

**Yeow, Aaron**

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**From:** Alan Leston <alanleston@gmail.com>  
**Sent:** Monday, July 14, 2014 12:30 PM  
**To:** Yeow, Aaron  
**Cc:** Will Ollison  
**Subject:** Comments on a proposed new FRM for O3  
**Attachments:** Comments on New O3 FRM 7\_14\_14.pdf

To: Aaron Yeow - DFO

I would like submit the attached comments for consideration by the CASAC-AMMS during their upcoming discussion (7/16/14) of a new Federal Reference Method (FRM) for ozone.

Please note that although the American Petroleum Institute has provided partial funding for the preparation of these comments, the recommendations and conclusions are my own.

If you should have any questions about the attached comments please call or email me at the addresses below.

Best regards,  
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# **Comments on CASAC-AMMS Recommendation Regarding New Federal Reference Methods for Ozone**

**July 14, 2014**

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## **INTRODUCTION**

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

1. What is the AMMS view on adding an additional O<sub>3</sub> 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<sub>3</sub> FRM will serve as an additional FRM to supplement the current Ethylene-Chemiluminescence method, which is no longer being produced or supported.
2. What is the AMMS views on establishing the Nitric Oxide-Chemiluminescence (NO-CL) method (currently an FEM) as the new, additional O<sub>3</sub> FRM?
3. Do any other ozone measurement methods exist that the AMMS recommends for consideration of possible promulgation as a new (additional) O<sub>3</sub> FRM?
4. What is the AMMS views on the use of low-cost sensor technology to supplement regulatory ozone monitoring (i.e., in rural areas)?

## COVER LETTER

Subsequent to the teleconference on 6/12/14 the AMMS, drafted a letter (7/1/14) to the EPA Administrator summarizing the results of its deliberations and recommendations. The following comments center on that 7/1/14 letter and use a page/line numbering format (Page/line numbers).

**(1/34-36)** The CASAC-AMMS voices support for retaining the current O3 FRM (ethylene-chemiluminescence) or (ET-CL) noting that,

*“...this approach is consistent with how most other obsolete FRMs have been treated by EPA....”*

Although EPA has adopted a second FRM for the measurement of SO<sub>2</sub>, that second method is an “automated” approach as opposed to the original “manual” FRM. The manual technique involves “wet chemistry” which is labor-intensive, requires the supply and disposal of chemical reagents, and has not been widely used in ambient monitoring for decades. In adopting automated ultraviolet fluorescence (UVF) as a second FRM, EPA noted<sup>2</sup> that canceling the manual FRM would invalidate all existing SO<sub>2</sub> FEMs. EPA further noted that it would rescind the manual method’s FRM status when,

*“...new SO<sub>2</sub> FRM analyzers have adequately permeated State monitoring networks...”*

However, as of June 18, 2014 EPA has not granted FRM status to any automated SO<sub>2</sub> instrument<sup>3</sup>. Also, on June 14, 1972 the EPA Administrator stated that the FRM for NO<sub>2</sub> (Jacobs-Hochheiser manual method) was deficient and would be withdrawn<sup>4</sup>. The original NO<sub>2</sub> manual FRM was supplanted with both an automated FRM and a manual FEM (sodium arsenate) in 1977<sup>3</sup>. EPA has, thus far, not employed a consistent approach to FRM replacement or augmentation.

Also, with multiple FRMs the issue of “authority” arises and ORD is seeking input on their proposed adoption of multiple O<sub>3</sub> FRMs (Charge Question 3). If multiple FRMs are adopted some monitoring agencies will collocate those FRMs at marginal sites that just attain or exceed the O<sub>3</sub> NAAQS. How will EPA/ORD designate a site if the collocated monitors disagree? This difficulty is not addressed in the AMMS “Consensus Responses to Charge Questions” p. 2, lines 31-34.

**(1/40-42)** ORD stated in its 5/5/14 presentation that considerable use of span “correction factors” (CFs) was made before comparing instrument performance. These CFs were based on daily zero/span checks performed on an automated basis. The zero response from all instruments at both locations was accurate and stable and no “zero” CFs were employed. During the RTP comparison (June/July, 2012) the candidate NO-CL and UV-drier instruments required no CFs but the daily performance checks on the ET-CL FRM were so variable that no “defensible CF” could be generated. During the Houston comparison two different CFs were applied to the ET-CL FRM instrument, a span CF was applied to the NO-CL data for the first half of the study, and no CF was used for the UV-SL instrument data.

Approval of a new O3 FRM has significant and long lasting implications and should be done in a manner that leaves no uncertainty as to its performance. For this reason the use of CFs should be avoided or extremely limited. Instruments displaying unstable behavior should be repaired or replaced. The unstable performance of the ET-CL FRM during ORD's RTP comparison was so extreme that the study results should be invalidated. The more recent (but limited) comparison data from ORD's RTP site show much improved performance with all instruments operating within 3.0% of ideal. This test should be extended and used in lieu of the earlier data from RTP.

Results from ORD's Houston study showed performance of the ET-CL FRM was within 4.0% of ideal and the NO-CL instrument was (apparently) mis-calibrated at the beginning of the study by 7%. A span CF generated due to a known calibration error is acceptable if it is not extreme, as was the case in Houston. However, in future studies ORD should take precautions to insure that its ET-CL instrument is stable and properly calibrated and use only data produced after stable operation has begun.

**(2/5-8)** The draft CASAC-AMMS letter has not taken into account comparative candidate instrument responses from (1) differences in humidity control and (2) dilution effects occurring among the three monitors (ET-CL, NO-CL and UV-SL). For example, in the 4/3/2014 ORD presentation to the AMMS the "interference equivalent" due to water vapor for the O3 FRM (ET-CL) is listed as "0.008 ppb". Interference equivalent testing procedures are called out in 40 CFR, Part 53, Subpart B. Table B-3 of Subpart B indicates that the testing of CL-type O3 monitors for water vapor shall be carried out in the absence of the pollutant of interest (i.e., O3). The presence of O3 is required in the ET-CL method to generate the chemiluminescence signal so it is impossible to test for water vapor effects in the absence of O3 and difficult to understand how any signal occurred during these water vapor interference tests.

Additionally, Table A2 of ASTM method D5149-02<sup>5</sup> (measurement of O3 via ET-CL) notes a positive 6%-12% bias (depending on ET-CL instrument type) at the 20,000 ppm absolute humidity test specified for the ET-CL monitor. Biases of this magnitude are inconsistent with the ORD results presented to the AMMS from LaPorte/Houston/TX (LAP) site which showed excellent agreement between the ET-CL monitor and both the NO-CL and UV-SL monitors. Daily high temperatures during the ORD study ranged from 90-100 degrees F. with dew points of 75-80 degree F<sup>6</sup>. Under such hot, humid conditions the ET-CL monitor should have over-reported O3 data by several percent. According to laboratory test results presented by ORD both the NO-CL and the UV-SL instruments have water vapor interferences of well under 1 ppb. So, during the LAP comparison the ET-CL instrument was exhibiting anomalous water vapor performance and may not have been representative of historic ET-CL instrument performance. ORD should present laboratory water vapor interference testing data collected with the ET-CL instrument at 20,000 ppm H2O in the presence of O3 that was mentioned by EPA staff during the 2<sup>nd</sup> AMMS teleconference and include field comparison data from its scheduled July-August 2014 testing in Denver. ORD noted in its 5/5/14 presentation that,

*"...deadlines associated with the now court ordered proposal date for the ozone NAAQS review will not permit inclusion of the results of the Denver 2014 field evaluation campaign in the proposed rulemaking package...."*

There is no requirement that replacement of the obsolete ET-CL FRM should coincide with revisions to the O3 NAAQS levels and appropriate time should be taken to make the O3 FRM change correctly.

ORD has proposed a  $\leq 5$  ppb humidity interference performance specification in the proposed NO-CL FRM description that requires a dryer to control sample air humidity. This humidity control requirement should be extended to UV method FEM performance specifications, noting that the UV-CL instrument accomplishes this goal by Nafion equalization of scrubbed and unscrubbed sample stream humidity to local ambient humidity rather than by drying these sample streams. EPA should also consider a more rigorous 30,000 ppm humidity test to determine the biasing of measured O3 levels in instruments that dry ambient sample streams since O3 concentrations might be expected to increase by up to 3% from removal of water vapor at Houston type locations.

AMMS also fails to consider sample dilution effects in the candidate UV-SL instrument resulting from its unsymmetrical addition of N2O flow to the scrubbed sample to halve N2O consumption. While this compromise laudably corrects about 98% of the conventional photometer Hg/VOC interference bias and reduces field unit O/M expense, CASAC should encourage 100% interference correction by recommending replumbing of an FRM version of the UV-SL for symmetric addition of N2O to both scrubbed and unscrubbed sample streams.

**(2/8-11)** The UV-SL technique (2B Technologies, Inc. Model 211) has recently been granted FEM certification by EPA<sup>3</sup>. As an FEM the Model 211 does not require further testing prior to its consideration as a candidate FRM. This recent development should be acknowledged earlier in the cover letter perhaps on page 2, at lines 8-11.

The draft CASAC cover letter also fails to mention ORD's review of performance specifications for candidate FEM automated methods which are contained in 40 CFR, Part 53, Subpart B, subsections 53.20-23 and its recommendations for updating those specifications. ORD undertook this effort in response to the third O3 ISA<sup>7</sup> which noted,

*“These specifications should be revised to more accurately reflect the necessary performance requirements for O3 monitors used to support the current NAAQS.”*

Performance specifications are summarized in Tables B-1 through B-3 of Subpart B and include details for testing candidate techniques for bias from interfering chemical species including water vapor. The 4/3/2014 ORD presentation (Slide 9) included proposed upgraded specifications that were favorably received by some AMMS members. One AMMS committee member wrote that mercury should be added to table B-1 and also cited a report<sup>8</sup> that provided a summary of reported interferences to UV photometers deployed in the current monitoring networks that would also be helpful additions to Subpart B. While a passing reference is made to adding mercury to Table B-1 in the AMMS Consensus Response to Charge Question 2, a more comprehensive approach is needed.

The major problems associated with current O3 measurement are; 1) the lack of a viable FRM (the genesis of this process) and 2) inadequate interference testing of FEM candidate monitors.

If the interference performance specifications in Subpart B are not adequately upgraded, the current interference-prone monitors will continue to deliver biased O<sub>3</sub> data and adoption of any new FRM will not improve the quality of ambient data. The cover letter should specifically call for such upgrading of the FEM/FRM testing protocols and inclusion of interfering species reported for current network monitors.

## CONSENSUS RESPONSES

The CASAC-AMMS attached a Consensus Report to the cover letter outlining the committee's overall response to the Charge Questions. The consensus report also included some specific member comments on material provided to the committee by ORD.

**(1/33-35)** By approving a second FRM, the CASAC-AMMS agrees that the current ET-CL method should retain its FRM status. Although this is presumed to allow currently deployed SLAMS/CASTNet instruments to remain in operation, how then will the more stringent performance specifications associated with the new FEM/FRM(s) come into general use? State, local and tribal (S/L/T) monitoring organizations will not seek new, better performing instruments in the absence of additional funding. Instrument manufacturers will continue producing existing models of FEMs unless better-performing models result in an equal or higher profit margin. Moreover, the ET-CL FRM itself will no longer pass the proposed new 5 ppb humidity interference performance specification without installation of humidity controls. Given the demonstrated improvement in monitoring accuracy, CASAC should recommend that EPA require prompt upgrading of existing UV network photometers with the recently FEM certified NO scrubber and humidity control technology. This approach has the advantage of being cost-effective and commercially available compared to a wholesale replacement of existing units with new monitors, as noted below.

**(4/-2)** The suggestion to include, “*loggable Relative Humidity (RH) measurements down-stream of the sample cell.*” is an excellent one. ORD should include this requirement in Appendix D-1 to 40 CFR Part 50 – Reference Measurement Principle and 9 Calibration Procedure for the Measurement of O<sub>3</sub> in the Atmosphere – NO—Chemiluminescence, NO-10 CL, Method.

**(4/29-30)** The AMMS is troubled by, “*a two ppb zero offset*” attributed to the UV-SL method and this is a justifiable concern. The offset may be a consequence of adding N<sub>2</sub>O to only the “reference” portion of the measurement and not both the reference and “sample” paths. This approach results in different ratios of O<sub>3</sub> (and interfering species) to diluent gas in each path and might be sufficient to introduce the noted offset. This could be verified by adding N<sub>2</sub>O to both paths.

ORD did not employ a UV-SL instrument in the early (June/July, 2012) RTP phase of their comparison study. The zero offset during the LAP phase of the study was +1.90 ppb for 1-hour data and +1.58 ppb for 8-hour data. The zero offset during the latest (April/May, 2014) study at RTP was +0.70 ppb for 1-hour data and -0.69 ppb for 8-hour data.

To date ORD has reported on 33 days of UV-SL performance (24 days at LAP and 9 days at RTP) a time period which is not sufficient to characterize UV-SL performance. ORD must continue characterizing both UV-SL and NO-CL instrument performance until a solid data base

of monitor behavior under varying climatic and geographic conditions is established. The Denver comparison, scheduled for the summer of 2014 should yield important data with respect to the questions about UV-SL instrument performance but ORD should be prepared to conduct additional comparisons before determining that either instrument is an appropriate FRM.

**(5/19-21)** The AMMS notes the inherent superiority of gas-phase scrubbers for UV-based O<sub>3</sub> monitors. The AMMS should recommend that EPA facilitate upgrading traditional UV-based monitors via the addition of an EPA-certified gas-phase (NO) scrubber technology. This approach is more efficient (and cost-effective) than simply grandfathering the biases of existing UV FEMs into the monitoring network or requiring expensive recertification by the new FRM.

**(5/24-25 & 27-28)** AMMS should note that both NO-CL and UV-SL instruments have associated cost and space requirements not just the UV-SL. There are also health and safety issues associated with the use of cylinders of high concentration NO that should also be called out.

## REFERENCES

1. EPA Memo, March 7, 2014, Timothy J. Buckley, Director HEASD, to Ed Hanlon, Designated Federal Officer, Clean Air Scientific Advisory Committee, EPA Science Advisory Board Staff Office.
2. **Federal Register** /Vol. 75, No. 119 /Tuesday, June 22, 2010 /Rules and Regulations.
3. List of Designated Reference and Equivalent Methods, June 18, 2014.  
[www.epa.gov/ttn/amtic/criteria.html](http://www.epa.gov/ttn/amtic/criteria.html) .
4. Evaluation of the Sodium Arsenite Method for Measurement of NO<sub>2</sub> in Ambient Air, Margeson, J.H., Beard M.E, and Suggs, J.C., J. of the Air Pollution Control Assoc., Vol. 27, No. 6, 1977.
5. Standard Test Method for Ozone in the Atmosphere: Continuous Measurement by Ethylene Chemiluminescence, Designation: D 5149 – 02, ASTM International, 100 Barr Harbor Drive, PO Box C700, West Conshohocken, PA 19428-2959,
6. Historical Weather for 2013 in Houston, Texas, USA,  
<http://weatherspark.com/history/30150/2013/Houston-Texas-United-States> .
7. Integrated Science Assessment for Ozone and Related Photochemical Oxidants, Third External Review Draft, June 2012, EPA/600/R-10/076C.
8. Spicer, C. W., Joseph, D. W. and Ollison, W. M., “A Re-Examination of Ambient Air Ozone Monitor Interferences”, J. Air & Waste Manage. Assoc., **60**: 2010, 1353–1364, doi:10.1031/1047-3289.60.11.1353.