Trace Level (TL) Audit/Calibration Issues for the Gases

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Objective: Discuss “old” vs. “new” audit and calibration approaches for $NO_{y,}$ and CO and SO2 and O3

- Non-Trace Level NPAP Auditor Values for NO_2, CO and SO_2 have been based on CO calibrations, followed by audit gas CO analyses.
- Historically, diluted multi-blend (MB) cylinders of CO, SO_2, and NO were used; GPT was used to create NO_2 from NO
- Issues with the Trace Level (TL) NO_y and CO analyzers, the calibrator, and the zero air generator may require another approach, based on NO_y calibration; testing the CO/No_y against the new method now.

NOy & CO Analyzers
Calibration Issues

- NO_y - Converter requires separate flow path; either need twice the calibration/audit gas, or have to do at different times (0-200 ppb f.s.)
- CO – Operators have seen *variable* zero and drift (^{0}C problem?) for affecting low (0-50 or 100 ppb) levels (at 0-5ppm f.s.)
- Calibrator – Problems have been observed and discussed regarding reliable O_3 generation for low NO_2 levels (1-5 ppb) by GPT

Tower-Mounted Station NO_y Converter Box

- Converter box's location on the tower; This picture demonstrates why the NO_y analyzer requires a flow path separate from the monitoring station's inlet
- An added challenge is that the tower must be lowered to do anything to the converter
  - From connecting for auditing (and calibration), to routine maintenance on the box
  - Or, do you calibrate from inside the station? This is not the way calibrations are to be done:

    CFR requires auditing/calibrating as near as possible to the monitoring mode

How Does OAQPS Audit?

- The long flow path is maintained, but not on a tower.

Continue Addressing Generation Equipment and Standards Issues –

Note: Reasons to look for an alternate to the CO-based NOy audit calibration and analysis

- Effect of heat on CO analyzer stability
  - This seems to be especially true at values less than ~25 – 50 ppb of drift (vs stability, at zero or other short term point calibration) We have been told about both short term single point flow calibrations, especially at 0; plus longer term drift (1 to 3 or more hours).
- Ozone Generation
  - Environics 9100 is only specified to 50 ppb
    - It means when MFP checks the device before shipping, they only check ozone down to 50ppb
    - So not guaranteed to be stable (or working) at lower concentrations
  - I am talking about this with at least some of our vendors. Environics is currently testing a new lamp for its ozone generators: This may or may not solve the problem.

Note: But what I need to tell you to give you a better perspective is that we used our 9100 for very low levels of O3 in 2010; It didn't work well, or at all; now we have had our MFC upgraded and when we got it back in May 2011, it did work well. But we just re-did the work in March 2012 with a group of regional EPA and contractor personnel, for using on trace level audits, and it did not work correctly.

Additional Generation Equipment and Standards Issue

- Zero Air Generation
  - HC Convertor can convert some HC to CO
  - Convertor is often a major source of heat (250-350 ^{o}C)

So, Can We Still Use CO-Based Calibration?

- Will the old method work for TL NO_y?
  - Maybe, down to each agency's method practical stable point for CO; but, *NOT* at the same time because we have to feed our audit gas to the station's NOy inlet up in a tower.
  - Using GPT, but *only* down to the agency's low point limit for stable (non-drifting), accurate O_3 generation
- What will work for TL NO_y?
  - For NOy generation, we were able to use the more stable NPN for the multi-blend that we dilute down; Coveat depending on stability, as indicated by 6 month re-certifications; That is, we don't have as much history with low level NPN cylinders, so we have to make sure our NPN cylinders hold their concentrations for a useful length of time.

To Test New NO_y Calibration Approach; What We Have Used Is:

- So for generation: Multi-Blend, 200 ppm CO,1 ppm NPN
- Dilution:0-20 cc/min (NPN) and 30 LPM Zero air (ZA)
- 30LPM ZA

Note: Since we have questions about low CO, low GPT as well as true NOy concentrations , we are looking at CO & NOy calibration and audit gas generation at the same time to see what each analyzer can tell us about the other's performance, at very low concentrations.

- Calibration for analysis:
- High Span: 160 ppb NPN + 4 ppm CO
- Low Span: 40 ppb NPN and 1 ppm CO

Note: Practically speaking, we may end up auditing CO/SO2 at one time, NOy at another.

Will This New Calibration Method Work for TL NO_y?

- If it can be shown that NPN (and simultaneous CO)-based calibration, instead of CO (?+ GPT)-based calibration, works reliably and accurately
- Local field testing is currently underway;1st try: seems OK
- NPN vs IPN: Gallon of liquid NPN has new safety issues; So, some vendors will suggest the use of IPN; This may not be necessary; it has not been for us, because of our vendor
- But the low and high span cylinders for the trace level calibration method only take about 5 µl (micro liters)/cylinder of either NPN or IPN

NPN Calibration Advantages

- Quicker - NO GPT needed
- No low-level ozone needed to do low audit points
- Easy to do MDL when desired
- Truer test of NO_y than by GPT, which is for NO_2
- If NO_2 convertor efficiency is desired, will not add a lot of time to do both GPT and NPN

Discussion and Best Practices

Regarding possible ozone issues, some will be mfr., or even mfr.-component- specific. Agencies, notify the NPAP Region Contacts and me of issues/problems

We are doing independent testing of what we have here:

- Calibrator and zero air generator against an ozone analyzer and CO analyzer,
- NO_y by GPT,
- NO_y by NPN; this will be tried in RTP 1st;if it works, then it will be tried in the EPA Regions, to see if it works under varied conditions; and
- Ozone for ozone and $NO_{y/x}$ GPT for lower level (LL) audit points (LL TL or LL SLAMS)