Observations and Experience in Maintaining Consistent Analyzer Performance at Low Concentrations of O_3, NO_x, SO_2, and CO

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Monitoring @ Low Ambient Concentrations

- Why
- What
- Sources of Error and Minimizing Their Effect
- Pollutant Specific Caveats

Monitoring @ Low Ambient Concentrations

Why?

Monitoring @ Low Ambient Concentrations – Why? NCore

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NCore Multipollutant Monitoring Network

NCore is a multi pollutant network that integrates several advanced measurement systems for particles, pollutant gases and meteorology. Most NC
start of the network on January 1, 2011.

Monitoring Objectives

The NCore Network addresses the following objectives:

- Timely reporting of data to public by supporting AIRNow, air quality forecasting, and other public reporting mechanisms;
- Support for development of emission strategies through air quality model evaluation and other observational methods;
- Accountability of emission strategy progress through tracking long-term trends of criteria and non-criteria pollutants and their precursors;
- Support for long-term health assessments that contribute to ongoing reviews of the NAAQS;
- Compliance through establishing nonattainment/attainment areas through comparison with the NAAQS;
- Support to scientific studies ranging across technological, health, and atmospheric process disciplines; and
- Support to ecosystem assessments recognizing that national air quality networks benefit ecosystem assessments and, in turn, benefit from

Measurements

Monitoring @ Low Ambient Concentrations – Why?
Ncore (continued)

Measurements

Parameter	Comments
PM2.5 speciation	Organic and elemental carbon, major ions and trace metals (24 hour average; every 3rd day); IMPROVE or CSN
PM2.5 FRM mass	24 hr. average at least every 3rd day
continuous PM2.5 mass	1 hour reporting interval; FEM or pre-FEM monitors
PM(10-2.5) mass	Filter-based or continuous
ozone (O3)	all gases through continuous monitors
carbon monoxide (CO)	capable of trace levels (low ppm and below) where needed
sulfur dioxide (SO2)	capable of trace levels (low ppb and below) where needed
nitrogen oxide (NO)	capable of trace levels (low ppb and below) where needed
total reactive nitrogen (NOy)	capable of trace levels (low ppb and below) where needed
surface meteorology	wind speed and direction (reported as "Resultant"), temperature, RH

Monitoring @ Low Ambient Concentrations– Why?
Auditing - 40 CFR Part 58 Appendix A

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Title 40: Protection of Environment

PART 58—AMBIENT AIR QUALITY SURVEILLANCE

Monitoring @ Low Ambient Concentrations – Why?
Auditing - 40 CFR Part 58 Appendix A

3.1.2.1 The evaluation is made by challenging the monitor with audit gas standards of known concentration from at least three audit levels. One point must be within two to three times the method detection limit of the instruments within the PQAOs network, the second point will be less than or equal to the 99th percentile of the data at the site or the network of sites in the PQAO or the next highest audit concentration level. The third point can be around the primary NAAQS or the highest 3-year concentration at the site or the network of sites in the PQAO. An additional 4th level is encouraged for those agencies that would like to confirm the monitors' linearity at the higher end of the operational range. In rare circumstances, there may be sites measuring concentrations above audit level 10. Notify the appropriate EPA region and the AQS program in order to make accommodations for auditing at levels above level 10.

Audit level	Concentration Range, ppm			
	O_3	SO_2	NO_2	CO
1	0.004-0.0059	0.0003-0.0029	0.0003-0.0029	0.020-0.059
2	0.006-0.019	0.0030-0.0049	0.0030-0.0049	0.060-0.199
3	0.020-0.039	0.0050-0.0079	0.0050-0.0079	0.200-0.899
4	0.040-0.069	0.0080-0.0199	0.0080-0.0199	0.900-2.999
5	0.070-0.089	0.0200-0.0499	0.0200-0.0499	3.000-7.999
6	0.090-0.119	0.0500-0.0999	0.0500-0.0999	8.000-15.999
7	0.120-0.139	0.1000-0.1499	0.1000-0.2999	16.000-30.999
8	0.140-0.169	0.1500-0.2599	0.3000-0.4999	31.000-39.999
9	0.170-0.189	0.2600-0.7999	0.5000-0.7999	40.000-49.999
10	0.190-0.259	0.8000-1.000	0.8000-1.000	50.000-60.000

What are "Low Ambient Concentrations" ?

Monitoring @ Low Ambient Concentrations - What

OAQPS Memo On 10 Audit Levels & Acceptance Criteria

Established November 18, 2010

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
RESEARCH TRIANGLE PARK, NC 27711

FEB 17 2011

OFFICE OF
AIR QUALITY PLANNING
AND STANDARDS

MEMORANDUM

SUBJECT: Guidance on Statistics for Use at Audit Levels 1 and 2 of the Expanded List of Audit Levels for Annual Performance Evaluation for SO_2, NO_2, O_3, and CO as Described in 40 CFR Part 58 Appendix A Section 3.2.2

FROM: Lewis Weinstock, Group Leader Lewis Weinstock
Mike Papp, QA Team Lead Mike Papp
Ambient Air Monitoring Group (C304-06)

TO: Air Monitoring Program Managers and Staff

On November 18, 2010, a technical memorandum[1] that allowed for the expansion of the performance evaluation audit levels from five (currently in CFR) to ten was distributed. The expansion allowed EPA to provide lower audit levels for use at NCore sites or sites reporting low routine concentrations and tightened up the span within each level to provide more choices of ranges where routine concentrations are being measured.

We have received comment from monitoring organizations and EPA Regions expressing concerns that the lower audit ranges will create large, unreasonable percent differences (PDs) if the same statistics and current acceptance limits are used. They are suggesting that EPA look to a different statistic at these lower audit ranges.

Using 1-point QC check data and annual performance evaluation data in AQS, recent NPAP through-the-probe data at NCore sites and some low concentration calibration information from our RTP Ambient Air Innovation Research Station (AIRS), EPA evaluated the effect of low-level concentrations against our current PD statistic. Attachment 1 provides the results of this evaluation.

[1] Expanded List of Audit Levels for Annual Performance Evaluation for SO_2, NO_2, O_3, and CO as Described in 40 CFR Part 58 Appendix A Section 3.2.2 http://www.epa.gov/ttn/amtic/cpreldoc.html

Monitoring @ Low Ambient Concentrations - What

OAQPS Memo On 10 Audit Levels & Acceptance Criteria - Summarized

EPA Ambient Air Audit Levels				
	Concentration in ppb			Conc. In ppm
Level	O3	SO2	NO2	CO
1	4-5.9	0.3-2.9	0.3-2.9	0.02-0.059
2	6-19	3-4.9	3-4.9	0.06-0.199
3	20-39	5-7.9	5-7.9	0.20-0.899
4	40-69	8-19.9	8-19.9	0.9-2.999
5	70-89	20-49.9	20-49.9	3-7.999
6	90-119	50-99.9	50-99.9	8-15.999
7	120-139	100-149.9	100-149.9	16-30.999
8	140-169	150-259.9	150-259.9	31-39.999
9	170-189	260-799.9	260-799.9	40-49.999
10	190-259	800-1000	800-1000	50-60
Audit Limits for SO2 & NO2 are ±15% and @ Levels 1 and 2 ±1.5 ppb				
Audit Limits for CO are ±15% and @ Levels 1 and 2 ±0.03 ppm				

Low Ambient Concentrations - QA/QC

The lower concentration limits we are discussing today will be:

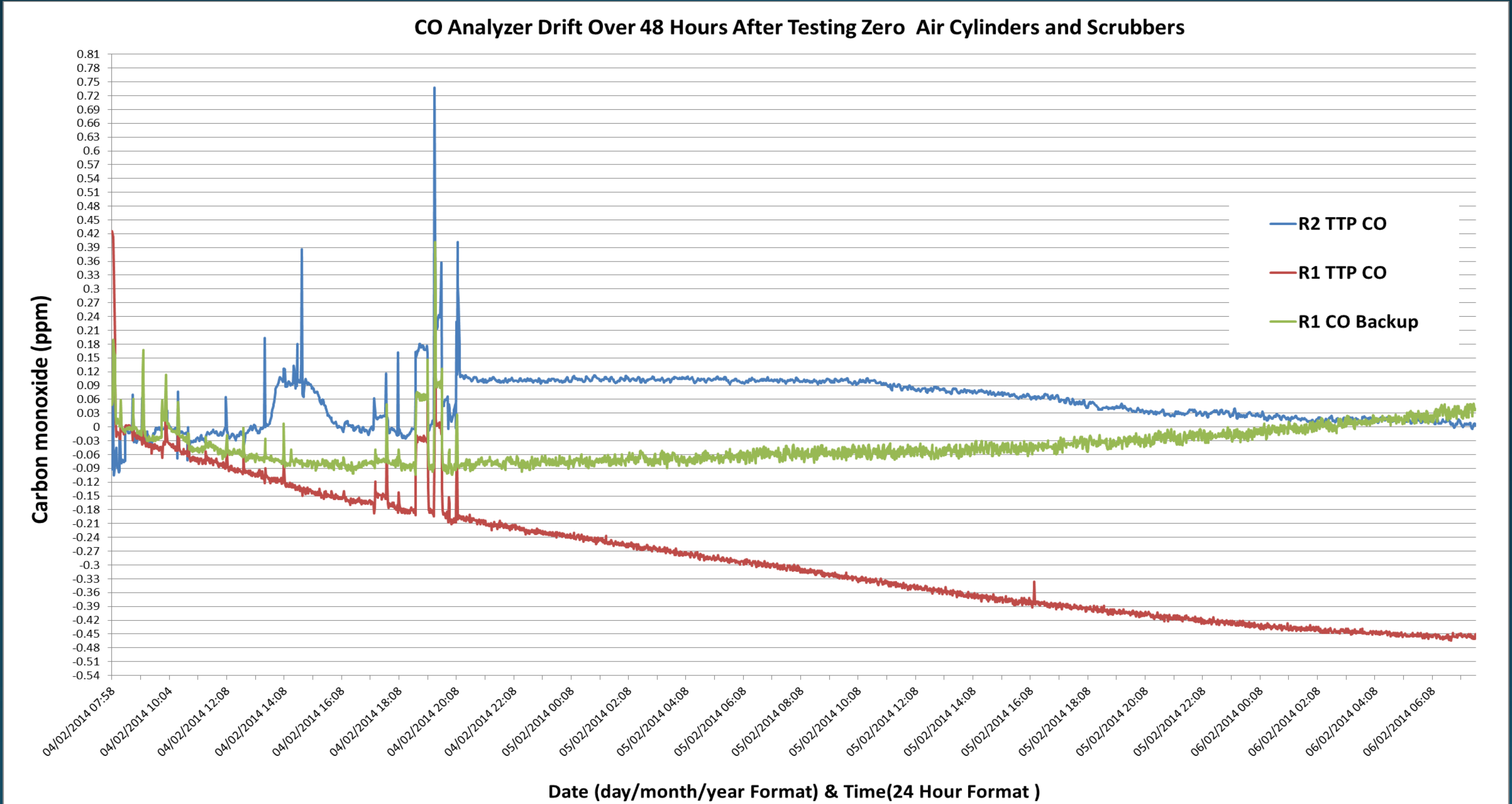
- O_3 = 5-20 ppb
- SO_2 & NO_2 = 1-8 ppb
- CO = 50 -250 ppb

These levels are @ audit levels 1-3. QA/QC @ Level 1 audit concentrations requires more equipment and benefits from previous experience at audit levels 2 and 3.

Low Ambient Concentration Monitoring/Auditing – Sources of Error

- Analyzer zero drift
- Flow measurement error increases at lower flow ranges
- Gas standard accuracy/impurities at low concentrations
- Zero gas contamination
- Gas manifold/flow path cleanliness

Minimizing Sources of Error – Zero Drift



Minimizing Sources of Error – Zero Drift

Adjusting Expectations

Minimizing Sources of Error – Zero Drift

Adjust Expectations - Zero Drift

Table 2. Zero Drift Results from Monitoring Organization Data Submittals

	Number of	Using Absolute Value SD			
Pollutant	Monitors	Avg ABS Zero	ABS SD	2*SD+Avg	3*SD+Avg
CO (ppm)	17	0.091	0.098	0.288	0.386
NO2 (ppb)	10	0.377	0.519	1.414	1.933
SO2 (ppb)	16	0.386	0.410	1.209	1.614
O3 (ppb)	49	0.585	0.571	1.716	2.282

Data published in QA Eye Issue 16, June 2014

Minimizing Sources of Error – Flow Measurement

Lower Part of Flow Range = Greater Bias

Comparison of ML-800 vs Definer 220

100 cc/min MFC

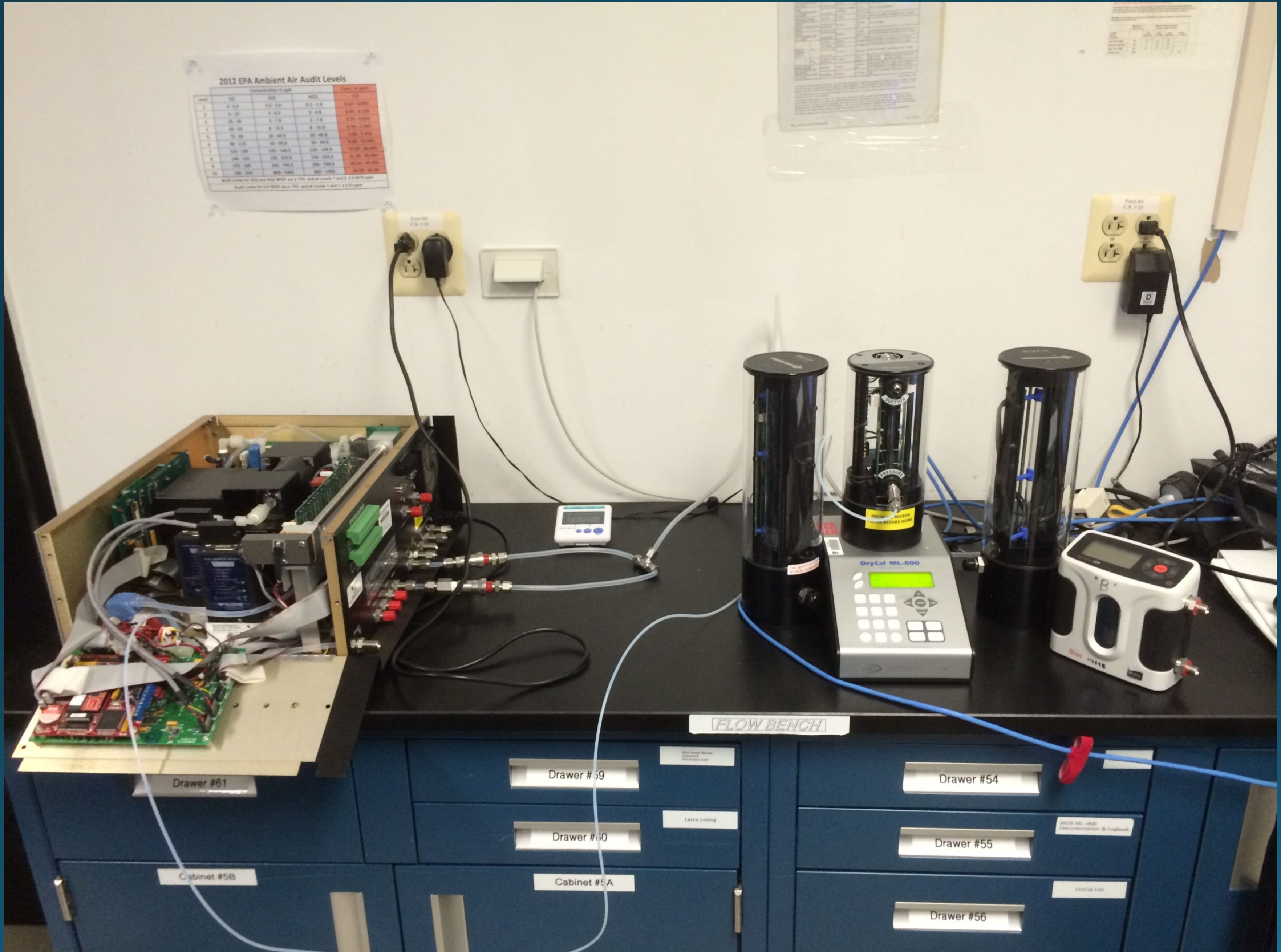
MFC Setting (cc/min)	EPA R2 ML-800 reading	R2 Definer 220	% error R2 Definer vs. ML-800	REGRESSION CORRECTED FLOW R2 Definer 220	REGRESSION CORRECTED FLOW % error R2 Definer vs. ML-800
100	99.23	98.98	-0.25%	99.11	-0.12%
90	89.28	89.16	-0.13%	89.30	0.02%
80	79.30	79.22	-0.10%	79.37	0.10%
70	69.36	69.09	-0.39%	69.25	-0.16%
60	59.43	59.30	-0.22%	59.48	0.08%
50	49.53	49.52	-0.02%	49.71	0.37%
40	39.56	39.41	-0.38%	39.61	0.14%
30	29.65	29.44	-0.71%	29.66	0.03%
20	19.72	19.41	-1.57%	19.64	-0.40%
10.5	10.31	9.99	-3.10%	10.23	-0.75%

10 cc/min MFC

MFC Setting (cc/min)	EPA R2 ML-800 reading	R2 Definer 220	% error R2 Definer vs. ML-800	REGRESSION CORRECTED FLOW R2 Definer 220	REGRESSION CORRECTED FLOW % error R2 Definer vs.
10	9.81	9.35	-4.69%	9.77	-0.42%
8	7.82	7.46	-4.59%	7.89	0.89%
6	5.85	5.41	-7.47%	5.85	0.04%
4	3.90	3.40	-12.82%	3.85	-1.28%
2	1.91	1.47	-23.04%	1.93	1.05%

Note the ability to correct Definer 220 bias @ low flow levels by calibrating with a superior flow standard.

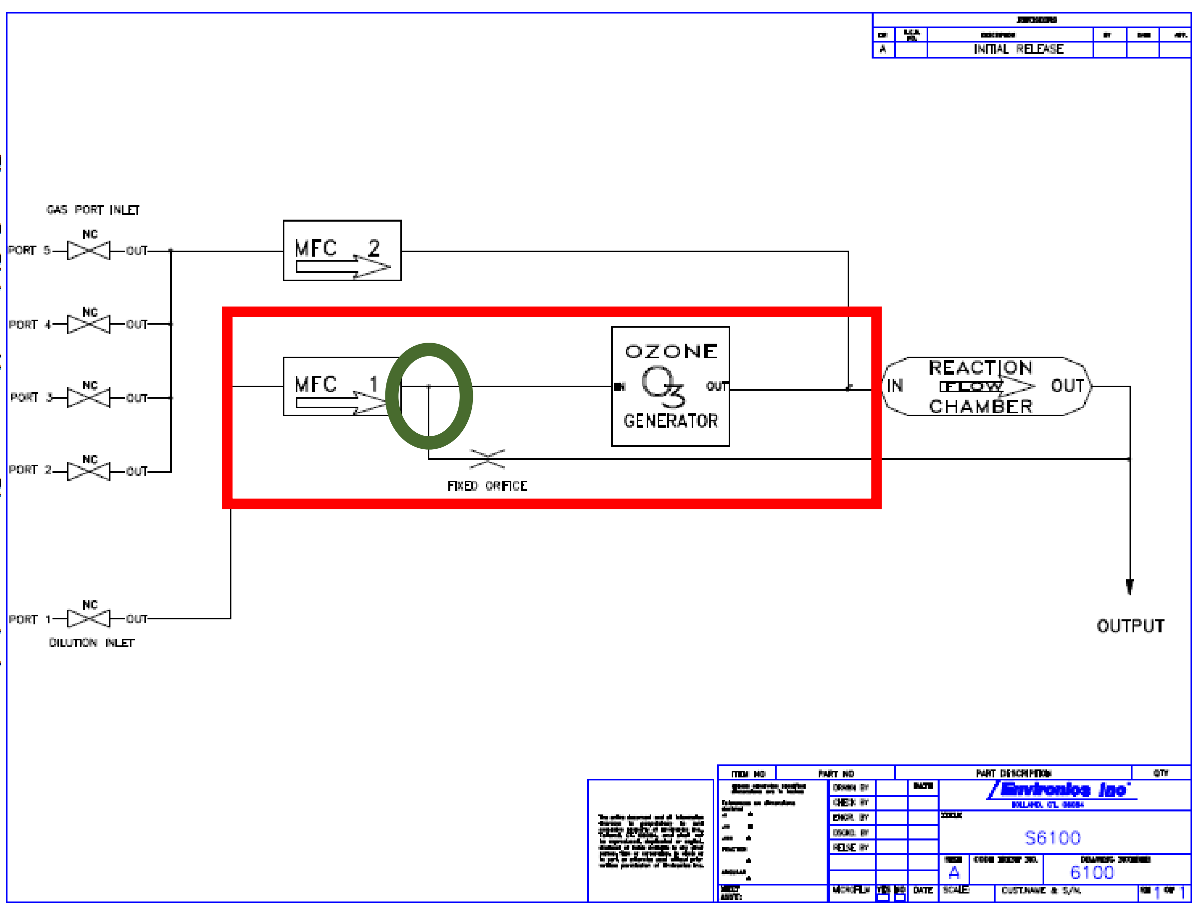
Minimizing Sources of Error – Flow Measurement



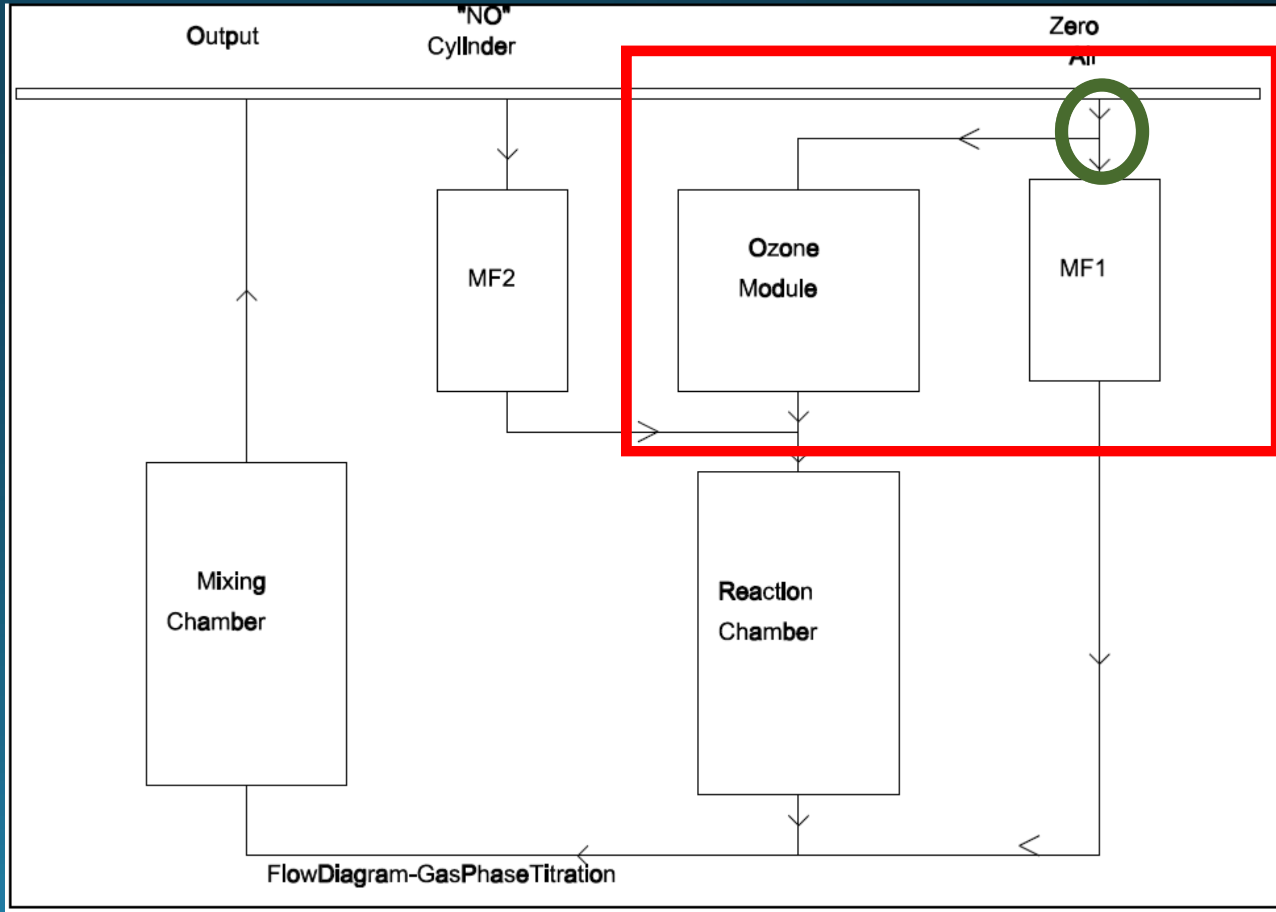
Minimizing Sources of Error – Flow Measurement

Use simple GPT devices. Exercise caution with devices that bypass the MFC for ozonator flow, because total diluent flow can only be measured at the output.

Simple Setup/post MFC bypass for O3



Caution- pre MFC bypass for O3



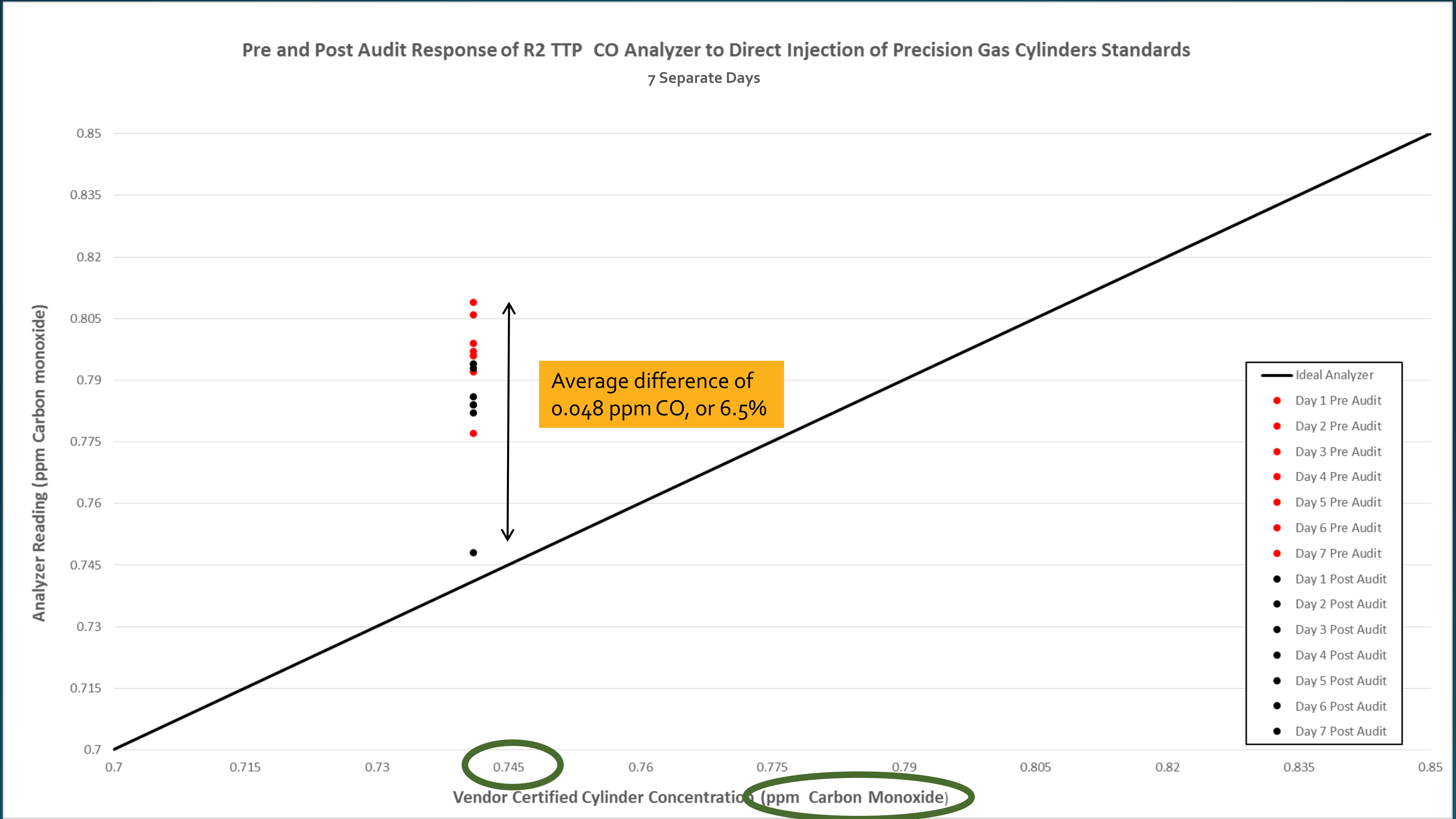
Minimizing Sources of Error – Flow Measurement

Avoid flows below 5 cc/min, unless you have access to BIOS ML-500/800 or DH Instrument Molbloc/Molbox or equivalent for calibration to 2 cc/min.

Have flow standards calibrated against higher quality standards at least annually.

Recommended to have access to a separate flow device(s) to compare against, to examine for drift/departure from calibration

Minimizing Sources of Error – Gas Standards



Minimizing Sources of Error – Gas Standards

- Use gas standards at levels that can be verified independently by NIST SRMs or equivalent.

- Practically, this means standards should not be lower than the following concentrations:

  SO_2 > 10 ppm

  NO/NOx >10 ppm; check for NO_2 impurity

  CO >400 ppm

  O_3 has no specific recommendation, as analyzer accuracy at low levels (5-30 ppb has not been a problem).

Note: At these concentrations, the cylinder standards will likely have a longer certification period, good for multiple years. Very Low level standards (single digit ppm) usually have 6-12 month certifications

Minimizing Sources of Error – Gas Standards

- Ideal cylinder concentrations for audit levels 1-5:

  - CO = 500 ppm
  - NO = 20 ppm
  - SO_2 = 10 ppm

When doing NO_2 GPT, titrate with O_3 until 50% of the NO is converted to NO_2. 50% of the gas should remain as NO. This is why there is 2x the NO concentration in the cylinder vs as SO_2.

  - O_3 = @ Higher flow rates (20L/min) lower O_3 concentrations are more easily generated due to the amount of dilution possible

Minimizing Sources of Error – Gas Standards

GPT device should have 3 MFC's at the following flow ranges:

- 0-20L/min diluent flow
- 0-100 cc/min pollutant flow
- 0-10 cc/min pollutant flow

Minimizing Sources of Error – Gas Standards Audit Level 1 Concentrations

- Using gas standards at the above stated concentrations, with a practical lower limit of 2 cc/min for the pollutant MFC, will require zero gas flow rates of 20L/min. With this setup, Level 1 audit concentrations are achievable.

$$\frac{(10 \text{ ppm } SO_2 \text{ gas std}) \times (2 \text{ cc/min MFC set})}{(20 \text{ L/min} + 2 \text{ cc/min})} = 1.0 \text{ ppb } SO_2 \text{ gas delivered}$$

$$\frac{20 \text{ ppm NOgas std}) \times (2 \text{ cc/min MFC set})}{(20 \text{ L/min} + 2 \text{ cc/min})} = 2.0 \text{ ppb NO gas delivered}$$

, titrate with O_3 @ 1.0 ppb to obtain 1.0 ppb NO_2

$$\frac{(500 \text{ ppm COgas std}) \times (2 \text{ cc/min MFC set})}{(20 \text{ L/min} + 2 \text{ cc/min})} = 0.0499 \text{ ppm CO gas delivered}$$

It is almost impossible to get > 24 L/min flows through the thick walled ¼ o.d. x 1/8" i.d. tubing used in most zero air generators. This is before using any additional scrubbers beyond purafill/charcoal. 30L/min specifications for zero air have not been found to be achievable.

Minimizing Sources of Error – Gas Standards
Audit Level 5 Concentrations

With the ideal cylinder blend, and a low MFC setting of 100 cc/min, Audit Level 5 levels can be achieved:

$$\frac{(10\ \text{ppm } SO_2 \text{ gas std}) \times (100\ \text{cc/min MFC set})}{(20\ \text{L/min} + 100\ \text{cc/min})} = 49.7\ \text{ppb } SO_2 \text{ gas delivered}$$

$$\frac{(20\ \text{ppm NOgas std}) \times (100\ \text{cc/min MFC set})}{(20\ \text{L/min} + 100\ \text{cc/min})} = 99.5\ \text{ppb NO gas delivered}$$

, titrate with O_3 @ 50 ppb to obtain 50 ppb NO_2

$$\frac{(500\ \text{ppm CO gas std}) \times (100\ \text{cc/min MFC set})}{(20\ \text{L/min} + 100\ \text{cc/min})}$$

2.49 ppm CO gas delivered

lowering diluent flow rate to 10L min yields

4.95 ppm CO (Audit Level 5)

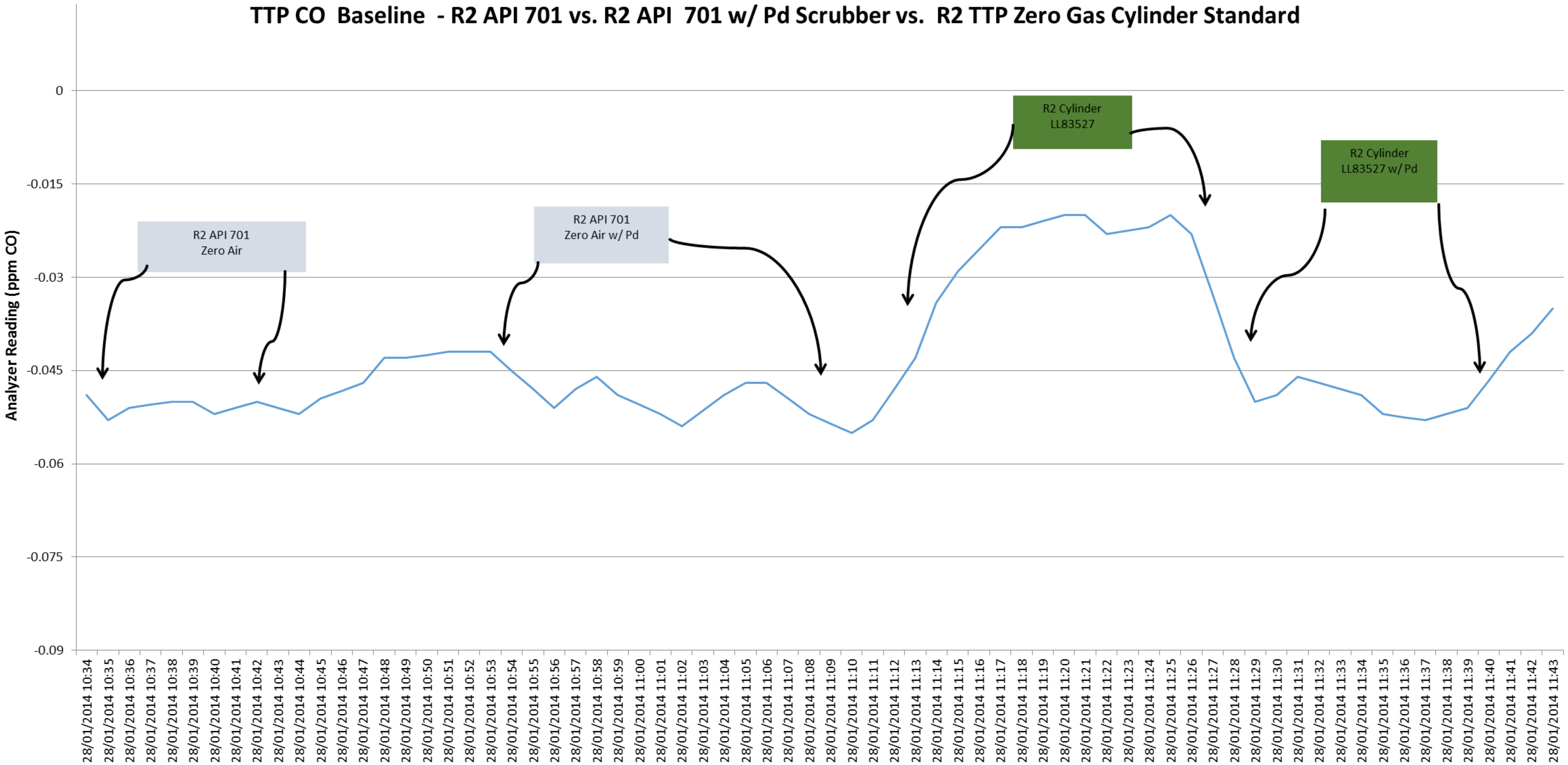
Minimizing Sources of Error – Gas Standards

For ozone, do not use an "all in one" GPT + photometer device.

Backpressure will cause inaccurate ozone readings at the higher flow rates needed.

Instead, use a GPT device with an ozone generator, and use an outboard ozone analyzer for determining the levels of ozone generated.

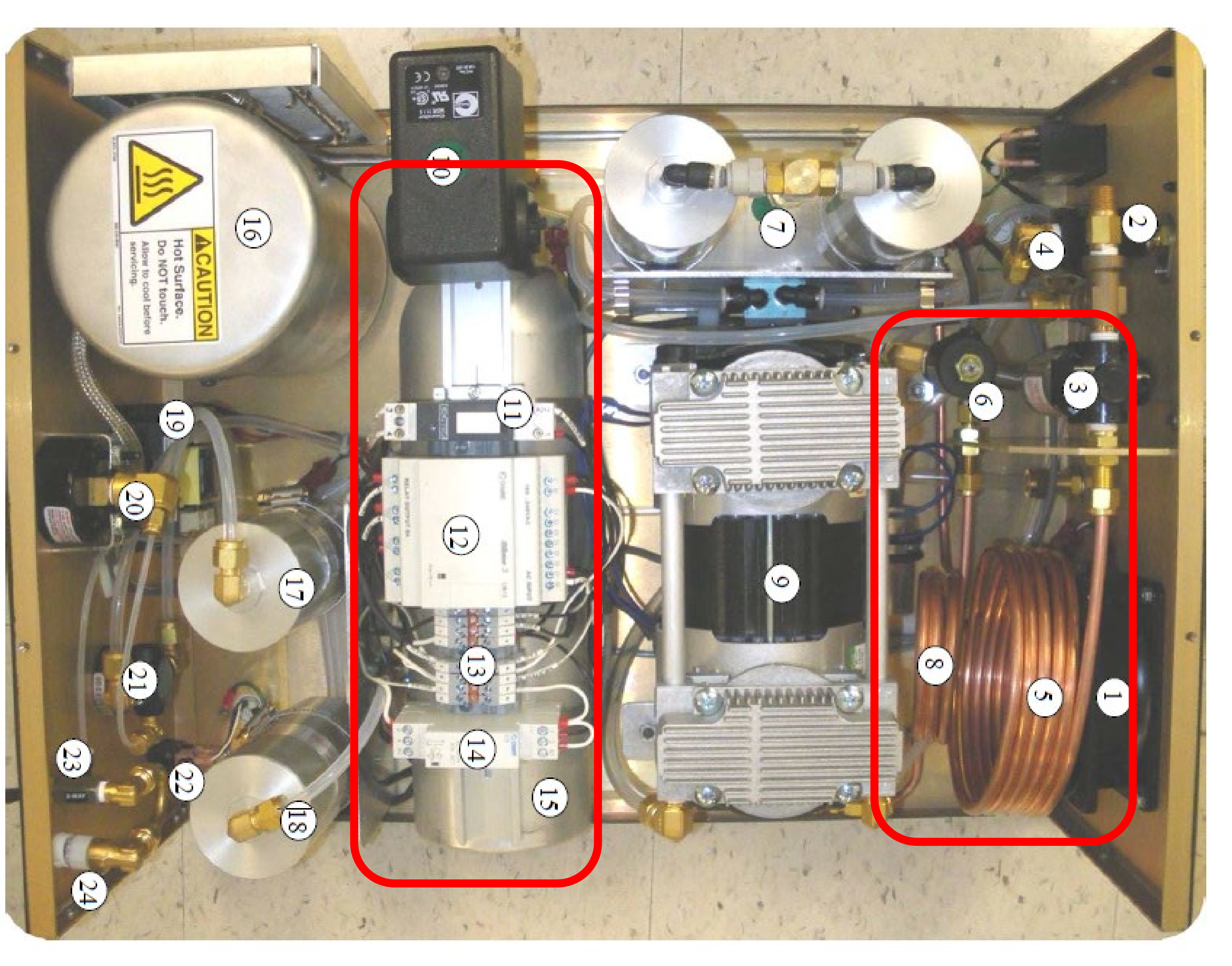
Minimizing Sources of Error – Zero Gas



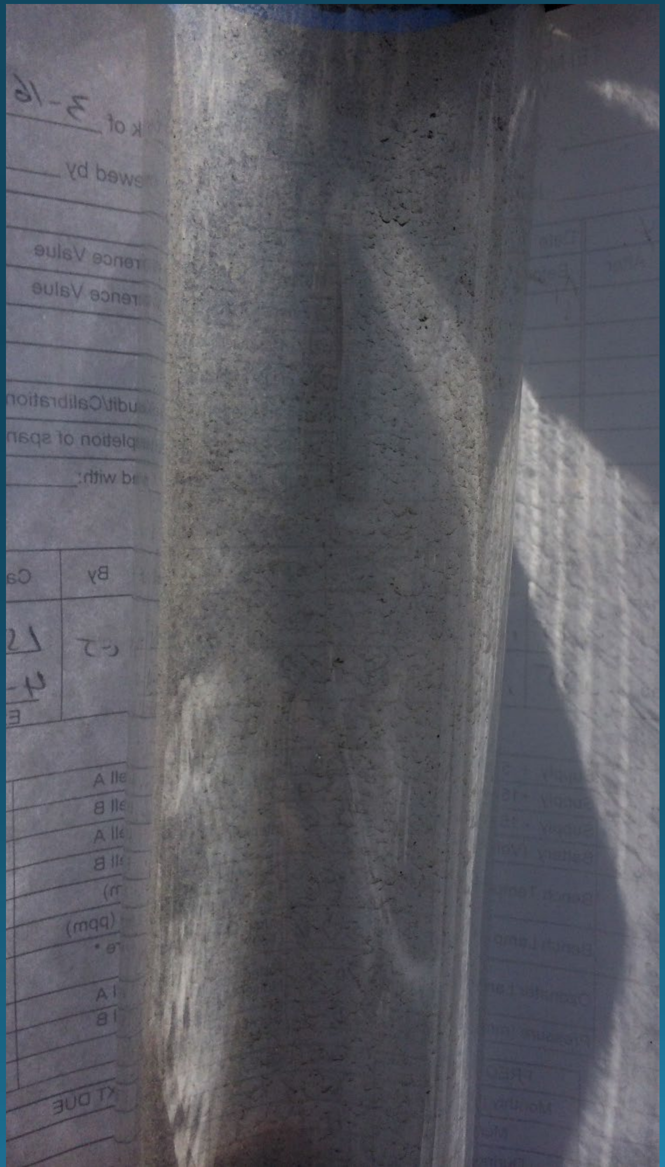
Minimizing Sources of Error – Zero Gas

- Scrub zero gas of all moisture – Environics/API type zero air supplies with compression drying (90 psi) is better than drierite/nafion alone.
- Use charcoal and purafill scrubbers.
- Use palladium on alumina for CO scrubbing.

Minimizing Sources of Error – Zero Gas



Minimizing Sources of Error – Manifold Cleanliness



Minimizing Sources of Error – Manifold Cleanliness

- Keep manifolds/tubing clean
- Keep flow rates high to minimize residence time.
- Manifold contamination usually eliminates a constant level of pollutant, independent of sample concentration.
- Manifold contamination is typically a surface area phenomenon. Affected by contact area x residence time.

Pollutant Specific Observations - O_3

- O_3 analyzers are very accurate and linear to 5 ppb (or lower)
- Valves and intricate tubing can catch dirt and scrub ozone.
- Do not use "all in one" GPT devices

Pollutant Specific Observations – SO_2

- SO_2 equilibration is at least 45 minutes – 1 hour for the first point.

- When switching MFC's to get lower flows (i.e. from 0-100 cc/min MFC to 0-10 cc/min MFC), the system needs to re-equilibrate for at least 30-45 minutes.

- Gas standards cylinder and regulator should be equilibrated under pressure and purged the night before an assay.

- SO_2 analyzers usually drift ± 1-2% about a mean. Let each analysis point fully equilibrate and take 10 or 15 minute averages if the drift is excessive.

Pollutant Specific Observations – NO_2

- NO_2 analyzers are very linear and accurate, even to very low (2 ppb) concentrations
- Determinations of NO_2 impurity in the standards cylinder are essential.
- Overnight equilibration of regulator is recommended.
- Multiple purges of the regulator (as many as 10 times) may be required in order to prevent the formation of NO_2 from ambient combination of NO w/ ambient O_2.
- Regulator purges should ideally be done with a 1/8" tube of >5 feet length attached, to minimize the possibility of re-entrainment of O_2 in the sample regulator.

Pollutant Specific Observations – CO

- CO analyzer drift of -0.100 ppm is typical, and can happen in minutes after a calibration.

- CO is relatively resistant to contamination degradation/absorption.

Conclusion

Accurate trace level monitoring/auditing can be achieved if careful consideration is given to:

- Expectations of drift
- GPT device choice and proper MFC range
  - 20L/100 cc/10 cc MFC's preferred
- Proper gas standards concentration selection
- Zero gas generator choice
- Manifold/sample train cleanliness
- Special caveats for individual pollutants