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Rapid Method for Acid Digestion of Glass-Fiber and Organic/Polymeric Composition Filters and Swipes Prior to Isotopic Uranium, Plutonium, Americium, Strontium, and Radium Analyses for Environmental Remediation Following Homeland Security Events

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Revision History

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RAPID METHOD FOR ACID DIGESTION OF GLASS-FIBER AND ORGANIC/POLYMERIC COMPOSITION FILTERS AND SWIPES PRIOR TO ISOTOPIC URANIUM, PLUTONIUM, AMERICIUM, STRONTIUM, AND RADIUM ANALYSES

1. Scope and Application

1.1. The method will be applicable to the digestion of air particulate filters, removable contamination swipes and smears, and other similar sample matrices that may contain non-refractory materials or the matrix substrate is not refractory, prior to the chemical separation procedures described in the following procedures (see Reference 16.3[1]):

1.1.1. Rapid Radiochemical Method for Americium-241 in Water for Environmental Remediation Following Homeland Security Events.

1.1.2. Rapid Radiochemical Method for Plutonium-238 and Plutonium-239/240 in Water for Environmental Remediation Following Homeland Security Events.

1.1.3. Rapid Radiochemical Method for Isotopic Uranium in Water for Environmental Remediation Following Homeland Security Events.

1.1.4. Rapid Radiochemical Method for Radium-226 in Water for Environmental Remediation Following Homeland Security Events

1.1.5. Rapid Radiochemical Method for Total Radiostrontium (Sr-90) in Water for Environmental Remediation Following Homeland Security Events.

1.2. The method is specific for the rapid dissolution of glass-fiber or organic composition filters, and the associated particulate deposition collected during air sampling events following a radiological or nuclear incident. **An alternate method for sodium carbonate fusion is presented separately in the document, *Rapid Method for Sodium Carbonate Fusion of Glass-Fiber and Organic/Polymeric Composition Filters and Swipes Prior to Isotopic Uranium, Plutonium, Americium, Strontium, and Radium Analyses***. Generally, the sodium carbonate fusion technique should be chosen when refractory constituents are suspected in the sampled particulates or when the acidic digestion procedure is otherwise deemed to be ineffective because of refractory residuals or constituents. The Incident Commander (or designee, IC) should be involved in the selection of the appropriate digestion technique.

1.3. Application of this method by any laboratory to an air particulate filter sample must be validated by the laboratory using the protocols provided in *Method Validation Guide for Qualifying Methods Used by Radioanalytical Laboratories Participating in Incident Response Activities* (see Reference 16.1). In the absence of project-specific guidance, measurement quality objectives (MQOs) may be based on the Analytical Action Levels (AALs) and Required Method Uncertainties (u_{MR}) found in the *Radiological Sample Analysis Guide for Incidents of National Significance — Radionuclides in Air*, Appendix I (see Reference 16.2).

[1] Revision 0.1 for all five rapid methods in water were released in October 2011 and are available at www.epa.gov/erln/radiation.html and www.epa.gov/narel/incident_guides.html. These revisions addressed typographical errors, improved wording consistency with other methods, and clarified some examples. There were no substantive changes to any of the methods.

1.4. As this method is a gross pre-treatment technique, to be used prior to other separation and analysis methods, the user should refer to those individual methods and any project-specific requirements for the determination of applicable measurement quality objectives.

1.5. The dissolution of glass-fiber filters by this method is expected to take approximately one hour. This is based on a sample consisting of one 47-mm diameter filter, loaded with approximately 10 mg airborne particulate material. For organic filter matrices, an additional one and one-half hours is expected for dry ashing the sample prior to dissolution. For the dissolution of larger filters, or filters loaded with significantly more particulate material, additional time and proportionately larger volumes of reagents may be required.

2. Summary of Method

2.1. The method is based on the complete dissolution of both the filter material and the deposited particulates.

2.2. In the case of glass-fiber filters, the siliceous filter as well as deposited silicates are dissolved with direct application of hydrofluoric acid. The addition of nitric and hydrochloric acids facilitates the dissolution of the remaining solids. The sample digestate is taken to dryness and re-dissolved in nitric acid in preparation for the ensuing chemical separation techniques.

2.3. For filters composed of organic materials, such as cellulose or polypropylene, the preliminary step of dry ashing in a 450 °C muffle furnace is taken to destroy the organic filter material. Dissolution of the organic material in the sample is essential to the success of the subsequent ion-exchange chromatography analytical separation methodologies.

3. Definitions, Abbreviations and Acronyms

3.1. Discrete Radioactive Particles (DRPs or “hot particles”). Particulate matter in a sample of any matrix where a high concentration of radioactive material is contained in a tiny particle (μm range).

3.2. *Multi-Agency Radiological Analytical Laboratory Protocol* (MARLAP) Manual (See Reference 16.4).

4. Interferences and Limitations

4.1. Filters that contain large amounts of particulate material may result in persistent undissolved particulates in the digestion process during Step 11.2.5. These samples may require repeated application of the digestion procedure to cause a complete dissolution of the particulates.

4.2. In some cases particulate material may become dislodged during shipping or handling and may be found loose in the shipping envelope or container. For these samples, care should be taken to ensure a quantitative transfer of the sample to the digestion vessel. In some cases, it may become necessary to include the envelope for ashing and digestion, to ensure a quantitative transfer of material. Irregularities in sample processing such as these should be thoroughly documented and reported in the case narrative.

4.3. Most glass-fiber filters contain significant amounts of barium, which may ultimately interfere with the separation and analysis of radium, where that analyte is required. Initial characterization of the filter matrix to determine the content of elemental barium may help the laboratory make decisions about the optimum sample aliquot that the separation method will successfully process.

4.4. Some filters, particularly glass-fiber filters contain measurable quantities of naturally occurring radionuclides, such as uranium. The radionuclides native to the filter matrix should be measured and this activity should be considered in the assessment of the particulate results.

Matrix blanks, prepared with new, uncontaminated filters should be requested by the incident commander to assess the concentration of radionuclides native to the filter material. This may be done outside the scope of the initial background determination for the project, especially if the manufacture or lot number changes during the project.

4.4.1. In the preparation and analysis of matrix blanks the laboratory should verify with the incident commander that a sufficient number of blank filters are provided for analysis, and that those filters are of the same manufacture and lot (if practicable) as those used in the incident sampling.

4.4.2. In the absence of specific direction from the incident commander or in the project specifications, at least three uncontaminated filter blanks will be processed at the beginning of each project and the results of these analyses will be properly identified and reported to the incident commander.

4.5. In the analysis of air filters, where the available sample is limited and irreplaceable, the laboratory is strongly encouraged to reserve an aliquant of the sample digestate to allow for unforeseen analysis requirements, and to guard against the loss of sample through failure of the method or laboratory error. It is acknowledged that the creation of a reserve aliquant may not be possible in all cases, particularly where very low detection limits are required and the entire sample must be used.

4.6. Samples for which the creation of a reserve aliquant is appropriate, as well as samples with elevated activity and samples that require multiple analyses from a single filter, may need to be split after dissolution. In these cases care should be taken to carefully measure the initial digestate and the split fractions to ensure that the sample aliquant for analysis is accurately determined. The creation of multiple aliquants of a sample should be thoroughly documented and reported in the case narrative.

4.7. Samples that require the creation of multiple aliquants, or samples that require analyses for which the addition of tracers and carriers necessary for other tests may be an interferent (e.g., gross alpha/beta analyses), may necessitate the addition of those tracers and carriers to the individual split fractions of the sample, after dissolution. This necessary addition of tracers or carriers after the sample dissolution should be thoroughly documented and reported in the case narrative.

4.8. The subsequent chemical separation methods, which are referenced in Section 1.1 above, specify a sample size (in liters), which is used in the associated calculation of activity, uncertainty, etc.

4.8.1. When this method is employed and the entire volume of digestate is processed in the subsequent chemical separation method a sample size of "1 filter" is used in lieu of the water volume in all calculations, with the final results reported in units of activity per filter, rather than activity per liter.

4.8.2. In cases where the filter digestate is split prior to analysis the fractional aliquant of the filter is used for the sample size.

4.9. In some cases the IC may provide air volumes to be assigned to each filter and may request that the results are reported in units of activity per volume of air.

4.9.1. In cases where the entire filter is used for analysis, the volume of air volume, generally in liters or cubic meters, is used in place of the "1 filter" sample size described above.

4.9.2. When the sample is split prior to analysis, the sample size must reflect the product of the total sample volume times the fractional aliquant of the filter used for analysis.

4.10. Where volumetric or areal sample sizes are provided by the IC and used in the calculation of sample activity concentrations, the laboratory should note in the case narrative whether the uncertainties associated with these volumetric or areal measurements are included in the calculated combined standard uncertainty using this method.

4.11. As with any analytical method, QC requirements may be superseded by the IC and the project specifications. Nonetheless, this method attempts to address QC requirements and considerations, particularly those associated with the unique nature of air filters.

4.12. Duplicate analyses are not generally possible in air filters. Consequently, this procedure does not address the preparation of duplicate samples for analysis.

4.13. Similarly, matrix spikes are not generally possible, nor are they required in this procedure. At the direction of the incident commander, a specific sample may be requested for spiking and analysis. While the IC may use these results to evaluate potential matrix effects in the sample, this is not considered a matrix spike by the laboratory, and the laboratory will not correct or control a batch of samples based on the results.

4.14. In the preparation of blank samples and LCSs, care should be taken to create these QC samples as early in the process as possible, and to follow the same tracer/carrier additions, digestion process, and sample splitting used for the filed samples.

4.15. This procedure uses hydrofluoric acid (HF) to digest glass filters and any siliceous material in the sample. Do not use glass beakers in this method. The use of HF in glass beakers will damage the beakers and could result in catastrophic failure of the beakers during use, as well as the introduction of uranium and other radioactive constituents of glass into the sample. Only PTFE (Teflon®) beakers, or others impervious to HF, are to be used with this procedure.

4.16. Depending on the specific composition and manufacture, the PTFE beakers used in the acid digestion portion of this procedure may have a melting point as low as 400 ºC,

with a recommended performance temperature as low as 200 ºC. Care should be taken to perform this portion of the procedure at operating temperatures of 200 ºC or lower.

4.17. During the dry-ashing portion (Step 11.1.5) of this procedure, care should be taken to ensure that the glass beakers and the ribbed watch glasses are sufficiently durable to withstand the furnace temperature of 450 °C.

4.18. Although this method is applicable to a variety of subsequent chemical separation procedures, it is not appropriate where the analysis of volatile constituents such as iodine or polonium is required. The user of this method must ensure that analysis is not required for any radionuclide that may be volatile under these sample preparation conditions, prior to performing this procedure.

5. Safety

5.1. General

5.1.1. Refer to your laboratory safety manual for concerns of contamination control, personal exposure monitoring and radiation dose monitoring.

5.1.2. Refer to the laboratory chemical hygiene plan (or equivalent) for general safety rules regarding chemicals in the workplace.

5.2. Radiological

5.2.1. Hot particles (DRPs)

5.2.1.1. Hot particles will be small, on the order of 1 mm or less. Discrete radioactive particles are typically not evenly distributed in the media and their radiation emissions are not uniform in all directions (anisotropic).

5.2.1.2. Filter media should be individually surveyed for the presence of these particles, and this information should accompany the samples during processing.

5.3. Procedure-Specific Non-Radiological Hazards

5.3.1. Particular attention should be paid to addressing issues surrounding the use and handling of hydrofluoric acid (HF). HF is an extremely dangerous chemical used in this procedure. Appropriate PPE must be obtained and used in strict accordance with the laboratory safety program specification. The laboratory is strongly encouraged to consider having an appropriate topical binding agent, such as calcium gluconate gel, immediately available in the laboratory area.

5.3.2. The acid digestion process alternately generates siliceous fluoride fumes and strong acidic vapors, which present extreme respiratory hazards, as well as other heath risks. The entire digestion process should be carried out in a laboratory fume hood.

6. Equipment and Supplies

For samples with elevated activity concentrations of these radionuclides, labware should be used only once due to potential for cross contamination. The laboratory safety manual should provide guidance for making these decisions.

6.1. Adjustable temperature laboratory hotplates.

6.2. Dispensing pipette, 5 mL delivery volume. Alternately, a bottle-top dispenser, small volume graduated cylinder, or any other device for delivering nominal 5 mL volumes of reagents into the sample beaker.

6.3. Teflon beakers, 250 mL capacity.

6.4. Teflon spatula or rubber policeman.

6.5. Tweezers or forceps.

6.6. For organic filter matrices, the following equipment will also be needed:

6.6.1. Muffle furnace, for heating to 450 ºC.

6.6.2. Beakers, 250 mL capacity, Pyrex or equivalent.

6.6.3. Watch glasses, ribbed. These should be large enough to cover the beakers during dry ashing.

7. Reagents and Standards

Note: Unless otherwise indicated, all references to water should be understood to mean Type I Reagent water (ASTM D1193, see Reference 16.5).

7.1. Boric Acid, H_3BO_3, available commercially.

7.2. Water.

7.3. Hydrochloric acid (12 M), Concentrated HCl, available commercially.

7.4. Hydrofluoric acid (28 M), Concentrated HF, available commercially.

7.5. Nitric acid (16 M), Concentrated HNO_3, available commercially.

7.6. (For samples requiring Sr analysis) Nitric acid (8 M): Add 500 mL of concentrated HNO_3 to 400 mL of water and dilute to 1 L with water.

7.7. Radioactive tracers/carriers (used as yield monitors) and spiking solutions.

Refer to the chemical separation method(s) to be employed upon completion of this dissolution technique. Any tracers/carriers that are used to monitor chemical yield should be added at the beginning of this procedure. This allows for the monitoring of chemical losses in the digestion process, as well as in the chemical separation method. Carriers used to prepare sample test sources but not used for chemical yield determination (e.g., lanthanum added for uranium fluoride precipitation), should be added where indicated.

8. Sample Collection, Preservation, and Storage

There are no special collection, preservation, or storage considerations for this method.

9. Quality Control

9.1. In all cases, where the subsequent chemical separation technique requires the addition of carriers and radioactive tracers for chemical yield determinations, these are to be added prior to beginning the dissolution procedure, unless there is good technical justification for doing otherwise.

9.2. Batch quality control results shall be evaluated and meet applicable analytical project specifications (APSs) prior to release of unqualified data. In the absence of project-defined APS or a project-specific quality assurance project plan (QAPP), the quality control sample acceptance criteria defined in the laboratory quality manual and procedures shall be used to determine acceptable performance for this method.

9.3. A laboratory control sample (LCS), which consists solely of the reagents used in this procedure and a known quantity of radionuclide spiking solution, shall be run with each batch of samples. The concentration of the LCS should be at or near the action level or level of interest for the project.

9.4. One reagent blank shall be run with each batch of samples. The reagent blank should consist solely of the reagents used in this procedure. The reagent blank should not include a blank filter.

The purpose and use of matrix blanks is described in Section 4.4. At the discretion of the IC, when matrix blanks are analyzed with each batch, and the native filter constituents are sufficiently well characterized so that incidents of laboratory contamination may be differentiated from native blank filter activity, the use of reagent blanks described in this section may be omitted.

9.5. In the case of organic-matrix filters, precaution should be taken to ensure that the tracers, carriers, and spiking solutions used in the QC samples remain soluble and do not preferentially adhere to the vessel during the dry-ashing process (Step 11.1). For samples that need to be dry-ashed, the tracers, carriers, and spiking solutions used in the QC samples should be spiked onto an analyte-free material, such as ashless filter paper.

9.6. This method does not define quality control parameters or acceptance criteria. Those quality control factors are defined in the individual separation methods that follow this technique.

10. Calibration and Standardization

10.1. Refer to the individual chemical separation and analysis methods for calibration and standardization protocols.

11. Procedure

11.1. For organic filter matrices, the preliminary step of destroying the filter by dry ashing is necessary prior to dissolution of the particulate material. For glass-fiber filters, skip to Step 11.2.

11.1.1. Remove the filter from its container or sleeve, using a clean forceps if necessary, and transfer the filter into a 250-mL glass beaker.

11.1.2. If any loose particulate material is present transfer that material to the beaker as well.

11.1.3. Add any necessary tracers or carriers, as prescribed in the subsequent chemical separation methods, adding the solution directly onto the filter material. The tracer solution should be absorbed into the filter material, if possible.

11.1.4. If the total volume of tracers used exceeds 2 mL, dry the sample on a hotplate before proceeding. Otherwise, proceed directly to the next step.

11.1.5. Cover the beaker with a ribbed watch glass and heat in a muffle furnace at 450 ºC for one hour, or until the sample is completely ashed.

11.1.6. Remove from furnace to cool, approximately 15 minutes.

11.1.7. When the beaker is cool, add 5 mL concentrated nitric acid and heat gently on a hot plate to dissolve the ashed material. Use a spatula or rubber policeman, if necessary, to dislodge the ashed material from the surface of the beaker.

11.1.8. Transfer the sample to a Teflon beaker.

11.1.9. Rinse the glass beaker and watch glass into the Teflon beaker using small portions of an additional 5 mL rinse of concentrated nitric acid.

11.1.10. Rinse the glass beaker again into the Teflon beaker using a 5 mL rinse of concentrated hydrochloric acid.

11.1.11. Add 5 mL concentrated HF to the Teflon beaker.

11.1.12. Go to Step 11.2.6.

11.2. For glass-fiber filters.

11.2.1. Remove the filter from its container or sleeve, using a clean forceps if necessary, and transfer the filter into a 250-mL Teflon beaker.

11.2.2. If any loose particulate material is present transfer that material to the beaker as well.

11.2.3. Add any necessary tracers or carriers, as prescribed in the subsequent chemical separation methods, adding the solution directly onto the filter material. The tracer solution should be absorbed into the filter material, if possible.

11.2.4. In a fume hood, carefully add 5 mL concentrated hydrofluoric acid. The reaction will be vigorous and will immediately destroy the glass filter material.

11.2.5. Add 5 mL each of concentrated nitric acid and concentrated hydrochloric acid.

11.2.6. Heat the beaker on a hotplate to a maximum of 200º C, taking the sample to dryness.

11.2.7. If the sample is to be analyzed for actinides, add approximately 0.5 g H_3BO_3, otherwise skip to Step 11.2.8.

11.2.8. Add 5 mL concentrated HNO_3 and continue heating to re-dissolve the residue and to effect a complete conversion to a nitrate environment.

11.2.9. Once the sample is dissolved, heat gently to dryness.

11.2.10. Proceed to the chemical separation methods. In all cases omit the initial addition of tracers and carriers used for yield determinations, as those reagents were added at the beginning of the digestion process.

Note: The counting time stated in Section 1.4 of the applicable rapid water method must be reevaluated for the required air filter or swipe MQOs as well as the expected chemical yield, aliquanting of the sample, and for air filters a nominal sample volume.

11.2.10.1. For actinide analyses, proceed directly to any of those methods listed in Steps 1.1.1, 1.1.2, or 1.1.3, proceeding directly to Step 11.2, "*Actinide Separations using Eichrom resins*."

11.2.10.2. For radium analysis, the sample will need to be converted to a hydrochloric matrix before continuing. Proceed directly to the method listed in Step 1.1.4, proceeding directly to Step 11.1.6, "*Reconstitute the sample with an additional 10 mL of hydrochloric acid…*"

11.2.10.3. For strontium analysis, dissolve sample residue in 5 mL 8 M HNO_3, then proceed directly to the method listed in Step 1.1.5, proceeding directly to Step 11.11, "*Set up a vacuum box for Sr-Resin™ columns…*"

12. Data Analysis and Calculations

12.1. Equations for determination of final result, combined standard uncertainty and radiochemical yield (if required) are found in the corresponding chemical separation and analysis methods.

12.2. In cases where the creation of a reserve aliquant is appropriate, as well as samples with elevated activity and samples that require multiple analyses from a single filter, the sample should be split after dissolution. In these cases care should be taken to carefully measure the mass or volume of the entire final digestate, and the mass or volume of the subsequent split fractions to ensure that the sample aliquant for analysis is accurately determined. The selection of equipment for volumetric and gravimetric measurements should reflect the analytical requirements; the uncertainty of the measurement should be controlled at a level that is consistent with the analysis Measurement Quality Objectives (MQOs). The creation of multiple aliquants of a sample should be thoroughly documented and reported in the case narrative.

12.3. The sample aliquant size for analysis is calculated:

$$V_a = V_s \times (D_a / D_s)$$

Where:

V_s = the original sample size, in the units designated by the IC (e.g., 100 cm^2, 68.5 m^3, etc.)

D_s = the mass or volume of the entire final digestate, created in Step 11.2.10 of this procedure (e.g. 100 g, 50 mL, etc.).

D_a = the mass or volume of the aliquant of digestate used for the individual analyses, as described in the various parts of Step 11.14 of this procedure

(e.g. 25 g, 5.0 mL, etc.). Note that the values for D_a must be in the same units used in D_s.

V_a = the sample aliquant size, used for analysis, in the units designated by the IC (e.g., 25 cm^2, 6.85 m^3, etc.).

12.4. The laboratory should ensure that the additional uncertainty associated with splitting the sample is included in the calculation of the standard uncertainty of the sample volume, generally referred to as $u(V_a)$ in the associated chemical separation methods described in Section 1.1 above. The laboratory should also note in the case narrative, or appropriate documentation, that this additional uncertainty has been incorporated into the final combined standard uncertainty (CSU) calculation.

13. Method Performance

13.1. Method validation results may be found in the attached appendices.

13.2. Expected turnaround time per batch:

13.2.1. For 47-mm diameter glass-fiber filters, the digestion should add approximately one hour to the time specified in the individual chemical separation methods.

13.2.2. For 47-mm organic matrix filters requiring dry ashing and digestion, approximately two and one-half hours should be required, in addition to the time specified in the individual chemical separation methods.

14. Pollution Prevention: This method utilizes the smallest volumes of inorganic acids that are reasonably expected to perform the required dissolution in the samples. This approach significantly reduces the acid volumes and the energy required for drying, as compared to conventional techniques that are standard in the industry.

15. Waste Management

15.1. For each sample analyzed, 20 – 25 mL concentrated inorganic acids, including nitric, hydrochloric, and hydrofluoric, are dried completely and the volatilized vapors are exhausted through the laboratory fume hood. The fume hood should be equipped with a water scrubber or other means for removing the acid vapors from the exhaust air. The resulting acidic effluent water should be evaluated to ensure that all local, state, and federal disposal requirements are met.

16. References

16.1. U.S. Environmental Protection Agency (EPA). 2009a. *Method Validation Guide for Qualifying Methods Used by Radiological Laboratories Participating in Incident Response Activities*. Revision 0. Office of Air and Radiation, Washington, DC. EPA 402-R-09-006, June. Available at: www.epa.gov/narel/incident_guides.html and www.epa.gov/erln/radiation.html.

16.2. U.S. Environmental Protection Agency (EPA). 2009b. *Radiological Laboratory Sample Analysis Guide for Incidents of National Significance–Radionuclides in Air*. Revision 0. Office of Air and Radiation, Washington, DC. EPA 402-R-09-007, June. Available at: www.epa.gov/narel/incident_guides.html and www.epa.gov/erln/radiation.html.

16.3. U.S. Environmental Protection Agency (EPA). 2010. *Rapid Radiochemical Methods for Selected Radionuclides in Water for Environmental Restoration Following Homeland Security Events*, Office of Air and Radiation, National Air and Radiation Environmental Laboratory. EPA 402-R-10-001, February. Revision 0.1 of rapid methods issued October 2011. Available at: www.epa.gov/narel/incident_guides.html and www.epa.gov/erln/radiation.html.

16.4. MARLAP. 2004. *Multi-Agency Radiological Laboratory Analytical Protocols Manual*. Volumes 1 – 3. Washington, DC: EPA 402-B-04-001A-C, NUREG 1576, NTIS PB2004-105421. July. Available at: www.epa.gov/radiation/marlap/.

16.5. ASTM D1193, "Standard Specification for Reagent Water" ASTM Book of Standards 11.01, current version, ASTM International, West Conshohocken, PA.

17. Flow Chart