Additional Preliminary Comments from Members of the CASAC Air Monitoring and Methods Subcommittee (AMMS) Review of Supplemental Material Submitted on May 5, 2014 by EPA Office of Research and Development Regarding EPA's Federal Reference Method for Ozone: Nitric Oxide (NO)-Chemiluminescence

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Purpose: These are additional preliminary comments from members of the CASAC Air Monitoring and Methods Subcommittee (AMMS), related to the AMMS's review of supplemental material submitted by the EPA Office of Research and Development on May 5, 2014 for consideration by AMMS members in relation to the CASAC AMMS review of EPA's recommended second Federal Reference Method for Ozone (Recommended Method: NO-Chemiluminescence).

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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 Ethylene FRM 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 now shows excellent agreement with the corrected FRM data.

Q #3:
The same corrected 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.

Request for clarification:
The revised FRM data from May 5th raise another question about the original data presented by ORD on April 3. Page 7 of that presentation shows some divergence in the NO-CL vs FRM data that was of concern to the AMMS during the April teleconference. The May 5th ORD material states that it was FRM drift that was causing the excessive scatter on page 7 (April 3). The UV-SL scatter plot for Houston on page 11 (April 3) does not show any obvious scatter, but it uses the same FRM data set (the same time period) as the page 7 plot. Thus one would expect that excessive FRM scatter to show up here also. But it doesn't; It appears that the hours in question where the FRM data were corrected (May 5 ORD material) were not included in the UV-SL vs FRM plot. It would be helpful if ORD could

explain why.

Dr. Judith C. Chow

Question 2. What is the AAMMS view on establishing the Nitric Oxide-Chemiluminescence (NO-CL) method (currently an FEM) as the new, additional O_3 FRM?

The light emitted by chemiluminescence from gas-phase chemical reaction of O_3 with nitric oxide (NO) (Figure 1) 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 1) 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.

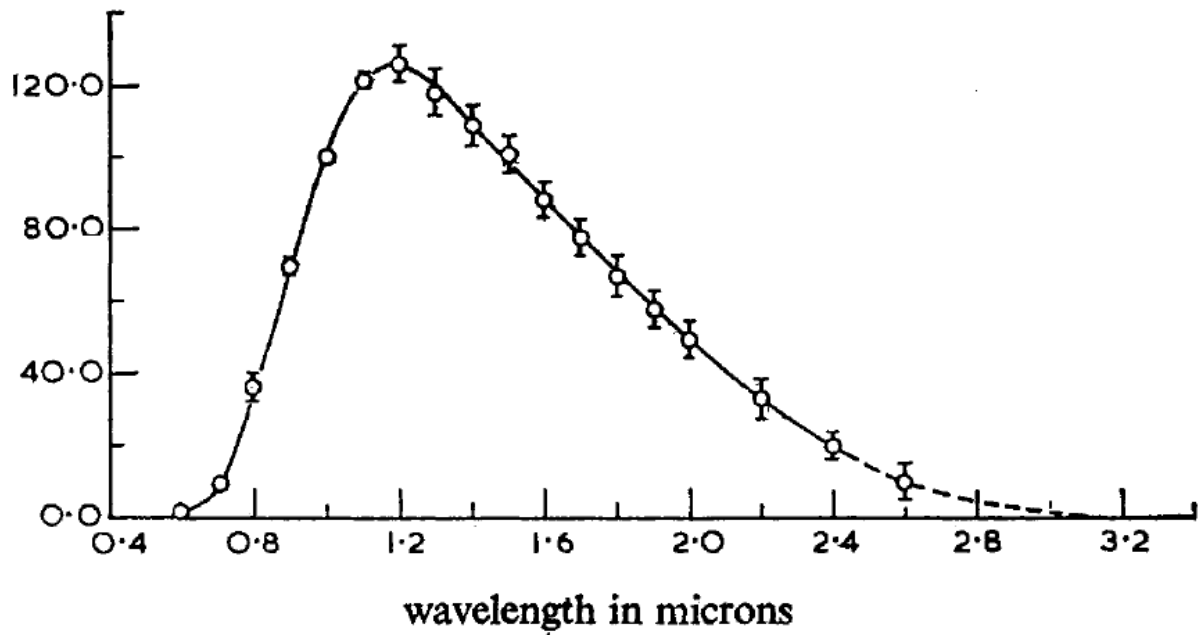

Figure 1. Relative intensity of light as a function of wavelength emitted by the NO-O_3 reaction (Figure 2 from Clough and Thrush, 1967).

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 2 and 3, 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.

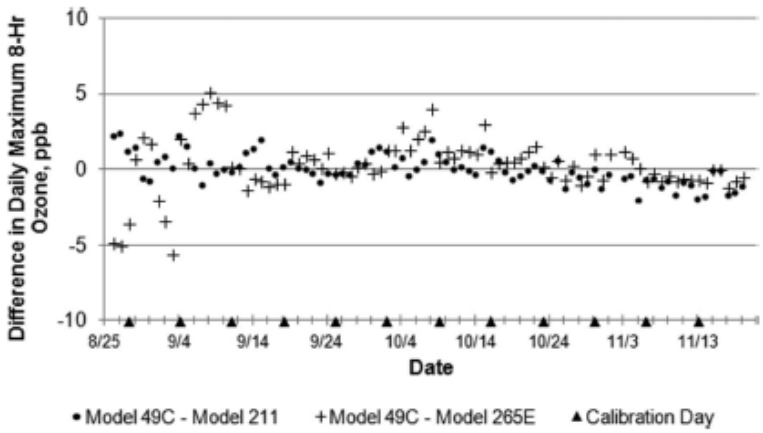

Figure 2. Differences between 8-hour moving average O_3 from Houston, TX for a standard UV FEM (Thermo 49C), a 2B Technologies Model 211 UV FEM, and a Teledyne 265E NO-CL FEM. Deviations of the 265E at the beginning of the sequence were unexplainable. If they were due to UV biases owing to removal of UV-absorbing gases in the O_3 scrubber, then the UV O_3 should always be higher than the NO-CL O_3. (Figure 3 of Ollison et al., 2013).

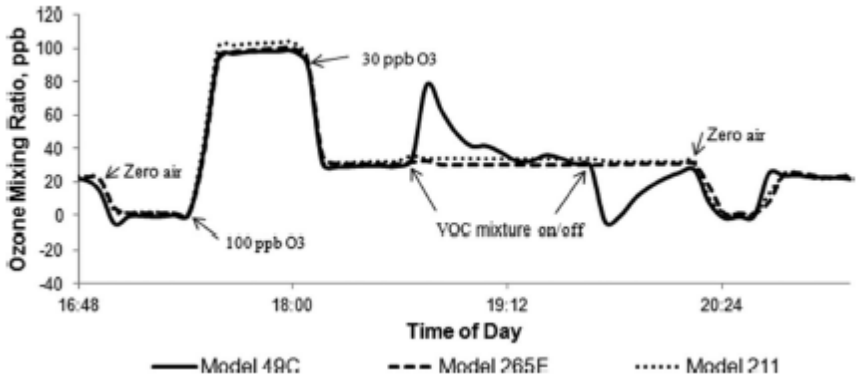

Figure 3. Response of the three Houston instruments to a mixture of VOCs injected into a stream containing 30 ppb O_3. The Model 49C shows a response to this mixture, indicating its removal by the O_3 scrubber, while the Model 211 shows no interference, indicating that it compensates for this potential interference. (Figure 8 of Ollison et al., 2013).

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.

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?

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 3, 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.

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Dr. Kenneth Demerjian

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 nominal and do not seem to account for the zero offset. ORD want to consider performing systematic zeroing (e.g., hourly) to see if this reduces the magnitude of the zero offset.

Dr. Rudolf Husar

I reviewed the additional data submitted by EPA on May 5th, 2014. I concluded that I am not qualified to evaluate and comment authoritatively on the new EPA analyses.

Dr. Peter H. McMurry

I commend Russell Long and coworkers for their excellent detective work and for the clarity of this report. In my opinion they have resolved several of the issues that troubled our subcommittee in our earlier deliberations.

Long et al. provide compelling evidence that scatter in results for NO-CL vs ET-CL (FRM) and UV-Drier vs ET-CL (FRM) was due to problems that were discovered with operation of the FRM instrument. Those problems included (i) a loose particle filter (8 data points) and (ii) different spans for the periods Sept. 4-15 and Sept 16-28. When the 8 flawed data points were eliminated and correct FRM spans were used, FRM ET-CL and NO-CL agreed to within 2% with very little scatter. FRM and SL-UV measurements were equally well correlated, although the SL-UV measurements exhibited a zero offset bias of ~2 ppb that could not be explained.

In my view, these new results clearly demonstrate the suitability of the NO-CL technique as an FRM. I no longer have the reservations that I may have expressed earlier.

These new results show that UV-SL is also likely to be suitable. However, the 2 ppb positive bias remains unexplained. Furthermore, additional field testing should be done before this method is certified as an FRM. Given the widespread use of UV absorption for O_3 measurements by state and local agencies, I would recommend that EPA complete the work required to certify SL-UV as an FRM. I recognize that, given court-imposed deadlines, it may not be possible to complete that certification now. Given the work that has been done already, however, it should be possible to complete the work that would assess SL-UV's suitability as an FRM within a year or so. I would like to see this happen.

Dr. Allen Robinson

The additional ORD analysis of the field data appears to alleviate some of the concerns raised by the initial AAMMS review. It is still not clear to me that the NO-CL or the UV-SL is the superior technology. The performance of the FRM in the first RTP deployment is concerning (slide 5). There is the 2 ppbv offset with UV-SL (slide 15 and 16) that is concerning.

Dr. Armistead (Ted) Russell

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