Preliminary Comments from Members of the Clean Air Scientific Advisory Committee (CASAC) Air Monitoring and Methods Subcommittee (AMMS)
Additional Preliminary Comments received on 2/16/11

Purpose: To review and provide advice on the scientific adequacy and appropriateness of EPA draft documents on monitoring and methods for Oxides of Nitrogen (NOx) and Sulfur (SOx).

Additional Preliminary Comments from Dr. George Allen

Trace SO_2 Monitoring Guidance for RAIN

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Introduction:

These notes are intended to provide guidance for operation of trace-level SO_2 analyzers employed in the Mane-Vu **R**egional **A**erosol **I**ntensive **N**etwork (RAIN) program. Due to the "emerging" nature of commercial trace-level gas monitors, feedback from instrument operators is essential to the creation of accurate and useful operating procedures. Send any comments to George Allen at NESCAUM.

Although the operating principles for trace-level SO_2 analyzers are the same as for ambient SO_2 analyzers, there are several aspects of operation and data acquisition/validation that are crucial for generating data of useful quality in the sub-ppb range. The majority of guidance here is related to insuring that low SO_2 concentration data, i.e., near the method's Limit of Detection (LOD), are handled in an optimal manner and that the data quality at these low concentrations is properly characterized.

It is critical to note that unlike compliance oriented monitoring, "true-trace" SO2 monitoring data quality is driven by 3 major items: the quality of the "zero-air", how the observed zero-air data are applied to the measured data, and how data near zero [both positive and negative] are handled during both data collection AND processing.
What's not as important: The ability to calibrate to very low SO2 levels (under 10 to 20 ppb) is NOT a significant factor in generating "true-trace" level quality SO2 data.

Method:

These notes apply to both the modified Thermo Model 43-CTL (standard optical bench with non-trace level PMT optical filter to retain good NO rejection) and to the Model 43-CTL-E (new longer optical bench and non-trace level PMT optical filter).

Method Goal:

The goal of this method is a "true" 1-hour average limit of detection (LOD) of less than 0.3 ppb (0.2 ppb if possible) where LOD is defined as twice the overall baseline uncertainty, and uncertainty includes both 2-sigma of random variability (drift) and any offsets (bias).

> *Notes: Method LOD here is driven only by baseline uncertainty (drift and offset), not analyzer noise. This guidance does not apply to the Teco continuous sulfate method, since its baseline is internally determined and the quality of the zero-air used during SO_2 calibrations of that system is not a significant factor in method performance.*

Operational Checks:

1. Is the instrument working properly?

Responses to zero gas should be stable (within 0.1 ppb) over intervals of 1-2 weeks. Note that recorded baseline values should be based on an average of at least 15 minutes of stable data to minimize the effect of short-term noise on the precision of the observed zero reading. Another useful indicator of instrument performance and longer-term stability is the actual gross value of the instrument's response to zero-air, often called the "scattered light" value. This is the instrument reading in ppb with no background value subtracted. While this value can always be calculated from the observed baseline value and the background setting of the instrument, this information is more readily assessed if the instrument's background setting is always left at 0 ppb. This results in a gross zero-air response of several ppb, but this is not a problem since this value is always subtracted out during data processing (see section on data processing below).

2. Is the zero-air free from contaminants?

There are two ways to check: A) multiple z-air sources and B) evaluation of ambient data.

A) Use multiple sources of zero-air; if different, the one with the lowest response is usually the best. Compare the response from high quality cylinder z-air to that obtained with scrubbed ambient air using 24x7 purged activated carbon. Note: carbon type is important; Barnebey & Sutcliffe Corp. (formerly Barneby-Cheney) type GI (www.bscarbon.com, Columbus OH, Tel. 1-888-800-1911) has been shown to work well. Alternatively, one could use a sodium carbonate coated denuder, such as the Sunset Laboratory model # DN-315 stainless steel concentric denuder (as used in the Teco 5020 sulfate analyzer); this may require additional 3/4" to 1/4" Teflon reducer fittings.

> *Notes: For charcoal and denuder zero-air systems, the inlet air must be outside air (gas manifold air is ok). Shelter air should never be used for any zero air source! Also, to the extent possible, all components of zero-air systems should be free of plastics or other materials which might out-gas hydrocarbons. See Appendix D of the Teco 43C-TL manual for approaches to generating trace-quality zero air.*

B) Evaluate ambient data during clean periods when measured levels approach zero. Simple monthly time-series plots of hourly ambient data are a good operational diagnostic tool. In most rural areas in the eastern US, hourly SO2 concentrations should often (several times per month) drop below 0.2 ppb during the night (from dry deposition). Reported hourly concentrations of baseline-corrected data are expected to be slightly negative on occasion (a data floor of 0.00 ppb is indicative of truncation), but never be more negative than -0.1 ppb. In cases where ambient data is significantly negative [indicating either instrument baseline drift or a problem with the system's zero-air quality], the system's baseline data should be corrected based on the lowest stable ambient reading during a given data processing interval.

3. Is data acquisition accurate at low-levels?

Digital data streams are strongly preferred for trace gas methods since analog systems may introduce significant offset errors or have insufficient resolution or cause truncation of small negative values.

If analog data acquisition must be used, set the data logger resolution (both acquisition and 1-hour average reporting) to 0.01 ppb; 0.1 ppb is not sufficient for generation of baseline data or for diagnostic use as described above.

The combination of analyzer analog output range and data logger analog to digital conversion resolution must provide resolution of at least 0.1 ppb (hourly averages composed of 1-minute or more frequent samples at this resolution will provide resolution substantially better than 0.1 ppb).

> *Note: the D/A resolution for the Teco 43CTL (and all Teco C-series instruments) is 10-bit (1024 values) and ranges from -2.3% to 100% of analog full scale output in 0.1% FS (0.001*FS) increments. For 500 ppb FS, the resolution is 0.5 ppb. To meet the resolution requirements here, the instrument's analog full scale must be no higher than 100 ppb.*

The analyzer/logger configuration combination used must be capable of recording and reporting small negative values (at least -1.0 ppb).

It is important that the final 1-hour analog dataset be compared to the internally stored digital data source when the system is first installed and on a regular basis afterwards. After any external offset corrections (logger or post-processing), the data from these two sources should agree to within 0.05 ppb. For the Teco 43 series analyzers, this requires that the stored data **"**record interval**"** be set to store 1-hour averages (the default is 5 minutes). This setting must be saved with the "set save params" command; otherwise the storage interval will return to the default of 5-minutes when the instrument is powered down. This is likely to require changing some DIP-switch settings on the system's back-plane circuit boards as detailed in the instrument's manual.

<u>Data processing/validation methods:</u>

1. Apply all available baseline measurements to the final data set.

It is critical to apply baseline (zero-air) check data to the final processed data set regardless of how small the correction is -- a correction of 0.1 ppb is significant. For data sets where the baseline is reasonably stable (drift or change between successive observations of less than 0.2 ppb), it is sufficient to apply the mean of adjacent baseline measurements to the data collected between them. In situations where the baseline drift between measurements is between 0.2 and 0.5 ppb, the data is best processed using a linear interpolation approach (either by day or by hour) unless there is reason to suspect that the baseline change occurred at a specific point in time. Drift of this magnitude should not normally occur; if it persists, the instrument needs service. For out of control situations where drift is larger than 0.5

ppb, the same interpolation technique can be used, but the data may need to be flagged and the instrument should be serviced immediately.

2. Preserve the "noise" at levels below the LOD.
This is essential to assess during review of final data sets. Small negative concentrations (to at least -0.2 ppb) after baseline corrections are applied must be retained in the validated hourly data set, although they can be flagged as below the LOD and/or as negative. They should not be set to zero or ½ the LOD; that should only be done as needed on analytical data sets, based on the data flags.

Calibrations:

It is desirable but not at all essential to calibrate this instrument at low SO_2 levels [less than 20 ppb]. Unlike some methods such as CO, the fluorescent SO_2 method is inherently linear down to 0 concentration. Appendix D of the Teco 43C-TL[E] manual has an excellent discussion on trace-level calibration issues.

If analog outputs are used and the instrument's full scale analog range is 100 ppb as suggested above, SO2 calibrations are limited to less than 100 ppb. Cylinders of SO_2 in the 20 ppm range are readily available and will allow concentrations to be generated between 20 and 80 ppb with normal (1000:1) dilution ratios. Alternatively, a second SO2 analog output channel with a higher range can be used only for calibration points that are off-scale on the logger channel that is used to collect ambient data. Dual-analog output range configurations can also be used to address this issue.

The biggest concern with lower concentration (less than 50 ppm) SO_2 cylinders is the potential for contamination by back-diffusion [room air -- oxygen and moisture -- getting into the cylinder] from a poorly purged regulator. **A**t low SO2 cylinder concentrations, contamination with even a small amount of moisture from back-diffusion can cause the SO_2 concentration to become unstable; the lower the cylinder concentration the more susceptible it is to any contamination from "abuse" [back-diffusion] in the field. However, it has been this author's experience that if properly prepared [Eg., stable over the first 1-2 months] and carefully handled in the field, even very low (500 ppb) cylinders of SO2 in 20% O_2 can be stable over 5 to 10 years or more.

The fundamental rule for insuring that low concentration cylinders of SO2 [or NO] are not contaminated during use by back-diffusion is as follows:
"Whenever the cylinder valve is open, there must be gas flow out of the cylinder".
In other words, "Never dead-end the cylinder".

If the "Never dead-end the cylinder" concept is always applied, it is impossible for any air or other contaminants to enter the cylinder. In practice, this rule means that there must always be a "path" for the cylinder gas to flow towards whenever the cylinder valve is open. From an operational point of view, this means that on startup for a span point, the LAST flow point opened is the cylinder valve, and

on shutdown the FIRST flow point closed is the cylinder valve. Nothing else matters in terms of preserving the cylinder's integrity.

If this principle is followed, the common practice of repeated vacuum purging of regulators is not necessary. A simple 1 or 2 time regulator flush is all that is needed, since the vacuum purge technique assumes that back-diffusion will occur.

This process assumes that manual calibrations are used, not automatic methods. Automatic zero and span checks may not be appropriate for trace gas methods. Additional precautions [regulator purging and conditioning] may be needed for automatic calibration setups.