



UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON D.C. 20460

OFFICE OF THE ADMINISTRATOR
SCIENCE ADVISORY BOARD

July 28, 2014

EPA-CASAC-14-007

The Honorable Gina McCarthy
Administrator
U.S. Environmental Protection Agency
1200 Pennsylvania Avenue, N.W.
Washington, D.C. 20460

Subject: Review of EPA's Recommendation for an Additional Federal Reference Method for
Ozone: Nitric Oxide-Chemiluminescence

Dear Administrator McCarthy:

In response to a request from the EPA's Office of Research and Development, the Clean Air Scientific Advisory Committee (CASAC) Air Monitoring and Methods Subcommittee (AMMS) held teleconferences on April 3 and June 12, 2014, to review the EPA's recommendation to add the Nitric Oxide-Chemiluminescence, or NO-CL, measurement method as a Federal Reference Method (FRM) for the measurement of ozone. CASAC's consensus responses to the agency's charge questions and the individual review comments from the CASAC AMMS are enclosed. CASAC's key points are highlighted below.

An FRM serves as the standard protocol for measuring ambient concentrations of pollutants regulated under the National Ambient Air Quality Standards (NAAQS) program. The existing FRM for Ozone (Ethylene-Chemiluminescence Method, or ET-CL) is no longer being manufactured or supported. In 2009, the EPA consulted a previous CASAC monitoring subcommittee (the Ambient Air Monitoring and Methods Subcommittee - AAMMS) on ambient air monitoring issues related to the Ozone NAAQS, including issues related to the development of a second FRM for measuring ozone. The agency considered the individual AAMMS member comments and now is recommending that the NO-CL measurement method should be a second Ozone FRM. In the current review, CASAC considered the EPA Office of Research and Development's (ORD) analysis and technical documentation on the NO-CL method, and the EPA recommendation to make this measurement method a second Ozone FRM.

Overall, CASAC agrees with the EPA that a new Ozone FRM should be added. The current FRM's ET-CL instrument is no longer commercially available for use in designating other ozone measurement methods as Federal Equivalent Methods (FEMs). CASAC also agrees that the current ET-CL FRM can remain on the EPA's list of designated reference and equivalent methods, and notes that this approach is consistent with how most other obsolete FRMs have been treated by EPA.

CASAC agrees that the NO-CL method is a good candidate for FRM status and CASAC is impressed by the laboratory evaluations, which show that the NO-CL method far exceeds 40 CFR Part 53

requirements for FRM designation, including laboratory tests for water vapor and other interferences. Following the additional EPA analyses reported in their May 5, 2014 summary, CASAC concludes that results of the EPA's field tests also support a case for FRM designation of the NO-CL method. However, before proceeding with FRM designation of the NO-CL method, CASAC recommends that the EPA thoroughly assess results of its additional field tests on the NO-CL method that EPA planned to conduct in Denver in late June 2014. CASAC also recommends that the EPA's proposed revision to Appendix D-1 of 40 CFR Part 50 (i.e., Reference Measurement Principle and Calibration Procedure for the Measurement of O₃ in the Atmosphere – NO-Chemiluminescence, NO-CL, Method; January 2, 2014 Draft) include more detail. CASAC recommends that the EPA include additional criteria within this Appendix for the NO-CL method, such as more detailed explanation of measurement principles and other information on the method as described in the response to charge questions.

CASAC recommends that EPA also continue evaluation of the ultraviolet-scrubberless measurement method (UV-SL) as a possible candidate for an FRM. The EPA recently designated the 2B Technologies Inc. Model 211 UV-SL monitor as an FEM, and EPA analyses presented to the CASAC AMMS at the May 5, 2014, meeting show excellent correlations between UV-SL and the ET-CL FRM, and between UV-SL and NO-CL. EPA needs to further test the UV-SL method to resolve an issue regarding the method's zero offset results. Furthermore, the UV-SL method has not been tested against the FRM in the field as thoroughly as would be desired to merit FRM designation at this time. CASAC recommends that the EPA complete the work that would be required to assess the UV-SL method's suitability as an FRM.

CASAC notes that other available systems to measure ozone—including quantum cascade laser based tunable multi-pass IR absorption spectroscopy, cavity ring down spectroscopy (CRDS) and cavity attenuated phase shift spectroscopy (CAPS)—are not practical at this time as FRMs. These approaches are relatively expensive, have complex operational requirements, and are not broadly in use by state agencies. However, rapid technology innovation may make these methods more practical for routine use in the near future, and if they can attain the specified criteria, then there is no reason why they should not be considered as candidate FRMs.

Sensors are low-cost, easy-to-use, portable air pollution monitors that can provide highly time-resolved data. However, low-cost sensor-based systems that are currently available for ozone measurement are not sufficiently developed to be considered as FRMs or FEMs at this time. While these sensors are not likely to replace regulatory monitors, they can provide useful data for many non-regulatory monitoring objectives.

Low-cost sensors tend to be small and operate with low power, so they can be deployed where more expensive regulatory monitors are not feasible (e.g., saturation monitoring). One of the EPA's most important research objectives is to more accurately assess personal exposure. Low-cost sensors may be useful for assessing personal exposure because many of them can be deployed to characterize exposures for a more representative population over a larger portion of a typical day. However, in order to aid the interpretation of their data, low-cost sensors need to be well characterized (precision, bias, interferences) and also evaluated through co-location with regulatory monitors.

CASAC appreciates the opportunity to provide input to the EPA on this issue. We look forward to receiving the agency's response.

Sincerely,

/signed/

Dr. H. Christopher Frey, Chair
Clean Air Scientific Advisory Committee

/signed/

Mr. George A. Allen, Chair
CASAC Air Monitoring and Methods
Subcommittee

Enclosures

NOTICE

This report has been written as part of the activities of the EPA's Clean Air Scientific Advisory Committee (CASAC), a federal advisory committee independently chartered to provide extramural scientific information and advice to the Administrator and other officials of the EPA. CASAC provides balanced, expert assessment of scientific matters related to issues and problems facing the agency. This report has not been reviewed for approval by the agency and, hence, the contents of this report do not necessarily represent the views and policies of the EPA, nor of other agencies within the Executive Branch of the federal government. In addition, any mention of trade names or commercial products does not constitute a recommendation for use. CASAC reports are posted on the EPA website at: <http://www.epa.gov/casac>.

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CASAC**

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*Did not participate in this Review.

Abbreviations and Acronyms

AMMS	Air Monitoring and Methods Subcommittee
CAA	Clean Air Act
CASAC	Clean Air Scientific Advisory Committee
CRDS	Cavity Ring Down Spectroscopy
CAPS	Cavity Attenuated Phase Shift Spectroscopy
CFR	Code of Federal Regulations
ET-CL Method	Ethylene-Chemiluminescence Method
EPA	U.S. Environmental Protection Agency
FEM	Federal Equivalent Method
FRM	Federal Reference Method
NAAQS	National Ambient Air Quality Standards
NO-CL Method	Nitric Oxide-Chemiluminescence Method
OAQPS	EPA Office of Air Quality Planning and Standards
ORD	EPA Office of Research and Development
O ₃	Ozone
SAB	EPA Science Advisory Board
UV-SL	Ultraviolet-Scrubberless Method

Consensus Responses to Charge Questions on EPA's Recommended Federal Reference Method for Ozone: Nitric Oxide-Chemiluminescence

Background

EPA scientists conduct methods evaluation research to assess ways of accurately and reliably measuring criteria pollutants in ambient air. These methods — called Federal Reference Methods (FRMs) — are descriptions of how to sample and analyze levels of criteria air pollutants, and are used by states and other monitoring organizations to assess implementation actions needed to attain National Ambient Air Quality Standards (NAAQS). The Clean Air Act requires the EPA to set NAAQS for six common air pollutants (i.e., particulate matter, ground-level ozone, carbon monoxide, sulfur oxides, nitrogen oxides, and lead).

An FRM serves as the standard protocol for measuring ambient concentrations of one or more of the six criteria air pollutants, and each of the pollutants has at least one FRM. FRMs are used to determine whether a given geographic region is in compliance with the NAAQS. To allow innovation and advance new technologies, the EPA also reviews, tests, and approves other methods, called Federal Equivalent Methods (FEMs), which are based on different measurement technologies than FRMs but must be as accurate as FRMs. FRMs thus serve as the “gold standard” against which the field- and laboratory-based performance of emerging monitoring technologies (i.e., FEM candidates) are compared. Given the importance of the roles of FRMs, when a new reference method is proposed as an additional FRM, it is crucial to ensure that its measurement performance is as good as or exceeds that of the current FRM.

The existing ozone (O₃) FRM is based on the Ethylene-Chemiluminescence (ET-CL) method. Analyzers implementing this method are no longer being manufactured or supported. The EPA's Office of Research and Development (ORD) reported that the last O₃ FRM analyzer was designated by the EPA in 1979, and most designated O₃ FRM analyzers now are either inoperative or too old to serve as an FRM.

In 2009, EPA consulted a previous Clean Air Scientific Advisory Committee (CASAC) monitoring subcommittee (the Ambient Air Monitoring & Methods Subcommittee - AAMMS) on ambient air monitoring issues related to the O₃ NAAQS, including issues related to the development of a second FRM for measuring O₃. During the 2009 consultation, several individual AAMMS members recommended that the EPA consider developing a new FRM for Ozone that is reasonably free of interferences and is commercially available. The agency considered the individual AAMMS member comments,¹ and now is recommending that the Nitric Oxide-Chemiluminescence, or NO-CL, Method should be a second O₃ FRM.

The NO-CL Method is currently an FEM, and the EPA noted that the NO-CL method's principle of operation is similar in concept to that of the current ET-CL FRM. The EPA has also stated that its analysis of the field and laboratory performance of the NO-CL method indicated that data from the NO-CL method closely parallel the ET-CL FRM. The EPA further stated that the NO-CL method has an

¹March 6, 2009 CASAC AAMMS Consultation on Ambient Air Monitoring Issues Related to the Ozone NAAQS, [http://yosemite.epa.gov/sab/sabproduct.nsf/64B88B99C37A68CF852575710072D8C0/\\$File/EPA-CASAC-09-005-unsigned.pdf](http://yosemite.epa.gov/sab/sabproduct.nsf/64B88B99C37A68CF852575710072D8C0/$File/EPA-CASAC-09-005-unsigned.pdf)

added benefit in that it is a current FEM and is fully-qualified for promulgation as an FRM. The EPA also recommends that the existing ET-CL FRM be retained to ensure continued authorization for the use of existing FEMs that were designated based on comparisons to the ET-CL FRM.

In this current review, the CASAC Air Monitoring and Methods Subcommittee (AMMS) reviewed EPA's analysis and technical documentation on the NO-CL method, and responded to four charge questions from the agency. The document reviewed by the CASAC AMMS is the technical portion of the package for the O₃ NAAQS Review that focuses on the EPA's recommended second FRM for O₃ (i.e., Appendix D-1 to 40 CFR Part 50 – Reference Measurement Principle and Calibration Procedure for the Measurement of O₃ in the Atmosphere – NO—Chemiluminescence, NO-CL, Method; January 2, 2014 Draft).

The CASAC AMMS reviewed supplemental material that the EPA presented during the April 3, 2014, CASAC AMMS teleconference call and supplemental material that EPA provided on May 5, 2014, for the CASAC consideration. CASAC's advice regarding its review of EPA's analysis, review of technical documentation on the NO-CL method, and its response to the EPA charge questions, is contained within this CASAC report.

Response to Charge Questions

CASAC focused on the following charge questions as part of its review, and provides the following responses to these charge questions.

Adding a New Ozone FRM

Charge Question 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.

CASAC agrees that the current O₃ FRM is out of date because the ET-CL-based instrument is no longer commercially available, and that a new O₃ FRM should be added. CASAC does not anticipate significant issues associated with having two FRM's for O₃ on the EPA list of FRM/FEM instruments; this is consistent with the EPA's approach when a new sulfur dioxide (SO₂) FRM was added as part of the 2010 SO₂ NAAQS revision regulation.²

²See *Federal Register* Notice (Volume 75, Number 119, page 35593): Appendix A–1 to Part 50—Reference Measurement Principle and Calibration Procedure for the Measurement of Sulfur Dioxide in the Atmosphere Ultraviolet Fluorescence Method.

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

Based upon review of all materials provided by EPA for the CASAC consideration, including supplemental material provided by EPA on May 5, 2014, CASAC agrees that the NO-CL method is a good candidate for FRM status.

During the April 3, 2014 AMMS teleconference call, the EPA presented its initial analyses of data collected on side-by-side comparisons with the current and proposed FRM. The EPA laboratory evaluations demonstrated that while the candidate NO-CL method met laboratory interference tests and other laboratory requirements for FRM designation, comparisons between the NO-CL and ET-CL appeared to have more scatter than expected and possible drift in one or both instruments. CASAC AMMS members encouraged the EPA to refine the analysis, and after the April teleconference EPA continued to analyze data to sort out sources of variability between candidate NO-CL analyzers and the ET-CL method. On May 5, 2014, EPA submitted its reanalysis of this data as supplemental material for CASAC's consideration.

The EPA's May 5, 2014 supplemental material indicates that the scatter that was apparent in the data presented previously to the CASAC AMMS was, in fact, due to problems with how the ET-CL FRM instrument was operated and not due to the instrument itself. Those problems included a change in instrument span that occurred on Sept. 16, 2013, and a loose particulate filter that led to eight inaccurate hourly measurements. When those problems were corrected, scatter was markedly reduced and correlations were found to be excellent. Subsequent to the April 3, 2014 teleconference call, EPA staff provided final data sets from the RTP and LAP field campaigns. Final data differed from preliminary data in that zero and span responses were used to adjust data from some of the analyzers, including the ET-CL FRM. Within the EPA's May 5, 2014 supplemental material, EPA staff also provided summary statistics for zero and span responses for all analyzers. Review of the final data sets indicates that the NO-CL analyzer exhibits acceptable zero and span variation. The NO-CL method also compares extremely well with the existing ET-CL FRM. These updated results make a convincing case for designation of the NO-CL method as an FRM.

Before proceeding with FRM designation of the NO-CL method, CASAC recommends that the EPA thoroughly assess results of its additional field tests on the NO-CL method that were planned for late June 2014 in Denver to ensure that the data from the candidate FRM are in good agreement with the existing FRM.

CASAC also notes that water vapor is an interferent in the NO-CL method and causes reduced signal due to quenching of the excited NO₂ molecule. This effect can reduce apparent O₃ concentrations by 10%, or more (Boylan et al., 2014), but is minimized in commercial NO-CL analyzers by drying the sample. Given this sensitivity to water vapor, CASAC agrees that periodic checks of onboard dryer performance may be warranted. This is best accomplished by requiring the method to include loggable Relative Humidity (RH) and temperature measurements down-stream of the sample cell.

The proposed revision to Appendix D-1 of 40 CFR Part 50 (i.e., Reference Measurement Principle and Calibration Procedure for the Measurement of O₃ in the Atmosphere – NO—Chemiluminescence, NO-

CL, Method; January 2, 2014 Draft) needs additional detail. Information similar to what is included within EPA's *Federal Register* Notice for the Ultraviolet Fluorescence Method for SO₂ should be included in Appendix D-1 to 40 CFR Part 50 for the NO-CL method. The EPA should further develop Appendix D-1 to include additional requirements, including information on the measured wavelength range for this method, a "schematic diagram" (see Fig. 1 for the SO₂ FRM), and relevant references to the method. Additional requirements that are not specified in Table B-1 of part 53.20 should be included in this Appendix, such as response linearity and operating environmental temperature test specifications. Mercury vapor interference limits for UV methods need to be included in Table B-1. See Dr. Judy Chow's individual comments for more details and relevant references.

CASAC also recommends that the EPA replace Reference 8, "Transfer standards for calibration of Ambient Air Monitoring Analyzers for Ozone" dated 2010 with the October 2013 version (U.S.EPA, 2013).

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

CASAC recommends that the EPA should identify monitors that are suitable for routine state and local agency monitoring networks. Monitors should be reliable, have minimal service requirements, not require excessive operator time, and not be cost-prohibitive or resource intensive.

In addition to the NO-CL method, the EPA should continue to consider and vigorously evaluate the Ultraviolet-Scrubberless Method (UV-SL) as an additional O₃ FRM, since UV-SL monitors based on light absorption have been shown to not have the level of interference problems that exist in the current light absorbance FEM monitors. 2B Technologies Inc. submitted the material needed to qualify the Model 211 monitor as an FEM, and on June 18, 2014, EPA designated the Model 211 as an FEM (79 FR 34734). The EPA analyses provided to the CASAC AMMS on May 5, 2014 show excellent correlations between UV-SL and the ET-CL FRM, and between UV-SL and NO-CL, albeit with an unexplained ~2 ppb zero offset for the UV-SL method. The 2B Tech Model 211 light absorption UV-SL O₃ monitor is described in 2B Technologies Inc. patent (Birks et al., 2013). It has been shown through research and publications to not have the level of interference problems that exist in current light absorbance FEM monitors. It is likely that the SL-UV method may be acceptable as a third FRM if the 2 ppb zero offset present in the EPA tests is resolved. If the EPA eventually proposes to make the UV-SL method an FRM, the agency should develop additional detail similar to what is included within EPA's *Federal Register* Notice for the Ultraviolet Fluorescence Method for SO₂ within Appendix D-1 to 40 CFR Part 50 for the UV-SL method and discussed in the response to Charge Question 2.

Like the NO-CL method, the UV-SL method requires a source of reagent NO. The 2B Tech Model 211 presently uses a photolysis cell to produce NO from a cylinder of pure N₂O, or potentially a cylinder of high concentration NO. In routine operation, the Model 211 consumes approximately 6 m³ per year of N₂O. This should be taken into account when considering cost and space requirements for deployment.

There are other measurement methods available to measure O₃, including quantum cascade laser based tunable multi-pass IR absorption spectroscopy, cavity ring down spectroscopy (CRDS) and cavity attenuated phase shift spectroscopy (CAPS) methods. The CRDS and CAPS methods measure O₃

indirectly via absorption of NO₂ from reacting O₃ with NO. However, monitors using these methods are relatively expensive and more complex in comparison to monitors using the UV-SL or NO-CL methods, and are not broadly in use throughout state agencies, and thus are not practical at this time for consideration as FRMs.

There are also low-cost/low-power sensor-based monitors that have been developed for O₃ measurement that are discussed in the response to Charge Question 4. These low-cost sensor-based monitors are probably not sufficiently developed to be considered as FRMs at this time.

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

Current U.S. NAAQS regulations require use of a narrow range of FRM/FEM monitoring equipment that is expensive, complex, and stationary. Sensors are low-cost (e.g., a few hundred dollars), easy-to-use, portable air pollution monitors that can provide highly time-resolved data. While FRM and FEMs are relatively expensive to operate and are likely to be deployed at locations that are specifically tied to a regulatory monitoring requirement, sensors can supplement this monitoring network to provide non-regulatory air quality monitoring data in locations where FRM/FEM monitors are either not cost-effective or not practical. Sensors need to be thoroughly evaluated to ensure that their performance specifications for precision, accuracy, sensitivity, interferences, and other criteria meet the necessary monitoring objectives.

Low-cost sensors may be useful for developing micro scale and personal exposure estimates that can augment neighborhood or urban scale regulatory monitors, if these sensors are of sufficient precision and accuracy and small and light enough for such applications. Their portability and low power requirements make them potentially useful for measuring air quality throughout a person's day, both indoors and outdoors. Actual exposure information is important because ambient standards are generally based on outdoor urban scale exposure which is not representative of actual exposures for a majority of the population. This is especially true for reactive pollutants such as O₃ which typically have very different indoor and outdoor concentrations. White (2009) also points out that monitoring requirements for regulatory and public health tracking may not align exactly. While health tracking seeks a more complete characterization of population exposure, including all the health-relevant species, regulatory monitoring places more weight on the measurement's absolute accuracy and pollutant specificity. For example, sensitivity to non-O₃ oxidants is considered an undesirable interference to FRM/FEM instruments. However, ozone is merely an indicator for a reactive mix of ozone and other photochemical oxidants that have health effects. Hence, low-cost sensors for photochemical oxidants could contribute to improved chemical exposure assessment.

A recent example of a cost-efficient technology for spatially dense ozone monitoring is described by Bart et al. (2014). A network using gas-sensitive semiconductor technology, solar power, and automated cell-phone communications was deployed and validated in a 50-sensor test-bed in British Columbia during 2012.

Low-cost O₃ sensors may also be suitable for research applications where cost, power requirement and instrument environmental considerations can limit or prohibit the use of FEM/FRM monitors. For

instance, high altitude balloon studies, studies of the influence of geographic features such as water bodies, mountains and canyons as well as studies of the spatial impact of NO_x sources are applications that may benefit from the use of low-cost sensors rather than regulatory monitors.

Currently available low-cost O₃ sensors may be useful in areas where there is sparse O₃ monitoring, such as in the rural intermountain west, or in urban settings with large spatial variations in concentration. In areas where spatial concentration gradients are smaller, measurements may require more accurate and precise instruments than sensors can presently provide.

Low-cost sensors do not need to meet the same specifications as regulatory monitors, since they are not used for determination of NAAQS compliance. However, in order to aid the interpretation of their data, low-cost sensors need to be well characterized (precision, bias, interferences) and also evaluated through co-location with regulatory monitors. It is unlikely that current low-cost sensor-based monitors would be appropriate as an additional (or replacement) O₃ FRM.

REFERENCES

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Appendix A

Compendium of Individual Comments by CASAC Air Monitoring and Methods Subcommittee Members on EPA’s Recommendation for an Additional Federal Reference Method for Ozone: Nitric Oxide-Chemiluminescence

MR. GEORGE A. ALLEN.....	A-2
DR. LINDA J. BONANNO	A-3
DR. JUDITH C. CHOW.....	A-4
DR. KENNETH DEMERJIAN	A-17
MR. ERIC S. EDGERTON.....	A-20
MR. HENRY (DIRK) FELTON.....	A-22
DR. PHILIP FINE	A-24
DR. PHILIP HOPKE.....	A-25
DR. RUDOLF HUSAR.....	A-28
DR. PETER H. MCMURRY	A-29
DR. ALLEN ROBINSON.....	A-30
DR. ARMISTEAD (TED) RUSSELL	A-32
DR. JAY TURNER	A-34
DR. YOUSHENG ZENG.....	A-36

Mr. George A. Allen

The revised test data provided to the AMMS by ORD on May 5 is very helpful and resolves issues regarding the NO-CL candidate FRM that were raised on the April 3 AMMS call and in the May 1 draft AMMS letter.

Q #2:

The May 5 ORD additional data analysis appear to resolve issues with performance of the NO-CL candidate FRM that we discussed on our call and in the first draft of the letter; the NO-CL candidate FEM used for that comparison had performance issues with span stability, and some hours when there was a leak in the FRM's particle filter holder have been removed. The LaPorte/Houston NO-CL vs. FRM comparison that was of concern during our initial call is shown on page 14 of the additional May 5 ORD analysis; the NO-CL method corrected data now show excellent agreement with the FRM data.

Q #3:

The same FRM data noted above are used to demonstrate the performance of the UV-SL candidate FRM at the Houston site on page 15, and on page 16 the 2 candidate FRMs are compared directly to each other. I agree with ORD that these tests show the UV-SL analyzer has a ~ 2 ppb offset (1.9 with the FRM, and 2.2 with the NO-CL candidate FRM analyzer). The offset for the NO-CL vs. FRM is 0.3 ppb (page 14). EPA does not report the statistical significance of these intercepts (is the intercept different than 0 at $p=.05$), but visually (given the large # of data points near zero ppb), the ~ 2 ppb offset of the UV-SL is likely to be significant (e.g., real). ORD does not provide any reason for the UV-SL positive intercept in the revised May 5 material for review. If it is significant and remains unexplained, this may be of concern in the context of recommending the UV-SL as an additional FRM.

Another topic for consideration is if EPA has performed sufficient testing of the UV-SL method to allow us to recommend that it be a FRM. The UV-SL has not been through as much testing (different sites, seasons, etc.) as the NO-CL method -- that's just what ORD has brought to the table. Given the court-ordered deadline for an ozone NAAQS NPRM of December 1, 2014 as well as the timing for finalizing this Advisory Report, there may not be time for ORD to do additional testing of the UV-SL method for the AMMS to consider.

Dr. Linda J. Bonanno

Charge Question 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.

Response: Good idea since the Ethylene method is out of date and as long as the NO method shows that it's the same or better than the FRM and it's not more prone to interferences and is easy to implement/practical for routine monitoring.

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

Response: Is it really worth the effort to make the NO FEM method an FRM method?

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

Response: UV method?

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

Response:

Are there plans to designate this technology as FRM or FEM?

Would measurements be used for designation purposes?

I'd just want to be sure that there's adequate evidence that the low-cost sensor technology performs same as FRM/FEM. Monitors in rural areas can record high levels of ozone because of the low concentration of scrubber gases (NO_x)

Dr. Judith C. Chow

Charge Question 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.

Response:

Adding O₃ FRMs would be useful since the Ethylene-Chemiluminescence FRMs (Beckman 950A, Bendix 8002, CSI 2000) that were used in U.S. monitoring networks during the 1970s–1980s, are no longer commercially available (Leston et al., 2005). Current performance criteria (Code of Federal Regulations, 2010) for O₃ Federal Equivalent Methods (FEM) allow 10 ppb as a minimum detection limit, 12 or 24 hour zero-span drifts of 20 ppb, interferences of 60 ppm, and precision of 10 ppb. These criteria are outdated and need to be revised to support the current 75 ppb O₃ National Ambient Air Quality Standards (NAAQS) as acknowledged in the Integrated Science Assessment for Ozone and Related Photochemical Oxidants (U.S.EPA, 2013a).

EPA should consider specifying FRM performance criteria (Chow, 1995; Watson et al., 1995) rather than specifying a measurement method or instrument design, such as the NO-CL. Such performance criteria should include specifications and tolerances for: 1) baseline stability; 2) span stability; 3) response linearity; 4) minimum detectable limits; 5) tolerance of known interfering species at normal ambient and extreme ambient concentrations; 6) response time; 7) flow control; and 8) sensitivity to environmental extremes (temperature, humidity, precipitation). The specifications should be the ideal, with tolerances that can be achieved with current technology. Tolerances could be reduced as future technologies allow. As noted above, the current FEM tolerances (Code of Federal Regulations, 2010) may have been appropriate for 1980s measurement technology, but they are much too loose for current technology. Any measurement principle or instrument design that meets these criteria would qualify as a FRM.

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

Response:

The light emitted by chemiluminescence from gas-phase chemical reaction of O₃ with nitric oxide (NO) (Figure 2 from Clough and Thrush, 1967) has long been used to quantify NO concentrations (NO_x) (Saltzman et al., 1956; Saltzman and Gilbert, 1959), and this method is defined as the FRM for NO₂ (Code of Federal Regulations, 1983). It seems logical, then, to use the same principle for the detection of O₃ when it is properly implemented. Interferences from HNO₃, PAN, and other nitrogen-containing species that are converted to NO (Dunlea et al., 2007; Villena et al., 2012; Winer et al., 1974; Xu et al., 2013) for this FRM are not an issue for O₃ detection. The Teledyne Model 265E (Teledyne API, 2011) is a commercially-available NO-CL analyzer and an FEM. The wavelengths monitored by this instrument are not specified, though Kalnajs and Avallone (2010) cite 830 nm as the detection wavelength while Stedman et al. (Stedman et al., 1972) cite 648 nm. It appears that detectors sensitive to the red to near-IR part of the spectrum are used in most method implementations (Minarro et al., 2011;

Ray et al., 1986; Ulanovsky et al., 2001; Zahn et al., 2012; Zhang et al., 2010). The NO-CL method has the advantage over the ethylene-chemiluminescence method since it has faster reaction rates, higher signal to noise (m/z) ratio, the ability to work under vacuum, requires a smaller reaction volume, and accommodates flexible operating conditions (Pearson and Stedman, 1980; Ridley et al., 1992).

Many compounds emit light upon reaction with O_3 (Hansen et al., 1977; Mihalatos and Calokerinos, 1995; Toda and Dasgupta, 2008; Zhang et al., 2010; Zhang et al., 1999), including ethylene which is the basis for the current CL FRM (Code of Federal Regulations, 1997). Light from these reactions is typically broad-band and extends from the UV to IR regions of the spectrum. These reactions do not appear to affect light from the NO- O_3 reaction (Figure 2 from Clough and Thrush, 1967) when it is assumed that such reactions have already taken place in the atmosphere prior to entering the sensing zone.

When the NO reactant concentration is much higher than ambient levels, the effect of ambient NO appears to be negligible. Interferences from water vapor (Pearson, 1990) are eliminated by sample drying at the inlet (Wilson and Birks, 2006) and reaction-quenching by changes in the atmospheric composition appear to be negligible. Improved sensitivity and specificity of the NO-CL method has been recognized (Parrish and Fehsenfeld, 2000), but its linear response to O_3 must be externally calibrated. A few comparisons between UV absorption and NO- or ethylene-chemiluminescence methods were examined (Arshinov et al., 2002; Ryerson et al., 1998; Williams et al., 2006). Good correlations were found by Ryerson et al. (1998) based on five field measurements of urban plume, but NO-CL method reported ~5% systematically low measurements from aircraft as compared to UV absorption. The disagreement between NO-CL and UV measurements was attributed to the deficiency in photon counting efficiency of the NO-CL.

There have been limited comparisons of the NO-CL method with UV absorption methods (Ollison et al., 2013; Williams et al., 2006) that are in more common use. The most recent, and interesting results, are summarized in Figures 3 and 8 of Ollison et al. (2013), demonstrating good agreement with one UV absorption system and poorer agreement with another. The disagreement was attributed to UV interferences rather than NO-CL interferences in an environment known to have high VOC levels.

Although the concept is good, the proposed revision to Appendix D-1 of Part 50 needs additional work. It is a small modification to the current O_3 FRM specification (Code of Federal Regulations, 1997), which is itself sketchy on the design and performance standards needed to specify a FRM. For example, UV light-emitting diodes (LEDs) and photodiode detectors are now available (Fowles and Wayne, 1981; SETI, 2014; Sglux, 2014) that might mitigate some of the temperature dependence of the mercury lamp. Modern methods of linear regression that consider errors in both variables should be considered for calculating slopes and intercepts of calibration curves (York, 1966). More modern measurements of O_3 UV absorption efficiencies and their variation with temperature should be evaluated (Barnes and Mauersberger, 1987; Bass and Paur, 1981; Malicet et al., 1995; Mauersberger et al., 1987; Voigt et al., 2001). The statement in Section 3 of Appendix D-1 that "...the NO-CL measurement system is relatively free of significant interferences from other pollutant substances that may be present in ambient air" needs to be tested under a wider variety of conditions than have been reported to date. Spicer et al. (2010) provide a good example of an array of ambient and laboratory tests that would be useful. Figures 1 and 2 of Appendix D-1 also need to be revised to specify the optics and source. Reference 8, "Transfer

standards for calibration of Ambient Air Monitoring Analyzers for Ozone” dated 2010 should be replaced with the October 2013 version (U.S.EPA, 2013b) at the same website.

EPA’s May 5, 2014 PowerPoint presentation (Long et al., 2014) provides insufficient documentation to arrive at the conclusion that “based upon the work that has been done to date and this subsequent data analysis, ORD is confident that the NO-CL method meets and exceeds all requirements for proposal of a new FRM for ozone.” A full technical report, of which there are several examples (Holowecky et al., 2008; Leston, 2014; Spicer et al., 2010; U.S.EPA, 1979; U.S.EPA, 1998; U.S.EPA, 2013b), which includes: 1) specification of performance criteria (see above); 2) literature review; 3) explanation of measurement principles, interferences, and currently available instruments; 4) laboratory tests; 5) field tests (including site selection to evaluate interferences and environmental effects); 6) data analysis; and 7) recommendations. Slides 5 and 6 show that the “FRM” is inferior to the collocated FEMs, although it is unclear why this is the case; nor is it clear what specific instruments were tested, how old they were, or how they were maintained. Slides 8, 10, and 17 show that the NO-CL and UV instruments measure well within reasonable performance criteria, and there is no reason to select one method over the other as a FRM.

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

Response:

Spectrophotometric determination of atmospheric O₃ also has a long history (Bravo and Lodge, 1964; Grosjean and Harrison, 1985; Stair, 1959). An additional O₃ FRM by UV absorption should be considered, as most O₃ monitoring networks in the U.S. (i.e., federal, state, local, and tribal) use a UV photometric FEM. Switching from ethylene-CL to the UV absorption method apparently reduced operational costs and improved safety by eliminating the compressed flammable ethylene gas. Appendix D-1 uses this principle as the transfer standard that is in turn related to UV primary standards (Norris et al., 2013; Viallon et al., 2006). These units are mostly based on the 254 nm emission line from a low pressure mercury (Hg) discharge lamp as the UV light source (Leston et al., 2005). The major objection to them as FRMs has been the potential absorption interferences at this wavelength from certain VOCs, water vapor, and mercury. As indicated in Figure 8 of Ollison et al., 2013, it appears that it is possible to compensate for these with appropriate sample pre-treatment and parallel absorbance cells.

For an intercomparison in Mexico City, Dunlea et al. (2006) did not observe positive or negative interferences on UV O₃ monitors, although the potential interference from oxidized or nitrated aromatics needs to be further tested. When UV O₃ monitors were compared with collocated research-grade open-path instruments (i.e., DOAS and FTIR measurements), up to 18% discrepancy was found. Interferences with UV O₃ measurements from fresh diesel emissions were found and attributed to fine particles ($d_p < 0.2 \mu\text{m}$) passing through the particulate filter and scattering/absorbing radiation within the detection cell. Ollison et al. (2013) and Johnson (2014) demonstrated the use of scrubbed O₃ with excess NO generated in situ by photolysis of added nitrous oxide (N₂O) in 2B Technologies Model 211. This process eliminated the need for a conventional O₃ scrubber. Different scrubbers (e.g., non-heated MnO₂, heated silver wool, or optimal heated metal scrubber) and interference by ultrafine particles in UV O₃ systems need to be further tested prior to consideration as an additional O₃ FRM.

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

Response:

It is a good idea to consider low cost sensor technology to supplement regulatory O₃ monitoring in rural or remote areas. These would also be useful for human exposure studies to determine how concentrations differ from urban-scale compliance monitors.

Early O₃ measurements monitored the cracks in a piece of bent rubber (Beatty and Juve, 1955; Bradley and Haagen-Smit, 1951; Soret, 1853), and these were indicative of different levels. More recently, passive samplers have been used for long-term averages and exposure studies, although variable diffusion rates increase concentration uncertainty (Bhangar et al., 2013; Cox, 2003; Geyh et al., 2000; Grosjean and Hisham, 1992; Manning et al., 1996; Monn and Hangartner, 1990; Plaisance et al., 2007; Varns et al., 2001). Ozonesondes (Brewer and Milford, 1960; Hogrefe et al., 1998; Johnson et al., 2008; Komhyr, 1969; Liu et al., 2006; Newchurch et al., 2003; Shiotani et al., 2002; Vomel and Diaz, 2010) use a buffered potassium iodide (KI) reaction (Byers and Saltzman, 1958; Hodgeson et al., 1971; Kopczynski and Bufalini, 1971) with coulometric or colorimetric detection. The disadvantage of this method is that it responds to all oxidants, not just O₃, and it has a limited capacity. Longer-lived electrochemical detectors are being developed (Knake and Hauser, 2002; Williams et al., 2013).

For remote environments, continuous monitors must be small, lightweight, low power, and easy to operate. Hintsa et al. (2004) tested two O₃ sensors (i.e., Physical Science Inc. [PSI; Andover, MA] and 2B Technologies [Golden, CO]) for O₃ monitoring at ocean buoys and towers. These sensors reported good precision (~1–1.5 ppm) and accuracy (~2%) with 4–4.5 Watts power required. The 2B Technologies O₃ monitor has been applied in the National Park Service network (<http://www.nature.nps.gov/air/Studies/portO3.cfm>), and a modified 2B Model 202 was also found to sustain low temperature (<–60 °C) in the Antarctic (Bauguitte et al., 2011).

2B Technology Personal Ozone Monitor (POM) with a 0.34 Kg weight and 3 Watt power requirement can be considered as a low-cost sensor (~\$5,000 vs. ~\$9,000–13,000 for a conventional O₃ monitor). An example of collocated comparisons at Sparks, NV, the monitoring site operated by the Washoe County Health Department, is shown in Figure 1 for a collocated comparison among three UV absorption O₃ monitors: 1) Teledyne API Model 400E; 2) 2B Technology Personal Ozone Monitor (POM); and 3) 2B Technology Model 205 for the period of 3/1–29/13 at Sparks, NV (Green et al., 2013)

The Sparks site is known to be affected by residential wood burning during cold nights (Chow et al., 1988). The effect of wood smoke VOCs (Huntzicker and Johnson, 1979) can be seen on the POM results for several nights in a higher concentration. These also seem to correspond to lower concentrations during the daytime. The three monitors tracked well, with correlations (R^2) of 0.82–0.93; larger intercepts (4.87 ppb) were found between the 2B Model POM and API 400E and between the 2B Models POM and 205 (intercept of 5.32 ppb) as shown in Figure 2. (Green et al., 2013)

O’Keeffe and Lewis (2007) used an optical fiber sensor to measure O₃ at both UV (254 nm) and visible (603 nm) absorption spectra. The sensitivity of optical fiber sensors is proportional to the path length of the gas cells. Optical fiber sensors minimize chemical and electromagnetic interference with relatively low cost.

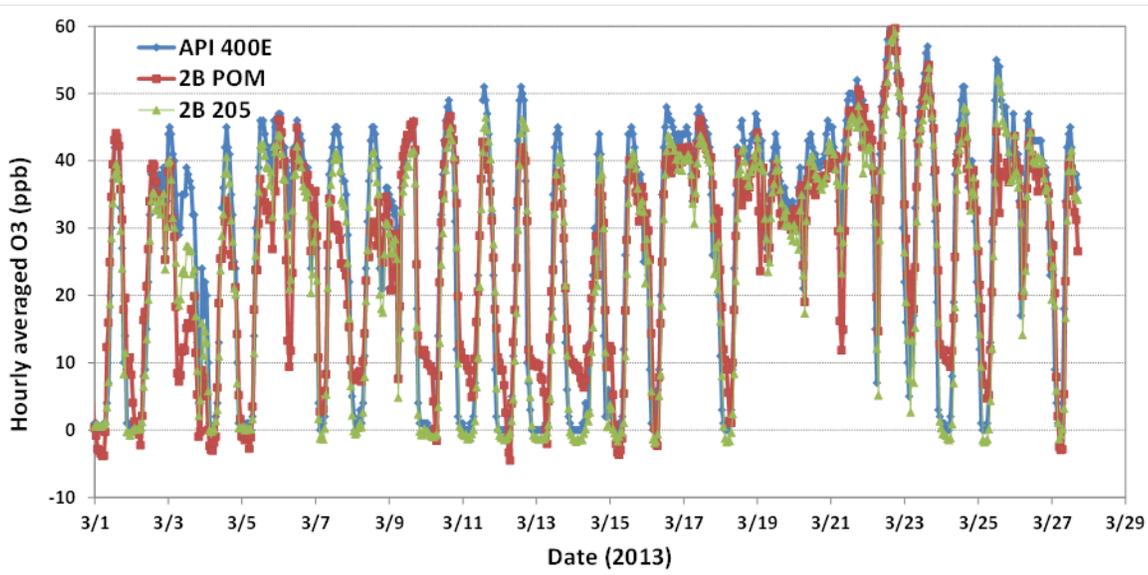


Figure 1. Collocated comparison among three UV absorption O₃ monitors: 1) Teledyne API Model 400E; 2) 2B Technology Personal Ozone Monitor (POM); and 3) 2B Technology Model 205 for the period of 3/1–29/13 at Sparks, NV (Green et al., 2013). The Sparks site is known to be affected by residential wood burning during cold nights (Chow et al., 1988) The effect of wood smoke VOCs (Huntzicker and Johnson, 1979) can be seen on the POM results for several nights in a higher concentration. These also seem to correspond to lower concentrations during the daytime.

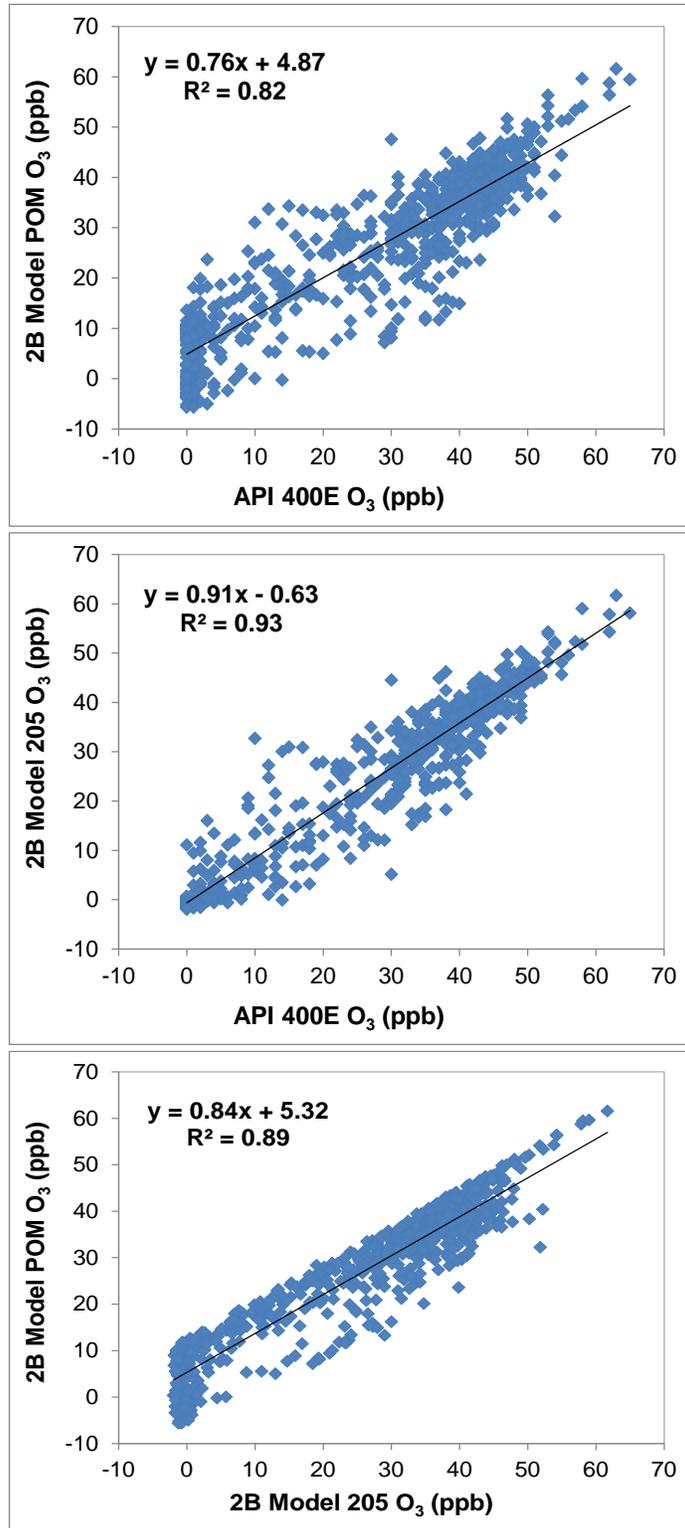


Figure 2. Collocated comparison of one hour averages for three collocated O₃ monitors: 1) Teledyne API Model 400E; 2) 2B Technology Personal Ozone Monitor (POM); and 3) 2B Technology Model 205 in Sparks, NV during 3/1–29/13 (Green et al., 2013).

Fowles and Wayne (1981) proposed the use of an LED to monitor O₃. Laboratory tests were conducted by Kalnajs and Avallone (2010), similar to the dual-cell UV absorption technique (Proffitt and McLaughlin, 1983) in the TEI 49 O₃ analyzer. The single low-pressure mercury-vapor UV light source is replaced with a pair of solid state UV LEDs. The LEDs provide a stable light source with adequate intensity without the need for temperature control and high-voltage power supply, and reduces energy consumption as compared to the conventional mercury-vapor lamp. Gubarev et al. (2013) introduced a low-cost, lightweight (2.4 Kg) microprocessor O₃ meter based on UV absorption at 254 nm using corona discharge and semiconductor O₃ sensor. The reported accuracy was <3% and the device required very low power (11 Watts). Washenfelder et al. (2011) measured O₃ by chemical conversion to NO₂ in excess NO with subsequent detection by cavity ring-down spectroscopy.

Darby et al. (2012) combined cavity-enhanced absorption spectroscopy (CEAS) with a low pressure mercury lamp to achieve low detection limit (8.4 ppb) for O₃. Gomez and Rosen (2013) reported a fast-response cavity-enhanced O₃ monitor based on incoherent broadband CEAS (IBB-CEAS) with ~1 ppb sensitivity at 0.1 s integration time. Gao et al. (2012) documented the development and testing of the NOAA-2 O₃ monitor using the polarized UV beam in the absorption cells to reduce cell length and a capillary mercury lamp to increase UV intensity. A chemiluminescence O₃ detector for airborne applications is also presented by Zahn et al. (2012).

Other techniques, including photoacoustic (Veres et al., 2005), solid state (Korotcenkov et al., 2007a; 2007b; 2009; 2014; Korotcenkov and Cho, 2012), and electrochemical cells cited above need to be further tested. The performance of several O₃ monitors employing several different operation principles is shown in Table 1 of Gomez and Rosen (2013). These low-cost, lightweight O₃ monitors need to be collocated with proven O₃ monitors (e.g., FRM or FEM) to assure their equivalence and comparability during O₃ measurements. Bowman (2013) calls attention to the need of an international O₃ air quality monitoring system that integrates a continuum of observations from local to global scale, including both ground- and satellite-based observations of O₃. Tests of low-cost O₃ microsensors should be part of the EPA tasks to verify the emerging technology.

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Dr. Kenneth Demerjian

Charge Question 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.

Response:

It seems that referring to the development of a new O₃ FRM as an additional FRM to supplement the current Ethylene-Chemiluminescence (ECL) method is confusing. If the ECL is no longer produced or supported, are we not proposing a replacement of the O₃FRM. I don't see that we have a choice but to establish a new O₃ FRM and decommission the current ECL FRM.

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

Response:

Establishing the Nitric Oxide-Chemiluminescence (NO-CL) method as the new O₃ FRM is a logical choice given the techniques track record and performance characteristics in NO monitoring instrumentation. That being said, much of the literature on (NO-CL) pertains to its application in NO measurement systems and not for ozone monitoring. Studies related to the design of CL reaction cells to optimize light gathering, achieve faster flows to reduce residence times and lower pressure have all improved NO detection limits and sensitivity. This collection of work has also identified interferences affecting detection limits and reported on a variety of intercomparison studies of (NO-CL) measurements related to the measurement of NO, NO₂, and NO_y. This work should be reviewed and relevant aspects to the proposed O₃ (NO-CL) FRM cited (see references below). Operational modifications have also been introduced (Ollison et al., 2013) to existing instrumentation (UV absorption and NO-CL) that mitigates some well known interferences and improves O₃ measurement accuracy. Further analyses and additional intercomparison studies performed by ORD on the NO-CL and UV-O₃ scrubberless (SL-UV) methodologies with the ECL FRM, suggest very similar performance statistics, with the possible exception regarding the high zero offset (~2.0ppb) observed in the SL-UV measurement method (see slides 15-16 ORD supplemental presentation). Although nightly zeroing (slide twelve) does not seem to explain the observed results, the presentation does not indicate how the chemical zeroing was performed (i.e., using NO from a cylinder or generated from the photolysis of N₂O, an option on the 2B Tech Model 211). If the photolysis of N₂O was the NO source, it is conceivable that it is the source of the zero offset. For example, O(¹D) generated in the photolysis of N₂O is a potential source of OH (via O(¹D) reaction with H₂O) which is highly reactive with other compounds (e.g., VOCs) forming oxidized products with uv absorbing properties in 254nm region.

Reported SL-UV interferences (e.g. xylene, SO₂, NO₂, H₂O) are low and do not seem likely to account for the zero offset. ORD may want to consider performing systematic zeroing (e.g., hourly) to see if this reduces the offset.

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

Response:

Based on the results presented in ORD intercomparison of the SL-UV method as discussed above, I would support its consideration as an additional O₃ FRM. Other techniques available for O₃ FRM status but rather expensive include Quantum Cascade Laser based tunable multi-pass IR absorption spectroscopy; cavity ring down spectroscopy (CRDS) and cavity attenuated phase shift spectroscopy (CAPS) both of the latter techniques measure ozone indirectly via NO₂ from reacting O₃ with NO.

The JSC Optec 3.02 P-A chemiluminescent ozone analyzer looks like a promising FEM

Regarding Guidance/Opinion on Emerging Measurement Methodologies: Recent application of an O₃ semiconductor gas sensor array network reported by Bart et al., 2014 is an interesting example of an emerging measurement methodology. Such techniques show promise in providing expansive spatial coverage and resolution of ozone concentrations at relatively low cost with some caveats (see response to CQ#4).

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

Response:

Deployment of low-cost sensor technology to improve spatial coverage of relative ozone concentrations is a useful strategy, if it is backed-up with selective placement of O₃ FEM(s) to support the absolute ozone calibration of the sensor array.

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Mr. Eric S. Edgerton

Charge Question 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.

Response: This makes sense, given the status of the of the ethylene-chemiluminescence method.

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

Response: NO-CL is a good choice for a new FRM. The reaction has long been used to measure NO and other components of NO_y at sub-ppb concentrations with minimal interference and good linearity over a broad dynamic range. Field tests performed by ORD show excellent agreement with the O₃ FRM, when data from both analyzers are corrected for zero and span response. In addition, the NO-CL method exhibits greater zero and span stability than the current O₃ FRM and the UV FEM. The one significant issue with NO-CL is variable water vapor (quenching). Boylan et al., 2014 show that water vapor interference is on the order of 4.2% per 10,000 ppm H₂O. This can be very significant, given that summertime H₂O concentrations can approach 40,000 ppm in the southeastern U.S. I believe the instrument design reduces this effect by drying sample air upstream of the reaction chamber. In practice, it may be advisable to verify dryer performance on a periodic basis. It might also be worthwhile revisiting the interference equivalent test procedure specified in 40 CFR Part 53. My interpretation of Table B-3, is that water vapor interference testing for the ethylene chemiluminescence (ET-CL) O₃ FRM is performed in zero air (i.e., no pollutant). This may be appropriate for ET-CL, but this is not the case for NO-CL.

Boylan, P., Helmig, D., and Park, J.H. Characterization and mitigation of water vapor effects in the measurement of ozone by chemiluminescence with nitric oxide. 2014. Atmos. Meas. Tech. 7: 1231-1244. doi:10.5194/amt-7-1231-2014, 2014.

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

Response: The scrubberless-UV (SL-UV) method tested by ORD shows great promise and easily exceeds current and proposed specifications for FRM status in 40 CFR Part 53. Field tests are somewhat limited to date. Further evaluation is strongly encouraged. It should be noted, however, that the commercially available SL-UV method as of May 2014 requires an external source of compressed N₂O, and that this imposes cost, space and safety considerations on those who operate the method. Other chemical and spectroscopic methods exist for the measurement of ozone, such as cavity ringdown, but I see no reason to designate these FRM as opposed to FEM.

Clean Air Scientific Advisory Committee (CASAC) Draft Report (7/18/14) -- Do not Cite or Quote --This draft has not been approved by the chartered CASAC and does not represent EPA policy.

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

Response: Given current capabilities, I see little value in the use of low-cost sensors to supplement regulatory ozone monitoring, except possibly when it comes to questions of site selection. In this case, screening with low-cost sensors might assist in locating appropriate sites for regulatory monitoring purposes.

Mr. Henry (Dirk) Felton

Charge Question 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.

Response:

FRMs are important and necessary for all criteria pollutants. These methods must be available to provide very accurate data no matter where they are used and no matter what concentrations of co-pollutants are in the ambient air. This is because the primary purpose of FRMs is to serve as a bench mark for developers of FEMs. Developers of new methods must be able to properly operate an FRM so they can evaluate prototypes that may lead to improved methods in the future.

FRMs are also necessary to provide data for areas where inadequacies in FEMs may cause their data to be questioned. Monitoring agencies may want to deploy an FRM to obtain data that in the context of the NAAQS are free from biases or interferences.

It is important that an FRM be available for every criteria pollutant even if it is not routinely deployed by regulatory agencies. The existing Ethylene-Chemiluminescence method should be revoked because it is not commercially available, it is not a method that can easily be assembled as needed and there are no vendors providing service for the few remaining instruments in existence. The existing FEMs that were approved based on comparisons to the Ethylene-Chemiluminescence should keep their approved status until a new FRM is approved that demonstrates a significant improvement over the prior method.

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

Response:

After consideration of ORD's follow-up data analysis it is evident that the NO-CL method is an acceptable FRM for Ozone. The variability (imprecision) in the initial data report was explained by inconsistencies in the operation of the ET-CL FRM and not the NO-CL instrument. ORD's evaluation of several other Ozone methods is very interesting. It is likely that the SL-UV method may be acceptable as a second FRM once the noise and zero offset issues are resolved.

One disadvantage of the ET-CL and NO-CL method is the requirement for a reagent. The currently available NO-CL instrument requires a 10,000 ppm cylinder of NO in order to operate. This concentration of NO combined with the size of most cylinders for these applications represent a safety issue for personnel in the buildings where these instruments are located. In regulatory monitoring networks, instruments are sometimes located in schools or other public

facilities where gasses with concentrations above safety thresholds are not permitted. This should not preclude the instrument from consideration as an FRM although it may limit where it can be deployed.

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

Response:

Low cost sensors are not well suited to the measurement of regional secondary pollutants that do not vary significantly over wide regions in ambient air. Taking meaningful measurements in rural areas often requires instruments that are more accurate and precise than instruments that are used to measure concentrations that are closer to ambient standards. The variability between a regulatory measurement and a sensor reading in many cases would overwhelm the spatial differences between Ozone measured at two different ambient locations within the same region.

Low cost sensors are well suited for use in developing personal exposure estimates that can be compared to data collected at neighborhood scale regulatory monitors. Sensors are often inexpensive, portable and operate with low power requirements which make them ideal for measuring air quality throughout a person's day no matter where they are. Actual exposure information is important because ambient standards are generally based on outdoor neighborhood scale exposures which are not representative of actual exposures for a majority of the population. This is especially true for reactive pollutants such as Ozone which typically have very different indoor and outdoor concentrations. Sensor accuracy and precision issues can be resolved with careful study design and collocation with regulatory monitors.

Sensors are also likely to be better suited for many research applications where power and instrument environmental considerations can prohibit the use of a FEM or FRM. For instance, the newly installed near road NO₂ monitors may provide a new opportunity to deploy low cost Ozone sensors at locations near NO_x sources which can provide data that are useful for research at locations that are not well suited to regulatory monitoring.

Dr. Philip Fine

Charge Question 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.

Response: It is critically important that there be an ozone FRM that is commercially available from one or more manufacturers. Potential future ozone FEMs will need to demonstrate equivalency using an FRM, and the FRM should be readily available, affordable, and easy to use.

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

Response: Given the timeframe of the upcoming ozone NAAQs regulation, I can support the designation of this method as an FRM. However, if there is time to explore other methods that may have better performance, and look deeper into the source of error of the NO-CL comparison data, then perhaps other methods may emerge as better FRM candidates (See below).

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

Response: While other methods are more prevalent in ambient networks (i.e the UV photometric ozone FEM) there may not be a pressing need for additional FRMs if the current one under consideration is approved. But as shown in the EPA presentation, the new UV scrubberless method may show better performance than the NO-CL method. If there is time to further test this new method and it proves superior to the NO-CL method, then I recommend strong consideration as an FRM instead of the NO-CL method. I don't see a need for multiple new FRMs going forward, given that the FEM designation provides an adequate option for other regulatory monitoring methods.

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

Response: Since the typical ozone measurement technologies are relatively expensive to operate, maintain, and calibrate, lower cost sensors for ozone or other ozone related-pollutants could prove very useful in assessing the spatial extent of ozone issues, especially in rural areas. However, before such technology is used for regulatory monitoring, or even as a supplement to regulatory monitoring, the sensor performance must be fully characterized in order to properly interpret the generated data. Sensor testing should include evaluations for accuracy, precision, interferences, sensitivity, longevity, drift, and calibration procedures.

Dr. Philip Hopke

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

Response:

Light absorption

There are systems based on light absorption that do not have the level of interference problems that exist in the current light absorbance FEM monitors. This commercially available system, the 2B Tech model 211, is described in their patent (Birks et al., 2013) and has been used by Ollison et al. (2014) and Johnson et al. (2014). It has a water vapor control system although that has not been well described in their literature. This system uses gas-phase scrubber technology with NO added to the sampled air to quantitatively react with ozone and remove it from the sample. A low concentration of NO is added to the sample to generate ozone-free, reference air. The light intensity is measured in the reference and sample modes with a dual beam optical system so that the concentration of ozone can be calculated directly from Beer's Law. Nitric oxide can be supplied from an external NO cylinder and will provide over a year of gas supply. Alternatively, nitric oxide can be generated inside the instrument using an optional photolytic NO generator through photolysis of nitrous oxide (N₂O) that would also be supplied by an external cylinder. They also have a moisture compensation system that removes any water issues. The prior versions of the 2B Tech ozone monitors had been given FEM status so this improved unit would appear to be a strong candidate to be an FRM. They have submitted the material needed to qualify the Model 211 as an FEM. In the data presented by EPA, the Model 211 provided a tighter fit to the ethylene chemiluminescence data than does the NO-CL system so in terms of being the best replacement for the current FRM, it represents superior performance relative to the proposed NO-CL system.

The Birks et al. (2013) patent also includes bromine atoms as another gas phase ozone scrubber. Although normally one does not want to designate a patented technology as an FRM, this system does appear to provide a good system for ozone measurement that is worth consideration.

Electrochemical

An electrochemical ozone sensor uses a porous membrane that allows ozone gas to diffuse into a cell containing electrolyte and electrodes. When ozone comes into contact with the electrolyte, a change in electrochemical potential occurs between the electrodes causing electrons to flow. Korotcenkov and Cho (2012) provide a review of a major class of these sensors.

In zero air, little or no electron flow occurs. As the presence of ozone increases, the electrical signal increases proportionally. The monitor interprets this signal and displays the ozone concentration in PPM (parts per million).

Advantages

Linear Response

- Good repeatability and accuracy
- Very quick response time - 1-2 Seconds
- Long battery life
- Can measure ozone accurately up to 20 ppm
- Moderate resistance to interference

Disadvantages

- Humidity can affect sensor readings
- Sensitive to EMF/RFI
- Limited sensor life (often max of 12-18 months), even if in storage
- Decreased accuracy at low ozone levels (below 0.1 ppm)

Semiconductor-Based Ozone Sensors:

Heated Metal Oxide Sensor (HMOS)/Gas Sensitive Semiconductor (GSS)

A heated metal oxide semiconductor (HMOS) sensor works by heating a small substrate to high temperature (around 300-deg F / 149-deg C). At this temperature, the substrate is very sensitive to ozone and exhibits a change in resistance that is proportional to the amount of ozone which contacts its surface. The circuitry of the monitor interprets this change in resistance and displays the corresponding ozone level on the display as either PPM or PPB.

Advantages

- Very responsive to low levels of ozone (below 0.1 ppm)
- Least expensive monitoring technology
- Excellent repeatability and accuracy
- Long Sensor Life if stored properly

Disadvantages

- Slow start-up (can require 8-24 hours warm-up time)
- Slower response time to ozone (compared to electrochemical)
- Very sensitive to interference
- Shorter battery life due to heated sensor element
- Not linear at ozone levels above 1 ppm
- Max. Temperature threshold of 122F or less (depending on model)

It is not clear that either electrochemical or semiconductor sensors would be suitable for long term monitoring applications such as is needed for an FRM.

References

Birks, J.W., Anderson, C., Williford, J. (2013) Ozone Monitor with Gas-Phase Ozone Scrubber, Patent No.: US 8,395,776 B2.

Johnson, T., Capel, J., Ollison, W. (2014) Measurement of microenvironmental ozone concentrations in Durham, North Carolina, using a 2B Technologies 205 Federal Equivalent Method monitor and an interference-free 2B Technologies 211 monitor, *Journal of the Air & Waste Management Association*, 64:360-371.

Korotcenkov, G., Cho, B.K. (2012) Ozone measuring: What can limit application of SnO₂-based conductometric gas sensors? *Sensors and Actuators B: Chemical* 161:28–44.

Ollison, W.M.; Crow, W.; Spicer, C.W. (2013). Field testing of new-technology ambient air ozone monitors. *J. Air Waste Manage. Assoc.*, **63**(7):855-863.

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Dr. Rudolf Husar

Charge Question 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.

Initial Response to Charge Question 1: Overall View on Adding an Additional O₃ FRM

Adding the NO-CL O₃ monitor as additional FRM instrument is necessary, sound and timely.

The necessity arises from the fact that the aging ozone monitors need to be replaced or augmented in the regulatory monitoring network. Since the current Ethylene-based CL O₃ monitors are not available (not manufactured) an additional FRM monitor is a necessity.

The choice of the NO-CL O₃ monitor is sound for the reasons stated by EPA: (1) It is based on the same sensing principle; (2) the data quality and operational performance is similar to the current FRM and (3) the instrument has already been approved and in use as an FEM for Ozone. Also, the chemiluminescence method has been in use since the mid-1960s.

Assuring high quality and extensive O₃ monitoring with the additional O₃ FRM is also timely from regulatory perspective. Currently, O₃ and PM_{2.5} are the key pollutants that are in need for significant regulatory actions. Over the recent decade, the US PM_{2.5} concentrations have declined dramatically and approaching the 'natural conditions' in many regions of the US. However, ozone remains to be a more persistent pollutant and health hazard. Intense O₃ monitoring is necessary for enforcing NAAQS, for the determination of the human-'natural' contributions to the ambient O₃ as well as the identification of the diverse and uncertain sources of the secondary O₃ pollutant.

Dr. Peter H. McMurry

I have read all of the materials that Ed Hanlon attached with his earlier emails.

My Background:

I have not personally carried out ambient O₃ measurements in recent years, but have previously used ethylene-O₃Chemiluminescence and UV absorption instruments for measuring O₃ in the atmosphere and in laboratory studies. I do not have any personal experience with the proposed O₃-NO Chemiluminescence FRM.

Charge Question 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.

My Response to Charge Question 1:

Given that:

- O₃ is a criteria pollutant;
- ethylene-O₃Chemiluminescence method is the only existing FRM for O₃;
- a commercial ethylene-O₃Chemiluminescence instrument has not been available for 20 years;

it seems clear to me that there is a need for either (i) a commercial version of an ethylene-O₃chemiluminescence instrument or (ii) a new FRM based on a different measurement principle. If a new FRM is to be adopted, factors that must be considered include availability, reliability, capital cost, operating cost, sensitivity, and accuracy (including potential interferences). Also, side-by-side measurements of O₃ with instruments based on the new FRM and the current ethylene-O₃chemiluminescence FRM should be made in diverse environments and in all seasons to document the existence and magnitudes of any potential biases.

Dr. Allen Robinson

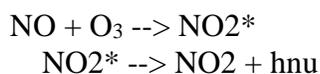
Charge Question 1: What is the AMMS view on adding an additional O₃ FRM (as Appendix D-1 of the 40 CFR Part 50 Federal Regulation) for the purpose of establishing a new FRM that is implemented in analyzers currently in production status? This new O₃ FRM will serve as an additional FRM to supplement the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

Response: Given the lack of commercial availability of existing O₃ FRM it seems important that the EPA establish commercially available O₃ FRM. It is not clear how EPA can meet the requirements of NAAQS certification without a commercially available O₃ FRM.

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

Response: The approach seems reasonable.

The NO chemiluminescence instrument runs on the reaction



Ordinarily such an instrument runs with a lot of O₃ to as to completely react away the NO.

So, I presume that what is being planned is to run an NO chemiluminescence instrument with a large excess of NO, so that the species being quantitatively titrated is O₃ and not NO. If so, there is no immediate reason to regard it as less accurate than the NO instrument, and the calibration should transfer. Therefore this seems suitable as an FRM method.

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

Response: No immediate suggestions come to mind.

*Charge Question 4: Guidance/Opinion on Emerging Measurement Methodologies:
What is the AMMS views on the use of low-cost sensor technology to supplement regulatory ozone monitoring (i.e., in rural areas)?*

Response: A low cost-sensor is potentially attractive to enhance the O₃ monitoring network. The key question is performance. These lower cost sensors do not have the performance of the more expensive FRM type sensors. Therefore EPA needs to carefully think about and clearly specify the required performance specifications. This seems especially important in more rural areas which may have lower O₃ levels, which may require improved performance. One can overcome some of the performance limitations of an individual sensor by deploying networks, but that will erode some of the cost savings.

Dr. Armistead (Ted) Russell

Charge Question 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.

Response: It is perfectly reasonable to move away from the ethylene chemiluminescent method given the circumstances as an FRM, and to a new method. It is not apparent why one should continue to include the old method and as an FRM except for continuity, or if there are no downsides to continue its inclusion.

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

Response: This makes sense. Though, as noted below, it might be good to consider additional sensors as well. One question I would have is if the proposed approach includes the best methods to minimize the impact of artifacts and biases.

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

Response: Given the widespread, and apparently successful, use of the UV-photometric instruments, why not consider that as an FRM? If I recall correctly, in past deliberations, we have recommended performance-based criteria for FRM status. On the other hand, if it continues as an FEM, and there are no major limitations to its use in regulatory monitoring relative to an FRM, it may not be worth making it an FRM as well.

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

Response: The main question here is what will be the purpose of these low cost sensors? Ozone is rather homogeneously distributed geographically, so there is actually less need to monitor in as many locations as some other pollutants. Thus, the need for low cost (and likely less accurate) sensors is diminished. However, that should not be construed as saying they should not be used in such an application when one can show that the combination of cost, power requirements,, accuracy, and other factors lead one to choose a low cost sensor. More specifically, EPA should not come out against using low cost sensors in applications where they might provide some benefits. However, unless their performance is proven to justify it, they should not be used in regulatory monitoring as it is not apparent that they can provide better estimates of the local concentrations than other methods involving some sort of spatial-temporal mapping and more accurate ozone monitors. The continued development of low cost sensors is strongly supported for other purposes, e.g., personal monitoring.

Clean Air Scientific Advisory Committee (CASAC) Draft Report (7/18/14) -- Do not Cite or Quote --This draft has not been approved by the chartered CASAC and does not represent EPA policy.

5. Comments on the additional data provided by ORD.

The additional data provided by ORD provide further support for the designation of NO-CL as an FRM.

Dr. Jay Turner

Charge Question 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.

Response: The proposal to establish an additional O₃ FRM is strongly supported. As clearly articulated in the supporting materials provided to the committee, instruments that conform to the existing FRM method are no longer commercially available. While it might seem convoluted to keep the obsolete FRM (Ethylene-Chemiluminescence method, hereafter simply called the “FRM”), the point was made that existing FEM designations were made by benchmarking against the Ethylene-Chemiluminescence method and thus it would be necessary to redesignate all of the existing FEM methods if the existing FRM was revoked. While revocation of the existing FRM would be a cleaner approach, the effort needed to redesignate the existing FRM methods is understandably difficult to justify. A migration to performance-based criteria would be a long-term solution.

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

Response: As discussed by the committee on April 3, the EPA performance evaluation (presentation materials from Russell Long *et al.*) demonstrates the Nitric Oxide-Chemiluminescence (NO-CL) method fared well in the laboratory evaluation (slide 9). The field data evaluated to date (slides 6-7) demonstrate small bias but considerable scatter between the methods for hourly data. Supplemental material dated May 5 made a compelling case that the major contributor to this scatter was from the FRM (RTP/AIRS study) and from initially not correcting the NO-CL and FRM data for variations in the night span check values (LaPorte/Houston study). Additional measurements conducted at RTP/AIRS in April/May 2014 demonstrate tight relationships between the NO-CL and FRM after correcting the latter for variations in nightly span check values.

Additional statistical measures of the scatter in the field evaluations data would be helpful. Scattergrams were provided for hourly data and it would be helpful to see the results for 8-hour average data. I presume the regressions in the evaluations are ordinary least squares (OLS) regressions. If so, the FRM measurement is being treated as absolute (no error) and it might be preferred to also use approaches that consider error in both the FRM and candidate measurements. Deming regression and orthogonal regression are examples of suitable approaches and the lead discussant for this charge question (Eric Edgerton) has previously published on their use. Regardless, confidence intervals should be provided for the regression slopes and intercepts.

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

Response: The UV method scrubberless ozone monitor (UV-SL) laboratory and field data appear quite promising. Based on the laboratory evaluation (slide 12), water vapor remains an interferent but at

~0.2 ppb equivalent is well below the current and proposed 40 CFR Part 53 specifications. The May 5 supplemental material further supports that high data quality can be achieved with the UV-SL method. EPA provided a reasonable explanation for proceeding at this time with the NO-CL designation as an FRM and possibly designating the UV-SL method as an FRM after additional testing.

I do not have access to ISO 13964:1998 (Air quality -- Determination of ozone in ambient air -- Ultraviolet photometric method) and am curious whether there are performance criteria in this document.

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

Charge Question 4: Guidance/Opinion on Emerging Measurement Methodologies: What is the AMMS views on the use of low-cost sensor technology to supplement regulatory ozone monitoring (i.e., in rural areas)?

There is currently some activity to develop low-cost O₃ sensor technologies. While they might not meet the specifications of an FEM, they could play a vital role if their performance is adequately evaluated. Next generation sensors for O₃ were showcased at the EPA-sponsored Air Sensors 2013 Workshop and are briefly discussed in a recent paper by Piedrahita *et al.* (*Atmos. Meas. Tech. Discuss.*, **7**, 2425–2457, 2014).

Dr. Yousheng Zeng

In review of the materials provided to the AMMS committee members and the current FRM for ozone (Appendix D to 40 CFR 50), some observations are made that have influenced my comments. These observations are first discussed below, and they are followed by my comments.

Observations:

1. Although this rulemaking effort is presented as adding the NO-CL as a new FRM for ozone, the draft rule (proposed Appendix D-1 to 40 CFR 50) has little to do with NO-CL. Other than mentioning the name of the method (NO-CL) in the beginning of the proposed Appendix D-1, there is no technical substance specific to the NO-CL measurement method. The technical substance is about how to accurately generate ozone standard for calibration of the NO-CL analyzer.
2. Similarly the existing FRM for ozone (Appendix D to 40 CFR 50) only mentions the ethylene-CL method in the beginning, and the rest of FRM is about how to accurately generate ozone standard to calibrate the ethylene-CL analyzer.
3. The core technical substance (i.e., procedures to generate calibration standard) of the existing FRM and the proposed new FRM is essentially same. The difference is that the proposed new FRM includes Sections 1 (Applicability), 2 (Principle), 3 (Interferences), and 5 (Frequency of Calibrations). These new sections do not add technical specifications to the reference method.

My Comments:

Based on the above observations, I do not see a need to re-designate the current FRM as Appendix D-2 and add a new FRM as Appendix D-1. Instead, it makes more sense to revise the current FRM and keep it in current designation of Appendix D, i.e., maintain only one FRM and keep it in Appendix D. The revisions will include:

1. Adding Section 1 (Applicability). However, do not limit it to the NO-CL method. Make it applicable to the ethylene-CL method, NO-CL method, or other methods that meet the requirements of this FRM and quality assurance procedures and guidance provided in 40 CFR 58.
2. Adding Section 2 (Principle) as proposed except removing Subsection 2.1 (or making it more generic and not limiting to NO-CL), and making Subsections 2.3 and 2.4 more generic and not limiting to NO-CL.
3. Adding Section 3 (Interferences) as proposed except making it more generic and not limiting to NO-CL.
4. Adding Section 5 (Frequency of Calibration) as proposed.

Ambient ozone monitoring methods (either current ethylene-CL FRM or proposed NO-CL FRM) consists of two parts, the analyzer and the calibration procedures that generate the standard. The analyzer part is method specific, i.e., either ethylene-CL or NO-CL. The calibration procedures are independent of the analyzers, and can be applicable to either analyzers (or even future new analyzers as long as they can pass the calibration procedures and quality assurance procedures). The focus of both the existing FRM and the proposed new FRM is the calibration procedures, which are independent of analyzers. The calibration procedures are essentially same. Why do we want to have two FRM's?

The advantages of revising the current FRM to allow both ethylene-CL and NO-CL based analyzer include:

1. Avoid unnecessary regulations.
2. The FRM for ozone will be more streamlined. It resolves the issue associated with obsolete ethylene-CL based analyzers and related legacy issues. At same time, it achieves the objective of promoting the NO-CL based method to the FRM status. It will be less disruptive to operations of monitoring agencies because this is what they have been doing for many years as FEM. It will be designated as FRM without significant substantive changes.
3. If worded properly, it may also allow other methods, including emerging methods, to be qualified as FRM, making the rule more adaptive for technological advancement.

If the EPA wants to promulgate a new FRM that is truly specific to the NO-CL method, it should significantly expand the technical content of the FRM to include

- Specific descriptions of the NO-CL method, making it distinguishable from the ethylene-CL method in Appendix D-2 (which also means that Appendix D-2 needs to be expanded in the same fashion), and
- Typical specifications for an analyzer such as detection limit, linearity range, precision, accuracy, zero and calibration drift, response time, etc.

Considering the fact that the existing FRM had worked well in decades without specificity regarding the analyzer part of the method, I am not advocating the approach of expanding the FRM to include the specific descriptions of the NO-CL method and analyzer-oriented specifications. What I am advocating is what I stated earlier, i.e., keep one FRM and list both ethylene-CL and NO-CL methods in the FRM.

During the April 3, 2014 AMMS public teleconference, several AMMS members expressed favorable opinions on the UV method, and some AMMS members expressed concerns on the NO-CL method. Based on the final outcome of the AMMS deliberation and consensus and the EPA's position, if the UV method is considered as FRM *in addition to* the NO-CL method, my recommendation to the EPA is to keep one FRM and list all three methods (ethylene-CL, NO-CL, and UV methods) in the FRM. If the outcome is to use the UV method *instead of* the NO-CL method, then the EPA can keep one FRM and list two methods (ethylene-CL and UV methods) in the FRM.