Gaseous Pollutants

NAAQS O3, CO, NO2 and SO2
Shelter Requirements

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

• Required 20-30Deg.C) range-and stable(+/-2Deg) 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
  – inverter
• Auxiliary generator
• Up to 20 amps each for instruments, AC=40
• Required operating range 115-125VAC

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Data System

- Allows you to track, store, process and, for modern systems, transmit multiple parameters at the same time. Example—see effect of Temp. on concentration! Older 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.
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
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
• For Reactive Gases, need Sampling Flowpath made of Non-reactive materials
• FEP Teflon or Borosilicate Glass; most 1/4”
• Minimize turns, fittings, that increase resistance (Change P)
• Use 316 SS for reactive gases only when P too high for Teflon
• Use SS for reactive gas regulators
• Brass Regulators OK for UP air, CO
Standards and Calibrators

• EPA Protocol Gas in Cylinders
• NIST SRPs *
• Zero Air
• Calibrations
• 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
• 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?
• Ambient Air Protocol Gas Verification Program-blind to vendor
Standard Reference Photometer (SRP)

- 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
- 1 NIST SRP in 8 of 10 EPA Regions
- All SLT “primary” commercial devices must be compared 1/yr to Regional SRPs
Zero Air (ZA)

- Part 58 AppB, 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 high concentrations to make ambient concentrations; & make and dilute ozone

- Sources: zero air generator (ZAG-ambient air scrubbers), or commercial cylinders.

- Best ZAG Feature: Regeneration Cycle

- Source: 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!
• 40 CFR Part 50, Appendices’ 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”

• Ozone proposal will revise Part 50 to describe calibration scale (expected to be out for review by the end of CY2014)
Full Scale (Operating Range) vs. Calibration Scale (or calibration range)

Historical Approach (real data example)

New Thinking

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<th>3</th>
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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.
• 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”)!
Lowering 1-Point QC Check
Concentration Range

• CO
  – Current: 1-10 ppm
  – Proposed: 0.5-5.0 ppm

• SO2, NO2, and O3,
  – Current: 0.01-0.1 ppm (10-100 ppb)
  – Proposed: 0.005-0.08 ppm (5-80 ppb)

Better reflects routine concentrations and should not be a burden to meet
If mean/median concentration is above/below the range select either the highest/lowest concentration of the range.
Performance Evaluations (PEs)

- CFR requires Annual (Agency) & 5 Year (National)
- Purpose: ID significant discrepancies (exceedances of NPAP TTP acceptance limits); are just a flag to tell SLTs to check and see if they have a problem with their monitoring system.
- For NPAP TTP, on the day of the audit, the auditor or audit results can indicate the area of the problem, for gas audits. But not for particulate audits. Auditors and SLTs have to wait for the post-sampling weigh lab results before have the audit results.
Why 2.4(NPAP), Not Just 3.2.2 (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?

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Annual PE by Agencies

- All SLTs have to get all sites done each year
- 3 levels required for SLTs, 4 recommended; 1st CFR table had 3 levels; most recent has 5. Guidance has 10, to allow more flexibility.
- Proposing to change the CFR to what is now in the guidance.
Annual PE by Agencies (Continued)

• NO2 by GPT requires 80 ppb NO remaining (that is, an excess)
• EPA is proposing to change the Excess NO (remaining) wording
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.
• Increased to 10 audit level concentrations
• Modified language so it is not a requirement to audit sites a 2\textsuperscript{nd} time in order to fulfill “audits in each qtr.”
• Removed requirement to audit points within 3 consecutive ranges per audit
• Revised “80\% bracketing language” for the 3 ranges per audit
  – 2 audit points at ranges between 10-80\% of routine concentrations
  – 3\textsuperscript{rd} audit point in a range at the NAAQS or above the highest 3 year concentration- whichever is greater

Removed requirement for Regional Administrator (or designee) approval for use of audit gases at ranges higher than the highest concentration in level 10: Added language to notify AQS to accommodate audits higher than level 10
• # sites and levels required
• Region decides what levels to do
• A little state implementation
• TTP Audit Workbook-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; If you get an AQS report with just levels before Dec, 2011, don’t think level 4 or 5 is the concentration it would be—and different for each gas!- after Dec., 2011!!
NPAP TTP

• All sites in 5 years, proposing 6, 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 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
  - 7 of 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
Guess the Year!!

• You may be surprised!
• The answer gives the reason why we still need to do NPAP: the agency annual audits did not raise any flags about these problems—only the NPAP TTP audits did.