Gaseous Pollutants

NAAQS O3,CO, NO2 and SO2

National Ambient Air Monitoring Conference
August 2016

Agenda

What you have to have for Monitoring & QA/QC

- Shelter and Equipment
- Gas Standards and SRP

What you have to do with these items:

- QC Checks
  - I point QC (3.1.1)-agencies do
  - Annual PE (3.1.2)-agencies do
  - NPAP (3.1.3)-Regions do; agencies can request Self-Implementation
- Ambient Air Protocol Gas Verification Program

Factors Affecting Monitoring and QA/QC Data Quality

Shelter Requirements

Issues of concern & to control:

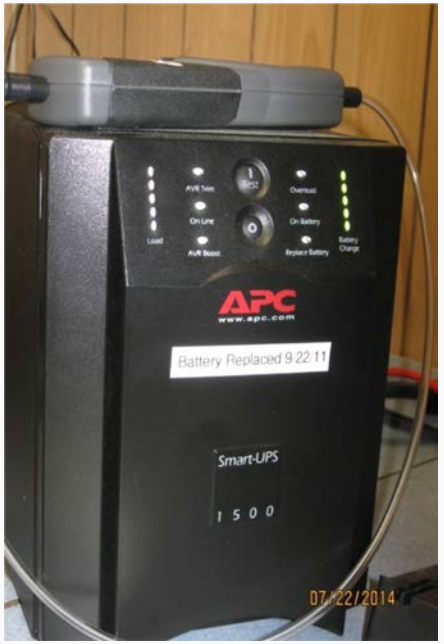
- Temperature (CFR Part 53.32)
- Power (CFR Part 53.32)
- Data System
- Isolation and Mounting
- Access
- Labeling

Temperature

- Required 20-30ºC range-and stable (+/-2º) within that range, especially for low level!!!- for operating NAAQS gas analyzers (+ZAG & Calibrator);for low level, best to track continuously on your data system right along with O3,CO,etc.
- Problems can occur, especially if T changes during measurement; PV=nRT Rules!
- Need AC (2 better than 1), insulation
- Fans-can reduce extremes quickly

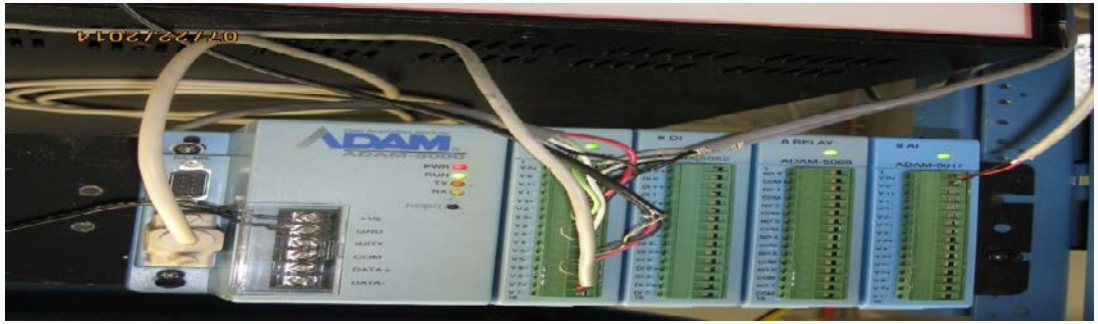
Power

- Uninterruptible Power Supply (battery back-up)
  - allows retention of data if power goes out, surges, or fluctuates
- As needed-
  - power line conditioner; especially if need generator
  - inverter
- Auxiliary generator-but cycling can be an issue
- Need Up to 20 amps ***each*** for instruments, AC=40
- Required operating range 115-125VAC



Data System

- Allows you to track, store, process and, for (wireless) modern systems, transmit multiple parameters at the same time. Example-see effect of Temp.(using, e.g., a Comet 7310), on concentration! Older data systems are analog, newer are digital.
- Can display/print concentrations as a string of #s or as a trace(=old strip charts), with annotations
- Digital allows remote performance monitoring, including zero, span and ambient data:1,5 min avgs.

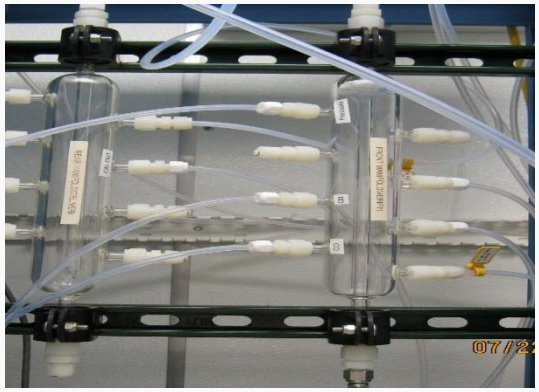


Isolation

- Isolate sensitive equipment from vibration-shock mounts on instrument racks, etc.
- Isolate people from physical & chemical hazards (cylinders); can make a cylinder compartment
- Wall mounts to secure cylinders from moving
- Clam shells to protect cylinder regulators
- CO alarm to protect against cylinder leaks and vehicle (power) or generator exhaust

Access

- Instrument racks: Need Space on either side, above and below; slide rails
  - Facilitates routine and corrective maintenance
- Need Counter work space, cabinets and drawers for parts
- Label all cords and flow path tubing



Probes, Manifolds, Lines, etc.

- For Reactive Gases, need Sampling Flowpath made of Non-reactive materials:40 CFR Part 58, App.E.9.a
- FEP Teflon or Borosilicate Glass; most 1/4”
- Minimize turns, fittings, that increase resistance (Change P)
- Use stainless steel for reactive gas regulators
- Brass Regulators OK for UP air, CO

Standards and Calibrators

- EPA Protocol Gas in Cylinders
- NIST SRPs *
- Zero Air
- Calibrators

These items are used to calibrate test gas analyzers and generate audit test gases.

* National Institute of Standards Technology in Gaithersburg, Maryland

EPA Protocol Gas in Cylinders

- NIST SRMs and NIST Traceable NAAQS CO, SO2, and NO in commercial compressed gas cylinders (2000 psig); in N2 or Air; Pressure significance-safety issue, and indicates amount left
- Grade of analysis: batch, individual, EPA protocol
- Greenbook, in EPA's TTN- a protocol for independent analysis verification
- Independent US Vendor Verification-who does an agency go to if they have ?? about the vendor's analysis?- EPA Regions 2 and 7,if schedule allows
- Ambient Air Protocol Gas Verification Program-blind to vendor (will talk about later)

EPA Protocol Gas in Cylinders-New Issue!!

- Some of the CFR–required concentrations for NPAP audits are lower than in the past

- This will now result in an increase in $$ and time for cylinder recertification, at least initially, and maybe for the for seeable future

New Cylinder Certification Issue-Why??

- We can’t count on these lower certified concentrations lasting as long as they did at higher concentrations, even if they are made by the very best vendors-let alone if they are made at a lower cost. And, NO BATCH ANALYSES!

Standard Reference Photometer (SRP) (Level 1 standards)

- NIST Traceable NAAQS O3-Use a UV wavelength in a NIST or commercial-made device (can't bottle ozone)
- 2 NIST SRPs in RTP vs 2 NIST SRPs in Gaithersberg
- 1 NIST SRP in 8 of 10 EPA Regions
- All SLT "primary" (Level 2 standards) commercial devices must be compared at least 1/yr to Regional SRPs

Why 2 Devices in NIST, RTP and Agencies (SLTs)

- You can’t keep ozone in a bottle, so you have to generate it continuously, then measure it
- Why 2: One stays in the home base lab, the other travels; have to bring the traveler back to the home base to make sure traveler has not changed; or, if it has, to recalibrate it
- If you know about 1950’s westerns, O3 is the Palladin of gas standards: Have SRP, will travel

Zero Air (ZA)

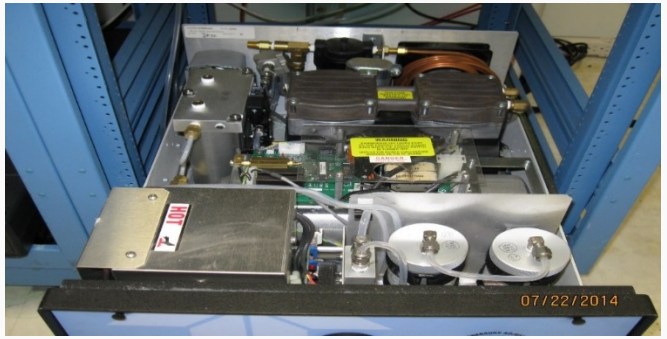
- Part 58 App A,sect.2.6.1,Gas Audit Standards must be NIST-traceable; but, no NIST Zero
- Part 50, Appendices for gases: must be free of contaminants which will cause a detectable response on the analyzer; or react with the gas being analyzed

Zero Air(cont'd.)

- ZA role: used to zero analyzers; dilute hi conc.to make ambient concentrations; & make and dilute ozone
- Sources: zero air generator (ZAG-ambient air scrubbers), or commercial cylinders.
- Best ZAG Feature: Regeneration Cycle
- So, sources vary a lot. So, need to document ALL info about your ZA
- Issues: ***Pressure restriction between ZAG & Cal; Must cycle, pre-turn off, or H2O into Cal; if ZAG converts some gas to CO, add 2nd converter?***

“Zero” Air

- Use same “0” for all 4 –CO, SO2, NO2 and O3
- Should identify ZA Acceptance criteria
- Can control problems by checking ZAG vs UP Air Cylinder, since ZAG can change, cylinder is less likely to; if ZAG “0” is “better,” use ZAG for your zero; and Document!
- NPAP ZAG is and has been better, data show



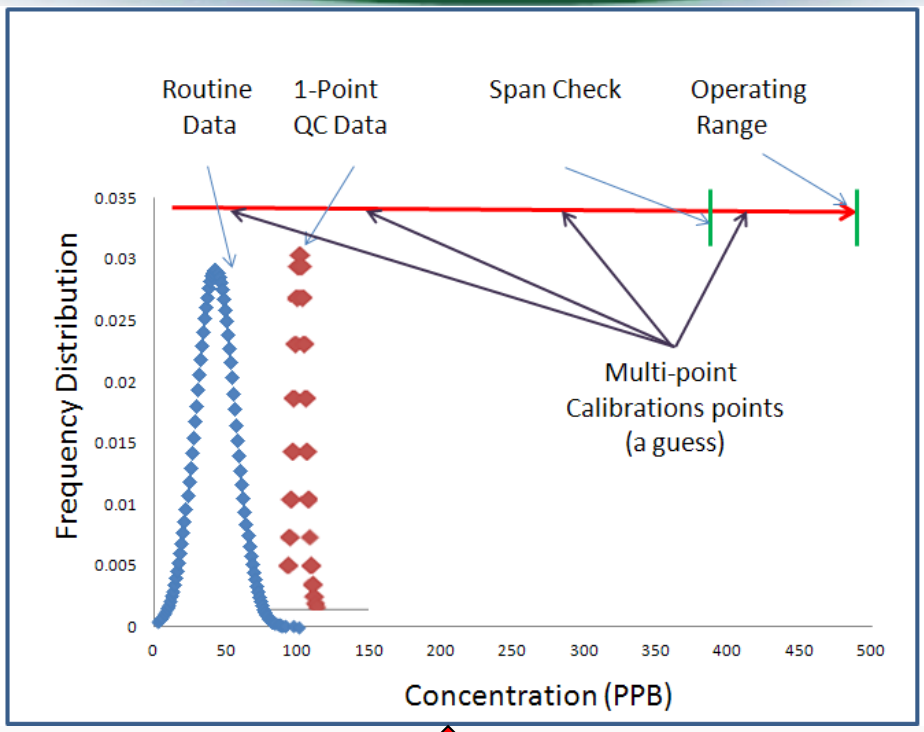
Calibrations

- 40 CFR Part 50, Appendices (A-SO2, C-CO, D-O3, & F-NO2)' sections on calibration, for 20-80% Full Scale (from 70's)
  - May not be appropriate for current ambient concentrations
  - Recent data challenges – "Calibration should have one point in the range of monitors concentrations"
- The QC (Sect. 9) and calibration section of the QA Handbook (Sect. 12) address the issue.
  - Using term "calibration scale" vs. "full scale"

1 Point Precision Check vs. Cal.

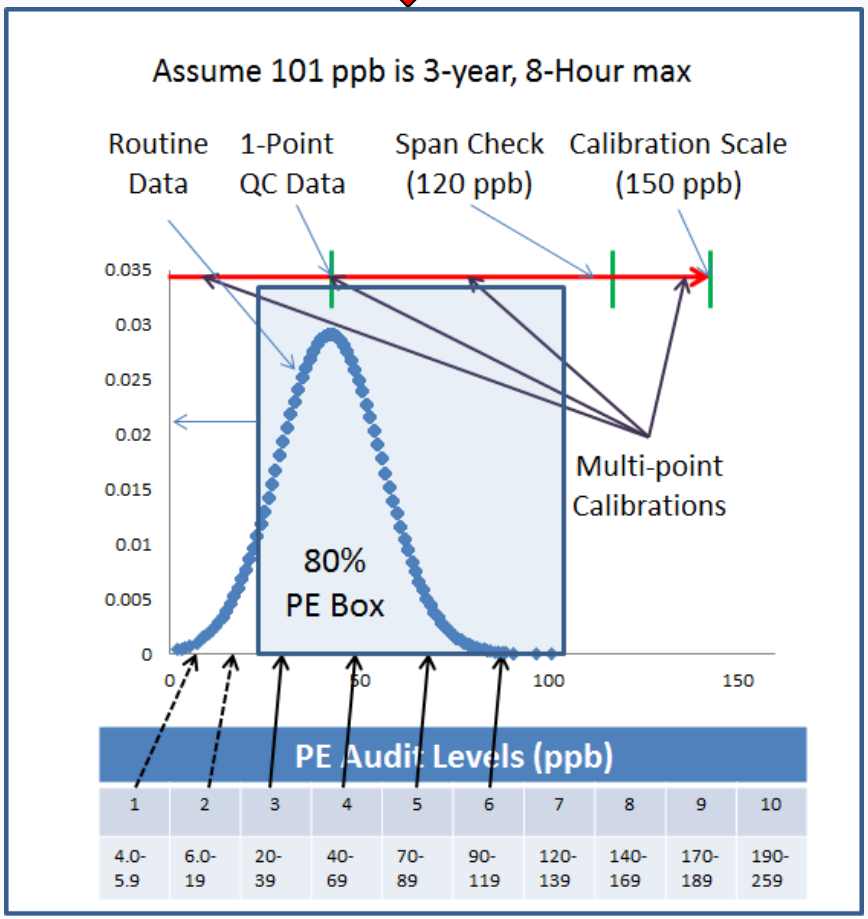
- 1970's (to Present) Part 50 Calibration Requirements vs 1 Pt. Check requirements are inappropriate for the 1 pt check, because CFR Calibration requires no points lower than 20 % FS. But many recent monitoring data are below 20% FS- especially for O3 ("low level")! So, Use NPAP to ***collect data on how well agencies use of 1970 calibration requirements is affecting the data they report to EPA***

Full Scale (Operating Range) vs. Calibration Scale (or calibration range)



Historical Approach
(real data example)

New Thinking



Lowering 1-Point QC Check Concentration Range Pg 17282 Sec. 3.1.1

- SO_2, NO_2, and O_3, Concentration Range
  - Previous: 0.01 - 0.1 ppm
  - Proposed/Final: 0.005 - 0.08 ppm

Finalized as proposed

- CO Concentration Range
  - Previous: 1 – 10 ppm
  - Proposed/Final: 0.5 - 5 ppm

Finalized as proposed

Changed from proposal

- Concentration selection
  - Proposed- based on mean/median concentration of site or network of sites
  - Final
    - The QC check gas concentration selected within the prescribed range should be related to the monitoring objectives for the monitor.
    - If NAAQS related one can select a higher range… but be mindful of your routine concentration
    - If monitoring at an NCore site or for trace level monitoring, the QC check concentration should be selected to represent the mean or median. If the mean or median concentrations at trace gas sites are below the MDL of the instrument the agency can select the lowest concentration in the prescribed range that can be practically achieved; ("practically" –gives agencies leeway to do what they need)

Annual Performance Evaluation - Part 1 Pg 17283 Sec. 3.1.2

- Required –each site annually; 3 ranges (levels) required, 4 recommended
- Increased to 10 audit level concentrations (up from 5)
- Modified language so that it's not a requirement to audit sites a second time in order to fulfill audits in each quarter.
- Removed requirement to audit three consecutive audit ranges
- Removed requirement for Regional Administrator (or designee) approval for use of audit gasses at ranges higher than the highest concentration in level 10.
  - Added language to notify AQS to accommodate audits higher than level 10

Finalized as proposed

Annual Performance Evaluation- Part 2 ,Pg 17283 Sec. 3.1.2

Changed from proposal

- Proposed- revised the previous "80% bracketing language" for the three levels/ranges required per audit
  - 2 audit points at (in the range of) 10-80% of routine concentrations
  - The third audit point at the NAAQS or above the highest 3-year concentration whichever is greater.
- Final
  - One point must be within two to three times the method detection limit of the instruments within the PQAOs network*, (minimally level 1)*
  - 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, and
  - 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.

Calibrators

- Vary between vendors. Some (more than 1) vendors can add a 3rd MFC to the regular range device that only has 2. Set up for Gas Phase Titration(GPT).
- Trace will need a 3rd MFC, compared to the 2 needed for regular range
- Regular range Calibrators may contain O3 Generators designed for regular range. Can/may need to be adjusted for lower level concentrations.
- EPA AAMG/QA did that for our Audit Trailer, Regions

Low End CO Issues for 1 Point QC Check range & Audits

"(Low end points) better reflect routine concentrations and should not be a burden to meet, ***if agencies get equipment and features needed"***

HOWEVER: Concentrations less than 1.0 ppm may vary with temperature (T)

If T drifts, the CO may drift, depending on how much the T change is, and how long it lasts

For CO Auditors, let CO analyzer warm up over night; can take a long time to stabilize

Annual PE by Agencies (Continued)

- NO2 by GPT requires NO remaining (that is, an excess); for 1970's-80's levels: 0.080ppm
- The amount of Excess NO (remaining) for GPT using chemiluminescent method depends on the concentration intended to be generated by the GPT
- This requirement should be kept in mind when deciding on what range (maximum concentration) to operate at.

EXCESS NO (Remaining)

- *3.1.2.2 The NO_2 audit techniques may vary depending on the ambient monitoring method. For chemiluminescence-type NO_2 analyzers, gas phase titration (GPT) techniques should be based on EPA guidance documents and monitoring agency experience. The NO_2 gas standards may be more appropriate than GPT for direct NO_2 methods that do not employ converters. Care should be taken to ensure the stability of such gas standards prior to use*

National Performance Audit Program NPAP

Goal

- Independently check to quantitatively show that agency monitoring data are adequate
- Adequate for what?- for the intended use of the monitoring data: decision making
- Regarding adequacy for ambient air monitoring, one of the goals is accuracy
- NPAP Tests Agency audit accuracy

Audits Test Measurement Accuracy

- Best Data: Points clustered around the true number-accurate and precise
- One Data problem: Points clustered, but not at the true number - precise but not accurate
- Worst: Points spread out wide, around but not at the true number- Neither accurate nor precise

Why NPAP and not Just Annual PEs?

- Independent Checking of the Checkers
- Independently quantifying the adequacy of each agency's audits (how well are they doing the audits)
- Purpose of audit and audit result acceptance criteria is to help agencies identify problems, NOT to invalidate data
- Quantification of data comparability at a national level
- If not EPA, then who?

NPAP

- # sites and levels required
- Region decides what levels to do
- A little state implementation
- TTP Audit Workbook, PEAT Replacement- Preliminary results to agency operator ON SITE
- Entry into AQS-Important note about Levels in AQS: Changed # of levels from 5 to 10 in Dec, 2011.

NPAP TTP

- All sites in 6 years, to allow for doing re- audits; all networks each year;# levels required may be more than SLTs, due to the need to do 2-3 points to bracket 1Point check level and 1 near/above NAAQS (see new wording in QA Handbook)
- Due to limitations in current Calibration requirements in Part 50, NPAP TTP can and will check lower end concentrations. This may be the only way we can identify the consequences of the current calibration requirement limitations.

So Why We Need to Do NPAP?

In 1 recent year since we started TTP in 2004:

- We found exceedances of our acceptance limit in 19 monitors in 18 sites, spread out in 8 of the 10 Regions; of these exceedances, 12 were for more than 1 point (level) per monitor
- 7of 8 Regions audited reported problems and follow up for 13 sites; no 2 problems were the same. There were 3 Equipment problems; 3 had material in the flow path; 3 had zero issues;3 had calibration issues;2 had unknown issues that were resolved
- ***To collect data on how well agencies use of 1970 calibration requirements is affecting the data they report to EPA today***