From: Alan Leston
Sent: Thursday, May 15, 2014 8:36 PM
To: Hanlon, Edward
Cc: Will Ollison
Subject: Comments on 4/3/14 teleconference

Dear Mr. Hanlon,
I would like to enter the attached comments into the meeting material for the CASAC-AMMS discussion regarding a new Federal Reference Method for Ozone:Nitric Oxide Chemiluminescence.

Please note that although my efforts in drafting these comments were partly funded by the American Petroleum Institute the conclusions and recommendations are my own.

Thank you for your consideration in this matter.

Best regards,
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Comments Regarding Adoption of a New Ozone Federal Reference Method

Prepared by:
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May 15, 2014

INTRODUCTION

In conjunction with the ongoing review of the National Ambient Air Quality Standard (NAAQS) for ozone (O3) the U.S. Environmental Protection Agency's (EPA) Office of Research and Development (ORD) is proposing a new Federal Reference Method (FRM) for ozone. ORD requested that the Air Monitoring and Methods Subcommittee (AMMS) panel of the Clean Air Scientific Advisory Committee (CASAC)[1] review its proposal during a public teleconference on April 3, 2014 and provided four "Charge Questions" to be addressed by the AMMS.

1. What is the AMMS view on adding an additional O3 FRM (as Appendix D-1 of the 40 CFR Part 50 Federal Regulation) for the purpose of establishing a new FRM that is implemented in analyzers currently in production status? This new O3 FRM will serve as an additional FRM to supplement the current Ethylene-Chemiluminescence method, which is no longer being produced or supported.

2. What is the AMMS views on establishing the Nitric Oxide-Chemiluminescence (NO-CL) method (currently an FEM) as the new, additional O3 FRM?

3. Do any other ozone measurement methods exist that the AMMS recommends for consideration of possible promulgation as a new (additional) O3 FRM?

4. What is the AMMS views on the use of low-cost sensor technology to supplement regulatory ozone monitoring (i.e., in rural areas)?

AMMS PANEL WRITTEN COMMENTS

Preliminary written responses from AMMS members to Charge Question 1 (Q1) supported adoption a new O3 FRM but with some concern expressed over adding an FRM instead of replacing the existing FRM due to possible disagreement between the two standards. EPA was requested to clarify its rationale for a dual-FRM approach and provide more detail in their proposed revisions to Table D-1, 40 CFR Part 50 associated with any new proposed FRM, including specifics such as measurement wavelength range, schematic diagrams, and a list of citations.

Panelist written comments on Q2 were mixed. Four of ten panel members addressing the question favored the NO/CL method approval while six thought approval to be premature, asking to see ongoing planned testing and a more in-depth analysis of existing test data. While one member noted several advantages of the NO/CL technique over the current FRM (Ethylene Chemiluminescence method – Eth/CL), e.g., a faster response rate, higher signal-to-noise ratio, smaller reaction volume, operation under reduced barometric pressures, and accommodation of "flexible operating conditions", another noted the hazards of working with 10,000 ppm nitric oxide (NO) cylinder mixtures.

With respect to Q3 identifying alternative FRM candidate methods, three members supported a "scrubberless" UV photometric method (UV/SL) that employs a gas-phase NO scrubber specifically and two additional members cited this "UV method" as having potential.

Written responses to Q4 invariably cited the need for extensive testing to fully characterize the performance of low cost sensors. Possible uses for such sensors included; microenvironmental measurements, personal exposure estimates, characterization of spatial gradients, and saturation monitoring around large/complex sources of near-ground level emissions.

EPA AMMS PANEL BRIEFING

Agency staff initially briefed the AMMS, outlining the candidate FRM testing activities undertaken by ORD to-date.

The NO/CL method was proposed since the O3 FRM (Eth/CL) instrument is currently no longer available from, nor supported by, any vendor. Moreover, the NO/CL chemiluminescence measurement principle is the same as the current FRM and has been tested and approved as an O3 FEM. The NO/CL monitor is commercially available and highly specific for O3 measurement, needing only the moisture drying system present on the commercial instrument to avoid water vapor interferences. In addition to the vendor FEM application performance testing, ORD has completed laboratory testing on the NO/CL technique and three field studies (Baltimore, Research Triangle Park and Houston) comparing the NO/CL method against the current Eth/CL FRM and other FEMs with a fourth Denver field study planned during summer of 2014.

Although no results from the Baltimore study were presented, results from the RTP field study, linearly regressed, showed that the NO/CL method was well correlated with the FRM with little

zero offset. However, some noise variability was evident at the 75 ppb level of the current 8-hour O3 NAAQS where the NO/CL response varied from 65 ppb to 78 ppb.

Good correlation and zero offset were observed in Houston for the NO/CL instrument and the noise was significantly lower than at RTP, ranging from 70-75 ppb at 75 ppb. No explanation was offered for the large variation in NO/CL monitor noise between the RTP and Houston sites. Laboratory results were also shown for the NO/CL instrument range, noise (20% & 80% of full scale), lower detection limit, interference equivalents, and zero/span drift and lag/rise/fall times. Although method "precision" is a required parameter for FRM/FEM testing[2], no precision testing results were presented.

Linear regressions were also presented for two additional field tested O3 measurement methodologies. A "scrubberless" UV absorption photometer equipped with a gas-phase NO scrubber (UV/SL) was well correlated with the FRM, had very low noise, and a zero offset of +1.9 ppb. The UV/SL technique was noted as "very promising" and ORD staff suggested that it should be considered as an additional FRM after designation as FEM and further evaluation by ORD in routine monitoring. A conventional FEM UV absorption photometer with a solid-phase scrubber showed good correlation with the FRM but was noisier than the UV/SL monitor with a +3.6 ppb zero offset.

Laboratory test data for a conventional FEM UV photometer with a solid-phase scrubber, a conventional FEM UV photometer with sample dryer, and a UV monitor with a gas-phase scrubber and dryer (UV/SL). In general, all three UV-based monitors meet EPA's new proposed FRM/FEM H2O, H2S, and CO2 interferent performance specifications, although precision measurements were not included for any monitor. A major exception was failure of the conventional FEM UV absorption photometer without a dryer to meet the proposed performance standard for water vapor interference. A dryer-modified conventional UV photometer was twice as noisy but showed 20-fold lower water vapor interference. EPA staff noted that because of this finding it was <u>critical</u> that O3 FEM monitors include moisture control. This requirement for moisture control was also included in the proposed Table D-1 for the NO/CL FRM. However germane these three interferents are to chemiluminescence monitors, the current interferences for which UV photometers must be tested are SO2, NO2, NO, m-xylene, and water vapor[3] and tests for those interferents were not presented.

AMMS PANEL DISCUSSION

In regards to maintaining the existing FRM one panel member noted past approaches taken to remove the current FRM flammability/explosion issue associated with the use and handling of compressed ethylene. The CSI 2000 portable O3 monitor employed "ethychem" (a blend of 90% CO2 and 10% ethylene)[4] to drop the concentration of compressed ethylene below the "lower explosive limit" and thus avoid that problem. However, the ethychem approach requires a higher gas flow due to the lower ethylene concentration and the ethylene output changes perceptibly with tank drawdown, requiring more frequent calibrations. Reagent cylinders have to be replaced much more frequently and would still require recalibration after each cylinder change due to variations in ethylene and impurity concentrations in commercially available cylinders. Any routinely useful Eth/CL method must avoid both the issues of flammability/explosion and frequent cylinder change out.

A panel member questions whether the gas-phase scrubber is truly more effective than the solid-phase scrubber or is only a sales-oriented point of view. The infirmities of the solid-phase scrubber have long been noted to remove more than "only ozone"[5,6] and have "memory" issues from previous use[7] while the gas-phase scrubber appears immune to such difficulties.

Another panel member noted the need for an FRM that performs well in both the field and laboratory. This is a very important consideration in light of the fact that the FEM UV photometric method (used at the vast majority of current ambient monitoring sites) has never been officially tested for the majority of species now reported to bias its performance [6].

In response to a panel member's inquiry as to whether it was EPA's intent to propose a new FRM as part of the 12/2014 O3 NAAQS draft revision, EPA staff agreed, noting that given this timeframe only the NO/CL method can be considered as a new O3 FRM since there is little time for further field testing and analysis of any other methods before publication of the proposed O3 NAAQS. However, panel members recommended the UV/SL method as an alternative FRM for a number of reasons:

- the scattergraph of NO/CL vs. FRM is noisier than the similar UV/SL vs. FRM graph – indicating that NO/CL is a less accurate method.

- the NO/CL method "…hasn't reached the level of performance that we (are) really looking for…."

- the issue of safety arises when using the high NO concentration required by the NO/CL method.

Panel members felt that the UV/SL method "…has potential…" but needs "…more evaluation…." and requested that EPA perform additional analyses on the scheduled upcoming field test and of existing data and resubmit these results:

- members requested that EPA include analyses of 8-hour data in the revised NO/CL field study presentation.

- members requested that additional clarification/analyses of the "Y-intercept" for both UV method plots in the EPA staff presentation.

- the Panel Chairman agreed to another teleconference if/when ORD prepares another report on the NO/CL method with the requested additional data and analyses.

Regarding Q4 panelists noted that low cost sensors do not necessarily have to meet FRM/FEM performance specifications but all such performance "issues" must be clearly defined and that such sensors are generally NOT suited for use in rural areas where O3 levels are generally low and gradients are small; however, panelists did note that low cost sensors are well-suited to personal exposure and possibly near-road studies.

There was general agreement among panel members that low cost sensors might be used to supply special gradient data.

Public Comments

In response to a panelist's concern over instrument exhaust NOx products, a public commenter noted that NOx "scrubbers" were already built into the NO/CL and UV/SL models currently available. Public comment also noted the potential high biasing of ambient O3 levels by inlet height differences (e.g., between urban SLAMS monitors at 3-4 meters vs. CASTNet instrument inlets at 10 meters above ground level) and the need to adjust O3 concentrations for barometric pressure effects, as is currently done for PM2.5 measurements, that lead to overestimates of exposure due to the reduced pollutant mass inhaled at higher altitudes resulting from use of pressure-invariant mixing ratios, rather than concentration measures of gaseous pollutant standards.

OTHER ISSUES

Although not addressed during the AMMS teleconference it is critical that EPA, and those advising EPA on technical matters, be aware of the issues surrounding O3 data precision and bias. As noted above, the precision of candidate FRM/FEM analyzers is a required performance specification but was absent in the EPA presentation. This oversight can be rather easily corrected when performing laboratory comparisons but if collection of precision data is not "planned into" field studies a valuable evaluation metric will be forever lost. EPA should capture instrument precision data during this summer's O3 instrument field study in Denver and include analyses of that data in the subsequent report. Available precision data should also be added to a revised staff presentation.

Also, previous CASAC discussions indicate that members are uncertain as to the precision and bias associated with ambient O3 data, especially the data for concentrations near the current O3 NAAQS. For example, during the March 27th CASAC Ozone Review Panel meeting teleconference - Day 3[8] a panel member noted that

> *"…EPA actually did an analysis of their ozone monitoring capabilities…when they took into account the instrument precision and accuracy, something… on the order of 2 ppb accuracy…."*

It is not clear which "analysis" the member is referring to. There have been at least two EPA-sponsored reports[9,10] addressing the magnitude of O3 measurement error. A 1997 report found

> *"…a conservative estimate for the typical error associated with an ozone concentration measurement in the real world is on the order of 4 ppb…."*

but cautioned that this estimate did not include instrument noise or other systematic errors such as interference effects or sample line degradation. When the authors examined actual precision data from 1995 and 1996 (all sites in the AIRS AMP 240 database) they found an

> *"…absolute error of ±4.8 ppb…"*

at an assumed concentration of 80 ppb. Although this empirical approach did include instrument noise and sample line degradation it did not take into account ambient air matrix interferences. Furthermore, the authors stated that

> "*…Much higher errors may occur, as the numbers in Table 2 represent average errors….*"

These results indicate the minimum measurement error associated with hourly O3 measurements near the level of the current O3 NAAQS is 4-5 ppb.

A second 2006 EPA report examined the measurement error associated with 8-hour O3 design values. The authors simulated measurement error with a model employing estimated 8-hour precision and a random bias. The 8-hour precision estimate was derived from 1-hour precision data assuming there was "no appreciable serial correlation" while the bias was based in part on a six month data set from a single O3 monitor. The model simulation resulted in an O3 design value uncertainty of 1.3 ppb. However, it is likely that measurement errors ARE serially correlated from one hour to the next and a small set of precision data from a single site is not a robust characterization of a nation-wide network of 1300 O3 monitors.

A report characterizing O3 measurement error using collocated monitors is available[11] and while it does not include a "bias" factor (or a measure of "precision" as EPA defines it) the report is instructive in estimating real world measurement error. The CASTNET 2010 Annual Report summarizes quarterly" precision" for the 2006-2009 period from four collocated sites.

The Mackville, KY site hosts two Thermo Scientific 49i monitors which are maintained by a single CASTNET operator. The Rocky Mountain site also contains two Thermo Scientific 49i monitors which are independently operated and serviced by different organizations, one by CASTNET and the other by the National Park Service. The site in Suffolk County, NY is part of the EPA-mandated State and Local Air Monitoring Station (SLAMS) network and hosts both Thermo Scientific 49i and Dasibi 1008 monitors maintained by a single operator. Finally, the SLAMS site in St. Louis County, MO contains two API 400 monitors overseen by a single operator.

Hourly data from these collocated monitors was reviewed for the period of interest and the mean absolute relative percent difference (MARPD) was calculated for each pair of hourly ambient data from each site. This approach is somewhat different than the EPA method for assessing precision in which a known quantity of O3 is generated (in clean, dry zero air) and introduced into the monitor. Precision at the St. Louis and Mackville sites were very good (3.8% and 1.4% respectively) while the Rocky Mountain site was 5.6% and the Suffolk site showed an 11.2% difference. On average, the four sites had a 5.5% difference over the entire range of concentrations measured. At the level of the current O3 NAAQS (75 ppb) this error would amount to 4.1 ppb.

Together these results demonstrate that measurement error in the routine operation of ambient O3 monitors is not trivial, especially given the number of different styles of FEM monitors used and the number of different agencies operating those monitors. However, none of these reports were designed, or able to evaluate, the error associated with interfering species known to exist[6]

in the ambient air matrix. In general, the minimum measurement error in 8-hour O3 averages appears to be ca. ±4 ppb but this minimum does not account for bias due to interferences. In addition, although the use of averaging results across the range of concentrations experienced at a few sites provides some perspective on measurement it is critical to understand the errors that exist at and above the O3 NAAQS concentrations and precision data to support such an analysis could not be found. Finally, estimating O3 monitor/network precision and bias with data generated during a limited part of the O3 diurnal cycle (i.e., the same time every night) while using ultra-dry calibration gases (which alters ambient air matrix effects) introduces a bias that can mask the source of serious measurement error.

SUMMARY

With respect to Charge Question 1 the AMMS subcommittee unanimously favored selecting a new FRM for O3. However, clarification was requested from EPA regarding the implications of simply adding an FRM vs. replacing the existing method.

On Charge Question 2 the subcommittee initially voiced written support for the NO/CL technique as the new FRM. However, during the teleconference few members spoke in favor of raising NO/CL to FRM status. The field comparison data gathered and presented by ORD raised panelist concerns about the level of noise shown by the NO/CL method and the lack of requested additional analyses which might have led to a better understanding of the source of that noise.

The subcommittee opinion on other suitable O3 FRM techniques (Charge Question 3) centered on the UV photometric method with a gas-phase scrubber (UV/SL) as a preferable alternate/additional candidate FRM, an opinion also expressed in both preliminary written comment and oral comment during the teleconference.

The concept of employing low cost O3 sensors, especially at rural areas (Charge Question 4) was met with calls for extensive testing to characterize each device's performance. It was noted that such devices did not have to meet FRM/FEM specifications in order to be useful in personal exposure or near road monitoring where collocated FRM/FEM data was available. Low cost sensors were also identified as being of useful in characterizing spatial gradients.

Subcommittee members offered several suggestions to ORD for bolstering NO/CL method data. Suggestions included, 1) examining the diurnal pattern of differences between the NO/CL and FRM methods (especially at Houston), 2) aggregating 1-hour data into 8-hour averages to better understand NO/CL method performance near the level of the NAAQS, 3) investigating co-pollutants in order to better understand the differing noise levels between the RTP and Houston sites, 4) identifying/reporting on issues that resulted in large "Y-intercept" values for both of the UV monitors tested, 5) adding mercury (a known interferent) to the list of interfering species for the UV method in Table B-2 and Table B-3, subpart B of Part 53.

In addition to the suggestions offered by the subcommittee the following suggestions are offered to help clarify issues related to adopting a new FRM for O3.

1) Explain why no data from the Baltimore field study was presented,

2) Include method "precision" results from laboratory studies (ORD presentation slides 9 & 12),

3) Explain why virtually all performance test results for the existing FRM were listed as "NA" on slide 9,

4) Include details on the monitor location(s) for data on slide 11 (i.e., field or lab),

5) Explain why UV monitors (slide 12) were tested for interference from water vapor, CO2 and H2S (interfering species for the CL method) and not SO2, NO2, NO, m-xylene and water vapor which are interfering test species in the UV method,

6) Regardless of whether the NO/CL method is designated as an FRM, EPA should require vendors to inform users of the hazards inherent in handling cylinders of compressed NO in the 10,000 ppm range – the NIOSH IDLH (Immediately Dangerous to Life or Health) level for NO is 100 ppm in comparison to the 1500 ppm IDLH for CO,

7) Clarify whether the Part 53 Subpart B Tables B-2 and B-3 (and any other related subparts) will be updated to include testing for all species now known to interfere with the UV method.

REFERENCES

1. EPA Memo, March 7, 2014, Timothy J. Buckley, Director HEASD, to Ed Hanlon, Designated Federal Officer, Clean Air Scientific Advisory Committee, EPA Science Advisory Board Staff Office.

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3. Table B-3 Subpart B of 40 CFR Part 53, http://www.ecfr.gov/cgi-bin/text-idx?SID=9567b18210024d612f8e45557157249e&tpl=/ecfrbrowse/Title40/40cfr53_main_02.tpl.

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5. Leston, A. and Ollison, W. M., "Estimated Accuracy of Ozone Design Values: Are They Compromised by Method Interferences?", in Tropospheric Ozone: Nonattainment and Design Values Issues, TR-23, Air & Waste Management Association, Pittsburgh, PA, 1993, 451-56.

6. Spicer, C. W., Joseph, D. W. and Ollison, W. M., "A Re-Examination of Ambient Air Ozone Monitor Interferences", J. Air & Waste Manage. Assoc., **60**: 2010, 1353–1364, doi:103155/1047-3289.60,11.1353.

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8. CQ Newsmaker Transcripts, "EPA Holds Meeting of the Clean Air Scientific Advisory Committee Ozone Review Panel, Day 3".

9. Memo, Hans P. Duel, Jonathan P. Cohen, SAI, 2 May, 1997 to Warren Freas, EPA, Re: Work Assignment 3-01, Determination of a Reasonable Systematic Error Estimate for Ozone Monitors.

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11. Clean Air Status and Trends Network 2010 Annual Report, EPA Contract No. EP-W-09-028, http://epa.gov/castnet/javaweb/docs/annual_report_2010.pdf .