.0050		58290	52473.8					
8709	06100112-15	AJ13657	☑	SE	16	1	☑	0.0073		86660	62016.7					
8710	06100112-16	AJ13658	☑	SE	17	1	☑	0.0079		60000	33805.9					
8711	06100112-17	AJ13659	☑	SE	18	1	☑	0.0099		92160	47244.8					
8712	CCV-02	AJ13659L	☑	L	NA	1	☑	NA	0.07	48550	1107.96	70	111			
8713	CCB-02	AJ13659B	☑	L	NA	1	☑	NA	0.07	2155	<71.286					

Analyst Review: QA Review:

Print Date: 04/04/2007

Page 1 of 1

Attachment 23.4
Example of a Certificate of Analysis

NEA
NORTHEAST ANALYTICAL LABS

CERTIFICATE OF ANALYSIS
09/11/2008
XYZ Company
1 Main Street
Any Town, NY 12345
CONTACT: Manager

MATRIX:	SEDIMENT	**PROJECT:**	Project Name here
DATE RECEIVED:	09/03/2008 **TIME:** 10:20	**LOCATION:**	Site Location here
SAMPLED BY:	.	**LAB ELAP#:**	11078
CUSTOMER PO:	N/A	**NEA LRF:**	08090043

NEA ID	CUSTOMER ID	METHOD	DATE-TIME SAMPLED	RESULTS	PQL	FLAG	UNITS	DATE ANALYZED
Total Organic Carbon								
AL14150	[redacted]	EPA Lloyd Kahn	08/28/2008 11:10	130000	640		mg/kg	09/11/2008
AL14151		EPA Lloyd Kahn	08/28/2008 11:10	120000	630		mg/kg	09/11/2008
AL14152		EPA Lloyd Kahn	08/28/2008 13:20	120000	570		mg/kg	09/11/2008
AL14153		EPA Lloyd Kahn	08/28/2008 14:35	98000	670		mg/kg	09/11/2008
AL14154		EPA Lloyd Kahn	08/28/2008 15:00	110000	640		mg/kg	09/11/2008
AL14155		EPA Lloyd Kahn	08/28/2008 15:32	130000	650		mg/kg	09/11/2008
AL14156		EPA Lloyd Kahn	08/28/2008 16:03	130000	640		mg/kg	09/11/2008
AL14157		EPA Lloyd Kahn	08/28/2008 17:58	62000	680		mg/kg	09/11/2008
AL14158		EPA Lloyd Kahn	08/28/2008 18:28	91000	640		mg/kg	09/11/2008
AL14159		EPA Lloyd Kahn	08/28/2008 18:51	69000	600		mg/kg	09/11/2008
AL14160		EPA Lloyd Kahn	08/29/2008 07:55	60000	660		mg/kg	09/11/2008
AL14161		EPA Lloyd Kahn	08/29/2008 08:22	36000	540		mg/kg	09/11/2008
AL14162		EPA Lloyd Kahn	08/29/2008 09:01	53000	610		mg/kg	09/11/2008
AL14163		EPA Lloyd Kahn	08/29/2008 10:30	130000	750		mg/kg	09/11/2008
AL14164		EPA Lloyd Kahn	08/29/2008 10:49	69000	610		mg/kg	09/11/2008
AL14165		EPA Lloyd Kahn	08/29/2008 11:08	100000	670		mg/kg	09/11/2008

Notes: ND (Not Detected). Denotes analyte not detected at a concentration greater than the PQL.
PQL (Practical Quantitation Limit). Denotes lowest analyte concentration reportable for the sample.

AUTHORIZED SIGNATURE:

William A. Kotas
Quality Assurance Officer

Robert E. Wagner
Laboratory Director

2190 Technology Drive Schenectady, NY 12308 Phone 518.346.4592 Fax 518.381.6055 Email : information@nealab.com

Attachment 23.5
MDL Results

Northeast Analytical, Inc.

Method Detection Limits

File Name: Q:\MDL\METALS\2007\MDL\TOC\[051007MDL_TOC_DC190.XLS]A
Date: 10-May-07

Compound:	Total Organic Carbon	Analysis:	EPA Lloyd Kahn
Matrix:	Soil/Solid	Instrument:	DC 190
Spike conc:	4.96 ug	Method:	Boat Injection/IR

NEA Sample ID	Preparation Date	File Name	Analysis Date	Measured Concentration ug	Percent Recovery (%)
AK03641	05/07/07	Run #1	05/10/07	2.91	58.7%
AK03642	05/07/07	Run #2	05/10/07	2.74	55.2%
AK03643	05/07/07	Run #3	05/10/07	3.15	63.5%
AK03644	05/07/07	Run #4	05/10/07	2.88	58.1%
AK03645	05/07/07	Run #5	05/10/07	3.23	65.1%
AK03646	05/07/07	Run #6	05/10/07	3.49	70.4%
AK03647	05/07/07	Run #7	05/10/07	3.14	63.3%
AK03648	05/07/07	Run #8	05/10/07	3.29	66.3%

Number (n):	8	
AVG:	3.10	ug
STDEV (s):	0.25	ug
%RSD:	7.92%	
MDL:	0.74	ug
VALID ?:	Y	

One sided Student's t values (t) at the 99% confidence level.

Number (n)	(t) value
7	3.143
8	2.998

APPENDIX 60
SOP FOR MASS OF SOLIDS ANALYSIS (NE277_01)

STANDARD OPERATING PROCEDURE

NORTHEAST ANALYTICAL INC.

NE277_01.DOC

REVISION NUMBER: 1

MASS OF SOLIDS FOR SEDIMENT SAMPLES

COPY # ___

NORTHEAST ANALYTICAL, INC.

STANDARD OPERATING PROCEDURE

LABORATORY PROCEDURE NE277_01.DOC

REVISION 1 (03/23/09)

Author:
Christina L. Braidwood (Quality Assurance Officer)

Reviewed by:

Robert E. Wagner
Laboratory Director

Approved by:

Christina Braidwood
Quality Assurance Officer

TABLE OF CONTENTS

1.0 IDENTIFICATION OF TEST METHOD

1.1 This Standard Operating Procedure (SOP) describes the analysis for sediment mass collected on primary traps using the mass of solids determination.

2.0 APPLICABLE MATRIX AND MATRICES

2.1 This method is applicable to sediment samples.

3.0 DETECTION LIMIT

3.1 The method reporting limit for this method is 0.1mg which is based on the sensitivity of the 4 place balance used to determine the weight of the sample.

4.0 SCOPE AND APPLICATION

4.1 Sediment from the river is collected on a primary trap and secondary trap. Trap design and placement and sample collection is the responsibility of the client.

4.2 Primary traps will be analyzed by this standard operating procedure through the mass of solids.

5.0 SUMMARY OF TEST METHOD

5.1 Traps are lowered gently to the bottom of the river, and allowed to rest on an approximately level area. The coordinates of the trap is specified by the user.

5.2 Sediment mass is measured using a primary trap and a secondary trap. The primary trap measures the mass of solids and the secondary trap is used to measure the PCB and TOC concentration of the material collected. The traps are retrieved upon completion of the dredging in a target upstream area. The traps are inspected at specified time intervals. When visible sediment is observed in the trap, it is withdrawn from the river, and water is decanted. The captured sediment will be placed in a laboratory container for determination of the mass of solids.

6.0 DEFINITIONS

6.1 **Mass-** a quantity or aggregate of matter.

6.2 **Trap-** a device pertaining to the collection of settleable sediment and allowing other matter to be omitted.

7.0 INTERFERENCES

7.1 Highly mineralized sediments containing significant concentrations of calcium, magnesium, chloride and/or sulfate may be hygroscopic and require prolonged drying, desiccation, and rapid weighing.

7.2 Samples containing high concentrations of bicarbonate are converted to carbonate. Drying may need to be prolonged to assure complete conversion.

7.3 Too much sample can crust over and trap water that will not be evaporated during the drying process. Care must be taken to avoid this situation by choosing the correct drying container.

7.4 All material in the trap must be included in the mass of solids determination.

8.0 SAFETY

8.1 Safety glasses and gloves are required. A lab coat or apron is strongly recommended. If samples contain known quantities of hazardous material, the dried sample is classified as hazardous waste and is subject to the procedures listed in SOP NE054 (Disposal of Hazardous Waste).

9.0 EQUIPMENT AND SUPPLIES

9.1 VWR model 1370FD model drying oven or equivalent

9.2 Analytical balance: Mettler model AG204 four place balance capable of weighing 0.0001g or equivalent. A four place balance will be used for samples that are low in weight.

9.3 Analytical balance: Mettler model PE16 16Kg capacity, capable of weighing 0.1g with a minimum capacity of 5 grams or equivalent. The larger capacity balance will be used for samples that are above the 200 grams capacity of the four place balance.

9.4 100 mL evaporating dishes (Coors p/n 60233) for samples that are small in mass.

9.5 Aluminum pans for drying samples that are large in mass.

9.6 Rinse bottle (Filled with laboratory grade water).

9.7 Portable dessicator. Purpose of the dessicator is to prevent the evaporating dishes from absorbing moisture while they are cooling. The desiccant material must be dried in the drying oven when the color of the desiccant is clear. Place the drying pan containing the dessicator material in the drying oven for a minimum of 1 hour. Transfer the material to the portable dessicator, and wait a minimum of 1 hour for the material to cool to room temperature before placing evaporating dishes in the portable dessicator.

9.8 Tweezers

9.9 Stainless steel spatula

10.0 REAGENTS AND STANDARDS

10.1 Laboratory grade water (RO water). Located in the Water Room.

11.0 SAMPLE COLLECTION, PRESERVATION, SHIPMENT, AND STORAGE

11.1 The analyst will be familiar with SOP NE227 (Sample Receiving Login & Storage Procedures).

11.2 Analysis should begin as soon as possible. However, there is no holding time applicable to this procedure. Samples require no preservation prior to analysis other than storage at 4 ± 2 ºC in the walk-in cooler to minimize microbiological decomposition of solids.

12.0 QUALITY CONTROL

12.1 **Standard Operating Procedure:** Analyst must read, understand, and use the latest version of the laboratory's SOPs that relate to their job responsibilities. The standard operating procedure must be read during their initial training, annually, and when the standard operating procedure is revised. Technicians should be familiar with the operation of the drying oven located in the Inorganics Laboratory. Technicians should be familiar with the maintenance of the portable desiccators and with the operation and maintenance of the analytical balance used for this procedure.

12.2 **Method Blank (MB)** - A method blank sample is analyzed once every batch of twenty samples or less. The method blank will consist of an empty drying container that is used to process samples.

12.3 **Field Duplicate (FD)- A** field duplicate is analyzed if provided.

13.0 CALIBRATION AND STANDARDIZATION

13.1 The scale must receive a calibration check daily. Please refer to SOP NE076 (Operation of Laboratory Balance and Calibration Check).

13.2 Oven Thermometer must to be calibrated yearly and the tolerance must be met. The correction factor must be applied.

13.3 The analyst must be familiar with usage of the portable dessicator. Drying agent must be adequate for dessicator. Refer to **Section 9.7** for desiccant usage.

14.0 PROCEDURE

14.1 Log into LIMS and create a batch for Mass of Solids test. Include the specified quality control samples described in **Section 12.0** under "Wetlab".

14.2 Prepare for Mass of Solids test by ramping drying oven to 104 ˚C.

14.3 Obtain the sample from storage and determine what size drying pan will be required based on sample size.

14.4 Prepare evaporating dishes by heating a clean, labeled dish to 104 ˚C ± 1˚C, for 1 hour in the drying oven. Cool dish by placing it into the dessicator and store until needed. Wait at least 1 hour for dish to equilibrate to room temperature. Weigh dish immediately before usage and record the weight of dish in LIMS. If the weight of the dish does not remain constant, return the dish into the dessicator and reweigh. Repeat **Section 14.2** until a constant weight is obtained (weight loss is 0.5 mg).

14.5 If the sample is large in weight (greater than 200 g), then an aluminum pan is used for drying and weighing purposes. Select the appropriate size pan and determine the weight empty on the large weight balance and record this weight in LIMs.

14.6 Carefully transfer the sediment sample from the jar to the drying dish

14.7 Rinse the sample jar with laboratory grade water to transfer all the sediment sample.

14.8 Depending on how much water is present, the sample may need to be dried in a chemical fume hood overnight before being placed into the drying oven.

14.9 Place sample into the drying oven at 104 ˚C ± 1˚C for 4 hours or until the sample evaporates to dryness by visual inspection. For large weight samples this drying may take overnight.

14.10 Remove sample from oven and place into dessicator for 1 hour.

14.11 Weigh evaporating dish with sample on the analytical balance until a constant weight is obtained (weight loss is 0.5 mg).

14.12 Enter data in required areas and finalize the LIMS logbook for Mass of Solids.

14.13 Create the Certification of Analysis (COA) after checking that the quality control samples were within quality acceptance limits.

14.14 After completion of the analysis run, the analyst reviews the logbook(s) and analytical data for completion. The supervisor must review the data in the logbook(s) and record their initials and date on the appropriate documents.

15.0 CALCULATIONS

15.1 Calculation for Mass of Solids (MOS):

MOS, g = Final dish weight, g – Initial dish weight, g

15.2 Calculation for Field Duplicate (precision to be calculated by client if the identity of the duplicate pairs is not known by the laboratory analysts):

$$\%RPD = \frac{(\text{sample result - duplicate result})}{(\text{sample result + duplicate result})} \times 200$$

16.0 METHOD PERFORMANCE

16.1 Laboratory audits will determine the compliance for method performance.

17.0 POLLUTION PREVENTION

17.1 Pollution prevention is practiced in the laboratory by minimizing usage of solvents and chemicals, so that disposal of waste generated is held to the smallest amount possible. This is directly linked to the types of procedures in place at the laboratory to reduce the volumes of solvents used.

17.2 Pollution prevention also relies on minimizing to the best extent the chemicals and solvents required to perform extraction and analysis procedures. The laboratory personnel strive to purchase chemicals and standards that will be consumed based on anticipated workload. For additional information about laboratory pollution prevention, please refer to laboratory SOP NE168.

18.0 DATA ASSESSMENT AND ACCEPTANCE CRITERIA FOR QUALITY CONTROL MEASURES AND CORRECTIVE ACTION FOR OUT OF CONTROL DATA

18.1 In situations where data is reported under out-of-control conditions, the data will be annotated with data qualifiers and/or appropriate descriptive comments defining the nature of the excursion in the sample case narrative. If warranted, a corrective action report (CAR) will be issued to define the problem, steps to correct the problem, and final resolution.

18.2 **Method Blank –** The level of target analyte in the method blank must be less than the reporting limit. If the Method Blank is greater than the reporting limit, the only associated samples that can be reported are the ones below the reporting limit, or more than ten times the level in the Method Blank.

18.3 **Field Duplicate- The** field duplicate must be within quality acceptance limits. The RPD should be $\leq$ 40% for results > 5X the RL. The difference between results should be < 2X the RL when at least one result is $\leq$ 5X the RL.

19.0 CORRECTIVE ACTIONS FOR OUT-OF-CONTROL DATA

19.1 Refer to table in **Section 20.2**.

20.0 CONTINGENCIES FOR HANDLING OUT OF CONTROL OR UNACCEPTABLE DATA

20.1 If quality control results are outside the acceptable quality control limits, the following procedures will be implemented:

20.1.1 The Quality Assurance Manager must be notified.

20.1.2 The data must be flagged with the appropriate qualifiers and addressed in the Case Narrative.

20.1.3 The client must be notified about the data.

20.2 Table for Corrective Actions for Out-of-Control Data

Quality Control Item	Corrective Action
Blank Contamination	1. Check previous samples for high analyte concentrations. 2. Reanalyze samples if possible. 3. Flag data. 4. Issue case narrative to client if necessary.
Field Duplicate sample results outside control limits	1. Put samples back to oven and reweigh as previous described. 2. Mix sample well and reanalyze samples if possible. 3. Flag data. 4. Issue case narrative to client if necessary.
Hold Time Excursion	1. Flag Data 2. Issue Case Narrative to client

21.0 WASTE MANAGEMENT

21.1 All applicable federal and state rules and regulations governing hazardous waste will be followed when disposing of laboratory waste generated during the execution of this method.

21.2 Please refer to standard operating procedure NE054 regarding how hazardous waste is handled and disposed of by the laboratory.

22.0 REFERENCES

22.1 "Methods of Chemical Analysis of Water and Wastes'," EPA-60/4-79-020, revised March 1983. Method #160.3

22.2 NYSDOH Environmental Laboratory Approval Program Manual item # 271

22.3 Standard Methods for the Examination of Water and Wastewater, 18th, 1992, APHA

23.0 ATTACHMENTS

No attachments for this SOP.

APPENDIX 61
SOP FOR PARTICLE-SIZE DISTRIBUTION OF CATALYTIC MATERIAL LASTER LIGHT SCATTERING BY ASTM D4464 (BR-GT-005, REV. 1)

Title: PARTICLE-SIZE DISTRIBUTION OF CATALYTIC MATERIAL LASER LIGHT SCATTERING (ASTM D4464)

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Approval Date: August 26, 2008

Facility Distribution No. Electronic **Distributed To: Facility Intranet**

The controlled copy of this SOP is the PDF copy of the SOP that is posted to the laboratory's SOP Directory. Printed copies of this SOP or electronic copies of this SOP distributed outside the facility are considered uncontrolled.

1.0 Scope and Application

1.1 This SOP describes the laboratory procedure for the determination of particle size distribution in catalyst and catalyst carrier particles. It is applicable to the particles sized above and below 30 to 300 um spherical diameter. Particle size determinations from this method may not agree with particle size distribution derived by other methods. Particle size distribution is strongly influenced by the physical employed by each test method. The result of any particle sizing method should be used only in a relative sense and should not be regarded as absolute when comparing results obtained by other methods.

2.0 Summary of Method

2.1 A portion of sample is dispersed in water or a compatible organic liquid and is circulated through the path of a laser light beam or some other suitable source of light. The particles pass through the beam and scatter it. Photodetector arrays collect the scattered light, which is converted to electrical signals to be analyzed using Fraunhofer Diffraction, or Mie Scattering, or both. Scattering information, typically, is analyzed assuming a spherical geometry for the particles. Calculated particle sizes are, therefore, presented as equivalent spherical diameters.

2.2 This SOP is based on the following reference method:

- ASTM D4464-00

Method modifications are listed in Section 15.0.

3.0 Definitions

3.1 Background- extraneous scattering of light by material present in the dispersion fluid other than the particles to be measured. It includes scattering by contamination in the measurement path.

3.2 Fraunhofer Diffraction- the optical theory that describes the low-angle scattering of light by particles that are large compared to the wavelength of the incident light.

3.3 Mie Scattering- the complex electromagnetic theory that describes the scattering of light by spherical particles. It is usually applied to particles with diameters that are close to the wavelength of the incident light. The real and imaginary indices of light refraction of the particles are needed.

3.4 Multiple Scattering- the re-scattering of light by a particle in the path of light scattered by another particle. This usually occurs in heavy concentrations of a particle dispersion.

4.0 Interferences

4.1 Air bubbles entrained in the circulating fluid will scatter light and then be reported as particles. Circulating fluids typically do not require degassing, but should be bubble-free on visual inspections.

4.2 Contaminants, such as non-aqueous solvent, oil or other organic coatings on the sample may emulsify in an aqueous carrier, scatter light, and be reported as part of the particle size distribution. Samples containing such contaminants may be analyzed in a non-aqueous carrier solvent to dissolve the contaminants or washed free of the contaminant with a compatible aqueous solvent.

4.3 Reagglomeration or settling of particles during analysis will cause erroneous results. Dispersions shall be prepared so a stable dispersion is maintained throughout the analysis.

4.4 Insufficient sample loading (obscuration) may cause electrical noise interference and poor data reproducibility. High sample loading may cause excessive light attenuation and multiple scattering, resulting in erroneous particle size distributions.

5.0 Safety

Employees must abide by the policies and procedures in the Corporate Environmental Health and Safety Manual (CW-E-M-001) and this document. This procedure may involve hazardous material, operations and equipment. This SOP does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, gloves, lab coats and closed-toe, nonabsorbent shoes are a minimum.

5.1 Specific Safety Concerns or Requirements

None

5.2 Primary Materials Used

Not Applicable

6.0 Equipment and Supplies

Catalog numbers listed in this SOP are subject to change at the discretion of the vendor. Analysts are cautioned to be sure equipment used meets the specification of this SOP.

- Malvern MasterSizer 2000 with Hydro 2000G wet-dispersion unit or equivalent
- 40ml glass vials with caps
- Disposable Pipettes, Fisher or equivalent
- Mechanical vortex machine

7.0 Reagents and Standards

- Deionized Water (DI Water)

8.0 Sample Collection, Preservation, Shipment and Storage

The laboratory does not perform sample collection so these procedures are not included in this SOP. Sampling requirements may be found in the published reference method.

Listed below are minimum sample size, preservation and holding time requirements:

Matrix	Sample Container	Minimum Sample Size	Preservation	Holding Time[1]	Reference
Solid	Glass Jar w/ Teflon Lid	50 g	4 ±2°C	None	ASTM D4464

Unless otherwise specified by client or regulatory program, after analysis, samples and extracts are retained for a minimum of 30 days after provision of the project report and then disposed of in accordance with applicable regulations.

9.0 Quality Control

Not Applicable

10.0 Procedure

Turn on the instrument and let it warm up for at least 30 minutes.

Check the dispersion unit to ensure that it is clean and filled with DI water.

Label a clean 40 mL vial with the sample's LAB ID.

Homogenize in the sample container in its container.

Transfer ~ 10 g of sample to its 40 mL vial.

Add enough DI water to the sample to fill the vial ~2/3 full.

Cap the vial and use the mechanical vortex machine to disperse the sample then inspect the sample to ensure that any agglomerations have been dispersed.

Open the instrument software program and select "Run Existing SOP" from the menu then select "STL-BTV-D4464" from the SOP list.

Save the data file using the SDG designation as the file name.

Follow the screen instructions for sample analysis. When the sample run is complete, select "Run this SOP again" from the menu. Repeat until all samples are analyzed.

Select "Measure" then open the "Accessories" tab. Briefly raise the pump RPM to 2000, then stop the pump and close the "Accessories" tab and the measurement window.

Check to ensure that the dispersion unit and cell are filled with clean DI water then turn the instrument off.

11.0 Calculations / Data Reduction

11.1 Calculations

Not applicable.

11.2 Data Review

11.2.1 Primary Review

Review your work for correctness, completeness and compliance to this SOP. Record any problems encountered during the analytical process on the bench sheet or complete a nonconformance report, when necessary. Set aside the paperwork for secondary review.

11.2.2 Secondary Review

Review the data to ensure the procedure performed is consistent with SOP and project specifications.

For additional guidance regarding the laboratory's protocol and required elements for data review refer to laboratory SOP BR-QA -019.

11.3 Data Reporting

Review project documents such as the environmental test request (ETR) analytical worksheets, Project Plan (PP), Project Memo or any other document/process used to communicate project requirements to ensure those project requirements were met. If project requirements were not met, immediately notify the project manager (PM) to determine an appropriate course of action.

Generate the data report in the deliverable format specified by the laboratory PM and release the report to report management.

Retain, manage and archive electronic and hardcopy data as specified in laboratory SOP BR-QA-014 Laboratory Records.

12.0 Method Performance

Not Applicable

13.0 Pollution Control

It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i.e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage and reagent stability). Employees must abide by the policies in Section 13 of the Corporate Safety Manual for "Waste Management and Pollution Prevention."

14.0 Waste Management

Waste management practices are conducted consistent with all applicable rules and regulations. Excess reagents, samples and method process wastes are disposed of in an accepted manner. Waste description rules and land disposal restrictions are followed. Waste disposal procedures are incorporated by reference to BR-EH-001. The following waste streams are produced when

this method is carried out.

- Solid Waste-Satellite Container: Solid Waste 5 Gallon Plastic Bucket (inside fume hood)

15.0 References / Cross-References

- Standard Test Method for Particle Size Distribution of Catalytic Material by Laser Light Scattering, ASTM D4464-00, Volume 04.08 Soil and Rock, American Society for Testing and Materials, Philadelphia, Pa., 2000.
- Corporate Environmental Health and Safety Manual (CW-E-M-001)
- Laboratory SOP BR-SL-001
- Laboratory SOP BR-QA-004
- Laboratory SOP BR-EH-001
- Laboratory SOP BR-QA-019

16.0 Method Modifications

None

17.0 Attachments

Not applicable,

18.0 Revision History

BR-GT-005, Rev. 1:

- Title Page: Updated approval signatures.
- All Sections: Converted to company template.

APPENDIX 62
SOP FOR DATA VALIDATION OF CONGENER PCB DATA LOW-LEVEL CALIBRATION METHOD (DVNE207_03)

1.0 OBJECTIVES

This standard operating procedure (SOP) describes procedures that the Environmental Standards data reviewers will use to validate PCB Congener data generated by Northeast Analytical, Inc.'s analytical SOP NE207_03 for the General Electric Company's Hudson River Remedial Action Monitoring Program. Validation will be performed to assess the compliance of the sample data to the analytical SOP as applicable to the General Electric Company's Hudson River Remedial Action Monitoring Program. In addition, the usability of the PCB Congener data provided by the analytical laboratory will be determined based on the general guidance provided in the "US EPA Contract Laboratory National Functional Guidelines for Organic Data Review" (10/1999; National Functional Guidelines) and "US EPA Contract Laboratory Program National Functional Guidelines for Superfund Organic Methods Data Review" (06/2008 National Functional Guidelines). It should be noted that the National Functional Guidelines apply strictly to data generated by the Contract Laboratory Program (CLP) protocol and are not directly applicable to validation of data generated by laboratory-developed analytical methods; therefore, this SOP presents the specific data qualification actions that will be used for validation.

The validation findings will be presented in a quality assurance review (QAR) that will be prepared for one or more sample delivery groups (SDGs). Copies of annotated analytical results summaries (Form I's), including any changes to the analytical results and data qualifier codes or a data summary spreadsheet of the qualified analytical results, will be included in the support documentation of the QAR.

2.0 EVALUATION TOOLS

Excel forms available in R:/Templates/Chemistry/XCELforms:

- Organic field duplicate comparisons Rev1-01.xls
- Organic field quadruplicate comparison Rev1-01.xls
- Organic field triplicate comparison Rev1-01.xls
- Aroclor.xls

Chemistry Applications:

- FIT
- Methods Database
- Target version 4.1 data processing software

3.0 REFERENCE DOCUMENTS

- US EPA Contract Laboratory Program National Functional Guidelines for Organic Data Review (10/1999).

- US EPA Contract Laboratory Program National Functional Guidelines for Superfund Organic Methods Data Review (06/2008).

- Northeast Analytical, Inc. (NEA)- Standard Operating Procedure for the Congener-Specific Polychlorinated Biphenyl (PCB) Analysis (Low-level Calibration Method) (SOP NE207_03, Rev. 03; 08/05/08).

- Region I, EPA-New England Data Validation Functional Guidelines for Evaluating Environmental Analyses (12/96).

- Region II, Standard Operating Procedure for the Validation of Organic Data Acquired Using SW-846 Method 8082 (SOP HW-23B, Rev. 1.0, May, 2002).

- Region III, Modifications to National Functional Guidelines for Organic Data Review (9/94).

4.0 PROCEDURE

4.1 EVALUATION OF METHOD COMPLIANCE

The data reviewer will assess the method compliance of the PCB Congener data based on an evaluation of information presented in the data package deliverables. Compliance to modified Green Bay Method analytical SOP as applicable to General Electric Company's Hudson River Remedial Action Monitoring Program (as directed by the Project Manager) will be evaluated as part of the assessment. In addition, the deliverables will be evaluated for reporting errors and inconsistencies. The findings of the method compliance assessment will be described in terms of deficiencies and comments about the data/deliverables. The deficiencies/comments will be presented in three subdivisions

(*i.e.*, correctable deficiencies, noncorrectable deficiencies, and comments) of the Organic Data Evaluation Section of the QAR. Each deficiency and comment discussed in the QAR will indicate any subsequent impact on the usability of the data or will identify aspect(s) of the data that could not be evaluated due to the deficiency.

The data reviewer should contact the project laboratory to request the correction of deficiencies prior to submittal of the QAR (if feasible and sanctioned by to General Electric Company). At a minimum, corrections required to allow for a full evaluation of the usability of the data should be requested. Such correctable deficiencies may include sample result errors, missing data deliverables, or calculation errors that would require a significant amount of the data reviewer's time to correct. Any laboratory resubmittals as a result of such requests will be discussed in the comments subdivision of the QAR and included as an attachment to the QAR.

4.2 DETERMINATION OF DATA USABILITY

The data reviewer will determine the usability of the PCB Congener data based on an evaluation of the information presented in the data package deliverables. The findings of the PCB data usability assessment will be presented in terms of data qualifications that the project team should consider in order to best utilize the data; these qualifications will be presented in the Organic Data Qualifier subsection of the QAR. Each qualification discussed in the QAR will indicate that the affected sample result(s) has been flagged with a representative qualifier code(s) to General Electric Company's database to provide, at a glance, an indication of the quantitative and qualitative reliability of each analytical result. In general, the qualifier statements will be presented in the QAR in the

following order: blank contamination, unusable results (R/UR), estimated results (J/UJ), tentative identifications of target compound results (N), field duplicate comparison, and a general qualifier for all results reported below the quantitation limit (if applicable to General Electric Company's Hudson River Remedial Action Monitoring Program).

The data reviewer's criteria for evaluating the usability of the PCB Congener data and the resultant qualifications will be as stipulated on the attached Table for the Validation of PCB (Congener) Data Generated by the project SOP for Congener-Specific PCB Analysis by modified Green Bay Method. It should be noted that the project manager should be consulted when "professional judgment" use is indicated on the attached table.

Quality Control Item	Usability Criteria	Action
Temperature Upon Receipt	4±2°C	If temperature is >10°C but ≤20°C, qualify positive results as estimated ("J") and qualify "not-detected results as estimated ("UJ"). If temperature is > 20°C, qualify positive results as estimated ("J") and qualify "not-detected" results as unusable ("UR"). Note time of collection relative to receipt at laboratory. Professional judgment should be used if < 8 hours has elapsed from collection to receipt at the laboratory to determine if qualification due to elevated temperature applies.
Technical Holding Time	Aqueous samples should be extracted within 365 days of sample collection. Sediment/soil samples should be extracted within 14 days of sample collection. Tissue samples (which have been frozen to <-18°C upon laboratory receipt) should be extracted within 1 year of sample collection. All matrices should be analyzed within 40 days after extraction.	If a holding time is exceeded, qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). If a holding time is grossly exceeded (*i.e.*, > twice the holding time), qualify positive results as estimated ("J") and qualify "not-detected" results as unusable ("UR").

Quality Control Item	Usability Criteria	Action
Initial Calibration	%RSD should be ≤20% for the three- or four-point calibration curve for each peak. In addition, the correlation coefficient (r) for each calibration curve must be ≥0.995. <u>Chromatographic Resolution</u> Peak valley heights between DB-1 peaks 14 and 15 must be equal to or less than half the height of peak 15. Also, DB-1 peaks 74 and 75 must be equal to or less than one-third the height of peak 74. Must be established initially.	If r is <0.995 but ≥0.85, qualify positive results as estimated ("J") and do not qualify "not-detected" results. Use professional judgment to qualify "not-detected" results as estimated ("UJ"). If r is <0.85, qualify positive results as estimated ("J") and qualify "not-detected" results as unusable ("UR"). Use professional judgment when evaluating the concentration intercept of a calibration curve. If the concentration intercept is positive, the samples should be evaluated for false positives. If the concentration intercept is negative, the sample should be evaluated for false negatives.

Quality Control Item	Usability Criteria	Action
Continuing Calibration Check (CCC) Standards	The %differences are calculated for Total PCBs and six selected PCB congener peaks (peaks 7, 116, 47, 93, 37 and 102which contain IUPAC #s 6, 205, 70, 174, 181, 104, 44, and 180) comparing the selected congener concentrations with the known concentrations. The % difference for Total PCBs must be ≤15%. The % differences for PCB congeners #s 6 and 205 (low-level peaks) must be ≤30%. The % differences for the other four medium and high-level peaks must be ≤15%. If a %difference fails, this may indicate unacceptable RRFs or an instrument problem. The area of the internal standard Octachloronapthalene (OCN) in the CCC standard must be within 50-150% of the average area for OCN among the initial calibration standards. Chromatographic Resolution Peak valley heights between DB-1 peaks 14 and 15 must be equal to or less than half the height of peak 15. Also, DB-1 peaks 74 and 75 must be equal to or less than one-third the height of peak 74. Must be established initially.	Qualification is for all samples on both sides of the out-of-criteria calibration standards. Professional judgment should be used to determine the impact of an out-of-criteria continuing calibration check relative to the PCB Congeners for which %differences have not been calculated. If Total PCBs has 15%<%D≤90% with the response indicating a sensitivity decrease, qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). If Total PCBs has %D>15% with the response indicating a sensitivity increase, qualify positive results as estimated ("J") and use professional judgment to qualify "not-detected" results. If the low-level PCB Congeners have 30%<%D≤90% with the response indicating a sensitivity decrease, qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). If the low-level PCB Congeners have %D>30% with the response indicating a sensitivity increase, qualify positive results as estimated ("J") and use professional judgment to qualify "not-detected" results. If the medium or high-level PCB Congeners have 15%<%D≤90% with the response indicating a sensitivity decrease, qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). If the medium or high-level PCB Congeners have %D>15% with the response indicating a sensitivity increase, qualify positive results as estimated ("J") and use professional judgment to qualify "not-detected" results. If Total PCBs or the select PCB Congeners have %D>90% with the response indicating a sensitivity decrease qualify positive results as estimated ("J") and qualify "not-detected" results as unusable ("UR"). Use professional judgment for qualification if the internal standard area for OCN or chromatographic resolution fails the usability criteria.

Quality Control Item	Usability Criteria	Action
Internal Standard – Octachloronaphthalene (OCN)	Area counts of the internal standard peaks for all CCCs, QC samples, and samples should be ±50% of the average internal standard area observed among the associated initial calibration standards. Retention time (RT) for any internal standard should be within the RT window.	If a sample area count is outside of criteria (±50% of the average area among the associated initial calibration standards), qualify positive results for compounds quantitated using that internal standard as estimated ("J") and qualify "not-detected" results for compounds quantitated using that internal standard as estimated ("UJ"). If extremely low sample area counts (<25% of the average area among the associated initial calibration standards) are reported, qualify positive results for compounds quantitated using the extremely low internal standard as estimated ("J") and qualify "not-detected" results for compounds quantitated using that internal standard as unusable ("UR"). If a CCC standard or QC sample area count is outside of the criteria (±50% of the average area among the associated initial calibration standards), use professional judgment to qualify data. If an internal standard RT is outside of the RT window and no peaks are observed in the sample chromatogram, qualification is not necessary. Use professional judgment if peaks are observed in the sample chromatogram.
Retention Time Windows (See Note #1 for additional information.)	All PCB congener(s) retention times (RTs) should be within the established RT windows in the CCCs. RT windows for samples are defined as the absolute RT of the Initial CCC Standard for a given analytical sequence ±0.07 minutes.	If the CCC RT windows are not within the specified RT windows, evaluate sample chromatograms for false positives and false negatives. If a constant drift in RT is observed in the bracketing CCC standards, the direction of the RT drift should be applied to the sample chromatograms.

Quality Control Item	Usability Criteria	Action
Blanks (See Note #2 for additional information.)	Summarize all results greater than the method detection limit (MDL) present in the blanks. The highest positive result associated with a sample should be utilized for evaluation of contamination.	If a target PCB Congener is found in the blank but not in the associated sample(s), no action is required. If a sample result is ≤5× the blank result, qualify the positive result as "not detected" ("UB") and revise the MDL to the value of the positive result. If the positive result qualified "UB" is <RL, the RL should be used as reported. If the positive result qualified "UB" is ≥RL, the value of the positive result should be used as the revised RL. If individual PCB congeners have been qualified "UB," adjust the associated Total PCB result to reflect that the individual PCB congener result should be considered "not-detected." If a sample result is >5× blank result, qualification is not required. If gross contamination exists (*i.e.*, saturated peaks on the GC), qualify the positive results as unusable ("R") due to interference.
Surrogates (See Note #3 for additional information.)	Use 60-140% for acceptance limits.	If the recoveries of one or more surrogates are > upper limit, qualify positive results as estimated ("J") and do not qualify "not-detected" results. If the recoveries of one or more surrogates are < lower limit but ≥10%, qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). If the recoveries of one or more surrogates are <10%, qualify positive results as estimated ("J") and qualify "not-detected" results as unusable ("UR").

Quality Control Item	Usability Criteria	Action
Laboratory Control Samples/Laboratory Control Sample Duplicate (LCS/LCSD)	For accuracy, use recovery limits of 60-140% for Total PCBs. For precision (if LCSD is provided), use RPD limits of 20% for aqueous samples and 40% for solid samples.	If the recovery is >140%, qualify positive results for all PCB Congeners and Total PCBs in all associated samples as estimated ("J") and do not qualify "not-detected" results. If the recovery is <60% but ≥10%, qualify positive results for all PCB Congeners and Total PCBs in all associated samples as estimated ("J") and qualify "not-detected" results in all associated samples as estimated ("UJ"). If the recovery is <10%, qualify positive results for all PCB Congeners and Total PCBs in all associated samples as estimated ("J") and qualify "not-detected" results in all associated samples as unusable ("UR"). If the precision exceeds the RPD criterion, qualify positive results in all associated samples as estimated ("J") and do not qualify "not-detected" results.

Quality Control Item	Usability Criteria	Action
Matrix Spike/Matrix Spike Duplicate (MS/MSD) (If performed)	For accuracy, use recovery limits of 60-140% for Total PCBs. For precision between MS and MSD, use criteria specified in the Field/ Laboratory Duplicate criteria (next item).	Data should not be qualified due to %Rs (or RPDs calculated on %Rs) that are outside of criteria if the original concentration of a PCB Congener is >4× the spiking level for that compound. RPDs calculated using MS/MSD results can be used to evaluate precision. If the recovery is >140%, qualify the positive results for all PCB Congeners and Total PCBs in the native sample as estimated ("J") and do not qualify the "not-detected" result. If the recovery is <60% but ≥10%, qualify the positive results for all PCB Congeners and Total PCBs in the native sample as estimated ("J") and qualify the "not-detected" result in the native sample as estimated ("UJ"). If the recovery is <10%, qualify the positive results for all PCB Congeners and Total PCBs in the native sample as estimated ("J") and qualify the "not-detected" result in the native sample as unusable ("UR"). If the precision criteria for any PCB Congener or Total PCBs are not met, qualify the positive result in the native sample as estimated ("J") and qualify the "not-detected" result in the native samples as estimated ("UJ"). If a field duplicate of the native sample was collected and analyzed, the field duplicate sample should also be qualified if an MS/MSD recovery or RPD is outside of criteria (as stated above for the native sample).
Field/Laboratory Duplicate (See Note #4 for additional information)	The RPD for water field duplicates should be ≤20% for results >5x the RL. The difference between results should be ≤ the RL when at least one result is ≤5x the RL. (Use ½ the RL as a numerical value for any "not-detected" results in the difference calculations).	If the criteria are not met, qualify positive results for the out-of-criteria compounds in the original sample and its duplicate as estimated ("J") and qualify "not-detected" results as estimated ("UJ").

Quality Control Item	Usability Criteria	Action
Percent Solids	Soil/sediment samples with less than 50% solid content require qualification.	If a soil/sediment sample has a percent solid content <50% but ≥10%, qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). Use professional judgment if a soil/sediment sample has a percent solid content <10%.
Compound Quantitation (See Notes #5 and 6 for additional information.)	Samples with results that exceed the instrument calibration range should be reanalyzed at a dilution. .	If a target PCB Congener result exceeds the instrument calibration range, qualify positive result as estimated ("J"). Use professional judgment to determine whether sample reanalyses and dilutions should be compared to the original analyses. If criteria (see field duplicate usability) between the original sample results and the reanalysis sample results are not met, qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). If a target PCB Congener is <RL but ≥MDL, qualify positive results as estimated ("J"). If any PCB Congener has been qualified as estimated due to any reason stated in this SOP, qualify the associated positive result for Total PCBs as estimated ("J").
System Performance (See Note #6 for additional information.)	Professional judgment should be used when assessing the degradation of system performance during analyses.	Use professional judgment to qualify the data if it is determined that system performance degraded during sample analyses.
Overall Assessment of Data	Assess overall quality of the data. Review available materials to assess the quality, keeping in mind the additive nature of the analytical problems.	Use professional judgment to determine the need to qualify data not qualified based on the QC previously discussed. Write a brief narrative to give the user an indication of the analytical limitations of the data. If sufficient information on the intended use and required quality of the data is available, include the assessment of the usability of the data within the given context.

Notes for the Validation of PCB (Congener) Data Generated by NEA's SOP for Congener-Specific PCB Analysis

1. If a RT shift is observed in an associated CCC and the sample chromatograms reveal peaks, use expanded RT windows and the surrogate shifts to evaluate for potential false positives and false negatives. If a possible false positive is observed, the reported positive sample result for the PCB Congener outside of the RT window may replace the MDL/RL and the result may be qualified as "not-detected" ("U"), depending on professional judgment. If a possible false negative is observed, the potential positive result may be quantitated and added to the result field and may be qualified as tentative ("N"), depending on professional judgment.

   If the chromatograms reveal peaks that interfere with potential detection of a target PCB Congener, qualify the MDL/RL for "not-detected" results as estimated ("UJ") or unusable ("UR"), depending on the level of the interference. Qualify reported positive results for the PCB Congener as unusable ("R") or raise the MDL and RL above the level of detection, depending on professional judgment.

   In addition to RT windows, the laboratory will be relying on its experience in pattern recognition of multi-peak response PCB chromatograms as well as historical data.

2. The frequency of equipment/rinse blanks is determined during the sampling event. The results of an equipment/rinse blank should be applied to all samples collected in the same day, unless only one blank was collected for a several-day sampling event. In instances where more than one blank is associated with a given sample, qualification should be

Notes for the Validation of PCB (Congener) Data Generated by NEA's SOP for Congener-Specific PCB Analysis

based upon a comparison with the associated blank having the highest concentration of a contaminant.

Instrument blank contamination should be applied to samples bracketing the contaminated instrument blank.

3. The surrogate recovery limits do not apply to samples analyzed at greater than five-fold dilutions. Qualification of the data is not necessary if the surrogate is diluted beyond detection. Generally, a greater than five-fold dilution will affect the ability to even detect the surrogate. Write a comment in the QAR addressing the issue that sample-specific method performance based on surrogate recoveries could not be evaluated due to the dilution required for sample analysis.

4. Duplicate samples may be collected and analyzed as an indication of overall precision. Field duplicate analyses measure both field and laboratory precision; therefore, the results may have more variability than laboratory duplicates that measure only laboratory performance. Laboratory duplicate results and field duplicate results apply only to the original sample and the laboratory/field duplicate. Solid duplicate results are expected to have greater variance than aqueous duplicate results.

5. If a sample result exceeds the instrument calibration range (lower dilution analysis) or is less than the RL (secondary dilution), do not utilize this result when comparing an original analysis and a diluted reanalysis.

Notes for the Validation of PCB (Congener) Data Generated by NEA's SOP for Congener-Specific PCB Analysis

6. Poor chromatographic performance affects both qualitative and quantitative results. Indications of substandard performance include:

- High background levels or shifts in absolute RTs of internal standards
- Excessive baseline rise at elevated temperature
- Extraneous peaks
- Loss of resolution
- Peak tailing or peak splitting that may result in inaccurate quantitation

Furthermore, one of the major sources of interference in PCB Congener analysis is co-extracted organochloride pesticides and associated pesticide breakdown products (*e.g.* DDT, DDD, DDE). Sulfuric acid, Florisil®, and sulfur cleanups (if performed) remove many non-target interferences but review the chromatographic pattern and peak RTs for potential interference.

APPENDIX 63
SOP FOR DATA VALIDATION OF ICP/MS METALS DATA (DV200.8)

1.0 OBJECTIVES

This standard operating procedure (SOP) describes procedures that the Environmental Standards data reviewers will use to validate inorganic data generated by US EPA Method 200.8 for the General Electric Company's Hudson River Remedial Action Monitoring Program. Validation will be performed to assess the compliance of the sample data to US EPA Method 200.8 and/or other reference documents (*e.g.*, analytical SOPs) as applicable to General Electric Company's Hudson River Remedial Action Monitoring Program. In addition, the usability of the inorganic data provided by the project laboratories will be determined based on the general guidance provided in the "US EPA Contract Laboratory National Functional Guidelines for Inorganic Data Review" (02/1994 and 10/2004; National Functional Guidelines). It should be noted that the National Functional Guidelines apply strictly to data generated by Contract Laboratory Program (CLP) protocol and are not directly applicable to validation of data generated by US EPA Method 200.8; this SOP presents the specific data qualification actions that will be used for validation.

The validation findings will be presented in a quality assurance review (QAR) that will be prepared for one or more sample delivery groups (SDGs). Copies of annotated analytical results summaries (Form I's), including any changes to the analytical results and data qualifier codes or a data summary spreadsheet of the qualified analytical results will be included in the analytical results section of the QAR.

2.0 EVALUATION TOOLS

Excel forms available in R:/Templates/Chemistry/XCELForms:

- Inorganic field duplicate comparison Rev 1-01.xls
- Inorganic triplicate comparison Rev 1-01.xls
- Total versus dissolved comparison Rev 1-01.xls

Chemistry Applications:

- FIT
- Methods Database

3.0 REFERENCE DOCUMENTS

- US EPA Contract Laboratory Program National Functional Guidelines for Inorganic Data Review (02/1994).

- US EPA Contract Laboratory Program National Functional Guidelines for Inorganic Data Review (10/2004).

- US EPA Method 200.8.

- Applicable project/laboratory analytical SOPs.

- Region I, EPA – New England Data Validation Functional Guidelines for Evaluating Environmental Analyses (12/96).

- Region II, Evaluation of Metals Data for the Contract Laboratory Program (CLP) (1/92) Validation of Inorganics.

- Region III, Modifications to Natural Functional Guidelines for Inorganic Data Review (9/94).

4.0 PROCEDURE

4.1 EVALUATION OF METHOD COMPLIANCE

The data reviewer will assess the method compliance of the inorganic data based on evaluation of information presented in the data package deliverables. Compliance with US EPA Method 200.8 and/or other reference documents (*e.g.*, analytical SOPs) as applicable to General Electric Company's Hudson River Remedial Action Monitoring Program (as directed by the Project Manager) will be evaluated as part of the assessment. In addition, the deliverables will be evaluated for reporting errors and inconsistencies. The findings of the method compliance assessment will be described in terms of deficiencies and comments about the data/deliverables. The deficiencies/comments will be presented in three subdivisions (*i.e.*, correctable deficiencies, noncorrectable deficiencies, and comments) of the Inorganic Data Section of the QAR. Each deficiency and comment discussed in the QAR will indicate any subsequent impact on the usability

of the data or will identify aspect(s) of the data that could not be evaluated due to the deficiency.

The data reviewer should contact the project laboratories to request the correction of certain deficiencies prior to submittal of the QAR (if feasible and sanctioned by General Electric Company). At a minimum, corrections required to allow for a full evaluation of the usability of the data should be requested. Such correctable deficiencies may include sample result errors, missing data deliverables, or calculation errors that would require a significant amount of the data reviewer's time to correct. In addition, the data reviewer should contact the project laboratories if feasible to request the correction of all correctable deficiencies that impact sample results or that the data reviewer was unable to correct prior to the submittal of the QAR, if time allows. Any laboratory resubmittals as a result of such requests will be discussed in the comments substation of the QAR and will be included as an attachment of the QAR.

4.2 DETERMINATION OF DATA USABILITY

The data reviewer will determine the usability of the inorganic data based on an evaluation of the information presented in the data package deliverables. The findings of the inorganic data usability assessment will be presented in terms of data qualifications that the project team should consider in order to best utilize the data. These qualifications will be presented in the Inorganic Data Qualifier subsection of the QAR. Each qualification will indicate that the affected sample result(s) has been flagged with a representative qualifier code(s) in the General Electric Company's database to provide, at a glance, an indication of the quantitative and qualitative reliability of each analytical result. In general, the qualifier statements will be presented in the QAR in the following

order: blank contamination, unusable results (R/UR), estimated results (J/UJ), field duplicate comparison, and a general qualifier for all results reported below the quantitation/reporting limit (if applicable to General Electric Company's Hudson River Remedial Action Monitoring Program).

The data reviewer's criteria for evaluating the usability of the inorganic data and the resultant qualifications will be as stipulated on the attached Table for the Validation of Metals Data Generated by US EPA Method 200.8. It should be noted that the Project Manager should be consulted when "professional judgement" use is indicated on the attached table.

Table for the Validation of Metals Generated by US EPA Method 200.8

Quality Control Item(s)	Usability Criteria	Action(s)
Temperature and Conditions Upon Receipt	Aqueous samples should be preserved with nitric acid to pH≤2. Solid samples should be preserved to 4±2°C.	If pH is >2 and the laboratory did not adjust the pH and allow the sample to sit for 16 hours before digestion, qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). Solid samples should not be qualified due to out-of-criteria temperature upon receipt.
Technical Holding Time	All matrices should be analyzed within 6 months of sample collection.	If holding time is exceeded, qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). If holding time is grossly exceeded (>1 year from date of sample collection), qualify positive results as estimated ("J") and qualify "not-detected" results as unusable ("UR").
Initial Calibration	Should be established with a minimum of one blank and three standards. Correlation coefficients (r) should be ≥0.995.	Use professional judgement if the minimum number of standards was not used or if instrument was not calibrated daily and/or not calibrated each time set up. If r is <0.995 but ≥0.85, qualify positive results as estimated ("J") and do not qualify "not-detected" results. If r is <0.85, qualify positive results as estimated ("J") and qualify "not-detected" results as unusable ("UR").
Instrument Performance (See Note #1 for additional information)	The coefficient of variation (C.V.) for multiple injections/integrations should be ≤20% for multiple injections/integrations when the result is >than the reporting limit (RL). Samples should not display negative results with absolute values >2× the method detection limit (MDL).	If C.V. is >20%, qualify positive results greater than the RL as estimated ("J") and do not qualify "not-detected" results. If a negative result >5× MDL, qualify the "not-detected" result as unusable ("UR"). If an analyte displays a negative result >2× MDL, qualify the "not-detected" result as estimated ("UJ").

Table for the Validation of Metals Generated by US EPA Method 200.8

Quality Control Item(s)	Usability Criteria	Action(s)
Initial Calibration Verification (ICV)	For accuracy, use recovery limits of 90-110%.	**Qualify samples for an entire analytical sequence.** If an analyte recovery is >110% but ≤125%, qualify positive results as estimated ("J") and do not qualify "not-detected" results. If an analyte recovery is <90% but ≥75%, qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). If an analyte recovery is >125%, qualify positive results as unusable ("R") and do not qualify "not-detected" results. If an analyte recovery is <75%, qualify positive results as estimated ("J") and qualify "not-detected" results as unusable ("UR").
Continuing Calibration Verification (CCV)	For accuracy, use recovery limits of 90-110% for the CCVs.	**Qualify samples analyzed before and after a non-compliant CCV.** If an analyte recovery is >110% but ≤125%, qualify positive results as estimated ("J") and do not qualify "not-detected" results. If an analyte recovery is <90% but ≥75%, qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). If an analyte recovery is >125%, qualify positive results as unusable ("R") and do not qualify "not-detected" results. If an analyte recovery is <75%, qualify positive results as estimated ("J") and qualify "not-detected" results as unusable ("UR").

Table for the Validation of Metals Generated by US EPA Method 200.8

Quality Control Item(s)	Usability Criteria	Action(s)
PQL/CRI/RLV Standard	For accuracy, use recovery limits of 80-120%.	**Qualify samples analyzed before and after a non-compliant PQL/CRI standard.** If an analyte recovery is >120%, qualify positive results ≤3× the spike level as estimated ("J") and do not qualify "not-detected" results. If an analyte recovery is <80% but ≥50%, qualify positive results ≤ 3× the spike level as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). If an analyte recovery is <50%, qualify positive results ≤3× the spike level as estimated ("J") and qualify "not-detected" results as unusable ("UR"). If an analyte recovery is >150%, qualify positive results ≤ 3× the spike level as unusable ("R"), qualify positive results >3× the spike level but ≤5× as the spike level estimated ("J"), and do not qualify "not-detected" results.
Initial Calibration Blank (ICB)/Continuing Calibration Blank (CCB)/Preparation Blank (PB)/Field Blank/Equipment Blank (See Note #2 for additional information.)	The highest positive result (greater than the MDL) in the blanks associated with a sample should be summarized and utilized for evaluation of contamination.	For ICBs and CCBs qualify samples per analytical sequence using professional judgment; for PBs, field blanks, and equipment blanks qualify per batch and for SDG. If an analyte is detected in the blank but not in the associated samples, no action is required. If a sample result is ≤5× the blank result, qualify the positive result as "not detected" ("UB") and revise the MDL to the value of the positive result. If the positive result qualified "UB" is ≤RL, the RL should be used as reported. If the positive result qualified "UB" is >RL, the value of the positive result should be used as the revised RL. If a sample result is >5× blank result, qualification is not required. If a blank has a negative result with an absolute value >2× MDL, qualify positive results ≤5× the absolute value of the blank result as estimated ("J") and qualify "not-detected" results as estimated ("UJ").

Table for the Validation of Metals Generated by US EPA Method 200.8

Quality Control Item(s)	Usability Criteria	Action(s)
Interference Check Sample Analysis (ICSA/ICSAB) (See Note #3 for additional information.)	For accuracy, use recovery limits of 80-120% for ICSA/ICSAB. The absolute value of analytes not present in ICSA solution should be <2× MDL.	Qualify samples analyzed before and after ICSA/ICSAB standard. Sample data are acceptable if the concentrations of interferents (*i.e.*, Al, Ca, Fe, and Mg) in the samples are ≤ 50% of the respective ICSA concentrations. For samples with concentrations of interferents (*i.e.*, Al, Ca, Fe, and Mg) >50% of the respective concentrations in the ICSA, qualify as follows: If an ICSAB recovery is > 120%, qualify positive results as estimated ("J") and do not qualify "not-detected" results. If an ICSAB recovery is 50-79%, qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). If an ICSAB recovery is <50%, qualify positive results as estimated ("J") and qualify "not-detected" results as unusable ("UR"). If positive results are observed in the ICSA for non-ICSA analytes that are >2× MDL, qualify positive results up to 5× ICSA concentration in samples with high (>50% ICSA interferents) interferents as estimated ("J") and do not qualify "not-detected" results. If negative results with an absolute value >2× MDL are observed in the ICSA for non-ICSA analytes, qualify positive results up to 5× the concentration observed in the ICSA in samples with high (>50% ICSA interferents) interferents as estimated ("J") and qualify "not-detected" results as estimated ("UJ").

Table for the Validation of Metals Generated by US EPA Method 200.8

Quality Control Item(s)	Usability Criteria	Action(s)
Laboratory Control Sample (LCS) (See Note #4 for additional information.)	For accuracy, use recovery limits of 85-115% for aqueous samples and 70-130% for solid samples.	For aqueous samples, if a recovery is >115% but ≤150%, qualify positive results as estimated ("J") and do not qualify "not-detected" results. For aqueous samples, if a recovery is <85% but ≥30%, qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). For aqueous samples, if a recovery is >150%, qualify all positive results as unusable ("R") and do not qualify "not-detected" results. For aqueous samples, if a recovery is <30%, qualify positive results as estimated ("J") and qualify "not-detected" results as unusable ("UR"). For solid samples, if a recovery is >130%, qualify positive results as estimated ("J") and do not qualify "not-detected" results. For solid samples, if a recovery is <70% but ≥30%, qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). For solid samples, if recovery is <30%, qualify positive results as estimated ("J") and qualify "not-detected" results as unusable ("UR").
Matrix Spike/Matrix Spike Duplicates (MS/MSD) (See Note #5 for additional information.)	For accuracy, use recovery limits of 70-130%. For precision, use the Field/ Laboratory Duplicate criteria (next page).	Data should not be qualified due to %Rs (or RPDs calculated using %Rs) that are outside of criteria if the original concentration of an analyte is >4× the spiking level for that analyte. RPDs calculated using MS/MSD results can be used to evaluate precision. If a recovery is >130%, qualify positive results in all associated samples as estimated ("J") and do not qualify "not-detected" results. If a recovery is <70% but ≥30%, qualify positive results in all associated samples as estimated ("J") and qualify "not-detected" results in all associated samples as estimated ("UJ"). If a recovery is <30%, qualify positive results in all associated samples as estimated ("J") and qualify "not-detected" results in all associated samples as unusable ("UR"). If the precision between recoveries exceeds the RPD criterion, qualify positive results in all associated samples as estimated ("J") and do not qualify "not-detected" results.
Serial Dilution Analysis	%D<10% if original undiluted concentration is >50× MDL.	If %D is >10%, qualify positive results as estimated ("J") and do not qualify "not-detected" results.

Table for the Validation of Metals Generated by US EPA Method 200.8

Quality Control Item(s)	Usability Criteria	Action(s)
Field Duplicate/Laboratory Duplicate (See Notes #5 and #6 for additional information.)	The RPD should be ≤20% for results >5x the RL. The difference between results should be ≤ the RL when at least one result is ≤5x the RL. (Use ½ the RL as the numerical value for any "not-detected" results in the RPD calculations).	If the criteria are not met, qualify positive results for non-compliant analyte in original sample and its duplicate as estimated ("J") and qualify "not-detected" results as estimated ("UJ").
Total vs. Dissolved Comparison	When the dissolved result is greater than the total result: use default limits of ± RL if at least one result is <10× RL. Use default limit of percent difference <10% if both results are ≥10× RL.	If the criteria are not met, qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). If at least one result is <10× RL and the difference is >5× RL, qualify positive results and "not-detected" results as unusable ("R/UR"). If both results are ≥10× RL and the percent difference is >50%, qualify positive results as unusable ("R").
Percent Solids	Soil/sediment samples with < 50% solid content require qualification.	If a soil/sediment sample has a percent solid content <50% but ≥10%, qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). Use professional judgement if a soil/sediment sample has a percent solid content <10%.
Analyte Quantitation	Samples with results that are >90% of the linear range should be reanalyzed at a dilution.	If a target analyte result is >90% of the linear range, qualify the positive result as estimated ("J"). If a target analyte result is <RL but ≥MDL, qualify positive results as estimated ("J").
Internal Standards	Intensities of the internal standards in the samples must be within 60-125% those in the associated calibration blank.	If the intensity of any internal standards in the samples is not within 60-125% that in the associated calibration blank and the laboratory did not dilute and reanalyze the sample, qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ") for elements associated with the internal standard.

Table for the Validation of Metals Generated by US EPA Method 200.8

Quality Control Item(s)	Usability Criteria	Action(s)
Overall Assessment of Data	Assess overall quality of the data. Review available materials to assess the quality, keeping in mind the additive nature of the analytical problems.	Use professional judgement to determine the need to qualify data not qualified based on the QC previously discussed. Write a brief narrative to give the user an indication of the analytical limitation of the data. If sufficient information of the intended use and required quality of the data is available, the reviewer should include the assessment of the usability of the data within the given content.

Notes for the Validation of Metals Data Generated by US EPA Method 200.8

1. Due to the nature of ICP/MS data, the MDL may be very low such that 5× the MDL may be below the project reporting limit (RL). If the MDL is very low, use professional judgment to determine if the RLs should be qualified due to negative sample results.

2. Generally, if more than one blank is associated with a given sample, qualification should be based upon a comparison with the associated blank having the highest concentration of a contaminant. Sample results should not be blank corrected.

   The frequency of field/equipment/rinse blanks is determined during the sampling event. The results of a field/equipment/rinse blank should be applied to all samples collected using the same equipment (equipment/rinse blanks only) on the same day (if only one blank was collected for a several-day sampling event, results would be applied to all samples in the SDG).

3. When comparing ICSA results to sample results, the units of each should be the same (*i.e.*, if the sample results are in mg/kg and the ICSA results are in µg/L, convert the ICSA results to mg/kg before comparing the results.) If the negative interference in the ICSA solution is comparable (similar level) to the negative values observed in the CCBs, the negative ICSA values should not be utilized for qualification. If the negative interference in the ICSA solution is not comparable to the negative values observed in the CCBs, the negative ICSA values should be utilized for qualification.

Notes for the Validation of Metals Data Generated by US EPA Method 200.8

4. The spike level for the solid LCS should be compared to the RL. Use professional judgement if the spike level is not sufficiently greater than the RL (*i.e.*, the lower recovery limit should not be less than the RL).

5. The laboratory may choose to analyze an MSD instead of a laboratory duplicate. The laboratory may include a post-digestion matrix spike (PDS) analysis. The PDS results are not utilized for qualification; however, the results are utilized to evaluate the MS/MSD recoveries.

6. Duplicate samples may be collected and analyzed as an indication of overall precision. Field duplicate analyses measure both field and laboratory precision; therefore, the results may have more variability than laboratory duplicates that measure only laboratory performance. Field duplicate sample results should only be applied to the original sample and its field duplicate. Laboratory duplicates should be applied to all samples in a batch. It is also expected that solid duplicate results will have a greater variance than aqueous duplicate results.

APPENDIX 64
SOP FOR DATA VALIDATION OF MERCURY DATA (DV1631)

1.0 OBJECTIVES

This standard operating procedure (SOP) describes procedures that the Environmental Standards data reviewers will use to validate mercury data generated by US EPA Method 1631 Revision E for General Electric Company's Hudson River Remedial Action Monitoring Program. Validation will be performed to assess the compliance of the sample data to US EPA Method 1631 Revision E, and/or other reference documents (*e.g.,* analytical SOPs) as applicable to General Electric Company's Hudson River Remedial Action Monitoring Program. In addition, the usability of the mercury data provided by the analytical laboratory(ies) will be determined based on the general guidance provided in the "US EPA Contract Laboratory Program National Functional Guidelines for Inorganic Data Review" (02/1994 and 10/2004; National Functional Guidelines). It should be noted that the National Functional Guidelines apply strictly to data generated by Contract Laboratory Program (CLP) protocol and are not directly applicable to validation of data generated by US EPA Method 1631 Revision E; this SOP presents the specific data qualification actions that will be used for validation.

The validation findings will be presented in a quality assurance review (QAR) that will be prepared for one or more sample delivery groups (SDGs). Copies of annotated analytical results summaries (Form I's), including any changes to the analytical results and data qualifier codes or a data summary spreadsheet of the qualified analytical results will be included in the analytical results section of the QAR.

2.0 EVALUATION TOOLS

Excel form available in R:/Templates/Chemistry/XCELForms:

- Inorganic field duplicate comparison Rev 1-01.xls
- Inorganic triplicate comparison Rev 1-01.xls
- Total versus dissolved comparison Rev 1-01.xls

Chemistry Applications:

- FIT
- Methods Database

3.0 REFERENCE DOCUMENTS

- US EPA Contract Laboratory Program National Functional Guidelines for Inorganic Data Review (02/1994).

- US EPA Contract Laboratory Program National Functional Guidelines for Inorganic Data Review (10/2004).

- US EPA Method 1631 Revision E.

- Applicable project/laboratory analytical SOP(s).

- Region I, EPA – New England Data Validation Functional Guidelines for Evaluating Environmental Analyses (12/96).

- Region II, Evaluation of Metals Data for the Contract Laboratory Program (CLP) (1/92) Validation of Inorganics.

- Region III, Modifications to National Functional Guidelines for Inorganic Data Review (9/94).

4.0 PROCEDURE

4.1 EVALUATION OF METHOD COMPLIANCE

The data reviewer will assess the method compliance of the mercury data based on evaluation of information presented in the data package deliverables. Compliance with US EPA Method 1631 Revision E, and/or other reference documents (*e.g.,* analytical SOPs) as applicable to the General Electric Company's Hudson River Remedial Action Monitoring Program (as directed by the Project Manager) will be evaluated as part of the assessment. In addition, the deliverables will be evaluated for reporting errors and inconsistencies. The findings of the method compliance assessment will be described in terms of deficiencies and comments about the data/deliverables. The deficiencies/comments will be presented in three subdivisions (*i.e.*, correctable deficiencies, noncorrectable deficiencies, and comments) of the Inorganic Data Section of the QAR. Each deficiency and comment discussed in the QAR will indicate any subsequent impact on the usability of the data or will identify aspect(s) of the data that could not be evaluated due to the deficiency.

The data reviewer should contact the project laboratories to request the correction of deficiencies prior to submittal of the QAR (if feasible and sanctioned by the General Electric Company). At a minimum, corrections required to allow for a full evaluation of the usability of the data should be requested. Such correctable deficiencies may include sample result errors, missing data deliverables, or calculation errors that would require a significant amount of the data reviewer's time to correct. Any laboratory resubmittals as a result of such request will be discussed in the comments subsection of the QAR and will be included as an attachment of the QAR.

4.2 DETERMINATION OF DATA USABILITY

The data reviewer will determine the usability of the mercury data based on an evaluation of the information presented in the data package deliverables. The findings of the mercury data usability assessment will be presented in terms of data qualifications that the project team should consider in order to best utilize the data. These qualifications will be presented in the Inorganic Data Qualifier Section of the QAR. Each qualification will indicate that the affected sample result(s) has been flagged with representative qualifier code(s) in the General Electric Company's database to provide, at a glance, an indication of the quantitative and qualitative reliability of each analytical result. In general, the qualifier statements will be presented in the QAR in the following order: blank contamination, unusable results (R/UR), estimated results (J/UJ), field duplicate comparison, and a general qualifier for all results reported below the quantitation/reporting limit (if applicable to General Electric Company's Hudson River Remedial Action Monitoring Program).

The data reviewer's criteria for evaluating the usability of the mercury data and the resultant qualifications will be as stipulated on the attached Table for the Validation of Mercury Data Generated by US EPA Method 1631 Revision E. It should be noted that the Project Manager should be consulted when "professional judgement" use is indicated on the attached table.

Table for the Validation of Mercury Data Generated by US EPA Method 1631 Revision E

Quality Control Item	Usability Criteria	Action(s)
Sample Preservation and Conditions Upon Receipt	Samples should be collected in unpreserved volatile vials and stored at 4±2°C.	Use professional judgment if the samples were not collected in appropriate bottles or did not have appropriate preservation.
Technical Holding Time	Preserved samples should be analyzed within 90 days. Unpreserved samples to be analyzed for total mercury must be preserved or analyzed within 48 hours of collection. If the sample is oxidized in the bottle, the time of preservation can be extended to 28 days.	If holding time is exceeded, qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). If holding time is grossly exceeded *i.e.*, twice the holding time), qualify positive results as estimated ("J") and qualify "not-detected" results as unusable ("UR").

Table for the Validation of Mercury Data Generated by US EPA Method 1631 Revision E

Quality Control Item	Usability Criteria	Action(s)
Initial Calibration (See Note #1 for additional information.)	The bubbler system calibration should include at least three bubbler blanks and five non-zero standards. Alternatively, the flow-injection system calibration should include at least three system blanks and five non-zero standards. The lowest calibration point must be the minimum level. The RSD should be ≤15% and the recovery of the lowest standard should be 75-125%.	Use professional judgement if the appropriate number of standards is not used. Qualify samples for an entire analytical sequence. If RSD>15%, qualify positive results as estimated ("J"). If the recovery of the lowest standard is >125%, qualify positive results that are less than the next highest standard with a 75-125% recovery in all associated samples in batch as estimated ("J") and do not qualify "not-detected" results. If the recovery of the lowest standard is 50%≤%R<75%, qualify positive results that are less than the next highest standard with a 75-125% recovery in the all associated samples in batch as estimated ("J") and qualify "not-detected" results in all associated samples in batch as estimated ("UJ"). If the recovery of the lowest standard is >150%, qualify positive results that are less than the next highest standard with a 75-125% recovery as unusable ("R") and do not qualify "not-detected" results. If the recovery of the lowest standard is <50%, qualify positive results that are less than the next highest standard with a 75-125% recovery in all associated samples as estimated ("J") and qualify "not-detected" results as unusable ("UR").
Quality Control Sample (QCS) (second source standard)	For accuracy, use recovery limits of 75-125%.	Qualify samples for an entire analytical sequence. If the recovery is >125% but ≤150%, qualify positive results as estimated ("J") and do not qualify "not-detected" results. If the recovery is <75% but ≥50%, qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). If the recovery is >150%, qualify positive results as unusable ("R") and do not qualify "not-detected" results. If the recovery is <50%, qualify positive results as estimated ("J") and qualify "not-detected" results as unusable ("UR").

Table for the Validation of Mercury Data Generated by US EPA Method 1631 Revision E

Quality Control Item	Usability Criteria	Action(s)
Initial Precision and Recovery (IPR)	For accuracy, use recovery limits of 79-121%. For precision, use limit of 21% RSD.	Qualify samples for an entire analytical sequence. If the recovery is >121% but ≤150%, qualify positive results as estimated ("J") and do not qualify "not-detected" results. If the recovery is <79% but ≥50%, qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). If the recovery is >150%, qualify positive results as unusable ("R") and do not qualify "not-detected" results. If the recovery is <50%, qualify positive results as estimated ("J") and qualify "not-detected" results as unusable ("UR"). If the precision exceeds the RSD criterion, qualify positive results as estimated ("J") and do not qualify "not-detected" results.
OngoingPrecision and Recovery (OPR)	Analyze prior to the analytical batch and at the end of the analytical sequence. For accuracy, use recovery limits of 77-123%.	Use professional judgment if OPR was not analyzed at the required frequency. Qualify samples bracketed by the OPR. If the recovery is >123% but ≤150%, qualify positive results as estimated ("J") and do not qualify "not-detected" results. If the recovery is <77% but ≥50%, qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). If the recovery is >150%, qualify positive results as unusable ("R") and do not qualify "not-detected" results. If the recovery is <50%, qualify positive results as estimated ("J") and qualify "not-detected" results as unusable ("UR").

Table for the Validation of Mercury Data Generated by US EPA Method 1631 Revision E

Quality Control Item	Usability Criteria	Action(s)
Bubbler Blanks/ System Blanks/Method Blanks Field Blank/Equipment Blank (See Note #2 for additional information.)	Each batch must have at least three bubbler blanks (bubbler system) or three system blanks (flow-injection system) and three method blanks. Each blank must contain <0.50 ng/L mercury. The mean result of the three bubbler blanks must be <0.25 ng/L with a standard deviation of <0.10 ng/L. The mean result of the three system blanks must be <0.5 ng/L with a standard deviation of <0.1 ng/L.	If the criteria for the bubbler or system blanks are not met, use professional judgment to qualify results (considering that the results for these blanks are subtracted from the sample results. For method blanks, field blanks, and equipment blanks, qualify per batch and/or SDG. The highest positive result (greater than the MDL) in the blanks associated with a sample should be summarized and utilized for the evaluation of contamination. If mercury is detected in blank but not in sample, no action is required. If a sample result is ≤5× the blank result, qualify the positive result as "not detected" ("UB") and revise the MDL to the value of the positive result. If the positive result qualified "UB" is ≤RL, the RL should be used as reported. If the positive result qualified "UB" is >RL, the value of the positive result should be used as the revised RL. If sample is >5× blank result, qualification is not required.
Laboratory Control Sample (LCS)	For accuracy, use recovery limits of 77-125%.	If a recovery is >125%, qualify positive results as estimated ("J") and do not qualify "not-detected" results. If a recovery is <77% but ≥30%, qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). If recovery is <30%, qualify positive results as estimated ("J") and qualify "not-detected" results as unusable ("UR").

Table for the Validation of Mercury Data Generated by US EPA Method 1631 Revision E

Quality Control Item	Usability Criteria	Action(s)
Matrix Spike/Matrix Spike Duplicates (MS/MSD)	Spiking level shall be 1-5 times the background concentration of the sample. Use 71-125% for accuracy and ≤ 24% RPD for precision.	Data should not be qualified due to %Rs (or RPDs calculated using %Rs) that are outside of criteria if the original concentration of an analyte is >4× the spiking level for that analyte. RPDs calculated using MS/MSD concentrations will be used to evaluate precision. If the recovery is >upper recovery limit, qualify positive results in all associated samples as estimated ("J") and do not qualify "not-detected" results. If the recovery is <lower recovery limit but ≥30%, qualify all positive results in all associated samples as estimated ("J") and qualify "not-detected" results in all associated samples as estimated ("UJ"). If the recovery is <30%, qualify positive results in all associated samples as estimated ("J") and qualify all "not-detected" results in all associated samples as unusable ("UR"). If the precision between recoveries exceeds the RPD criterion, qualify positive results in all associated samples as estimated ("J") and do not qualify "not-detected" results.
Laboratory Duplicate	Use limit of 24% RPD for aqueous samples for sample results ≥5× RL. Use default limit of ± RL for aqueous samples when at least one sample value is <5× RL. (Use ½ the RL as the numerical value for a "not-detected" result in the RPD calculation.)	If the field duplicate criteria are not met, qualify positive results for the non-compliant analyte in the original sample and its duplicate as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). If the laboratory duplicate criteria are not met, qualify positive results in the all associated samples in batch as estimated ("J") and qualify "not-detected" results in all associated samples in batch as estimated ("UJ").

Table for the Validation of Mercury Data Generated by US EPA Method 1631 Revision E

Quality Control Item	Usability Criteria	Action(s)
Total vs. Dissolved Comparisons	When the dissolved result is greater than the total result: use default limits of ± RL when at least one result is <10× RL. Use default limits of percent differences <10% when both results are ≥ 10× RL.	If the criteria are not met, qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). If at least one result is <10× RL and the differences is >5× RL, qualify positive and "not-detected" results as unusable ("R/UR"). If both results are ≥10× RL and the percent difference is >50%, qualify positive results as unusable ("R").
Analyte Quantitation	Samples with results that are > the calibration range should be reanalyzed at a dilution.	If a target analyte result is > the calibration range, qualify the positive result as estimated ("J"). If a target analyte result is <RL but ≥MDL, qualify positive results as estimated ("J").
Overall Assessment of Data	Assess overall quality of the data. Review available materials to assess the quality, keeping in mind the nature of the analytical problems.	Use professional judgement to determine the need to qualify data that were not qualified based on the QC previously discussed. Write a brief narrative to give the user an indication of the analytical limitation of the data. If sufficient information on the intended use and required quality of the data is available, include the assessment of the usability of the data within the given context.

Notes for the Validation of Mercury Data Generated by US EPA Method 1631 Revision E

1. For the flow-injection system calibration, if the calibration range is other than 0.5 to 100 ng/L, follow the US EPA 1631 Revision E requirements in Section 10.4.

2. Generally, if more than one blank is associated with a given sample, qualification should be based upon a comparison with the associated blank having the highest concentration of a contaminant. Sample results should not be blank corrected (with the exception of the bubbler/system blanks).

   The frequency of equipment blanks is determined during the sampling event. The results of a equipment/rinse blank should be applied to all samples collected using the same equipment (equipment/rinse blanks only) on the same day (if only one blank was collected for a several-day sampling event; results would be applied to all samples in the SDG).

APPENDIX 65
SOP FOR DATA VALIDATION OF WET CHEMISTRY DATA (DVWETCHEM)

1.0 OBJECTIVES

This standard operating procedure (SOP) describes procedures that Environmental Standards' data reviewers will use to validate wet chemistry and conventional parameter data generated by the ASTM and US EPA Methods for General Electric Company's Hudson River Remedial Action Monitoring Program. Validation will be performed to assess the compliance of the sample data to the applicable ASTM and US EPA Method and/or other reference documents (*e.g.*, analytical SOP) as applicable to General Electric Company's Hudson River Remedial Action Monitoring Program. In addition, the usability of the wet chemistry and conventional parameter data provided by the analytical laboratories will be determined based on the general guidance provided in the "US EPA Contract Laboratory Program National Functional Guidelines for Inorganic Data Review" (02/1994 and 10/2004) (National Functional Guidelines). It should be noted that the National Functional Guidelines applies strictly to data generated by the Contract Laboratory Program (CLP) protocol. As such, it is not directly applicable to validation of data generated by ASTM and US EPA Methods; therefore, this SOP presents the specific data qualification actions that will be used for validation.

The validation findings will be presented in a quality assurance review (QAR) that will be prepared from one or more sample delivery groups (SDGs). Copies of annotated analytical results summaries (Form I's), including any changes to the analytical results and data qualifier codes, or a data summary spreadsheet of the qualified analytical results will be included in the analytical results section of the QAR.

2.0 EVALUATION TOOLS

Excel forms available in R:/Templates/Chemistry/XCELForms:

Inorganic field duplicate comparison Rev1-01.xls
Inorganic field triplicate comparison Rev1-01.xls

Chemistry Applications:

FIT
Methods Database

3.0 REFERENCE DOCUMENTS

- US EPA Contract Laboratory Program National Functional Guidelines for Inorganic Data Review (02/1994).

- US EPA Contract Laboratory Program National Functional Guidelines for Inorganic Data Review (10/2004).

- ASTM and US EPA Methods.

- Applicable project/laboratory analytical SOP(s).

- Region II, Evaluation of Metals Data for the Contract Laboratory Program (CLP) (1/92) Validation of Inorganics.

- Region I, EPA – New England Data Validation Functional Guidelines for Evaluating Environmental Analyses (12/96).

- Region III, Modifications to Natural Functional Guidelines for Inorganic Data Review (9/94).

4.0 PROCEDURE

4.1 EVALUATION OF METHOD COMPLIANCE

The data reviewer will assess the method compliance of the wet chemistry and conventional parameter data based on an evaluation of information presented in the data package deliverables. Compliance to the ASTM or US EPA Method and/or other reference documents (*e.g.*, analytical SOPs) as applicable to General Electric Company's Hudson River Remedial Action Monitoring Program (as directed by the Project Manager) will be evaluated as part of the assessment. In addition, the deliverables will be evaluated for reporting errors and inconsistencies. The findings of the method compliance assessment will be described in terms of deficiencies and comments about the data/deliverables. The deficiencies/comments will be presented in three subdivisions (*i.e.*, correctable deficiencies, noncorrectable deficiencies, and comments) of the Inorganic and Conventional Parameter Data Evaluation Section of the QAR. Each deficiency and comment discussed in the QAR will indicate any subsequent impact on

the usability of the data or any certain aspect(s) of the data that could not be evaluated due to the deficiency.

The data reviewer should contact the project laboratories to request the correction of deficiencies prior to the submittal of the QAR (if feasible and sanctioned by General Electric Company). At a minimum, corrections necessary for a full evaluation of the usability of the data should be requested. Such correctable deficiencies may include sample result errors, missing data deliverables, or calculation errors that would take a significant amount of the data reviewer's time to correct. Any laboratory resubmittals as a result of such requests will be discussed in the comments subdivision of the QAR and included as an attachment to the QAR.

4.2 DETERMINATION OF DATA USABILITY

The data reviewer will determine the usability of the wet chemistry and conventional parameter data based on an evaluation of the information presented in the data package deliverables. The findings of the wet chemistry and conventional parameter data usability assessment will be described in terms of certain qualifications of the data that the project team should consider in order to best utilize the data. These qualifications will be presented in the Inorganic and Conventional Parameter Data Qualifier subsection of the QAR. Each qualification discussed in the QAR will indicate that the affected sample result(s) has been flagged with representative qualifier code(s) in the General Electric Company's database to provide, at a glance, an indication of the quantitative and qualitative reliability of each analytical result. In general, the qualifier statements will be presented in the QAR in the following order: blank contamination, common contaminants

that were not qualified, unusable results (R/UR), estimated results (J/UJ), field duplicate comparison, and a general qualifier for all results reported below the quantitation limit (if applicable to General Electric Company's Hudson River Remedial Action Monitoring Program).

The data reviewer's criteria for evaluating the usability of the wet chemistry and conventional parameter data and the resultant qualifications will be as stated in the attached Table for the Validation of Wet chemistry and Conventional Parameter Data Generated by ASTM and US EPA Procedures. It should be noted that the Project Manager should be consulted when directed to use "professional judgement" in the attached table.

Notes for the Validation of Wet Chemistry and Conventional Parameter Data Generated by the ASTM and US EPA Procedures

Quality Control Item	Usability Criteria	Action
Temperature and Conditions Upon Receipt	QAPP-specified.	For samples that are required to be stored at 4°±2°C: If temperature >10°C, but ≤20°C, qualify positive results as estimated ("J") and qualify "not-detected results as estimated ("UJ"). If temperature >20°C, qualify positive results as estimated ("J") and qualify "not-detected" results as unusable ("UR"). Note time of collection relative to receipt at laboratory. Professional judgment should be used if less than 8 hours had lapsed from collection to receipt to determine if the qualification above applies. If aqueous samples have pH values outside of required criteria, qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ").
Technical Holding Time	Samples should be analyzed within the QAPP-specified holding times.	If the sample analysis was performed >holding time but ≤ 2 × the holding time, qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). If the sample analysis was performed >2 × the holding time, qualify positive results as estimated ("J") and qualify "not-detected" results as unusable ("UR").
Initial Calibration (See Note #1 for additional information)	Laboratory-specified limit or use default of correlation coefficient (r) (linear) or coefficient of determination (COD) (quadratic) ≥0.995 if limits are not provided.	Use professional judgement when evaluating correlation coefficients and coefficients of determination (r or COD). If r or COD <0.995 (or laboratory limit) but ≥0.85, qualify positive results as estimated ("J") and do not qualify "not-detected" results. If r or COD <0.85, qualify positive results as estimated ("J") and qualify "not-detected" results as unusable ("UR").
Independent Calibration Verification Standard (ICV) and Continuing Calibration Verification Standard (CCV)	ICV and CCV Recoveries (%R) should be 85-115% for dissolved and suspended organic carbon. Laboratory-specified limits if performed for other parameters (not applicable to all parameters).	If the ICV or CCV %R>upper limit qualify positive results as estimated ("J") and do not qualify "not-detected" results. If the ICV or CCV 55%≤%R<lower limit qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). If the ICV or CCV %R <55%, qualify positive results as estimated ("J") and qualify "not-detected" results as unusable ("UR").

Notes for the Validation of Wet Chemistry and Conventional Parameter Data Generated by the ASTM and US EPA Procedures

Quality Control Item	Usability Criteria	Action
Blanks (Preparation and/or Continuing Calibration Blanks) (See Note #2 for additional information)	Summarize all results greater than the method detection limit (MDL) present in the blanks. The highest positive result associated with a sample should be utilized for evaluation of contamination.	If a target analyte is found in blank but not in the associated sample(s) no action is needed. If sample >RL, but <5× blank result, qualify the positive results as "not detected" ("UB"). If sample is positive, but <RL and <5× blank result, qualify the positive result as "not-detected" ("UB"). If sample result >5× blank result no qualification is necessary.
Laboratory Control/In-House Reference Sample	For accuracy, use QAPP-specified limits.	Data should not be qualified due to %Rs that are outside of criteria if the original concentration of a compound is > 4 × spiking level for that compound. If the recovery is >upper limit, qualify positive results in all associated samples in batch as estimated ("J") and do not qualify "not-detected" results. If the recovery is 30%≤%R<lower limit, qualify positive results in the all associated samples in batch as estimated ("J") and qualify "not-detected" results in all associated samples in batch as estimated ("UJ"). If the recovery is <30%, qualify positive results in all associated samples as estimated ("J") and qualify "not-detected" results as unusable ("UR").
Laboratory Fortified Matrix Sample (MS)	For accuracy, use QAPP-specified limits.	Data should not be qualified due to %Rs that are outside of criteria if the original concentration of a compound is > 4 × spiking level for that compound. If the recovery is >upper limit, qualify positive results in all associated samples in batch as estimated ("J") and do not qualify "not-detected" results. If the recovery is 30%≤%R<lower limit, qualify positive results in the all associated samples in batch as estimated ("J") and qualify "not-detected" results in all associated samples in batch as estimated ("UJ"). If the recovery is <30%, qualify positive results in all associated samples as estimated ("J") and qualify "not-detected" results as unusable ("UR").

Notes for the Validation of Wet Chemistry and Conventional Parameter Data Generated by the ASTM and US EPA Procedures

Quality Control Item	Usability Criteria	Action
Field/Laboratory Duplicate (See Note #3 for additional information)	Use QAPP-specified limits for Field Duplicate comparison. Use laboratory-specified limits for Laboratory Duplicate (Use ½ the RL as the numerical value for comparison if the analyte was "not-detected")	If the field duplicate criteria are not met, qualify positive results for the non-compliant analyte in the original sample and its duplicate as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). If the laboratory duplicate criteria are not met, qualify positive results in the all associated samples in batch as estimated ("J") and qualify "not-detected" results in all associated samples in batch as estimated ("UJ").
Percent Solids	Soil/sediment samples with less than 50% solid content require qualification.	If a soil/sediment sample has a percent solid content <50% but ≥10%, qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). Use professional judgement if a soil/sediment sample has a percent solid content <10%.
Overall Assessment of Data	Assess overall quality of the data. Review available materials to assess the quality, keeping in mind the additive nature of the analytical problems.	Use professional judgment to determine the need to qualify data that were not qualified based on the QC previously discussed. Write a brief narrative to give the user an indication of the analytical limitations of the data. If sufficient information on the intended use and required quality of the data is available, the reviewer should include his assessment of the usability of the data within the given context.

Notes for the Validation of Wet Chemistry and Conventional Parameter Data Generated by ASTM and US EPA Procedures

1. Use professional judgement when evaluating the concentration intercept of a calibration curve. If the concentration intercept is positive then the samples should be evaluated for false positives. If the concentration intercept is negative then the samples should be evaluated for false negatives.

2. The frequency of field/equipment/rinse blanks is determined during the sampling event. The results of a field/equipment/rinse blank should be applied to all samples collected using the same equipment (equipment/rinse blanks only) on the same day (unless only one was collected for a several-day sampling event; results would be applied to all samples in the SDG). In instances where more than one blank is associated with a given sample, qualification should be based upon a comparison with the associated blank having the highest concentration for a contaminant.

3. Duplicate samples may be taken and analyzed as an indication of overall precision. Field duplicate analyses measure both field and laboratory precision; therefore, the results may have more variability than laboratory duplicates which measure only laboratory performance. Field duplicate sample results should only be applied to the original sample and its field duplicate. Laboratory duplicate should be applied to all samples in a batch. It is also expected that solid duplicate results will have a greater variance than aqueous duplicate results.

APPENDIX 66
SOP FOR DATA VALIDATION OF CONGENER PCB DATA (DVNE013_09)

1.0 OBJECTIVES

This standard operating procedure (SOP) describes procedures that the Environmental Standards data reviewers will use to validate PCB Congener data generated by Northeast Analytical, Inc.'s analytical SOP NE013_08 for the General Electric Company's Hudson River Remedial Action Monitoring Program (RAMP). Validation will be performed to assess the compliance of the sample data to the analytical SOP as applicable to the General Electric Company's Hudson River SSAP. In addition, the usability of the PCB Congener data provided by the analytical laboratory will be determined based on the general guidance provided in the "US EPA Contract Laboratory National Functional Guidelines for Organic Data Review" (10/1999; National Functional Guidelines) and "US EPA Contract Laboratory Program National Functional Guidelines for Superfund Organic Methods Data Review" (06/2008 National Functional Guidelines). It should be noted that the National Functional Guidelines apply strictly to data generated by the Contract Laboratory Program (CLP) protocol and are not directly applicable to validation of data generated by laboratory-developed analytical methods; therefore, this SOP presents the specific data qualification actions that will be used for validation.

The validation findings will be presented in a quality assurance review (QAR) that will be prepared for one or more sample delivery groups (SDGs). Copies of annotated analytical results summaries (Form I's), including any changes to the analytical results and data qualifier codes or a data summary spreadsheet of the qualified analytical results, will be included in the support documentation of the QAR.

2.0 EVALUATION TOOLS

Excel forms available in R:/Templates/Chemistry/XCELforms:

- Organic field duplicate comparisons Rev1-01.xls
- Organic field quadruplicate comparison Rev1-01.xls
- Organic field triplicate comparison Rev1-01.xls
- Aroclor.xls

Chemistry Applications:

- FIT
- Methods Database
- Target version 4.1 data processing software

3.0 REFERENCE DOCUMENTS

- US EPA Contract Laboratory Program National Functional Guidelines for Organic Data Review (10/99).

- US EPA Contract Laboratory Program National Functional Guidelines for Superfund Organic Methods Data Review (06/2008).

- Northeast Analytical, Inc. (NEA)- Standard Operating Procedure for the Congener-Specific Polychlorinated Biphenyl (PCB) Analysis (SOP NE013_09, Rev. 09; 02/20/2009).

- Region I, EPA-New England Data Validation Functional Guidelines for Evaluating Environmental Analyses (12/96).

- Region II, Standard Operating Procedure for the Validation of Organic Data Acquired Using SW-846 Method 8082 (SOP HW-23B, Rev. 1.0, May, 2002).

- Region III, Modifications to National Functional Guidelines for Organic Data Review (9/94).

4.0 PROCEDURE

4.1 EVALUATION OF METHOD COMPLIANCE

The data reviewer will assess the method compliance of the PCB Congener data based on an evaluation of information presented in the data package deliverables. Compliance to NEA's analytical SOP as applicable to General Electric Company's Hudson River SSAP (as directed by the Project Manager) will be evaluated as part of the assessment. In addition, the deliverables will be evaluated for reporting errors and inconsistencies. The findings of the method compliance assessment will be described in terms of deficiencies and comments about the data/deliverables. The deficiencies/comments will be presented in three subdivisions (*i.e.*, correctable deficiencies, noncorrectable deficiencies, and comments) of the Organic Data Evaluation Section of the QAR. Each deficiency and

comment discussed in the QAR will indicate any subsequent impact on the usability of the data or will identify aspect(s) of the data that could not be evaluated due to the deficiency.

The data reviewer should contact the project laboratory to request the correction of deficiencies prior to submittal of the QAR (if feasible and sanctioned by to General Electric Company). At a minimum, corrections required to allow for a full evaluation of the usability of the data should be requested. Such correctable deficiencies may include sample result errors, missing data deliverables, or calculation errors that would require a significant amount of the data reviewer's time to correct. Any laboratory resubmittals as a result of such requests will be discussed in the comments subdivision of the QAR and included as an attachment to the QAR.

4.2 DETERMINATION OF DATA USABILITY

The data reviewer will determine the usability of the PCB Congener data based on an evaluation of the information presented in the data package deliverables. The findings of the PCB data usability assessment will be presented in terms of data qualifications that the project team should consider in order to best utilize the data; these qualifications will be presented in the Organic Data Qualifier subsection of the QAR. Each qualification discussed in the QAR will indicate that the affected sample result(s) has been flagged with a representative qualifier code(s) to General Electric Company's database to provide, at a glance, an indication of the quantitative and qualitative reliability of each analytical result. In general, the qualifier statements will be presented in the QAR in the

following order: blank contamination, unusable results (R/UR), estimated results (J/UJ), tentative identifications of target compound results (N), field duplicate comparison, and a general qualifier for all results reported below the quantitation limit (if applicable to General Electric Company's Hudson River RAMP).

The data reviewer's criteria for evaluating the usability of the PCB Congener data and the resultant qualifications will be as stipulated on the attached Table for the Validation of PCB (Congener) Data Generated by NEA's SOP for Congener-Specific PCB Analysis. It should be noted that the project manager should be consulted when "professional judgment" use is indicated on the attached table.

Table for the Validation of PCB (Congener) Data Generated by NEA's SOP for Congener-Specific PCB Analysis

Quality Control Item	Usability Criteria	Action
Temperature Upon Receipt	4±2°C	If temperature is >10°C but ≤20°C, qualify positive results as estimated ("J") and qualify "not-detected results as estimated ("UJ"). If temperature is > 20°C, qualify positive results as estimated ("J") and qualify "not-detected" results as unusable ("UR"). Note time of collection relative to receipt at laboratory. Professional judgment should be used if < 8 hours has elapsed from collection to receipt at the laboratory to determine if qualification due to elevated temperature applies.
Technical Holding Time	Aqueous samples should be extracted within 365 days of sample collection. Sediment/soil samples should be extracted within 14 days of sample collection. Tissue samples (which have been frozen to <-18°C upon laboratory receipt) should be extracted within 1 year of sample collection. All matrices should be analyzed within 40 days after extraction.	If a holding time is exceeded, qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). If a holding time is grossly exceeded (*i.e.*, > twice the holding time), qualify positive results as estimated ("J") and qualify "not-detected" results as unusable ("UR").

Table for the Validation of PCB (Congener) Data Generated by NEA's SOP for Congener-Specific PCB Analysis

Quality Control Item	Usability Criteria	Action
Initial High Level Linearity Verification (To confirm linearity; not used for quantitation)	%RSD should be ≤20% for the three relative response factors (RRFs). Chromatographic Resolution Peak valley heights between DB-1 peaks 14 and 15 must be equal to or less than half the height of peak 15. Also, DB-1 peaks 74 and 75 must be equal to or less than one-third the height of peak 74. Must be established initially.	If both the Low- and High-Level Linearity Verifications have been performed and only one of the verifications do not meet criteria, qualify positive results based on the concentration range and use the Low-Level Linearity Verification to assess "not-detected" results. If target PCB Congeners have 20%< %RSD ≤50%, qualify positive results as estimated ("J") and do not qualify "not-detected" results. If target PCB Congeners have 50%< %RSD ≤90%, qualify positive results as estimated ("J") and use professional judgment to qualify "not-detected" results. If target PCB Congeners have %RSD > 90%, qualify positive results as estimated ("J") and qualify "not-detected" results as unusable ("UR").
Initial Low Level Linearity Verification (To confirm linearity; not used for quantitation)	%RSD should be ≤20% for the three RRFs. Chromatographic Resolution Peak valley heights between NEA DB-1 peaks 14 and 15 must be equal to or less than half the height of peak 15. Also, NEA DB-1 peaks 74 and 75 must be equal to or less than one-third the height of peak 74. Must be established initially.	If both the Low- and High-Level Linearity Verifications have been performed and only one of the verifications do not meet criteria, qualify positive results based on the concentration range that failed and use the Low-Level Linearity Verification to assess "not-detected" results. If target PCB Congeners have 20%< %RSD ≤50%, qualify positive results as estimated ("J") and do not qualify "not-detected" results. If target PCB Congeners have 50%< %RSD ≤90%, qualify positive results as estimated ("J") and use professional judgment to qualify "not-detected" results. If target PCB Congeners have %RSD > 90%, qualify positive results as estimated ("J") and qualify "not-detected" results as unusable ("UR"). Use professional judgment for qualification if the chromatographic resolution fails the usability criterion.

Table for the Validation of PCB (Congener) Data Generated by NEA's SOP for Congener-Specific PCB Analysis

Quality Control Item	Usability Criteria	Action
Initial 72-hour Retention Time Window Measurement (See Note #1 for additional information.)	Initial RT windows are established to assist in PCB peak assignment. Three high-level Continuing Calibration Check standards and three Supplemental Congener Standards are analyzed over at least 72-hours. The mean RT and the standard deviation of each of the GC peaks are calculated. RT window is ± 3× the determined standard deviation or a default of 0.07 minute is applied (whichever is larger).	If the initial RT windows are not calculated correctly, use professional judgment for qualification.

Table for the Validation of PCB (Congener) Data Generated by NEA's SOP for Congener-Specific PCB Analysis

Quality Control Item	Usability Criteria	Action
Continuing Calibration Check (CCC) Standards	The %differences are calculated for Total PCBs and six selected PCB congeners (peaks 7, 116, 47, 93, 37 and 102which contain IUPAC #s 6, 205, 70, 174, 181, 104, 44, and 180) comparing the selected congener concentrations with the known concentrations. The % difference for Total PCBs must be ≤ 15%. The % differences for PCB congeners #s 6 and 205 (low-level peaks) must be ≤30%. The % differences for the other four medium and high-level peaks must be ≤15%. If a %difference fails, this may indicate unacceptable RRFs or an instrument problem. The area of the internal standard Octachloronapthalene (OCN) in the CCC standard must be within 50-150% of the average area for OCN among the initial calibration standards. <u>Chromatographic Resolution</u> Peak valley heights between DB-1 peaks 14 and 15 must be equal to or less than half the height of peak 15. Also, DB-1 peaks 74 and 75 must be equal to or less than one-third the height of peak 74. Must be established initially.	Qualification is for all samples on both sides of the out-of-criteria calibration standards. Professional judgment should be used to determine the impact of an out-of-criteria continuing calibration check relative to the PCB Congeners for which %differences have not been calculated. If Total PCBs have 15%<%D≤90% with the response indicating a sensitivity decrease, qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). If Total PCBs have %D>15% with the response indicating a sensitivity increase, qualify positive results as estimated ("J") and use professional judgment to qualify "not-detected" results. If the low-level PCB Congeners have 30%<%D≤90% with the response indicating a sensitivity decrease, qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). If the low-level PCB Congeners have %D>30% with the response indicating a sensitivity increase, qualify positive results as estimated ("J") and use professional judgment to qualify "not-detected" results. If the medium or high-level PCB Congeners have 15%<%D≤90% with the response indicating a sensitivity decrease, qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). If the medium or high-level PCB Congeners have %D>15% with the response indicating a sensitivity increase, qualify positive results as estimated ("J") and use professional judgment to qualify "not-detected" results. If Total PCBs or the select PCB Congeners have %D>90% with the response indicating a sensitivity decrease qualify positive results as estimated ("J") and qualify "not-detected" results as unusable ("UR"). Use professional judgment for qualification if the internal standard area for OCN or the chromatographic resolution fails the usability criteria.

Table for the Validation of PCB (Congener) Data Generated by NEA's SOP for Congener-Specific PCB Analysis

Quality Control Item	Usability Criteria	Action
Internal Standard – Octachloronaphthalene (OCN)	Area counts of the internal standard peaks for all CCCs, QC samples, and samples should be ±50% of the average internal standard area observed among the associated initial calibration standards. Retention time (RT) for any internal standard should be within the RT window.	If a sample area count is outside of criteria (±50% of the average area among the associated initial calibration standards), qualify positive results for compounds quantitated using that internal standard as estimated ("J") and qualify "not-detected" results for compounds quantitated using that internal standard as estimated ("UJ"). If extremely low sample area counts (<25% of the average area among the associated initial calibration standards) are reported, qualify positive results for compounds quantitated using the extremely low internal standard as estimated ("J") and qualify "not-detected" results for compounds quantitated using that internal standard as unusable ("UR"). If a CCC standard or QC sample area count is outside of criteria (±50% of the average area among the associated initial calibration standards), use professional judgment to qualify data. If an internal standard RT is outside of the RT window and no peaks are observed in the sample chromatogram, qualification is not necessary. Use professional judgment if peaks are observed in the sample chromatogram.
Retention Time Windows (See Note #1 for additional information.)	All target compound retention times (RTs) should be within the established RT windows. RT windows for samples are defined as the absolute RT of the Initial Continuing Calibration Check Standard for a given analytical sequence ±3× the standard deviation determined in the 72-hour period. If this RT window is less than 0.07 minute then a default of 0.07 minute is applied.	If the CCCstandard RT windows are not within the specified RT windows, evaluate sample chromatograms for false positives and false negatives. If a constant drift in RT is observed in the bracketing CCC standards, the direction of the RT drift should be applied to the sample chromatograms.

Table for the Validation of PCB (Congener) Data Generated by NEA's SOP for Congener-Specific PCB Analysis

Quality Control Item	Usability Criteria	Action
Blanks (See Note #2 for additional information.)	Summarize all results greater than the method detection limit (MDL) present in the blanks. The highest positive result associated with a sample should be utilized for evaluation of contamination.	If a target PCB Congener is found in the blank but not in the associated sample(s), no action is required. If a sample result is ≤5× the blank result, qualify the positive result as "not detected" ("UB") and revise the MDL to the value of the positive result. If the positive result qualified "UB" is <RL, the RL should be used as reported. If the positive result qualified "UB" is ≥RL, the value of the positive result should be used as the revised RL. If individual PCB congeners have been qualified "UB," adjust the associated Total PCB result to reflect that the individual PCB congener result should be considered "not-detected." If a sample result is >5× blank result, qualification is not required. If gross contamination exists (*i.e.*, saturated peaks on the GC), qualify the positive results as unusable ("R") due to interference.
Surrogates (See Note #3 for additional information.)	60-140 %R (sediment residuals split GEHR8082 extract spiked with TCMX and DCB). 70-130 %R (mGBM extract for special studies spiked with 2,2',3,3',4,4',5,6,6'-Nonachlorobiphenyl).	If the recoveries of one or more surrogates are > upper limit, qualify positive results as estimated ("J") and do not qualify "not-detected" results. If the recoveries of one or more surrogates are < lower limit but ≥10%, qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). If the recoveries of one or more surrogates are <10%, qualify positive results as estimated ("J") and qualify "not-detected" results as unusable ("UR").

Table for the Validation of PCB (Congener) Data Generated by NEA's SOP for Congener-Specific PCB Analysis

Quality Control Item	Usability Criteria	Action
Laboratory Control Samples/Laboratory Control Sample Duplicate (LCS/LCSD)	50-150 %R for Total PCB (sediment residuals split GEHR8082 extract spiked with Aroclors 1221 and 1242); 70-130 %R for Total PCB (mGBM extract for special studies spiked with Aroclor 1242).	If the recovery is >upper limit, qualify positive results for all PCB Congeners and Total PCBs in all associated samples as estimated ("J") and do not qualify "not-detected" results. If the recovery is <lower limit but ≥10%, qualify positive results for all PCB Congeners and Total PCBs in all associated samples as estimated ("J") and qualify "not-detected" results in all associated samples as estimated ("UJ"). If the recovery is <10%, qualify positive results for all PCB Congeners and Total PCBs in all associated samples as estimated ("J") and qualify "not-detected" results in all associated samples as unusable ("UR"). If the precision exceeds the RPD criterion, qualify positive results in all associated samples as estimated ("J") and do not qualify "not-detected" results.

Table for the Validation of PCB (Congener) Data Generated by NEA's SOP for Congener-Specific PCB Analysis

Quality Control Item	Usability Criteria	Action
Matrix Spike/Matrix Spike Duplicate (MS/MSD) (If performed)	For accuracy, use recovery limits of 50-150 %R for Total PCB (sediment residuals split GEHR8082 extract spiked with Aroclors 1221 and 1242) or 70-130 %R for Total PCB (mGBM extract for special studies spiked with Aroclor 1242). For precision between MS and MSD, use criteria specified in the Field/ Laboratory Duplicate criteria (next item).	Data should not be qualified due to %Rs (or RPDs calculated on %Rs) that are outside of criteria if the original concentration of a PCB Congener is >4× the spiking level for that compound. RPDs calculated using MS/MSD results can be used to evaluate precision. If the recovery is >upper limit, qualify the positive results for all PCB Congeners and Total PCBs in the native sample as estimated ("J") and do not qualify the "not-detected" result. If the recovery is <lower limit but ≥10%, qualify the positive results for all PCB Congeners and Total PCBs in the native sample as estimated ("J") and qualify the "not-detected" result in the native sample as estimated ("UJ"). If the recovery is <10%, qualify the positive results for all PCB Congeners and Total PCBs in the native sample as estimated ("J") and qualify the "not-detected" result in the native sample as unusable ("UR"). If the precision criteria for any PCB Congener or Total PCBs are not met, qualify the positive result in the native sample as estimated ("J") and qualify the "not-detected" result in the native samples as estimated ("UJ"). If a field duplicate of the native sample was collected and analyzed, the field duplicate sample should also be qualified if an MS/MSD recovery or RPD is outside of criteria (as stated above for the native sample).

Table for the Validation of PCB (Congener) Data Generated by NEA's SOP for Congener-Specific PCB Analysis

Quality Control Item	Usability Criteria	Action
Field/Laboratory Duplicate (See Note #4 for additional information)	The RPD for solid field duplicates should be ≤40% for results >5× the RL. The difference between results should be ≤ 2× the RL when at least one result is ≤5× the RL. Precision is assessed for all congeners detected in the original sample and/or its duplicate and for Total PCBs. (Use ½ the RL as a numerical value for any "not-detected" results in the difference calculations). The difference is not calculated for any congener or Total PCBs that are not detected in both the original sample and its duplicate.	If the criteria are not met, qualify positive results for the out-of-criteria compounds in the original sample and its duplicate as estimated ("J") and qualify "not-detected" results as estimated ("UJ").
Percent Solids	Soil/sediment samples with less than 10% solid content require qualification.	If a soil/sediment sample has a percent solid content <10%, qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ").
Compound Quantitation (See Notes #5 and 6 for additional information.)	Samples with results that exceed the instrument calibration range should be reanalyzed at a dilution. .	If a target PCB Congener result exceeds the instrument calibration range, qualify positive result as estimated ("J"). Use professional judgment to determine whether sample reanalyses and dilutions should be compared to the original analyses. If criteria (see field duplicate usability) between the original sample results and the reanalysis sample results are not met, qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). If a target PCB Congener is <RL but ≥MDL, qualify positive results as estimated ("J"). If any PCB Congener has been qualified as estimated due to any reason stated in this SOP, qualify the associated positive result for Total PCBs as estimated ("J").

Table for the Validation of PCB (Congener) Data Generated by NEA's SOP for Congener-Specific PCB Analysis

Quality Control Item	Usability Criteria	Action
System Performance (See Note #6 for additional information.)	Professional judgment should be used when assessing the degradation of system performance during analyses.	Use professional judgment to qualify the data if it is determined that system performance degraded during sample analyses.
Overall Assessment of Data	Assess overall quality of the data. Review available materials to assess the quality, keeping in mind the additive nature of the analytical problems.	Use professional judgment to determine the need to qualify data not qualified based on the QC previously discussed. Write a brief narrative to give the user an indication of the analytical limitations of the data. If sufficient information on the intended use and required quality of the data is available, include the assessment of the usability of the data within the given context.

Notes for the Validation of PCB (Congener) Data Generated by NEA's SOP for Congener-Specific PCB Analysis

1. If a RT shift is observed in an associated CCC and the sample chromatograms reveal peaks, use expanded RT windows and the surrogate shifts to evaluate for potential false positives and false negatives. If a possible false positive is observed, the reported positive sample result for the PCB Congener outside of the RT window may replace the MDL/RL and the result may be qualified as "not-detected" ("U"), depending on professional judgment. If a possible false negative is observed, the potential positive result may be quantitated and added to the result field and may be qualified as tentative ("N"), depending on professional judgment.

   If the chromatograms reveal peaks that interfere with potential detection of a target PCB Congener, qualify the MDL/RL for "not-detected" results as estimated ("UJ") or unusable ("UR"), depending on the level of the interference. Qualify reported positive results for the PCB Congener as unusable ("R") or raise the MDL and RL above the level of detection, depending on professional judgment.

   In addition to RT windows, the laboratory will be relying on its experience in pattern recognition of multi-peak response PCB chromatograms as well as historical data.

2. The frequency of equipment/rinse blanks is determined during the sampling event. The results of an equipment/rinse blank should be applied to all samples collected in the same day, unless only one blank was collected for a several-day sampling event. In instances where more than one blank is associated with a given sample, qualification should be

Notes for the Validation of PCB (Congener) Data Generated by NEA's SOP for Congener-Specific PCB Analysis

based upon a comparison with the associated blank having the highest concentration of a contaminant.

Instrument blank contamination should be applied to samples bracketing the contaminated instrument blank.

3. The surrogate recovery limits do not apply to samples analyzed at greater than five-fold dilutions. Qualification of the data is not necessary if the surrogate is diluted beyond detection. Generally, a greater than five-fold dilution will affect the ability to even detect the surrogate. Write a comment in the QAR addressing the issue that sample-specific method performance based on surrogate recoveries could not be evaluated due to the dilution required for sample analysis.

4. Duplicate samples may be collected and analyzed as an indication of overall precision. Field duplicate analyses measure both field and laboratory precision; therefore, the results may have more variability than laboratory duplicates that measure only laboratory performance. Laboratory duplicate results and field duplicate results apply only to the original sample and the laboratory/field duplicate. Solid duplicate results are expected to have greater variance than aqueous duplicate results.

5. If a sample result exceeds the instrument calibration range (lower dilution analysis) or is less than the RL (secondary dilution), do not utilize this result when comparing an original analysis and a diluted reanalysis.

Notes for the Validation of PCB (Congener) Data Generated by NEA's SOP for Congener-Specific PCB Analysis

6. Poor chromatographic performance affects both qualitative and quantitative results. Indications of substandard performance include:

- High background levels or shifts in absolute RTs of internal standards
- Excessive baseline rise at elevated temperature
- Extraneous peaks
- Loss of resolution
- Peak tailing or peak splitting that may result in inaccurate quantitation

Furthermore, one of the major sources of interference in PCB Congener analysis is co-extracted organochloride pesticides and associated pesticide breakdown products (*e.g.* DDT, DDD, DDE). Sulfuric acid, Florisil®, and sulfur cleanups (if performed) remove many non-target interferences but review the chromatographic pattern and peak RTs for potential interference.

APPENDIX 67
SOP FOR DATA VALIDATION OF AROCLOR PCB DATA (DV AROCLOR)

1.0 OBJECTIVES

This standard operating procedure (SOP) describes procedures that the Environmental Standards data reviewers will use to validate Aroclor PCB data generated by SW-846 Method 8082, USEPA Method 608, or USEPA Method 508 for the General Electric Company's Hudson River Remedial Action Monitoring Program (RAMP). Please note that Environmental Standards data reviewers will use DVGEHR8082 instead of this SOP to validate Aroclor PCB data generated by Method GEHR8082 for General Electric Company's Hudson River RAMP. Validation will be performed to assess the compliance of the sample data to the applicable method and/or reference documents (*e.g.*, analytical SOPs) as applicable to the General Electric Company's Hudson River RAMP. In addition, the usability of the Aroclor PCB data provided by the analytical laboratories will be determined based on the general guidance provided in the "US EPA Contract Laboratory National Functional Guidelines for Organic Data Review" (10/1999; National Functional Guidelines) and "US EPA Contract Laboratory Program National Functional Guidelines for Superfund Organic Methods Data Review" (06/2008 National Functional Guidelines). It should be noted that the National Functional Guidelines apply strictly to data generated by the Contract Laboratory Program (CLP) protocol and are not directly applicable to validation of data generated by SW-846 Method 8082, USEPA Method 608, or USEPA Method 508; therefore, this SOP presents the specific data qualification actions that will be used for validation.

The validation findings will be presented in a quality assurance review (QAR) that will be prepared for one or more sample delivery groups (SDGs). Copies of annotated analytical results summaries (Form I's), including any changes to the analytical results and data qualifier codes or a data summary spreadsheet of the qualified analytical results, will be included in the support documentation of the QAR.

2.0 EVALUATION TOOLS

Excel forms available in R:/Templates/Chemistry/XCELforms:

- Organic field duplicate comparisons Rev1-01.xls
- Organic field quadruplicate comparison Rev1-01.xls
- Organic field triplicate comparison Rev1-01.xls
- Aroclor.xls

Chemistry Applications:

- FIT
- Methods Database
- Target version 4.1 data processing software

3.0 REFERENCE DOCUMENTS

- US EPA Contract Laboratory Program National Functional Guidelines for Organic Data Review (10/1999).

- US EPA Contract Laboratory Program National Functional Guidelines for Superfund Organic Methods Data Review (06/2008).

- SW-846 Method 8082.

- USEPA 608

- Applicable project/analytical laboratory SOP(s).

- Region I, EPA-New England Data Validation Functional Guidelines for Evaluating Environmental Analyses (12/96).

- Region II, Standard Operating Procedure for the Validation of Organic Data Acquired Using SW-846 Method 8082 (Rev 2. 12/96).

- Region III, Modifications to National Functional Guidelines for Organic Data Review (9/94).

4.0 PROCEDURE

4.1 EVALUATION OF METHOD COMPLIANCE

The data reviewer will assess the method compliance of the PCB data based on an evaluation of information presented in the data package deliverables. Compliance to SW-846 Method 8082, USEPA Method 608, and/or USEPA Method 508 and/or other reference documents (*e.g.,* analytical SOPs) as applicable to General Electric Company's Hudson River RAMP (as directed by the Project Manager) will be evaluated as part of the assessment. In addition, the deliverables will be evaluated for reporting errors and inconsistencies. The findings of the method compliance assessment will be described in terms of deficiencies and comments about the data/deliverables. The deficiencies/ comments will be presented in three subdivisions (*i.e.,* correctable deficiencies,

noncorrectable deficiencies, and comments) of the Organic Data Evaluation Section of the QAR. Each deficiency and comment discussed in the QAR will indicate any subsequent impact on the usability of the data or will identify aspect(s) of the data that could not be evaluated due to the deficiency.

The data reviewer should contact the project laboratories to request the correction of deficiencies prior to submittal of the QAR (if feasible and sanctioned by to General Electric Company). At a minimum, corrections required to allow for a full evaluation of the usability of the data should be requested. Such correctable deficiencies may include sample result errors, missing data deliverables, or calculation errors that would require a significant amount of the data reviewer's time to correct. Any laboratory resubmittals as a result of such requests will be discussed in the comments subdivision of the QAR and included as an attachment to the QAR.

4.2 DETERMINATION OF DATA USABILITY

The data reviewer will determine the usability of the PCB data based on an evaluation of the information presented in the data package deliverables. The findings of the PCB data usability assessment will be presented in terms of data qualifications that the project team should consider in order to best utilize the data; these qualifications will be presented in the Organic Data Qualifier subsection of the QAR. Each qualification discussed in the QAR will indicate that the affected sample result(s) has been flagged with a representative qualifier code(s) to General Electric Company's database to provide, at a glance, an indication of the quantitative and qualitative reliability of each analytical result. In general, the qualifier statements will be presented in the QAR in the following order: blank contamination (UB), unusable results (R/UR), estimated results (J/UJ),

tentative identifications of target compound results (N), field duplicate comparison, and a general qualifier for all results reported below the quantitation limit (if applicable to General Electric Company's Hudson River RAMP).

The data reviewer's criteria for evaluating the usability of the PCB data and the resultant qualifications will be as stipulated on the attached Table for the Validation of PCB (Aroclor) Data Generated by SW-846 Method 8082, USEPA Method 608, USEPA Method 508. It should be noted that the project manager should be consulted when "professional judgement" use is indicated on the attached table.

Table for the Validation of PCB (Aroclor) Data Generated by SW-846 Method 8082, USEPA Method 608, and USEPA Method 508

Quality Control Item	Usability Criteria	Action
Temperature Upon Receipt	4±2°C	If temperature is >10°C but ≤20°C, qualify positive results as estimated ("J") and qualify "not-detected results as estimated ("UJ"). If temperature is > 20°C, qualify positive results as estimated ("J") and qualify "not-detected" results as unusable ("UR"). Note time of collection relative to receipt at laboratory. Professional judgement should be used if < 8 hours has elapsed from collection to receipt at the laboratory to determine if qualification due to elevated temperature applies.
Technical Holding Time	Aqueous samples should be extracted within 365 days of sample collection. Sediment/soil samples should be extracted within 14 days of sample collection. Air samples should be extracted within 7 days of sample collection. Soil/sediment and tissue samples (which have been frozen to <-10°C upon laboratory receipt) should be extracted within 1 year of sample collection. All matrices should be analyzed within 40 days after extraction.	If a holding time is exceeded, qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). If a holding time is grossly exceeded (*i.e.*, > twice the holding time), qualify positive results as estimated ("J") and qualify "not-detected" results as unusable ("UR").

Table for the Validation of PCB (Aroclor) Data Generated by SW-846 Method 8082, USEPA Method 608, and USEPA Method 508

Quality Control Item	Usability Criteria	Action
Initial Calibration (See Note #1 for additional information.)	%RSD should be ≤20%. For the calibration curve, r (linear) or coefficient of determination (COD; quadratic) must be ≥0.99.	If target Aroclors have 20%< %RSD ≤50%, qualify positive results as estimated ("J") and do not qualify "not-detected" results. If target Aroclors have 50%< %RSD ≤90%, qualify positive results as estimated ("J") and use professional judgement to qualify "not-detected" results. If target Aroclors have %RSD > 90%, qualify positive results as estimated ("J") and qualify "not-detected" results as unusable ("UR"). Use professional judgment when evaluating correlation coefficients (r) and coefficients of determination (COD). If r (linear) or COD (quadratic) is <0.99 but ≥0.85, qualify positive results as estimated ("J") and do not qualify "not-detected" results. If r or COD is <0.85, qualify positive results as estimated ("J") and qualify "not-detected" results as unusable ("UR").
Continuing Calibration Verification (CCV) (See Note #2 for additional information.)	%drift or %difference should be ≤15% (or %recovery within ±15%).	Qualification is for all samples on both sides of the out-of-criteria calibration standards. If target Aroclors have 15%<%D≤90% (or 10%≤%R<85%), with the response indicating a sensitivity decrease, qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). If target Aroclors have %D>15% with the response indicating a sensitivity increase (or %R>115%), qualify positive results as estimated ("J") and use professional judgement to qualify "not-detected" results. If target Aroclors have %D>90% with the response indicating a sensitivity decrease (or %R<10%), qualify positive results as estimated ("J") and qualify "not-detected" results as unusable ("UR").

Table for the Validation of PCB (Aroclor) Data Generated by SW-846 Method 8082, USEPA Method 608, and USEPA Method 508

Quality Control Item	Usability Criteria	Action
Retention Time Windows (See Note #3 for additional information.)	All target Aroclor peak retention times (RTs) should be within the established RT windows. RT windows should be estimated or defined by the laboratory or 3× the standard deviation of three non-sequential standards over a 72-hour period.	If the CCV RT windows are not within the specified RT windows, evaluate sample chromatograms for false positives and false negatives. If a constant drift in RT is observed in the bracketing CCV, the direction of the RT drift should be applied to the sample chromatograms.
Blanks (See Note #4 and Note #9 for additional information.)	Summarize all results greater than the method detection limit (MDL) present in the blanks. The highest positive result associated with a sample should be utilized for evaluation of contamination.	If a target Aroclor is found in the blank but not in the associated sample(s), no action is required. If a sample result is ≤5× the blank result, qualify the positive result as "not detected" ("UB") and revise the MDL to the value of the positive result. If the positive result qualified "UB" is <RL, the RL should be used as reported. If the positive result qualified "UB" is ≥RL, the value of the positive result should be used as the revised RL. If individual Aroclors have been qualified "UB," adjust the associated Total PCB result to reflect that the Aroclor result should be considered "not-detected." If a sample result is >5× blank result, qualification is not required. If gross contamination exists (*i.e.*, saturated peaks on the GC), qualify the positive results as unusable ("R") due to interference.
Surrogates (See Note #5 for additional information.)	Use recovery limits provided in the method performance tables in the QAPP.	If the recoveries of one or more surrogates are > the QAPP upper acceptance limit, qualify positive results as estimated ("J") and do not qualify "not-detected" results. If the recoveries of one or more surrogates are < the QAPP lower acceptance limit but ≥10%, qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). If the recoveries of one or more surrogates are <10%, qualify positive results as estimated ("J") and qualify "not-detected" results as unusable ("UR").

Table for the Validation of PCB (Aroclor) Data Generated by SW-846 Method 8082, USEPA Method 608, and USEPA Method 508

Quality Control Item	Usability Criteria	Action
Matrix Spike/Matrix Spike Duplicate (MS/MSD) (If performed)	Use recovery limits provided in the method performance tables in the QAPP. For precision, use the criteria for Field/ Laboratory Duplicate (next page).	Data should not be qualified due to %Rs (or RPDs calculated on %Rs) that are outside of criteria if the original concentration of an Aroclor is >4× the spiking level for that compound. RPDs calculated using MS/MSD results can be used to evaluate precision. If the recovery is > the QAPP upper acceptance limit, qualify the positive result in the native sample as estimated ("J") and do not qualify the "not-detected" result. If the recovery is < the QAPP lower acceptance limit but ≥10%, qualify the positive result in the native sample as estimated ("J") and qualify the "not-detected" result in the native sample as estimated ("UJ"). If the recovery is <10%, qualify the positive result in the native sample as estimated ("J") and qualify the "not-detected" result in the native sample as unusable ("UR"). If the precision between recoveries exceeds the RPD criterion, qualify the positive result in the native sample as estimated ("J") and do not qualify the "not-detected" result. One or more Aroclors may be present in the MS/MSD. If the %R for the Aroclor(s) utilized in the MS/MSD are outside of criteria, the impact on the other Aroclors should be evaluated. If only one Aroclor is present in the MS/MSD, all Aroclors and Total PCB should be qualified (as stated above). If multiple Aroclors are present in the MS/MSD, the impact depends upon the retention times of the other Aroclors. The retention times should be evaluated to determine which Aroclor will affect the other Aroclors. For example, if Aroclor-1016 and Aroclor-1260 are present in the MS/MSD, Aroclors-1221, -1232, -1242, and -1248 usually fall within the retention times of Aroclor-1016 and Aroclors-1248 and Aroclor-1254 usually falls within the retention times of Aroclor-1260 [therefore, for Aroclor-1016, Aroclors-1221, -1232, -1242, and -1248 should be qualified (as stated above), and for Aroclor-1260, Aroclors-1248 and -1254 should be qualified (as stated above)].

Table for the Validation of PCB (Aroclor) Data Generated by SW-846 Method 8082, USEPA Method 608, and USEPA Method 508

Quality Control Item	Usability Criteria	Action
Laboratory Control Samples (LCS)	Use recovery limits provided in the method performance tables in the QAPP.	If the recovery is > the QAPP upper acceptance limit, qualify positive results in all associated samples as estimated ("J") and do not qualify "not-detected" results. If the recovery is < the QAPP lower acceptance limit but ≥10%, qualify positive results in all associated samples as estimated ("J") and qualify "not-detected" results in all associated samples as estimated ("UJ"). If the recovery is <10%, qualify positive results in all associated samples as estimated ("J") and qualify "not-detected" results in all associated samples as unusable ("UR"). One or more Aroclors may be present in the LCS. If the %R for the Aroclor(s) utilized in the LCS are outside of criteria, the impact on the other Aroclors should be evaluated. If only one Aroclor is present in the LCS, all Aroclors and Total PCB should be qualified (as stated above). If multiple Aroclors are present in the LCS, the impact depends upon the retention times of the other Aroclors. The retention times should be evaluated to determine which Aroclor will affect the other Aroclors. For example, if Aroclor-1016 and Aroclor-1260 are present in the LCS, Aroclors-1221, -1232, -1242, and -1248 usually fall within the retention times of Aroclor-1016 and Aroclors-1248 and Aroclor-1254 usually falls within the retention times of Aroclor-1260 [therefore, for Aroclor-1016, Aroclors-1221, -1232, -1242, and -1248 should be qualified (as stated above), and for Aroclor-1260, Aroclors-1248 and -1254 should be qualified (as stated above)].

Table for the Validation of PCB (Aroclor) Data Generated by SW-846 Method 8082, USEPA Method 608, and USEPA Method 508

Quality Control Item	Usability Criteria	Action
Field/Laboratory Duplicate (See Note #6 for additional information)	Use precision limit of 20% RPD (%RSD for triplicate and quadruplicate analyses) for aqueous samples and 40% RPD (%RSD for triplicate and quadruplicate analyses) for solid and air samples when both sample results are ≥5× RL. Use precision limit of ± RL difference for aqueous samples (±2× RL difference for solid samples) between results when at least one sample value is <5× RL (including when one result is a "not-detected" result). Use one-half the RL as a numerical value for any "not-detected" result in the difference calculation. If both results are "not-detected", a quantitative assessment of duplicate precision is not performed.	If the criteria are not met, qualify positive results for the out-of-criteria compounds in the original sample and its duplicate as estimated ("J") and qualify "not-detected" results as estimated ("UJ").
Percent Solids	Sediment/soil samples with less than 50% solid content require qualification.	If a sediment/soil sample has a percent solid content <50% but ≥10%, qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). Use professional judgement if a sediment/soil sample has a percent solid content <10%.

Table for the Validation of PCB (Aroclor) Data Generated by SW-846 Method 8082, USEPA Method 608, and USEPA Method 508

Quality Control Item	Usability Criteria	Action
Compound Quantitation and Qualitative Identification (See Notes #3, #7, and #8 for additional information.)	Samples with results that exceed the instrument calibration range should be reanalyzed at a dilution. All sample chromatograms must be evaluated to determine whether the laboratory correctly identified the correct Aroclor based upon pattern recognition, peak retention times, and qualititative matching with the associated calibration standards.	If a target Aroclor result exceeds the instrument calibration range, qualify positive result as estimated ("J"). Use professional judgment to determine whether sample reanalyses and dilutions should be compared to the original analyses. If criteria (see field duplicate usability) between the original sample results and the reanalysis sample results are not met, qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). If a target Aroclor is <RL but ≥MDL, qualify positive results as estimated ("J"). It any positive result for a target Aroclor has been qualified as estimated ("J") due to any reason in this SOP, qualify the associated Total PCBs result as estimated ("J"). Use professional judgement to determine whether qualititative identifications are accurate and whether data qualification is necessary.
System Performance (See Note #8 for additional information.)	Professional judgement should be used when assessing the degradation of system performance during analyses.	Use professional judgment to qualify the data if it is determined that system performance degraded during sample analyses.
Overall Assessment of Data	Assess overall quality of the data. Review available materials to assess the quality, keeping in mind the additive nature of the analytical problems.	Use professional judgment to determine the need to qualify data not qualified based on the QC previously discussed. Write a brief narrative to give the user an indication of the analytical limitations of the data. If sufficient information on the intended use and required quality of the data is available, include the assessment of the usability of the data within the given context.

Notes for the Validation of PCB (Aroclor) Data Generated by SW-846 Method 8082, USEPA Method 608, and USEPA Method 508

1. If the initial calibration curve %RSD>50%, the linearity of the first three initial calibration standards should be evaluated. If the first three initial calibration standards for the compound are linear (*i.e.*, r ≥0.99), do not qualify "not-detected" results. If the first three initial calibration standards for the compound are not linear, qualify "not-detected" results as estimated ("UJ").

   Use professional judgment when evaluating the concentration intercept of a calibration curve. If the concentration intercept is positive, the samples should be evaluated for false positives. If the concentration intercept is negative, the sample should be evaluated for false negatives.

2. If instrument instability (*i.e.*, several continuing calibration standards with compounds exhibiting both increasing and decreasing sensitivity throughout an analytical sequence) is observed in the analysis of sequential continuing calibration standards, "not-detected" results may be qualified as estimated ("UJ") due to instrument sensitivity of a continuing calibration standard response that is greater than the initial calibration standard response (increase in instrument sensitivity).

   If the continuing calibration verification standard is %D>15% in the direction of increased instrument sensitivity and it is determined that "not-detected" results should not be qualified, the data reviewer should note this within the QAR support documentation.

Notes for the Validation of PCB (Aroclor) Data Generated by SW-846 Method 8082, USEPA Method 608, and USEPA Method 508

The Aroclor in the continuing calibration verification (CCV) standard analysis may be alternated among the Aroclors and also may be based on any Aroclors observed in the samples. The CCV standard analysis also may utilize only Aroclor-1016 and Aroclor-1260. If the %D>15% for the Aroclor(s) utilized in the CCV, the impact on the other Aroclors should be evaluated. If multiple CCVs with multiple Aroclors bracket the samples, the impact depends upon the retention times of the other Aroclors. The retention times should be evaluated to determine which Aroclor will affect the other Aroclors. For example, if Aroclor-1016 and Aroclor-1260 are present in the CCVs, Aroclors-1221, -1232, -1242, and -1248 usually fall within the retention times of Aroclor-1016 and Aroclors-1248 and Aroclor-1254 usually falls within the retention times of Aroclor-1260 [therefore, if %D>15% for Aroclor-1016, Aroclors-1221, -1232, -1242, and -1248 should be qualified (as stated above), and if %D>15% for Aroclor-1260, Aroclors-1248 and -1254 should be qualified (as stated above)].

3. Use professional judgment when evaluating sample chromatograms. The Aroclor patterns should be evaluated when an RT shift is observed. If the Aroclor pattern is present, qualification is not necessary. If a RT shift is observed in an associated CCC and the sample chromatograms reveal peaks, use expanded RT windows and the surrogate shifts to evaluate for potential false positives and false negatives. If a possible false positive is observed, the reported positive sample result for the Aroclors outside of the RT window may replace the MDL/RL and the result may be qualified as "not-detected" ("U"), depending on professional judgment. If a possible false negative is observed, the potential positive result may be quantitated and added to the result field and may be qualified as tentative ("N"), depending on professional judgment.

Notes for the Validation of PCB (Aroclor) Data Generated by SW-846 Method 8082, USEPA Method 608, and USEPA Method 508

If the chromatograms reveal peaks that interfere with potential detection of a target Aroclor, qualify the MDL/RL for "not-detected" results as estimated ("UJ") or unusable ("UR"), depending on the level of the interference. Qualify reported positive results for the PCB Congener as unusable ("R") or raise the MDL and RL above the level of detection, depending on professional judgment.

4. The frequency of equipment/rinse blanks is determined during the sampling event. The results of a equipment/rinse blank should be applied to all samples collected in the same day, unless only one blank was collected for a several-day sampling event. In instances where more than one blank is associated with a given sample, qualification should be based upon a comparison with the associated blank having the highest concentration of a contaminant.

   Instrument blank contamination should be applied to samples bracketing the contaminated instrument blank.

5. The surrogate recovery limits do not apply to samples analyzed at greater than five-fold dilutions. Qualification of the data is not necessary if the surrogate is diluted beyond detection. Generally, a greater than five-fold dilution will affect the ability to even detect the surrogate. Write a comment in the QAR addressing the issue that sample-specific method performance based on surrogate recoveries could not be evaluated due to the dilution required for sample analysis.

Notes for the Validation of PCB (Aroclor) Data Generated by SW-846 Method 8082, USEPA Method 608, and USEPA Method 508

6. Duplicate samples may be collected and analyzed as an indication of overall precision. Field duplicate analyses measure both field and laboratory precision; therefore, the results may have more variability than laboratory duplicates that measure only laboratory performance. Laboratory duplicate results and field duplicate results apply only to the original sample and the laboratory/field duplicate. Solid duplicate results are expected to have greater variance than aqueous duplicate results.

7. If a sample result exceeds the instrument calibration range (lower dilution analysis) or is less than the RL (secondary dilution), do not utilize this result when comparing an original analysis and a diluted reanalysis.

8. Poor chromatographic performance affects both qualitative and quantitative results. Indications of substandard performance include:

   - High background levels or shifts in absolute RTs of internal standards
   - Excessive baseline rise at elevated temperature
   - Extraneous peaks
   - Loss of resolution
   - Peak tailing or peak splitting that may result in inaccurate quantitation

APPENDIX 68
SOP FOR DATA VALIDATION OF HEXAVALENT CHROMIUM DATA (DV 7196A/7199)

1.0 OBJECTIVES

This standard operating procedure (SOP) describes procedures that Environmental Standards' data reviewers will use to validate hexavalent chromium data generated by SW-846 Methods 7196A and 7199 for General Electric Company's Hudson River Remedial Action Monitoring Program. Validation will be performed to assess the compliance of the sample data to the applicable SW-846 Methods and/or other reference documents (*e.g.*, analytical SOPs) as applicable to General Electric Company's Hudson River Remedial Action Monitoring Program. In addition, the usability of the hexavalent chromium data provided by the analytical laboratories will be determined based on the general guidance provided in the "US EPA Contract Laboratory Program National Functional Guidelines for Inorganic Data Review" (02/1994 and 10/2004) (National Functional Guidelines). It should be noted that the National Functional Guidelines applies strictly to data generated by the Contract Laboratory Program (CLP) protocol. As such, it is not directly applicable to validation of data generated by SW-846 Methods 7196A and 7199; therefore, this SOP presents the specific data qualification actions that will be used for validation.

The validation findings will be presented in a quality assurance review (QAR) that will be prepared from one or more sample delivery groups (SDGs). Copies of annotated analytical results summaries (Form I's), including any changes to the analytical results and data qualifier codes, or a data summary spreadsheet of the qualified analytical results will be included in the analytical results section of the QAR.

2.0 EVALUATION TOOLS

Excel forms available in R:/Templates/Chemistry/XCELForms:

- Inorganic field duplicate comparison Rev 1-01.xls
- Inorganic triplicate comparison Rev 1-01.xls
- Total versus dissolved comparison Rev 1-01.xls

Chemistry Applications:

FIT
Methods Database

3.0 REFERENCE DOCUMENTS

- US EPA Contract Laboratory Program National Functional Guidelines for Inorganic Data Review (02/1994).

- US EPA Contract Laboratory Program National Functional Guidelines for Inorganic Data Review (10/2004).

- SW-846 Methods 7196A and 7199.

- Applicable project/laboratory analytical SOP(s).

- Region II, Evaluation of Metals Data for the Contract Laboratory Program (CLP) (1/92) Validation of Inorganics.

- Region I, EPA – New England Data Validation Functional Guidelines for Evaluating Environmental Analyses (12/96).

- Region III, Modifications to Natural Functional Guidelines for Inorganic Data Review (9/94).

4.0 PROCEDURE

4.1 EVALUATION OF METHOD COMPLIANCE

The data reviewer will assess the method compliance of the hexavalent chromium data based on an evaluation of information presented in the data package deliverables. Compliance to the SW-846 Methods 7196A and 7199 and/or other reference documents (*e.g.*, analytical SOPs) as applicable to General Electric Company's Hudson River Remedial Action Monitoring Program (as directed by the Project Manager) will be evaluated as part of the assessment. In addition, the deliverables will be evaluated for reporting errors and inconsistencies. The findings of the method compliance assessment will be described in terms of deficiencies and comments about the data/deliverables. The deficiencies/comments will be presented in three subdivisions (*i.e.*, correctable deficiencies, noncorrectable deficiencies, and comments) of the Inorganic and Conventional Parameter Data Evaluation Section of the QAR. Each deficiency and comment discussed in the QAR will indicate any subsequent impact on the usability of

the data or any certain aspect(s) of the data that could not be evaluated due to the deficiency.

The data reviewer should contact the project laboratories to request the correction of deficiencies prior to the submittal of the QAR (if feasible and sanctioned by General Electric Company). At a minimum, corrections necessary for a full evaluation of the usability of the data should be requested. Such correctable deficiencies may include sample result errors, missing data deliverables, or calculation errors that would take a significant amount of the data reviewer's time to correct. Any laboratory resubmittals as a result of such requests will be discussed in the comments subdivision of the QAR and included as an attachment to the QAR.

4.2 DETERMINATION OF DATA USABILITY

The data reviewer will determine the usability of the hexavalent chromium data based on an evaluation of the information presented in the data package deliverables. The findings of the hexavalent chromium data usability assessment will be described in terms of certain qualifications of the data that the project team should consider in order to best utilize the data. These qualifications will be presented in the Inorganic and Conventional Parameter Data Qualifier subsection of the QAR. Each qualification discussed in the QAR will indicate that the affected sample result(s) has been flagged with representative qualifier code(s) in the General Electric Company's database to provide, at a glance, an indication of the quantitative and qualitative reliability of each analytical result. In general, the qualifier statements will be presented in the QAR in the following order: blank contamination, unusable results (R/UR), estimated results (J/UJ), field duplicate

comparison, and a general qualifier for all results reported below the quantitation/reporting limit (if applicable to General Electric Company's Hudson River Remedial Action Monitoring Program).

The data reviewer's criteria for evaluating the usability of the hexavalent chromium data and the resultant qualifications will be as stated in the attached Table for the Validation of Hexavalent Chromium Data Generated by SW-846 Methods 7196A and 7199. It should be noted that the Project Manager should be consulted when directed to use "professional judgement" in the attached table.

Notes for the Validation of Hexavalent Chromium Data Generated by SW-846 Methods 7196A and 7199

Quality Control Item	Usability Criteria	Action
Temperature and Conditions Upon Receipt	Aqueous samples should be preserved to 4±2°C.	If temperature >10°C, but ≤20°C, qualify positive results as estimated ("J") and qualify "not-detected results as estimated ("UJ"). If temperature >20°C, qualify positive results as estimated ("J") and qualify "not-detected" results as unusable ("UR"). Note time of collection relative to receipt at laboratory. Professional judgment should be used if less than 8 hours had lapsed from collection to receipt to determine if the qualification above applies.
Technical Holding Time	Aqueous samples should be analyzed within 24 hours of collection.	If the sample analysis was performed >holding time but ≤ 2 × the holding time, qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). If the sample analysis was performed >2 × the holding time, qualify positive results as estimated ("J") and qualify "not-detected" results as unusable ("UR").
Initial Calibration (See Note #1 for additional information)	Should be established with a minimum of one blank and three standards. Correlation coefficient (r) (linear) should be ≥0.999 (for IC analyses).	Use professional judgement if the minimum number of standards was not used or if instrument was not calibrated daily and/or not calibrated each time set up. If r is <0.995 but ≥0.85, qualify positive results as estimated ("J") and do not qualify "not-detected" results. If r is <0.85, qualify positive results as estimated ("J") and qualify "not-detected" results as unusable ("UR").
Instrument Performance (for IC analyses)	The relative standard deviation (RSD) for duplicate injections should be <20% when the result is >than the reporting limit (RL).	If RSD is >20%, qualify positive results greater than the RL as estimated ("J") and do not qualify "not-detected" results.

Notes for the Validation of Hexavalent Chromium Data Generated by SW-846 Methods 7196A and 7199

Quality Control Item	Usability Criteria	Action
Independent Calibration Verification Standard (ICV) and Continuing Calibration Verification Standard (CCV)	ICV and CCV Recoveries (%R) should be 90-110%.	If the ICV or CCV %R>110% but ≤125%, qualify positive results as estimated ("J") and do not qualify "not-detected" results. If the ICV or CCV %R<90% but ≥75%, qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). If the ICV or CCV %R>125%, qualify positive results as unusable ("R") and do not qualify "not-detected" results. If the ICV or CCV %R<75%, qualify positive results as estimated ("J") and qualify "not-detected" results as unusable ("UR").
Blanks (Preparation and/or Continuing Calibration Blanks/ Field Blank/Equipment Blank) (See Note #2 for additional information)	Summarize all results greater than the method detection limit (MDL) present in the blanks. The highest positive result associated with a sample should be utilized for evaluation of contamination.	For continuing calibration blanks qualify samples per analytical sequence using professional judgment; for preparation blanks, field blanks, and equipment blanks qualify per batch and for SDG. If an analyte is detected in the blank but not in the associated samples, no action is required. If a sample result is ≤5× the blank result, qualify the positive result as "not detected" ("UB") and revise the MDL to the value of the positive result. If the positive result qualified "UB" is ≤RL, the RL should be used as reported. If the positive result qualified "UB" is >RL, the value of the positive result should be used as the revised RL. If a sample result is >5× blank result, qualification is not required.
Laboratory Control Sample (LCS)	For accuracy, use recovery limits of 85-115%.	If the recovery is >115%, qualify positive results as estimated ("J") and do not qualify "not-detected" results. If the recovery is <85% but ≥50%, qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). If the recovery is <30%, qualify positive results as estimated ("J") and qualify "not-detected" results as unusable ("UR").

Notes for the Validation of Hexavalent Chromium Data Generated by SW-846 Methods 7196A and 7199

Quality Control Item	Usability Criteria	Action
Matrix Spike/Matrix Spike Duplicates (MS/MSD) (See Note #3 for additional information)	For accuracy, use recovery limits of 85-115%. For precision, use limit of 20% RPD.	Data should not be qualified due to %Rs (or RPDs calculated using %Rs) that are outside of criteria if the original concentration of a compound is > 4 × spiking level for that compound. If the recovery is >115%, qualify positive results in all associated samples in batch as estimated ("J") and do not qualify "not-detected" results. If the recovery is 30%≤%R<85%, qualify positive results in the all associated samples in batch as estimated ("J") and qualify "not-detected" results in all associated samples in batch as estimated ("UJ"). If the recovery is <30%, qualify positive results in all associated samples as estimated ("J") and qualify "not-detected" results as unusable ("UR"). If the precision between recoveries exceeds the RPD criterion, qualify positive results in all associated samples as estimated ("J") and do not qualify "not-detected" results.
Post-Digestion Spike (PDS) (for colorimetric analyses)	Use recovery limits of 85-115%.	If the recovery is >115%, qualify positive result in associated sample as estimated ("J") and do not qualify "not-detected" result. If the recovery is 40%≤%R<85%, qualify positive result in associated sample as estimated ("J") and qualify "not-detected" result in associated sample as estimated ("UJ"). If the recovery is <40%, qualify positive result in associated sample as estimated ("J") and qualify "not-detected" result as unusable ("UR").

Notes for the Validation of Hexavalent Chromium Data Generated by SW-846 Methods 7196A and 7199

Quality Control Item	Usability Criteria	Action
Field/Laboratory Duplicate (See Note #4 for additional information)	Use QAPP-specified limits for Field Duplicate comparison. For Laboratory Duplicate comparison use limit of 20% RPD for aqueous samples for sample results ≥5× RL. Use default limit of ± RL for aqueous samples when at least one sample value is <5× RL. (Use ½ the RL as the numerical value for comparison if the analyte was "not-detected")	If the field duplicate criteria are not met, qualify positive results for the non-compliant analyte in the original sample and its duplicate as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). If the laboratory duplicate criteria are not met, qualify positive results in the all associated samples in batch as estimated ("J") and qualify "not-detected" results in all associated samples in batch as estimated ("UJ").
Total vs. Dissolved Comparison	When the dissolved result is greater than the total result: use default limits of ± RL if at least one result is <10× RL. Use default limit of percent difference <10% if both results are ≥10× RL.	If the criteria are not met, qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). If at least one result is <10× RL and the difference is >5× RL, qualify positive results and "not-detected" results as unusable ("R/UR"). If both results are ≥10× RL and the percent difference is >50%, qualify positive results as unusable ("R").
Analyte Quantitation	Samples with results that are > the calibration range should be reanalyzed at a dilution.	If a target analyte result is > the calibration range, qualify the positive result as estimated ("J"). If a target analyte result is <RL but ≥MDL, qualify positive results as estimated ("J").
Overall Assessment of Data	Assess overall quality of the data. Review available materials to assess the quality, keeping in mind the additive nature of the analytical problems.	Use professional judgment to determine the need to qualify data that were not qualified based on the QC previously discussed. Write a brief narrative to give the user an indication of the analytical limitations of the data. If sufficient information on the intended use and required quality of the data is available, the reviewer should include his assessment of the usability of the data within the given context.

Notes for the Validation of Hexavalent Chromium Data Generated by SW-846 Methods 7196A and 7199

1. Use professional judgment when evaluating the concentration intercept of a calibration curve. If the concentration intercept is positive then the samples should be evaluated for false positives. If the concentration intercept is negative then the samples should be evaluated for false negatives.

2. The frequency of field/equipment/rinse blanks is determined during the sampling event. The results of a field/equipment/rinse blank should be applied to all samples collected using the same equipment (equipment/rinse blanks only) on the same day (unless only one was collected for a several-day sampling event; results would be applied to all samples in the SDG). In instances where more than one blank is associated with a given sample, qualification should be based upon a comparison with the associated blank having the highest concentration for a contaminant.

3. If low-concentration as well as high-concentration pre-digestion matrix spikes were prepared and analyzed, the low-concentration samples will be evaluated according to the low-concentration pre-digestion matrix spike recoveries and the high-concentration samples will be evaluated according to the high-concentration pre-digestion matrix spike recoveries.

   It should be noted that hexavalent chromium data may be acceptable for use, despite recoveries outside of limits in the matrix spike analyses. The analysis for ancillary parameters (oxidation reduction potential, ferrous iron, total organic carbon, pH, sulfides, biological oxygen demand, and/or chemical oxygen demand) in the unspiked sample aids in establishing the tendency of hexavalent chromium to exist or not exist in the unspiked

Notes for the Validation of Hexavalent Chromium Data Generated by SW-846 Methods 7196A and 7199

sample and assists in the interpretation of matrix spike recoveries which are outside of criteria. If samples have been analyzed for any of the aforementioned parameters, the results must be evaluated to make a determination of reducing/oxidizing tendencies in the sample matrix prior to any qualification of data.

4. Duplicate samples may be taken and analyzed as an indication of overall precision. Field duplicate analyses measure both field and laboratory precision; therefore, the results may have more variability than laboratory duplicates which measure only laboratory performance. Field duplicate sample results should only be applied to the original sample and its field duplicate. Laboratory duplicate should be applied to all samples in a batch.

APPENDIX 69
SOP FOR DATA VALIDATION OF AROCLOR PCB DATA BY GEHR8082 (DV GEHR8082)

1.0 OBJECTIVES

This standard operating procedure (SOP) describes procedures that the Environmental Standards data reviewers will use to validate PCB data generated by Method GEHR8082 for the General Electric Company's Hudson River Remedial Action Monitoring Program (RAMP). Validation will be performed to assess the compliance of the sample data to Method GEHR8082 and/or other reference documents (*e.g.*, analytical SOPs) as applicable to the General Electric Company's Hudson River RAMP. In addition, the usability of the PCB data provided by the analytical laboratories will be determined based on the general guidance provided in the "US EPA Contract Laboratory National Functional Guidelines for Organic Data Review" (10/1999; National Functional Guidelines) and "US EPA Contract Laboratory Program National Functional Guidelines for Superfund Organic Methods Data Review" (06/2008 National Functional Guidelines). It should be noted that the National Functional Guidelines apply strictly to data generated by the Contract Laboratory Program (CLP) protocol and are not directly applicable to validation of data generated by Method GEHR8082; therefore, this SOP presents the specific data qualification actions that will be used for validation.

The validation findings will be presented in a quality assurance review (QAR) that will be prepared for one or more sample delivery groups (SDGs). Copies of annotated analytical results summaries (Form I's), including any changes to the analytical results and data qualifier codes or a data summary spreadsheet of the qualified analytical results, will be included in the support documentation of the QAR.

2.0 EVALUATION TOOLS

Excel forms available in R:/Templates/Chemistry/XCELforms:

- Organic field duplicate comparisons Rev1-01.xls
- Organic field quadruplicate comparison Rev1-01.xls
- Organic field triplicate comparison Rev1-01.xls
- Aroclor.xls

Chemistry Applications:

- FIT
- Methods Database
- Target version 4.1 data processing software

3.0 REFERENCE DOCUMENTS

- US EPA Contract Laboratory Program National Functional Guidelines for Organic Data Review (10/1999).

- US EPA Contract Laboratory Program National Functional Guidelines for Superfund Organic Methods Data Review (06/2008).

- Analytical SOP GEHR8082.

- SW-846 Method 8082.

- Region I, EPA-New England Data Validation Functional Guidelines for Evaluating Environmental Analyses (12/96).

- Region II, Standard Operating Procedure for the Validation of Organic Data Acquired Using SW-846 Method 8082 (Rev 2. 12/96).

- Region III, Modifications to National Functional Guidelines for Organic Data Review (9/94).

4.0 PROCEDURE

4.1 EVALUATION OF METHOD COMPLIANCE

The data reviewer will assess the method compliance of the PCB data based on an evaluation of information presented in the data package deliverables. Compliance to Method GEHR8082 and/or other reference documents (*e.g.,* analytical SOPs) as applicable to General Electric Company's Hudson River RAMP (as directed by the Project Manager) will be evaluated as part of the assessment. In addition, the deliverables will be evaluated for reporting errors and inconsistencies. The findings of the method compliance assessment will be described in terms of deficiencies and comments about the data/deliverables. The deficiencies/comments will be presented in three subdivisions (*i.e.*, correctable deficiencies, noncorrectable deficiencies, and comments) of the Organic Data Evaluation Section of the QAR. Each deficiency and comment discussed in the QAR will indicate any subsequent impact on the usability of

the data or will identify aspect(s) of the data that could not be evaluated due to the deficiency.

The data reviewer should contact the project laboratories to request the correction of deficiencies prior to submittal of the QAR (if feasible and sanctioned by to General Electric Company). At a minimum, corrections required to allow for a full evaluation of the usability of the data should be requested. Such correctable deficiencies may include sample result errors, missing data deliverables, or calculation errors that would require a significant amount of the data reviewer's time to correct. Any laboratory resubmittals as a result of such requests will be discussed in the comments subdivision of the QAR and included as an attachment to the QAR.

4.2 DETERMINATION OF DATA USABILITY

The data reviewer will determine the usability of the PCB data based on an evaluation of the information presented in the data package deliverables. The findings of the PCB data usability assessment will be presented in terms of data qualifications that the project team should consider in order to best utilize the data; these qualifications will be presented in the Organic Data Qualifier subsection of the QAR. Each qualification discussed in the QAR will indicate that the affected sample result(s) has been flagged with a representative qualifier code(s) to General Electric Company's database to provide, at a glance, an indication of the quantitative and qualitative reliability of each analytical result. In general, the qualifier statements will be presented in the QAR in the following order: blank contamination (UB), unusable results (R/UR), estimated results (J/UJ), tentative identifications of target compound results (N), field duplicate comparison, and a

general qualifier for all results reported below the quantitation limit (if applicable to General Electric Company's Hudson River RAMP).

The data reviewer's criteria for evaluating the usability of the PCB data and the resultant qualifications will be as stipulated on the attached Table for the Validation of PCB (Aroclor) Data Generated by Method GEHR8082. It should be noted that the project manager should be consulted when "professional judgement" use is indicated on the attached table.

Table for the Validation of PCB (Aroclor) Data Generated by GEHR8082

Quality Control Item	Usability Criteria	Action
Temperature Upon Receipt	4±2°C	If temperature is >10°C but ≤20°C, qualify positive results as estimated ("J") and qualify "not-detected results as estimated ("UJ"). If temperature is > 20°C, qualify positive results as estimated ("J") and qualify "not-detected" results as unusable ("UR"). Note time of collection relative to receipt at laboratory. Professional judgement should be used if < 8 hours has elapsed from collection to receipt at the laboratory to determine if qualification due to elevated temperature applies.
Technical Holding Time	Aqueous samples should be extracted within 365 days of sample collection. Solid/soil samples should be extracted within 14 days of sample collection. All matrices should be analyzed within 40 days after extraction. Frozen archive samples should be extracted and analyzed within one year of sample collection.	If a holding time is exceeded, qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). If a holding time is grossly exceeded (*i.e.*, > twice the holding time), qualify positive results as estimated ("J") and qualify "not-detected" results as unusable ("UR").
Initial Calibration (See Note #1 for additional information.)	%RSD should be ≤20% and a calibration curve should be generated. For the calibration curve, r (linear) or coefficient of determination (COD; quadratic) must be ≥0.99.	If target Aroclors have 20%< %RSD ≤50%, qualify positive results as estimated ("J") and do not qualify "not-detected" results. If target Aroclors have 50%< %RSD ≤90%, qualify positive results as estimated ("J") and use professional judgement to qualify "not-detected" results. If target Aroclors have %RSD > 90%, qualify positive results as estimated ("J") and qualify "not-detected" results as unusable ("UR"). Use professional judgement when evaluating correlation coefficients (r) and coefficients of determination (COD). If r (linear) or COD (quadratic) is <0.99 but ≥0.85, qualify positive results as estimated ("J") and do not qualify "not-detected" results. If r or COD is <0.85, qualify positive results as estimated ("J") and qualify "not-detected" results as unusable ("UR").

Table for the Validation of PCB (Aroclor) Data Generated by GEHR8082

Quality Control Item	Usability Criteria	Action
Continuing Calibration Verification (CCV) (See Note #2 for additional information.)	%drift or %difference should be ≤15%.	Qualification is for all samples on both sides of the out-of-criteria calibration standards. If target Aroclors have 15%<%D≤90% with the response indicating a sensitivity decrease, qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). If target Aroclors have %D>15% with the response indicating a sensitivity increase, qualify positive results as estimated ("J") and use professional judgment to qualify "not-detected" results. If target Aroclors have %D>90% with the response indicating a sensitivity decrease qualify positive results as estimated ("J") and qualify "not-detected" results as unusable ("UR").
Retention Time Windows (See Note #3 for additional information.)	All target Aroclor peak retention times (RTs) should be within the established RT windows. RT windows should be estimated or defined by the laboratory or 3× the standard deviation of three non-sequential standards over a 72-hour period.	If the CCV RT windows are not within the specified RT windows, evaluate sample chromatograms for false positives and false negatives. If a constant drift in RT is observed in the bracketing CCV, the direction of the RT drift should be applied to the sample chromatograms.

Table for the Validation of PCB (Aroclor) Data Generated by GEHR8082

Quality Control Item	Usability Criteria	Action
Blanks (See Note #4 and Note #9 for additional information.)	Summarize all results greater than the method detection limit (MDL) present in the blanks. The highest positive result associated with a sample should be utilized for evaluation of contamination.	If a target Aroclor is found in the blank but not in the associated sample(s), no action is required. If a sample result is ≤5× the blank result, qualify the positive result as "not detected" ("UB") and revise the MDL to the value of the positive result. If the positive result qualified "UB" is <RL, the RL should be used as reported. If the positive result qualified "UB" is ≥RL, the value of the positive result should be used as the revised RL. If individual Aroclors have been qualified "UB," adjust the associated Total PCB result to reflect that the Aroclor result should be considered "not-detected." If a sample result is >5× blank result, qualification is not required. If gross contamination exists (*i.e.*, saturated peaks on the GC), qualify the positive results as unusable ("R") due to interference.
Surrogates (See Note #5 for additional information.)	Use 60-140% as limits.	If the recoveries of one or more surrogates are > upper limit, qualify positive results as estimated ("J") and do not qualify "not-detected" results. If the recoveries of one or more surrogates are < lower limit but ≥10%, qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). If the recoveries of one or more surrogates are <10%, qualify positive results as estimated ("J") and qualify "not-detected" results as unusable ("UR").

Table for the Validation of PCB (Aroclor) Data Generated by GEHR8082

Quality Control Item	Usability Criteria	Action
Matrix Spike/Matrix Spike Duplicate (MS/MSD) (IF REQUESTED)	For accuracy, use recovery limits of 60-140%. For precision, use RPD limits of 20% for aqueous samples and 40% for solid samples.	Data should not be qualified due to %Rs (or RPDs calculated on %Rs) that are outside of criteria if the original concentration of an Aroclor is >4× the spiking level for that compound. RPDs calculated using MS/MSD results can be used to evaluate precision. If the recovery is >140%, qualify the positive result in the native sample as estimated ("J") and do not qualify the "not-detected" result. If the recovery is <60% but ≥10%, qualify the positive result in the native sample as estimated ("J") and qualify the "not-detected" result in the native sample as estimated ("UJ"). If the recovery is <10%, qualify the positive result in the native sample as estimated ("J") and qualify the "not-detected" result in the native sample as unusable ("UR"). If the precision exceeds the RPD criterion, qualify the positive result in the native sample as estimated ("J") and do not qualify the "not-detected" result. One or more Aroclors may be present in the MS/MSD. If the %R for the Aroclor(s) utilized in the MS/MSD are outside of criteria, the impact on the other Aroclors should be evaluated. If only one Aroclor is present in the MS/MSD, all Aroclors and Total PCB should be qualified (as stated above). If multiple Aroclors are present in the MS/MSD, the impact depends upon the retention times of the other Aroclors. The retention times should be evaluated to determine which Aroclor will affect the other Aroclors. For example, if Aroclor-1221 and Aroclor-1242 are present in the MS/MSD, Aroclors-1221and -1232 usually fall within the retention times of Aroclor-1221 and Aroclors-1232, -1242, -1248 -1254 and -1260 usually falls within/closest to the retention times of Aroclor-1242 [therefore, for Aroclor-1221, Aroclors-1221and -1232 should be qualified (as stated above), and for Aroclor-1242, Aroclors-1232, -1242, -1248 -1254 and -1260 should be qualified (as stated above)].

Table for the Validation of PCB (Aroclor) Data Generated by GEHR8082

Quality Control Item	Usability Criteria	Action
Laboratory Control Samples (LCS)	For accuracy, use recovery limits of 50-150%.	If the recovery is >150%, qualify positive results in all associated samples as estimated ("J") and do not qualify "not-detected" results. If the recovery is <50% but ≥10%, qualify positive results in all associated samples as estimated ("J") and qualify "not-detected" results in all associated samples as estimated ("UJ"). If the recovery is <10%, qualify positive results in all associated samples as estimated ("J") and qualify "not-detected" results in all associated samples as unusable ("UR"). One or more Aroclors may be present in the LCS. If the %R for the Aroclor(s) utilized in the LCS are outside of criteria, the impact on the other Aroclors should be evaluated. If only one Aroclor is present in the LCS, all Aroclors and Total PCB should be qualified (as stated above). If multiple Aroclors are present in the LCS, the impact depends upon the retention times of the other Aroclors. The retention times should be evaluated to determine which Aroclor will affect the other Aroclors. For example, if Aroclor-1221 and Aroclor-1242 are present in the LCS, Aroclors-1221and -1232 usually fall within the retention times of Aroclor-1221 and Aroclors-1232, -1242, -1248 -1254 and -1260 usually falls within/closest to the retention times of Aroclor-1242 [therefore, for Aroclor-1221, Aroclors-1221and -1232 should be qualified (as stated above), and for Aroclor-1242, Aroclors-1232, -1242, -1248 -1254 and -1260 should be qualified (as stated above)].

Table for the Validation of PCB (Aroclor) Data Generated by GEHR8082

Quality Control Item	Usability Criteria	Action
Performance Evaluation Samples (PE)	For accuracy, use recovery limits of 50-150%.	If the recovery is >150%, qualify positive results in all associated samples as estimated ("J") and do not qualify "not-detected" results. If the recovery is <50% but ≥10%, qualify positive results in all associated samples as estimated ("J") and qualify "not-detected" results in all associated samples as estimated ("UJ"). If the recovery is <10%, qualify positive results in all associated samples as estimated ("J") and qualify "not-detected" results in all associated samples as unusable ("UR"). One or more Aroclors may be present in the PE. If the %R for the Aroclor(s) utilized in the PE are outside of criteria, the impact on the other Aroclors should be evaluated. If only one Aroclor is present in the PE, all Aroclors and Total PCB should be qualified (as stated above). If multiple Aroclors are present in the PE, the impact depends upon the retention times of the other Aroclors. The retention times should be evaluated to determine which Aroclor will affect the other Aroclors. For example, if Aroclor-1221 and Aroclor-1242 are present in the PE, Aroclors-1221and -1232 usually fall within the retention times of Aroclor-1221 and Aroclors-1232, -1242, -1248 -1254 and -1260 usually falls within/closest to the retention times of Aroclor-1242 [therefore, for Aroclor-1221, Aroclors-1221and -1232 should be qualified (as stated above), and for Aroclor-1242, Aroclors-1232, -1242, -1248 -1254 and -1260 should be qualified (as stated above)].

Table for the Validation of PCB (Aroclor) Data Generated by GEHR8082

Quality Control Item	Usability Criteria	Action
Field/Laboratory Duplicate (See Note #6 and Note #9 for additional information)	Use precision limit of 20% RPD (%RSD for triplicate and quadruplicate analyses) for aqueous samples and 40% RPD (%RSD for triplicate and quadruplicate analyses) for solid samples when both sample results are ≥5× RL. Use precision limit of ± RL difference (±2× RL difference for solid samples) between results when at least one sample value is <5× RL (including when one result is a "not-detected" result). Use one-half the RL as a numerical value for any "not-detected" result in the difference calculation. If both results are "not-detected", a quantitative assessment of duplicate precision is not performed.	If the criteria are not met, qualify positive results for the out-of-criteria compounds in the original sample and its duplicate as estimated ("J") and qualify "not-detected" results as estimated ("UJ").
Percent Solids	Solid samples with less than 10% solid content require qualification.	If a solid sample has a percent solid content <10%, qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ").

Table for the Validation of PCB (Aroclor) Data Generated by GEHR8082

Quality Control Item	Usability Criteria	Action
Compound Quantitation and Qualititative Identification (See Notes #3, #7, and #8 for additional information.)	Samples with results that exceed the instrument calibration range should be reanalyzed at a dilution. All sample chromatograms must be evaluated to determine whether the laboratory correctly identified the correct Aroclor based upon pattern recognition, peak retention times, and qualititative matching with the associated calibration standards.	If a target Aroclor result exceeds the instrument calibration range, qualify positive result as estimated ("J"). Use professional judgement to determine whether sample reanalyses and dilutions should be compared to the original analyses. If criteria (see field duplicate usability) between the original sample results and the reanalysis sample results are not met, qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). If a target Aroclor is <RL but ≥MDL, qualify positive results as estimated ("J"). Use professional judgement to determine whether qualitative identifications are accurate and whether data qualification is necessary.
System Performance (See Note #8 for additional information.)	Professional judgement should be used when assessing the degradation of system performance during analyses.	Use professional judgement to qualify the data if it is determined that system performance degraded during sample analyses.
Overall Assessment of Data	Assess overall quality of the data. Review available materials to assess the quality, keeping in mind the additive nature of the analytical problems.	Use professional judgement to determine the need to qualify data not qualified based on the QC previously discussed. Write a brief narrative to give the user an indication of the analytical limitations of the data. If sufficient information on the intended use and required quality of the data is available, include the assessment of the usability of the data within the given context.

Notes for the Validation of PCB (Aroclor) Data Generated by GEHR 8082

1. If the initial calibration curve %RSD>50%, the linearity of the first three initial calibration standards should be evaluated. If the first three initial calibration standards for the compound are linear (*i.e.*, r ≥0.99), do not qualify "not-detected" results. If the first three initial calibration standards for the compound are not linear, qualify "not-detected" results as estimated ("UJ").

   Use professional judgement when evaluating the concentration intercept of a calibration curve. If the concentration intercept is positive, the samples should be evaluated for false positives. If the concentration intercept is negative, the sample should be evaluated for false negatives.

   The initial calibration is performed using five-point initial calibration curves for Aroclor-1221, Aroclor-1242, and Aroclor-1254 because these Aroclors are the target compounds for the project. Single-point calibrations for each of the other Aroclors should be analyzed at or just above the quantitation limits for pattern recognition. Curves (linear not through the origin or a quadratic) should be generated and relative standard deviations (%RSDs) must be ≤20%. If positive results are detected, other than the three Aroclors in the multi-peak initial calibration curves, in the samples, then a five-point initial calibration curve should be analyzed for the Aroclor in question and the extracts must be re-injected. Surrogates will be added to the Aroclor-1254 initial calibration curve and all surrogates in the samples/blanks/QC samples/CCVs will be quantitated based on the Aroclor-1254 initial calibration.

Notes for the Validation of PCB (Aroclor) Data Generated by GEHR 8082

2. If instrument instability (*i.e.*, several continuing calibration standards with compounds exhibiting both increasing and decreasing sensitivity throughout an analytical sequence) is observed in the analysis of sequential continuing calibration standards, "not-detected" results may be qualified as estimated ("UJ") due to instrument sensitivity of a continuing calibration standard response that is greater than the initial calibration standard response (increase in instrument sensitivity).

   If the continuing calibration standard is %D>15% in the direction of increased instrument sensitivity and it is determined that "not-detected" results should not be qualified, the data reviewer should note this within the QAR support documentation.

   The continuing calibration verification standard analysis utilizes only Aroclor-1221, Aroclor-1242, and Aroclor-1254; therefore, if the %D>15% for these three Aroclors, the impact on the other Aroclors (-1016, -1232, -1248, and -1260) should be evaluated. The impact depends upon the retention times of the other Aroclors. The retention times should be evaluated to determine which Aroclor (-1221, -1242, or -1254) will affect the other Aroclors. Usually, Aroclors-1016, Aroclor-1221, Aroclor-1232, Aroclor-1242, and Aroclor-1248 fall within similar retention times and Aroclor-1248, Aroclor-1254, and Aroclor-1260 fall within similar retention times; therefore, if %D>15% for Aroclor-1242 or Aroclor-1221, then –1016, -1232, and -1248 should be qualified (as stated above), and if %D>15% for Aroclor-1254, then Aroclor-1248 and Aroclor-1260 should be qualified (as stated above).

Notes for the Validation of PCB (Aroclor) Data Generated by GEHR 8082

3. Use professional judgment when evaluating sample chromatograms. The Aroclor patterns should be evaluated when an RT shift is observed. If the Aroclor pattern is present, qualification is not necessary. If the chromatograms reveal peaks corresponding to target compounds of interest using expanded RT windows and the surrogate compounds do not display a similar shift in RT, reported positive sample results for the compound outside of the RT window are replaced with the RL and qualified as "not-detected" ("U").

   If the chromatograms reveal peaks that interfere with potential detection of a target compound, qualify reported positive results for the compound as unusable ("R").

4. The frequency of equipment/rinse blanks is determined during the sampling event. The results of a equipment/rinse blank should be applied to all samples collected in the same day, unless only one blank was collected for a several-day sampling event. In instances where more than one blank is associated with a given sample, qualification should be based upon a comparison with the associated blank having the highest concentration of a contaminant.

   If a sample result qualified "UB" is <RL and the laboratory did not report the RL on the data tables or Form I, the positive result (*e.g.*, 8 μg/L) should be replaced with the RL (*e.g.*, 10 μg/L).

   Instrument blank contamination should be applied to samples bracketing the contaminated instrument blank.

Notes for the Validation of PCB (Aroclor) Data Generated by GEHR 8082

5. The surrogate recovery limits do not apply to samples analyzed at greater than five-fold dilutions. Qualification of the data is not necessary if the surrogate is diluted beyond detection. Generally, a greater than five-fold dilution will affect the ability to even detect the surrogate. Write a comment in the QAR addressing the issue that sample-specific method performance based on surrogate recoveries could not be evaluated due to the dilution required for sample analysis.

6. Duplicate samples may be collected and analyzed as an indication of overall precision. Field duplicate analyses measure both field and laboratory precision; therefore, the results may have more variability than laboratory duplicates that measure only laboratory performance. Laboratory duplicate results and field duplicate results apply only to the original sample and the laboratory/field duplicate. Soil duplicate results are expected to have greater variance than aqueous duplicate results.

7. If a sample result exceeds the instrument calibration range (lower dilution analysis) or is less than the RL (secondary dilution), do not utilize this result when comparing an original analysis and a diluted reanalysis.

8. Poor chromatographic performance affects both qualitative and quantitative results. Indications of substandard performance include:

   - High background levels or shifts in absolute RTs of internal standards
   - Excessive baseline rise at elevated temperature

Notes for the Validation of PCB (Aroclor) Data Generated by GEHR 8082

- Extraneous peaks
- Loss of resolution
- Peak tailing or peak splitting that may result in inaccurate quantitation

9. The RL will be defined on a project-specific basis. If the project-required RL is less than the low calibration standard concentration, the Project Manager should be consulted for instructions about application of qualification related to the RL.

APPENDIX 70
SOP FOR DATA VALIDATION OF MERCURY DATA (DV 245.1)

1.0 OBJECTIVES

This standard operating procedure (SOP) describes procedures that the Environmental Standards data reviewers will use to validate mercury data generated by US EPA Method 245.1 for General Electric Company's Hudson River Remedial Action Monitoring Program. Validation will be performed to assess the compliance of the sample data to US EPA Method 245 and/or other reference documents (*e.g.,* analytical SOPs) as applicable to General Electric Company's Hudson River Remedial Action Monitoring Program. In addition, the usability of the mercury data provided by the analytical laboratory(ies) will be determined based on the general guidance provided in the "US EPA Contract Laboratory Program National Functional Guidelines for Inorganic Data Review" (02/1994 and 10/2004; National Functional Guidelines). It should be noted that the National Functional Guidelines apply strictly to data generated by Contract Laboratory Program (CLP) protocol and are not directly applicable to validation of data generated by US EPA Method 245.1; this SOP presents the specific data qualification actions that will be used for validation.

The validation findings will be presented in a quality assurance review (QAR) that will be prepared for one or more sample delivery groups (SDGs). Copies of annotated analytical results summaries (Form I's), including any changes to the analytical results and data qualifier codes or a data summary spreadsheet of the qualified analytical results will be included in the analytical results section of the QAR.

2.0 EVALUATION TOOLS

Excel form available in R:/Templates/Chemistry/XCELForms:

- Inorganic field duplicate comparison Rev 1-01.xls
- Inorganic triplicate comparison Rev 1-01.xls
- Total versus dissolved comparison Rev 1-01.xls

Chemistry Applications:

- FIT
- Methods Database

3.0 REFERENCE DOCUMENTS

- US EPA Contract Laboratory Program National Functional Guidelines for Inorganic Data Review (02/1994).

- US EPA Contract Laboratory Program National Functional Guidelines for Inorganic Data Review (10/2004).

- US EPA Method 245.1.

- Applicable project/laboratory SOP(s).

- Region I, EPA – New England Data Validation Functional Guidelines for Evaluating Environmental Analyses (12/96).

- Region II, Evaluation of Metals Data for the Contract Laboratory Program (CLP) (1/92) Validation of Inorganics.

- Region III, Modifications to National Functional Guidelines for Inorganic Data Review (9/94).

4.0 PROCEDURE

4.1 EVALUATION OF METHOD COMPLIANCE

The data reviewer will assess the method compliance of the mercury data based on evaluation of information presented in the data package deliverables. Compliance with US EPA Method 245.1 and/or other reference documents (*e.g.,* analytical SOPs) as applicable to the General Electric Company's Hudson River Remedial Action Monitoring Program (as directed by the Project Manager) will be evaluated as part of the assessment. In addition, the deliverables will be evaluated for reporting errors and inconsistencies. The findings of the method compliance assessment will be described in terms of deficiencies and comments about the data/deliverables. The deficiencies/comments will be presented in three subdivisions (*i.e.*, correctable deficiencies, noncorrectable deficiencies, and comments) of the Inorganic Data Section of the QAR. Each deficiency and comment discussed in the QAR will indicate any subsequent impact on the usability of the data or will identify aspect(s) of the data that could not be evaluated due to the deficiency.

The data reviewer should contact the project laboratories to request the correction of deficiencies prior to submittal of the QAR (if feasible and sanctioned by the General Electric Company). At a minimum, corrections required to allow for a full evaluation of the usability of the data should be requested. Such correctable deficiencies may include sample result errors, missing data deliverables, or calculation errors that would require a significant amount of the data reviewer's time to correct. Any laboratory resubmittals as a result of such request will be discussed in the comments subsection of the QAR and will be included as an attachment of the QAR.

4.2 DETERMINATION OF DATA USABILITY

The data reviewer will determine the usability of the mercury data based on an evaluation of the information presented in the data package deliverables. The findings of the mercury data usability assessment will be presented in terms of data qualifications that the project team should consider in order to best utilize the data. These qualifications will be presented in the Inorganic Data Qualifier Section of the QAR. Each qualification will indicate that the affected sample result(s) has been flagged with representative qualifier code(s) in the General Electric Company's database to provide, at a glance, an indication of the quantitative and qualitative reliability of each analytical result. In general, the qualifier statements will be presented in the QAR in the following order: blank contamination, unusable results (R/UR), estimated results (J/UJ), field duplicate comparison, and a general qualifier for all results reported below the quantitation/reporting limit (if applicable to General Electric Company's Hudson River Remedial Action Monitoring Program).

The data reviewer's criteria for evaluating the usability of the mercury data and the resultant qualifications will be as stipulated on the attached Table for the Validation of Mercury Data Generated by US EPA Method 245.1. It should be noted that the Project Manager should be consulted when "professional judgement" use is indicated on the attached table.

Table for the Validation of Mercury Data Generated by US EPA Method 245.1

Quality Control Item	Usability Criteria	Action(s)
Temperature and Conditions Upon Receipt	Aqueous samples should be preserved to pH ≤2 with HNO_3. Solid/soil samples should be preserved to 4±2°C.	If pH is >2 and the laboratory did not adjust the pH and allow the sample to sit for 16 hours before digestion, qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). Solid/soil samples should not be qualified due to out-of-criteria temperatures.
Technical Holding Time	Aqueous and soil/sediment matrices should be analyzed within 28 days of sample collection. Tissue matrices (which have been frozen to <-18°C upon receipt at the laboratory) should be analyzed within one year of sample collection.	If holding time is exceeded, qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). If holding time is grossly exceeded *i.e.*, twice the holding time), qualify positive results as estimated ("J") and qualify "not-detected" results as unusable ("UR").
Initial Calibration (See Note #1 for additional information.)	Calibration should be daily and each time the instrument is set up, with at least one blank and five standards. The correlation coefficient (r) should be ≥ 0.995.	Use professional judgement if the appropriate number of standards is not used or if the instrument was not calibrated daily and/or not calibrated each time set up. If the r is <0.997 but ≥0.850, qualify positive results as estimated ("J") and do not qualify "not-detected" results. If r is <0.850, qualify positive results as estimated ("J") and qualify "not-detected" results as unusable ("UR").
Instrument Performance	Samples should not display negative results with an absolute value >2× the method detection limit (MDL).	If a negative result with an absolute value >2× MDL is observed, qualify the "not-detected" result as estimated ("UJ").

Table for the Validation of Mercury Data Generated by US EPA Method 245.1

Quality Control Item	Usability Criteria	Action(s)
Quality Control Sample (QCS)/Initial Calibration Verification (ICV)	For accuracy, use recovery limits of 95-105%.	**Qualify samples for an entire analytical sequence.** If an analyte recovery is >105% but ≤125%, qualify positive results as estimated ("J") and do not qualify "not-detected" results. If an analyte recovery is <95% but ≥75%, qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). If an analyte recovery is >125%, qualify positive results as unusable ("R") and do not qualify "not-detected" results. If an analyte recovery is <75%, qualify positive results as estimated ("J") and qualify "not-detected" results as unusable ("UR").
Instrument Performance Check (IPC)/Continuing Calibration Verification (CCV)	For accuracy, use recovery limits of 90-110% for the subsequent IPCs/CCVs.	**Qualify samples analyzed before and after a non-compliant CCV.** If an analyte recovery is >110% but ≤125%, qualify positive results as estimated ("J") and do not qualify "not-detected" results. If an analyte recovery is <90% but ≥75%, qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). If an analyte recovery is >125%, qualify positive results as unusable ("R") and do not qualify "not-detected" results. If an analyte recovery is <75%, qualify positive results as estimated ("J") and qualify "not-detected" results as unusable ("UR").

Table for the Validation of Mercury Data Generated by US EPA Method 245.1

Quality Control Item	Usability Criteria	Action(s)
PRDL/CRA/RLV standard	For accuracy, use recovery limits 80-120%.	Qualify samples analyzed before and after a non-compliant PRDL/CRA standard. If the recovery is >120% but ≤150%, qualify positive results ≤ 2 × the spike level as estimated ("J") and do not qualify "not-detected" results. If the recovery is <80% but ≥ 50%, qualify positive results ≤ 2 × the spike level as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). If the recovery is <50%, qualify positive results ≤ 2 × the spike level as estimated ("J") and qualify "not-detected" results as unusable ("UR"). If the recovery is >150%, qualify positive results ≤ 2 × the spike level as unusable ("R"), qualify positive results >2× the spike level but ≤5× the spike level as estimated ("J"), and do not qualify "not-detected" results.
Initial Calibration Blank (ICB)/ Continuing Calibration Blank (CCB)/ Preparation Blank (PB)/Field Blank/Equipment Blank (See Note #2 for additional information.)	The highest positive result (greater than the MDL) in the blanks associated with a sample should be summarized and utilized for the evaluation of contamination.	For ICBs and CCBs, qualify samples per analytical sequence using professional judgment; for PBs, field blanks, and equipment blanks, qualify per batch and/or SDG. If mercury is detected in blank but not in sample, no action is required. If a sample result is ≤5× the blank result, qualify the positive result as "not detected" ("UB") and revise the MDL to the value of the positive result. If the positive result qualified "UB" is ≤RL, the RL should be used as reported. If the positive result qualified "UB" is >RL, the value of the positive result should be used as the revised RL. If sample is >5× blank result, qualification is not required. If a blank has a negative result with an absolute value >2 × MDL, qualify positive results ≤ 5 × the absolute value of the blank result as estimated ("J") and qualify "not-detected" results as estimated ("UJ").

Table for the Validation of Mercury Data Generated by US EPA Method 245.1

Quality Control Item	Usability Criteria	Action(s)
Laboratory Fortified Blank (LFB)/Laboratory Control Sample (LCS) (See Note #3 for additional information.)	For accuracy, use recovery limits of 85-115% for aqueous samples and 70-130% for solid samples.	For aqueous samples, if the recovery is >115% but ≤150%, qualify positive results as estimated ("J") and do not qualify "not-detected" results. For aqueous samples, if the recovery is <85% but ≥30%, qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). For aqueous samples, if the recovery is >150%, qualify positive results as unusable ("UR") and do not qualify "not-detected" results. For aqueous samples, if the recovery is <30%, qualify positive results as estimated ("J") and qualify "not-detected" results as unusable ("UR"). For solid samples, if the recovery is >130%, qualify positive results as estimated ("J") and do not qualify "not-detected" results. For solid samples, if the recovery is <70% but ≥30%, qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). For solid samples, if the recovery is <30%, qualify positive results as estimated ("J") and qualify "not-detected" results as unusable ("UR").

Table for the Validation of Mercury Data Generated by US EPA Method 245.1

Quality Control Item	Usability Criteria	Action(s)
Matrix Spike/Matrix Spike Duplicates (MS/MSD) (See Note #4 for additional information.)	For accuracy use recovery limits of 70-130%. For precision, use the criteria for Field/Laboratory Duplicates (next item).	Data should not be qualified due to %Rs (or RPDs calculated using %Rs) that are outside of criteria if the original concentration of an analyte is >4× the spiking level for that analyte. RPDs calculated using MS/MSD results can be used to evaluate precision. If the recovery is >130%, qualify positive results in all associated samples as estimated ("J") and do not qualify "not-detected" results. If the recovery is <70% but ≥30%, qualify all positive results in all associated samples as estimated ("J") and qualify "not-detected" results in all associated samples as estimated ("UJ"). If the recovery is <30%, qualify positive results in all associated samples as estimated ("J") and qualify all "not-detected" results in all associated samples as unusable ("UR"). If the precision between recoveries exceeds the RPD criterion, qualify positive results in all associated samples as estimated ("J") and do not qualify "not-detected" results.
Field Duplicate/Laboratory Duplicate (See Notes #4 and #5 for additional information.)	The RPD should be ≤20% for results >5x the RL. The difference between results should be ≤ the RL when at least one result is ≤5x the RL. (Use ½ the RL as the numerical value for a "not-detected" result in the RPD calculation.)	If the criteria are not met, qualify positive results for the non-compliant analyte in original sample and its duplicate as estimated ("J") and qualify "not-detected" results as estimated ("UJ").

Table for the Validation of Mercury Data Generated by US EPA Method 245.1

Quality Control Item	Usability Criteria	Action(s)
Total vs. Dissolved Comparisons	When the dissolved result is greater than the total result: use default limits of ± RL when at least one result is <10× RL. Use default limits of percent differences <10% when both results are ≥ 10× RL.	If the criteria are not met, qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). If at least one result is <10× RL and the differences is >5× RL, qualify positive and "not-detected" results as unusable ("R/UR"). If both results are ≥10× RL and the percent difference is >50%, qualify positive results as unusable ("R").
Percent Solids	Soil/sediment samples with less than 50% solid content require qualification.	If a soil/sediment sample has a percent solid content <50% but ≥10%, qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). Use professional judgement if a soil/sediment sample has a percent solid content <10%.
Analyte Quantitation	Samples with results that are > the calibration range should be reanalyzed at a dilution.	If a target analyte result is > the calibration range, qualify the positive result as estimated ("J"). If a target analyte result is <RL but ≥MDL, qualify positive results as estimated ("J").
Overall Assessment of Data	Assess overall quality of the data. Review available materials to assess the quality, keeping in mind the nature of the analytical problems.	Use professional judgement to determine the need to qualify data that were not qualified based on the QC previously discussed. Write a brief narrative to give the user an indication of the analytical limitation of the data. If sufficient information on the intended use and required quality of the data is available, include the assessment of the usability of the data within the given context.

Notes for the Validation of Mercury Data Generated by US EPA Method 245.1

1. Use professional judgement when evaluating the concentration intercept of a calibration curve. If the concentration intercept is positive, samples should be evaluated for false positives. If the concentration intercept is negative, samples should be evaluated for false negatives. Furthermore, samples should not display negative values >2× the MDL.

   The laboratory may utilize a non-linear regression curve fit. Due to different software programs, it may not be possible to reproduce the laboratory results.

2. Generally, if more than one blank is associated with a given sample, qualification should be based upon a comparison with the associated blank having the highest concentration of a contaminant. Sample results should not be blank corrected.

   The frequency of equipment blanks is determined during the sampling event. The results of a equipment/rinse blank should be applied to all samples collected using the same equipment (equipment/rinse blanks only) on the same day (if only one blank was collected for a several-day sampling event; results would be applied to all samples in the SDG).

3. The spike level for the solid LCS/LFB should be compared to the RL. Use professional judgment if the spike level is not sufficiently greater than the RL (*i.e.*, the lower recovery limit should not be less than the RL).

4. The laboratory may choose to analyze a matrix spike duplicate instead of a laboratory duplicate.

Notes for the Validation of Mercury Data Generated by US EPA Method 245.1

5. Duplicate samples may be collected and analyzed as an indication of overall precision. Field duplicate analyses measure both field and laboratory precision; therefore, the results may have more variability than laboratory duplicates that measure only laboratory performance. Field duplicate sample results should only be applied to the original sample and its field duplicate. Laboratory duplicate results should be applied to all samples in a batch. It is expected that solid duplicate results will have a greater variance than aqueous duplicate results.

APPENDIX 71
SOP FOR PERFORMANCE AND REPORTING OF FIELD AUDITS

1.0 OBJECTIVES

This Standard Operating Procedure (SOP) describes the procedures that the auditor will use for performing field audits and the reporting of the audit findings. Field audits will be performed to provide GE with an indication of the quality of the field services that are being provided by the field contractor(s) as part of the Remedial Action Monitoring Program (RAMP) and to ensure that the field contractor(s) are adhering to project requirements. This SOP applies to the contractor(s) involved in field data collection and the auditor.

2.0 EQUIPMENT

Not applicable.

3.0 SUPPORTING SOPs and DOCUMENTS

Applicable Field Sampling SOPs

Quality Assurance Project Plan (QAPP)

Health and Safety Plan

4.0 PROCEDURE

4.1 SCHEDULING

The frequency of field audits will be identified in the appropriate QAPP. When it has been determined that the performance of a field audit is necessary, the auditor will coordinate a date and time for the audit with GE which consider both the field schedule and any deadline necessary to meet the needs of the RAMP. The majority of the audits will be unannounced to the field contractors.

4.2 PRE-AUDIT PREPARATION

Once a field audit is scheduled, the auditor will review the applicable QAPP and determine and review the applicable SOPs. The auditor will also prepare an audit checklist relevant to the specific task being performed. The individual sampling and field procedures SOPs applicable to the tasks being audited will provide the specific criteria against which the audit will be performed.

4.3 GENERAL AUDIT APPROACH

Upon arrival at the project site, the auditor will initiate a meeting with the appropriate field personnel (site manager) to give a brief introduction of what they can expect to occur during the field audit. This introduction focuses on several key points. The auditor(s) will identify that they will be performing the audit with the aid of a checklist that has been prepared by the auditor.

The checklist guides the auditor(s) through the field task in the basic order that events are expected to occur. Another key point that will be made is that the auditor(s) will focus their questions toward the field personnel who actually perform the work and **not** their supervisors. Field supervisors may be present during the audit but may not answer the questions for the field personnel unless specifically requested to provide an answer. In addition, the auditor will ask questions regarding appropriate general field service protocols during this initial meeting.

The field audit checklist should include the following 9 sections as appropriate to the activities being performed. The field audit will be performed in the basic order defined by the checklist, depending on the task being performed. Subdivisions of the following sections will be necessary and will be dependent on the type of work being performed.

The approach of the audit on the following topics is described in greater detail in the subsequent sections of this SOP. The narrative of the field audit report will also follow the subject order of the checklist but will give the audit findings and recommendations in sufficient detail that the checklist will not be included with the report.

1. Field Documentation/Records
2. Decontamination Procedures
3. Sampling/Field Procedures
4. Sample Containers
5. Sample Packaging and Shipment
6. Chain-of-Custody
7. Health and Safety/Personal Protective Equipment
8. Other
9. Summary

Finally, following the audit, the auditor(s) will convene another meeting with the field management personnel in order to debrief them on the audit findings. The debriefing meeting should accomplish several goals. First, the field personnel must be made aware of the major points of the audit findings. This way, any statements made in the field audit report will not be a surprise to the contractor, and the contractor is given a chance to respond to the findings before the report is written. Their responses can then be incorporated into the field audit report by the auditor. Secondly, the auditor(s) should emphasize that recommendations will be made even to the best of contractors. The major goals of a field audit is to determine the quality of services being provided by the contractor, document that appropriate procedures are being used, and to identify problems (or potential problems) so that appropriate corrective action can be initiated by the contractor. The extent of the impact of the recommendation(s) will be indicated in

the report. Additionally, the audit should stress when correct field procedures were in use.

4.4 FIELD DOCUMENTATION/RECORDS

The auditor(s) must evaluate the contractor's documentation procedures throughout the audit, and should verify that all pertinent information is being neatly recorded in a logbook for all field events. The minimum information to be entered in the logbook should include: on-site personnel and their arrival and departure times; weather conditions; calibration and background settings of monitoring equipment; location of collected samples; time of collection; the required sample analysis; relevant observations; photograph log; adherence to and/or deviations from the QAPP; and other pertinent information.

4.5 DECONTAMINATION PROCEDURES

The auditor(s) will verify that the decontamination areas are established in a clean portion of the site and that correct decontamination procedures are being followed. The personnel performing the decontamination of the sampling equipment should be using the decontamination materials specified in the appropriate SOP and should be performed in the exact order listed in the SOP. Care should be taken to limit the amount of decontamination wastes generated during the cleaning process. The decontamination wastes should be properly managed and stored per SOP until appropriate disposal arrangements are made.

4.6 SAMPLE CONTAINERS

The auditor(s) will verify that the contractor is using laboratory supplied, pre-cleaned sample containers for analytical samples. The containers should be of the proper type

(i.e. glass, plastic, metal), volume, and material (i.e. amber or clear glass). Any cracked or broken sample containers should not be used and should be discarded. The appropriate preservatives should already be placed in the sample containers by the laboratory, or they may be added to the sample containers in the field. Once the sample is collected and placed in the sample container, the container should be legibly labeled or preprinted with the following information; sample ID, date, time, sampler's initials, analysis, and project name and number.

4.7 SAMPLING/FIELD PROCEDURES

The auditor(s) must evaluate the procedures the contractor utilizes during the collection of samples and other field activities. Samples may be collected from various medias (i.e., surface water and fish) and for various purposes (i.e., chemical analysis). The method of sample collection will also vary and will require assorted types of equipment to insure the proper collection of the sample. The auditor(s) must verify that a proper method of sample collection and proper equipment are being used for the media being sampled and the intended purpose of the sample collection. Deviations to the applicable QAPP should be noted by the auditor(s).

4.8 SAMPLE PACKAGING AND SHIPMENT

After environmental samples have been collected, placed in sample containers, labeled and temporarily stored on-site, they should be packaged and shipped to the laboratory for chemical analysis per SOP. The auditor(s) will verify that the transport device (e.g., ice chest) to be used for shipment of the samples is cleaned of any obvious debris and old shipping labels are removed. The auditor(s) will check to see that the transport device is lined with an absorbent material and a plastic bag. The samples will be checked to see if they are individually wrapped or protected and properly aligned in the transport device so

that they do not touch each other. The samples should then be packed using an approved packing material and iced down (with the exception of liquid samples for metal analysis) with sufficient "wet" ice or ice pack to keep the samples at 4 degrees Celsius. Packing tape and signed custody seals should be used to seal the transport device. Shipping air bills and content caution content labels (e.g., Fragile, This End Up, etc.) should be attached to the outside of the shipping container.

4.9 CHAIN-OF-CUSTODY

The auditor(s) will verify that the chain-of-custody record and procedures are being properly completed per SOP. As soon as practicable after sample collection, the following information must be recorded on the chain-of-custody form; project name and number, sampler(s), sample ID, date, time, type of sample (grab or composite), number of containers, sample analysis, remarks, and signature (when being relinquished). The field audit will include a determination that proper handling and transfer of chain-of-custody documentation is occurring.

4.10 HEALTH AND SAFETY/PERSONAL PROTECTIVE EQUIPMENT

The auditor(s) will observe the field personnel to verify that they are following the guidelines of the Health and Safety Plan. The auditor will make only general observations about the health and safety practices. The auditor(s) will check to see that the field personnel are wearing the specified protective clothing and equipment for the level of protection specified by the health and safety officer. The auditor(s) will also verify that the appropriate types of personal monitoring equipment is being used, and that personnel using the equipment are knowledgeable with the operation of the equipment.

4.11 OTHER

Due to the wide range of field services being performed on this project, the above discussed list of items may not always completely address the extent of the audit. At the auditor's discretion, other checklist items may be added to ensure that a complete audit is performed.

4.12 SUMMARY

The auditor(s) must summarize the major points of the field audit findings and the overall evaluation of the quality of service provided by the contractor. The summary should also reflect the overall attitude that the contractor has toward quality assurance and quality control.

4.13 REPORT FORMAT

The field audit report must contain the following sections in the following order. It must also contain a completed checklist as an attachment.

1. Introduction
2. Executive Summary
3. Audit Findings

The introduction should summarize who performed the audit, when the audit was performed, the name and address of the contractor, and the contractor's role in the RAMP. The Executive Summary should address the major findings of the field audit along with the possible impact on the quality of the contractor's service. The Audit Findings should follow the major headings of the checklist summarizing the findings

presented on the checklist along with any recommendations for improvement or corrective action. The report will be signed by the auditor(s) who performed the audit.

5.0 TRAINING

The auditor's conducting the field audit must have demonstrated knowledge in field quality assurance/quality control practices. This knowledge will include experience in geological and hydrogeological investigations, sample collection of various media, health and safety training, and technical report writing.

APPENDIX 72
SOP FOR PERFORMANCE AND REPORTING OF ANALYTICAL LABORATORY AUDITS

1.0 OBJECTIVES

This Standard Operating Procedure (SOP) describes the procedures that the auditor will use for performing analytical laboratory audits and the reporting of the audit findings. Analytical laboratory audits will be performed to provide GE with an indication of the quality of the data that are being provided by the laboratories as part of the Remedial Action Monitoring Program (RAMP) and to ensure that the laboratories are adhering to project requirements. This SOP applies to the laboratories and the auditor.

2.0 EQUIPMENT

Not applicable.

3.0 SUPPORTING SOPs and DOCUMENTS

Applicable Analytical SOPs.

Quality Assurance Project Plan (QAPP).

Health and Safety Plan

Applicable Laboratory Quality Assurance Manual (LQAM)

4.0 PROCEDURE

4.1 SCHEDULING

The frequency of laboratory audits will be identified in the appropriate QAPP. When it has been determined that the performance of a laboratory audit is necessary, the auditor will initiate contact with the designated project laboratory. The auditor and the laboratory will mutually determine a date and time for the audit which is convenient for both parties and which is within any deadline necessary to meet the needs of the QAPP. If necessary, unannounced audits may be performed.

4.2 PRE-AUDIT PREPARATION

At the time the laboratory audit is scheduled, the auditor will request any laboratory documents that would aid in the effectiveness of the audit if received prior to the audit. Such documents will include the LQAM and all analytical Standard Operating Procedures (SOPs) which are applicable to the analytical work being performed by the laboratory.

Prior to the audit, the auditor will review all documents provided by the laboratory. In the laboratory audit report, a statement will be made as to the appropriateness and thoroughness of these documents in terms of the needs of the QAPP. In addition, the auditor will take notes upon this initial review that will aid in verifying that the laboratory is following the procedures described in the documents. Any deviations from the documents will also be noted in the laboratory audit report.

4.3 GENERAL AUDIT APPROACH

Upon arrival at the designated project laboratory, the auditor will initiate a meeting with the appropriate laboratory personnel (analytical laboratory supervisor(s) and quality assurance supervisor) to give a brief introduction of what they can expect to occur during the laboratory audit. This introduction focuses on several key points. The auditor(s) will identify that they will be performing the audit with the aid of a checklist that has been prepared by the auditor. The checklist will not be provided to the laboratory at any time.

This checklist guides the auditor(s) through the laboratory in the basic order that samples are processed through the laboratory starting with sample receipt and ending with data reporting. Another key point that will be made is that the auditor(s) will focus their questions toward the technicians and analysts who actually perform the work and **not** their supervisors. Laboratory

supervisors may be present during the laboratory audit but may not answer the questions for the technicians/analysts unless the technicians/analysts cannot answer a given question. In addition, the auditor will ask questions regarding appropriate general laboratory information during this initial meeting.

The audit checklist is a proprietary document and has not been included with this SOP. It contains significant specific detail on the audit criteria and evaluation. The laboratory evaluation checklist includes the following eight sections. The laboratory audit will be performed in the basic order defined by the checklist, depending on the layout of the laboratory being audited. Subdivisions of the following sections will be necessary and will be dependent on the types of analytical work being performed for the RAMP at the designated laboratory. The approach of the audit on the following topics is described in greater detail in the subsequent sections of this SOP. In addition to the following topics, the auditor(s) will also be evaluating the overall sample tracking throughout the audit and the communication between the various sections of the laboratory (with a special regard to how holding times are met). The narrative of the laboratory audit report will also follow the subject order of the checklist but will give the audit findings and recommendations in sufficient detail that the checklist will not be included with the report.

1. Organization and Personnel
2. Sample Receipt and Storage Area
3. Sample Preparation Area
4. Sample Analysis Instrumentation
5. Documentation
6. Quality Control Manual
7. Data Handling
8. Summary

Finally, following the audit, the auditor(s) will initiate another meeting with the appropriate laboratory personnel in order to debrief them on the audit findings. The debriefing meeting should accomplish several goals. First, the laboratory personnel must be made aware of the major points of the audit findings. This way, any statements made in the laboratory audit report will not be a surprise to the laboratory and the laboratory is given a chance to respond to the findings before the report is written. Their responses can then be incorporated into the laboratory audit report. Secondly, the auditor(s) should emphasize that recommendations will be made even to the best of laboratories. The major goal of a laboratory audit is to determine the quality of data which is currently being generated by the laboratory and to identify problems (or potential problems) so that appropriate corrective action can be initiated by the laboratory. However, laboratory audits are also attended to give all laboratories, no matter their level of quality, ideas on how to become a better laboratory. The extent of the impact of the recommendation(s) will be indicated in the report.

4.4 ORGANIZATION AND PERSONNEL

The auditor(s) must evaluate the size and experience of the organization and the number, working hours, experience, and education of the personnel in the context of the RAMP analytical work which is being performed by the laboratory being audited. The general information about the organization and personnel should be addressed by the auditor(s) during the initial introduction meeting. The experience and education of the personnel are best evaluated at a later date by obtaining the staff's resumes during this introductory meeting. However, if the resumes or some other similar summaries are not available, questions of this nature must be asked by the auditor(s) throughout the audit.

4.5 SAMPLE RECEIPT AND STORAGE AREA

The auditor(s) should interview the designated sample custodian in this area of the laboratory. If a sample custodian has not been designated by the laboratory, the auditor(s) must interview any personnel responsible for receiving and logging in samples upon receipt at the laboratory. The auditor(s) must determine whether the laboratory personnel do anything to compromise the integrity of the samples during the check-in process, such as subjecting samples to any procedures which might lead to contamination or allowing temperature-preserved samples to warm to room temperature. In addition, the auditor(s) must verify that the laboratory personnel check and record all appropriate information regarding the condition of the samples upon receipt (i.e., Chains-of-Custody, cooler temperature, preservation, etc.). Furthermore, the auditor(s) must determine whether the sample storage area(s) are kept at the proper well-documented temperatures without any possibility of cross-contamination of samples. Finally, the auditor(s) must verify that the laboratory properly documents the condition of the samples upon receipt and that the information is determined from the check-in procedure. It must also be determined whether the tracking system in which the samples have been logged is adequate to ensure that holding times are being met.

4.6 SAMPLE PREPARATION AREA

The auditor(s) must evaluate the overall appearance and appropriateness of the size of the sample preparation area and the condition of the facility and equipment in the sample preparation area. The auditor(s) must verify that the equipment, water, and standards used in sample preparation are appropriately calibrated, stored, and/or maintained and that all appropriate information regarding these issues is properly documented. While in this area, the auditor(s) must interview the sample preparation technicians responsible for the preparations for the analyses of concern for the RAMP. During the interviews, the auditor(s) must determine whether the sample preparation technicians follow good laboratory practices as well as the required analytical preparation methods. The auditor(s) must evaluate whether the laboratory is introducing the appropriate type and number of quality control samples at this point and that the sample technicians' procedures or equipment do not introduce possible contamination (i.e., glassware is cleaned properly) or inaccuracies (i.e., proper glassware and standards are used correctly). The auditor(s) must also evaluate the laboratory's sample tracking system through this area to verify that holding times are properly tracked. Finally, the auditor(s) must verify whether all preparation procedures are appropriately documented.

4.7 SAMPLE ANALYSIS INSTRUMENTATION

In the various sample analysis instrumentation areas of the laboratory, the auditor(s) must interview the analyst(s) responsible for the analyses of concern for the RAMP. When possible, analysts will also be observed performing assigned tasks. The auditor(s) must evaluate whether the instrumentation used for the analyses of concern for the RAMP is appropriate and is properly maintained. Through the interviews with the analysts and observations of actual tasks, it must be determined if each instrument is calibrated (according to the associated analytical method) with well-documented calibration standards at the required frequency and that these instrument calibrations are properly documented. The auditor(s) must determine if method

detection limit studies have been performed on each instrument used for analysis. In addition, the auditor(s) must determine if standards and quality control samples are being analyzed at an appropriate frequency and whether appropriate quality control limits are being utilized for these analyses. The analysts' practices must be evaluated for their attention to the quality control results and to the possibility of instrument carryover. The auditor(s) must evaluate whether appropriate corrective actions are being taken when standard or quality control results are out of the method-required or laboratory-determined limits. Finally, the auditor(s) must determine whether all the analysis procedures and results are properly documented.

4.8 DOCUMENTATION

The auditor(s) must evaluate the laboratory's documentation procedures throughout the audit. It should be determined if well-labeled, neat, bound notebooks are being used to document and trace standards, calibrations, laboratory procedures, and any other routine quality control check. The auditor(s) must examine notebooks and observe whether they have been properly reviewed at the laboratory and that there are no obliterations.

The auditor(s) must also evaluate the data package preparation practices. Such practices include the system used for the collection of various hard copy data, validation of results prior to data package release, completeness checks, generation of cover letters or case narratives, and retention of data packages at the laboratory.

4.9 QUALITY CONTROL MANUAL

The appropriateness and thoroughness of the laboratory's quality control manual, as well as the LQAM and analytical SOPs, must be evaluated prior to the audit. However, throughout the audit, the auditor(s) must verify if the laboratory is actually following the practices defined in their documents. Any deviations from the documented procedures must be discussed in the laboratory audit report.

4.10 DATA HANDLING

The auditor(s) must determine whether the laboratory's data handling procedures are adequate. Proper data handling techniques include the checking of calculations by a second person, documenting calculations, recording all corrective actions taken on rejected data, and properly documenting detection limits and quality control results. In addition, data must be retained at the laboratory for an appropriate amount of time.

4.11 SUMMARY

The auditor(s) must summarize the major points of the laboratory audit findings and the overall impact on the quality of the data issued from the laboratory. The summary should also reflect the overall attitude that the laboratory has toward quality assurance and quality control.

4.12 REPORT FORMAT

The laboratory audit report must contain the following sections in the following order. It must also contain a completed checklist as an attachment.

1. Introduction
2. Executive Summary
3. Audit Findings

The introduction should summarize who performed the audit, when the audit was performed, the name and location of the laboratory, and the laboratory's role in the RAMP. The Executive Summary should address the major findings of the laboratory audit along with the possible impact on the laboratory's data quality. The Audit Findings should follow the major headings of the checklist summarizing the findings presented on the checklist along with any recommendations for improvement or corrective action. The report will be signed by the auditor(s) who performed the audit.

5.0 TRAINING

The auditors conducting the laboratory audit must have demonstrated knowledge in laboratory quality assurance/quality control practices. This knowledge will include experience in analytical data validation and having conducted at least two prior laboratory audits.