Trace Level (TL) Audit/Calibration Issues for NO_y and CO

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Objective: Discuss “old” vs. “new” audit and calibration approaches for NO_y

- 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 CO/NO_y now

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 - Variable zero and drift (^{0}C problem?) for reliable low (0-50 ppb) levels (at 0-5ppm f.s.)
- Calibrator - Problems observed in 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 demonstrates why the NO_y analyzer requires a flow path separate from the monitoring station's inlet
- 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

How Does OAQPS Audit?

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

Generation Equipment and Standards Issues

- Effect of heat on CO analyzer stability
  - This is especially true at values less than ~25 – 50 ppb of drift (vs stability, at zero or other short term point calibration)
- Ozone Generation
  - Environics 9100 is only specified to 50 ppb
    - Not guaranteed to be stable at lower concentrations
  - Environics currently testing a new lamp for its ozone generators

Generation Equipment and Standards Issues

- Zero Air Generation
  - HC Convertor can convert some HC to CO
  - Convertor is often a major source of heat (250-350 ºC)

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
  - Using GPT, *only* down to the agency's low point limit for stable (non-drifting), accurate O_3 generation
- What will work for TL NO_y?
  - Using the more stable NPN for the multi-blend (with or without CO); depending on stability, as indicated by 6 month re-certifications

New NO_y Calibration Approach

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

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

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; some vendors will suggest the use of IPN.
- 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

- 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, and
  - Ozone for ozone and $NO_{y/x}$ GPT for lower level (LL) audit points (LL TL or LL SLAMS)