Preliminary Comments from Members of the CASAC Air Monitoring and Methods Subcommittee (AMMS) Review of EPA's Federal Reference Method for Ozone: Nitric Oxide (NO)-Chemiluminescence Received as of March 28, 2014

Purpose: These are Preliminary Comments from Members of the CASAC Air Monitoring and Methods Subcommittee (AMMS), related to the AMMS's review of EPA's Ozone National Ambient Air Quality Standard (NAAQS) documentation that focuses on the EPA Office of Research and Development's recommended second Federal Reference Method for Ozone (Recommended Method: NO-Chemiluminescence).

Dr. Linda J. Bonanno 2
Dr. Judith C. Chow 3
Dr. Kenneth Demerjian 17
Mr. Henry (Dirk) Felton 19
Dr. Philip Fine 21
Dr. Philip Hopke 22
Dr. Rudolf Husar 25
Dr. Peter H. McMurry 26
Dr. Allen Robinson 27
Dr. Yousheng Zeng 29

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Response: Good idea since the Ethylene method is out of date and as long as the NO method shows that it's the same or better than the FRM and its not more prone to interferences and is easy to implement/practical for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

Dr. Judith C. Chow

Charge Question 1. What is the AMMS view on adding an additional O_3 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 O_3 FRM will serve as an additional FRM to supplement the current Ethylene-Chemiluminescence method, which is no longer being produced or supported.

Response:

Adding O_3 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 O_3 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 O_3 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 O_3 FRM?

Response:

The light emitted by chemiluminescence from gas-phase chemical reaction of O_3 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 NO_2(Code of Federal Regulations, 1983). It seems logical, then, to use the same principle for the detection of O_3 when it is properly implemented. Interferences from HNO_3, 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 O_3 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) O_3 FRM?

Response:

Spectrophotometric determination of atmospheric O_3 also has a long history (Bravo and Lodge, 1964; Grosjean and Harrison, 1985; Stair, 1959). An additional O_3 FRM by UV absorption should be considered, as most O_3 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 O_3 monitors, although the potential interference from oxidized or nitrated aromatics needs to be further tested. When UV O_3 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 O_3 measurements from fresh diesel emissions were found and attributed to fine particles (d_p<0.2 µm) 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 O_3 with excess NO generated in situ by photolysis of added nitrous oxide (N_2O) in 2B Technologies Model 211. This process eliminated the need for a conventional O_3 scrubber. Different scrubbers (e.g., non-heated MnO_2, heated silver wool, or optimal heated metal scrubber) and interference by ultrafine particles in UV O_3 systems need to be further tested prior to consideration as an additional O_3 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 O_3 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 O_3 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 O_3, 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 O_3 sensors (i.e., Physical Science Inc. [PSI; Andover, MA] and 2B Technologies [Golden, CO]) for O_3 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 O_3 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 O_3 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 O_3 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 O_3 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.

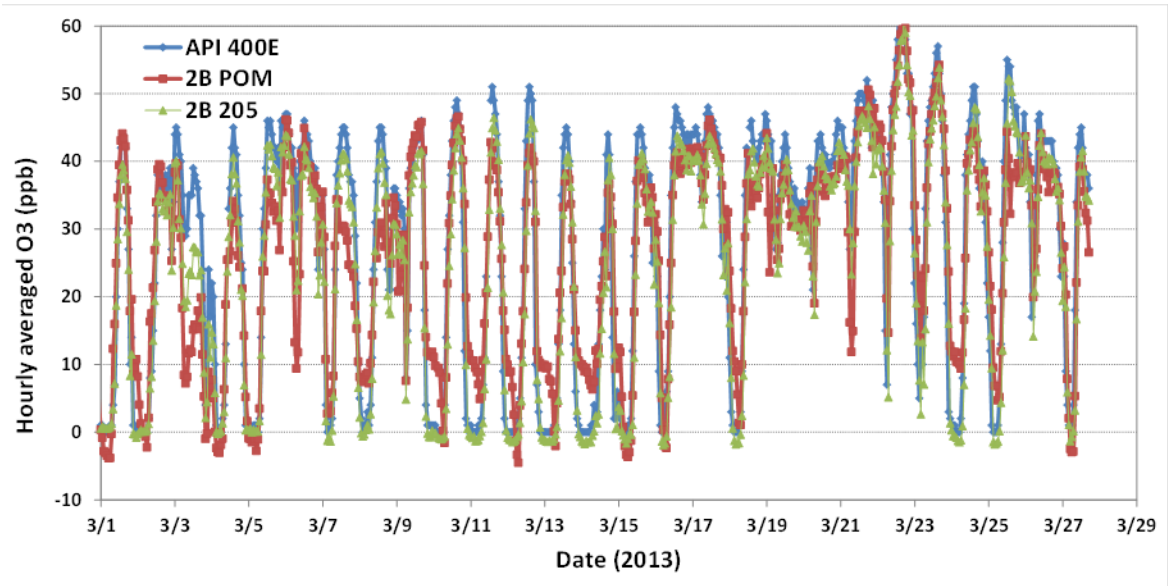

Figure 1. Collocated comparison among three UV absorption O_3 monitors: 1) Teledyne API Model 400E; 2) 2B Technology Personal Ozone Monitor (POM); and 3) 2B Technology Model 205 for the period of 3/1–29/13 at Sparks, NV (Green et al., 2013). The Sparks site is known to be affected by residential wood 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.

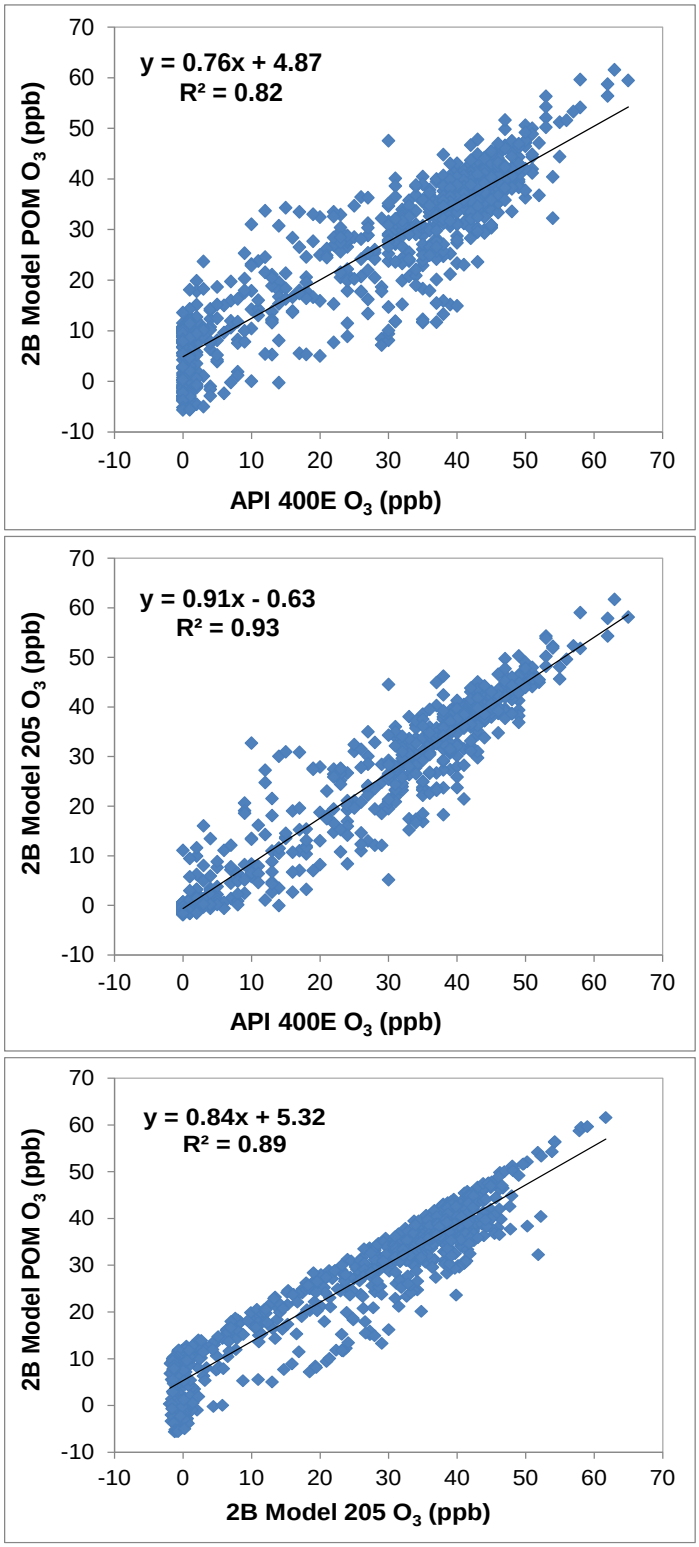

Figure 2. Collocated comparison of one hour averages for three collocated O_3 monitors: 1) Teledyne API Model 400E; 2) 2B Technology Personal Ozone Monitor (POM); and 3) 2B Technology Model 205 in Sparks, NV during 3/1–29/13 (Green et al., 2013).

Fowles and Wayne (1981) proposed the use of an LED to monitor O_3. 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 O_3 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 O_3 meter based on UV absorption at 254 nm using corona discharge and semiconductor O_3 sensor. The reported accuracy was <3% and the device required very low power (11 Watts). Washenfelder et al. (2011) measured O_3 by chemical conversion to NO_2 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 O_3. Gomez and Rosen (2013) reported a fast-response cavity-enhanced O_3 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 O_3 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 O_3 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 O_3 monitors employing several different operation principles is shown in Table 1 of Gomez and Rosen (2013). These low-cost, lightweight O_3 monitors need to be collocated with proven O_3 monitors (e.g., FRM or FEM) to assure their equivalence and comparability during O_3 measurements. Bowman (2013) calls attention to the need of an international O_3 air quality monitoring system that integrates a continuum of observations from local to global scale, including both ground- and satellite-based observations of O_3. Tests of low-cost O_3microsensors 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 O3 FRM. I don't see that we have a choice but to establish a new 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:

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 NOy. 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.

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:

I do not have any specific suggestions for an additional O3 FRM. Techniques available but rather expensive include Quantum Cascade Laser based tunable multi-pass IR absorption spectroscopy; cavity ring down spectroscopy (CRDS) and cavity attenuated spectroscopy (CAPS) both of the latter

techniques measure ozone indirectly via D 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: I recently reviewed a manuscript out of Canada that reported on an O3 semi-conductor sensor network array deployed in Frasier Valley. I am not sure of the status of the paper, but this would be an example of Emerging Measurement Methodologies.

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. Henry (Dirk) Felton

Charge Question 1: Overall View on Adding an Additional O3 FRM:
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 acceptable to approve the NO-Chemiluminescence method as an FRM for Ozone. It is important that an FRM be available for every criteria pollutant even if it is not routinely deployed by regulatory agencies. 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.

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 models in existence.

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

Response:

It is acceptable to approve the NO-Chemiluminescence method as an FRM for Ozone as long as regulatory agencies are not precluded from operating FEMs based on UV absorption. The currently available NO-Chemiluminescence instrument may not be a viable monitoring option for many regulatory agencies. This instrument requires a 10,000 ppm cylinder of NO as a reagent. 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.

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:

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 NO_2 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

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: I support the designation of this method as an 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: 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 in approved.

Request for Guidance/Opinion on Emerging Measurement Methodologies

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 Johnson et al. (2014). 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 supplied by an external cylinder. 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.

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.cas

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)

<u>Semiconductor-Based Ozone Sensors:</u>

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 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.

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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 PM2.5 are the key pollutants that are in need for significant regulatory actions. Over the recent decade, the US PM2.5 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-O3 Chemiluminscence 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.

<u>My Response to Charge Question 1:</u>

Given that:

- O3 is a criteria pollutant;
- ethylene-O3 Chemiluminscence method is the only existing FRM for O3;
- a commercial ethylene-O3 Chemiluminscence 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-O3 chemiluminescence 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-O3 chemiluminescence 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: Overall View on Adding an Additional O3 FRM:
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: Views on establishing the NO-CL method as the new, additional O3 FRM:
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

NO + O3 --> NO2*
NO2* --> NO2 + hnu

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 chemiluminesence 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: Other O3 Measurement Methods for Consideration as a New Additional O3 FRM:
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. Yousheng Zeng

In review of the materials provided to the AMMS committee members on March 5, 2014 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.