

4/1/14 Additional Preliminary Draft Comments for Deliberations of the CASAC Air Monitoring and Methods Subcommittee  
Subcommittee Review of EPA’s Federal Reference Method for Ozone: Nitric Oxide (NO)-Chemiluminescence. Please Do  
not Cite or Quote. These comments are preliminary and do not represent CASAC consensus comments nor EPA Policy.

**Additional 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 April 1, 2014**

**Purpose:** These are Additional 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).

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## **Mr. George A. Allen**

### Clarification on not removing old FRM.

It would be helpful if EPA could be explicit as to why they are not removing the old Ethylene-CL FRM from the method list at

<http://www.epa.gov/ttn/amtic/criteria.html> - specifically

<http://www.epa.gov/ttnamti1/files/ambient/criteria/reference-equivalent-methods-list.pdf>

It is my understanding that if the E-CL FRM was removed, all FEMs based on it (essentially all instruments in the current O3 monitoring network) would lose their FEM designation. There is clear precedent for keeping obsolete FRMs (and other obsolete FEMs) on the method list. When EPA promoted the Ultraviolet Fluorescence Method for SO2 from an FEM to an FRM as part of the most recent SO2 NAAQS review [Appendix A-1 to Part 50, FR Vol. 75, No. 119, pg 35593, 6/22/2010], the existing manual Reference Method for SO2 (Pararosaniline Method) was retained. It is my understanding that once a method or instrument is designated as an FRM or FEM, it is never removed from the method list.

### Description of the proposed NO-CL FRM.

The proposed text for the rule that describes the NO-CL method is relatively brief. Additional detail similar to what is included for the Ultraviolet Fluorescence Method for SO2 in the FR notice cited above should be included, such as information on the measured wavelength range for this method, a "schematic diagram" (see Fig. 1 for the SO2 FRM), and relevant references to this method.

**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

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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.

## **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), 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.

*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 Nitric Oxide-Chemiluminescence (NO-CL) method is adequately robust and its establishment as an additional O3 FRM is supported. The draft presentation (Russell Long *et al.*) provides some but not all of the evaluation details because it is a work in progress, and I look forward to the completed ambient evaluation (e.g. the summer 2014 study in Denver). It is not clear why the July 2011 Baltimore study results are not included. 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 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.

*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 commonly used – especially the FEM-designated UV methods – the proposed adoption of the Nitric Oxide-Chemiluminescence method is appropriate and should be adequate for the foreseeable future.

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*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: There is currently some activity to develop low-cost O<sub>3</sub> 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 O<sub>3</sub> 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).