

1
2 The Honorable Gina McCarthy
3 Administrator
4 U.S. Environmental Protection Agency
5 1200 Pennsylvania Avenue, N.W.
6 Washington, D.C. 20460
7

8 Subject: Review of EPA's Recommendation for an Additional Federal Reference Method for
9 Ozone: Nitric Oxide-Chemiluminescence
10

11 Dear Administrator McCarthy:
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13 In response to a request from the EPA's Office of Research and Development, the Clean Air Scientific
14 Advisory Committee (CASAC) Air Monitoring and Methods Subcommittee (AMMS) held
15 teleconferences on April 3 and June 12, 2014 to review EPA's recommendation to add the Nitric Oxide-
16 Chemiluminescence, or NO-CL, measurement method as a Federal Reference Method (FRM) for the
17 measurement of ozone. The CASAC's consensus responses to the agency's charge questions and the
18 individual review comments from the CASAC AMMS are enclosed. The CASAC's key points are
19 highlighted below.
20

21 An FRM serves as the standard protocol for measuring ambient concentrations of pollutants regulated
22 under the National Ambient Air Quality Standards (NAAQS) program. The existing FRM for Ozone
23 (Ethylene-Chemiluminescence Method, or ET-CL) is no longer being manufactured or supported. In
24 2009, EPA consulted a previous CASAC Monitoring Subcommittee (Ambient Air Monitoring and
25 Methods Subcommittee - AAMMS) on ambient air monitoring issues related to the Ozone NAAQS,
26 including issues related to the development of a second FRM for measuring ozone. The Agency
27 considered the individual AAMMS member comments, and now is recommending that the NO-CL
28 measurement method should be a second Ozone FRM. In the current review, CASAC considered
29 EPA's Office of Research and Development's (ORD) analysis and technical documentation on the NO-
30 CL method, and ORD's recommendation for making this measurement method a second Ozone FRM.
31

32 Overall, CASAC agrees with ORD that a new Ozone FRM should be added. The current FRM's ET-CL
33 instrument is no longer commercially available for use in designating other ozone measurement methods
34 as Federal Equivalent Methods (FEMs). CASAC also agrees that the current ET-CL FRM can remain
35 on the ORD's list of designated reference and equivalent methods, and notes that this approach is
36 consistent with how most other obsolete FRMs have been treated by EPA.
37

38 CASAC agrees that the NO-CL method is a good candidate for FRM status, and CASAC is impressed
39 by the laboratory evaluations, which show that the NO-CL method far exceeds current laboratory test
40 requirements for FRM designation. Following the additional EPA ORD analyses reported in their May
41 5, 2014 summary, CASAC concludes that results of ORD's field tests also make a compelling case for
42 FRM designation of the NO-CL method. CASAC also concludes that ORD's proposed revision to
43 Appendix D-1 of 40 CFR Part 50 (i.e., Reference Measurement Principle and Calibration Procedure for
44 the Measurement of O₃ in the Atmosphere – NO-Chemiluminescence, NO-CL, Method; January 2, 2014
45 Draft) needs to include more detail. CASAC suggests that ORD include additional performance criteria
46 within this Appendix for the NO-CL method, a more detailed explanation of measurement principles,

1 and other information on the method as described in the response to charge question within this CASAC
2 report.

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4 CASAC recommends that ORD also consider the ultraviolet-scrubberless measurement method (UV-
5 SL) as an FRM. The ORD analyses presented to the CASAC AMMS at the May 5, 2014 meeting reveal
6 excellent correlations between UV-SL and the ET-CL FRM, and between UV-SL and NO-CL, albeit
7 with an unexplained ~2 ppb zero offset for the UV-SL method. The UV-SL instrument also has a
8 modestly higher laboratory test interference from water vapor than the NO-CL monitor. Furthermore,
9 the UV-SL method has not been tested against the FRM in the field as thoroughly as would be desired to
10 merit FRM designation at this time. CASAC recommends that EPA ORD complete the work that would
11 be required to assess the UV-SL method's suitability as an FRM.

12
13 CASAC notes that other available systems to measure ozone, including quantum cascade laser based
14 tunable multi-pass IR absorption spectroscopy, cavity ring down spectroscopy (CRDS) and cavity
15 attenuated phase shift spectroscopy (CAPS), and are not practical at this time as FRMs. These
16 approaches are relatively expensive, have complex operational requirements, and are not broadly in use
17 by state agencies. However, rapid technology innovation may make these methods more practical for
18 routine use in the near future, and if they can attain the specified performance criteria, then there is no
19 reason why they should not be considered as candidate FRMs. Low-cost sensor-based systems that are
20 currently available for ozone measurement are not sufficiently developed to be considered as FRMs or
21 FEMs at this time. While these sensors are not likely to replace regulatory monitors, they can provide
22 useful data for many non-regulatory monitoring objectives. Sensors tend to be low in cost and operate
23 with low power, so they can be deployed where more expensive regulatory monitors are not required
24 (e.g., saturation monitoring). One of ORD's most important research objectives is to more accurately
25 assess personal exposure. Low-cost sensors are ideal for assessing personal exposure because many of
26 them can be deployed to characterize exposures for a more representative population over a larger
27 portion of a typical day. CASAC emphasizes that these low-cost ozone sensors require very careful
28 study design including an explicit plan to demonstrate sensor accuracy and precision.

29
30 Lastly, CASAC commends the EPA staff scientists who have been involved with ORD's evaluations
31 associated with adding a second FRM for measuring ozone.

32
33 CASAC appreciates the opportunity to provide input to the EPA on this issue. We look forward to
34 receiving the Agency's response.

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36 Sincerely,

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

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

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45 Enclosures

NOTICE

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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:

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21
22 *Did not participate in this Review.
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1 **Abbreviations and Acronyms**

| | | |
|----|----------------|--|
| 2 | AMMS | Air Monitoring and Methods Subcommittee |
| 3 | CAA | Clean Air Act |
| 4 | CASAC | Clean Air Scientific Advisory Committee |
| 5 | CRDS | Cavity Ring Down Spectroscopy |
| 6 | CAPS | Cavity Attenuated Phase Shift Spectroscopy |
| 7 | CFR | Code of Federal Regulations |
| 8 | ET-CL Method | Ethylene-Chemiluminescence Method |
| 9 | EPA | U.S. Environmental Protection Agency |
| 10 | FEM | Federal Equivalent Method |
| 11 | FRM | Federal Reference Method |
| 12 | NAAQS | National Ambient Air Quality Standards |
| 13 | NO-CL Method | Nitric Oxide-Chemiluminescence Method |
| 14 | OAQPS | EPA Office of Air Quality Planning and Standards |
| 15 | ORD | EPA Office of Research and Development |
| 16 | O ₃ | Ozone |
| 17 | SAB | EPA Science Advisory Board |
| 18 | UV-SL | Ultraviolet-Scrubberless Method |
| 19 | | |

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 (particulate matter, ground-level ozone, carbon monoxide, sulfur oxides, nitrogen oxides, and lead).

An FRM serves as the standard protocol for measuring ambient concentration of the six criteria air pollutants, and each of the pollutants has at least one FRM. FRMs are used to assess the quality of monitoring data 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 sampling and/or analyzing 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, and analyzers implementing this method are no longer being manufactured or supported. EPA's Office of Research and Development (ORD) reported that the last O₃ FRM analyzer was designated by EPA in 1979, and most designated O₃ FRM analyzers now are either inoperative or too old to serve as a FRM.

In 2009, EPA consulted a previous Clean Air Scientific Advisory Committee (CASAC) Monitoring Subcommittee (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. Following the consultation, the agency considered the individual AAMS member comments¹, 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 a FEM, and ORD noted that the NO-CL method's principle of operation is similar in concept to that of the current ET-CL FRM. ORD 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 parallels the ET-CL FRM. ORD further stated that the NO-CL method has an added

¹ March 6, 2009 CASAC AMMS 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)

1 benefit in that it is a current FEM and is fully-qualified for promulgation as a FRM. ORD also
2 recommends that the existing ET-CL FRM be retained to ensure continued authorization for the use of
3 existing FEMs that were designated based on comparisons to the ET-CL FRM.
4

5 In this current review, the CASAC Air Monitoring and Methods Subcommittee (AMMS) reviewed
6 ORD's analysis and technical documentation on the NO-CL method, and responded to four charge
7 questions provided by ORD to the AMMS. The document reviewed by the CASAC AMMS is the
8 technical portion of the package for the O₃ NAAQS Review that focuses on ORD's recommended
9 second FRM for O₃(i.e., Appendix D-1 to 40 CFR Part 50 – Reference Measurement Principle and
10 Calibration Procedure for the Measurement of O₃ in the Atmosphere – NO—Chemiluminescence, NO-
11 CL, Method; January 2, 2014 Draft). In addition, the CASAC AMMS reviewed supplemental material
12 that ORD presented during the April 3, 2014 CASAC AMMS teleconference call, and supplemental
13 material that ORD provided on May 5, 2014 for the CASAC consideration. CASAC's advice regarding
14 its review of ORD's analysis, review of technical documentation on the NO-CL method, and its
15 response to ORD's charge questions, is contained within this CASAC report.
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17 **Response to Charge Questions**

18
19 CASAC focused on the following charge questions as part of its review, and provides the following
20 responses to these charge questions.
21

22 **Adding a New Ozone FRM**

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24 *Charge Question 1. What is the AMMS view on adding an additional O₃ FRM (as Appendix D-1 of the*
25 *40 CFR Part 50 Federal Regulation) for the purpose of establishing a new FRM that is implemented in*
26 *analyzers currently in production status? This new O₃ FRM will serve as an additional FRM to*
27 *supplement the current Ethylene-Chemiluminescence method, which is no longer being produced or*
28 *supported.*
29

30 CASAC agrees that the current O₃ FRM is out of date because the ET-CL based instrument is no longer
31 commercially available, and that a new O₃ FRM should be added. CASAC does not anticipate
32 significant issues associated with having two FRM's for O₃ on the EPA list of FRM/FEM instruments;
33 this is consistent with EPA's approach when a new sulfur dioxide (SO₂) FRM was added as part of the
34 2010 SO₂ NAAQS revision regulation.²
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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).

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

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

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8 During the April 3, 2014 AMMS teleconference call, ORD presented data on side-by-side comparisons
9 with the current and proposed FRM. Results from the ORD laboratory evaluations of the NO-CL
10 method demonstrate that the candidate NO-CL method was reasonably interference-free, exceeded
11 laboratory requirements for FRM designation, and provided support for meaningful tightening of FRM
12 requirements in 40 CFR Part 53. However, preliminary results of field tests that occurred for
13 approximately 1 month each at Research Triangle Park (RTP), NC and Laporte/Houston (LAP), TX did
14 not make a compelling case for FRM designation of the NO-CL method, since comparisons between
15 NO-CL and ET-CL show a disquieting amount of scatter at both sites and hints of drift in one or both
16 instruments. Close inspection of scatterplots presented by ORD at the April 3, 2014 meeting from LAP,
17 where four analyzers were deployed, indicated that the drift was most likely associated with the NO-CL
18 analyzer. The CASAC AMMS encouraged ORD to continue assessing existing data to sort out sources
19 of variability between candidate NO-CL analyzers and the ET-CL method.

20
21 After the April teleconference, ORD continued to analyze data from RTP and LAP to sort out sources of
22 variability between candidate NO-CL analyzers and the ET-CL method. For the Houston, TX site, ORD
23 investigated the basis for the series of points that appeared to be outliers in data presented by ORD at the
24 April meeting. On May 5, 2014, ORD submitted its reanalysis of this data as supplemental material for
25 the CASAC consideration.

26
27 ORD's May 5, 2014 supplemental material indicates that scatter that was apparent in the data presented
28 previously to the CASAC AMMS was, in fact, due to problems with how the ET-CL FRM instrument
29 was operated and not due to the instrument itself. Those problems included a change in instrument span
30 that occurred on Sept. 16, 2013, and a loose particulate filter that lead to eight inaccurate hourly
31 measurements. When those problems were corrected, scatter was markedly reduced and correlations
32 were found to be excellent. Subsequent to the April 3, 2014 teleconference call, ORD staff provided
33 final data sets from the RTP and LAP field campaigns. Final data differed from preliminary data in that
34 zero and span responses were used to adjust data from some of the analyzers, including the ET-CL
35 FRM. Within ORD's May 5, 2014 supplemental material, ORD staff also provided summary statistics
36 for zero and span responses for all analyzers. Review of the final data sets indicates that the NO-CL
37 analyzer exhibits acceptable zero and span variation, and compares extremely well with the existing ET-
38 CL FRM. These updated results make a convincing case for designation of the NO-CL method as an
39 FRM.

40
41 CASAC also notes that water vapor is an interferent in the NO-CL method and causes reduced signal
42 due to quenching of the excited NO₂ molecule. This effect can reduce apparent O₃ concentrations by
43 10%, or more (Boylan et al., 2014), but is minimized in commercial NO-CL analyzers by drying the
44 sample. Given sensitivity to water vapor, CASAC agrees that periodic checks of onboard dryer

1 performance may be warranted. This is best accomplished by requiring the method to include loggable
2 Relative Humidity (RH) measurements down-stream of the sample cell.

3
4 The proposed revision to Appendix D-1 of 40 CFR Part 50 (i.e., Reference Measurement Principle and
5 Calibration Procedure for the Measurement of O₃ in the Atmosphere – NO—Chemiluminescence, NO-
6 CL, Method; January 2, 2014 Draft) needs additional detail. Information similar to what is included
7 within EPA’s Federal Register Notice for the Ultraviolet Fluorescence Method for SO₂ should be
8 included in Appendix D-1 to 40 CFR Part 50 for the NO-CL method. ORD should further develop
9 Appendix D-1 to include additional requirements, including information on the measured wavelength
10 range for this method, a “schematic diagram” (see Fig. 1 for the SO₂ FRM), and relevant references to
11 the method. Additional performance requirements that are not specified in Table B-1 of part 53.20
12 should be included in this Appendix, such as response linearity and operating environmental temperature
13 test specifications. Mercury vapor interference limits for UV methods need to be included in Table B-1.
14 See Dr. Judy Chow’s individual comments for more details and relevant references.

15
16 CASAC also recommends that ORD replace Reference 8, “Transfer standards for calibration of Ambient
17 Air Monitoring Analyzers for Ozone” dated 2010 with the October 2013 version (U.S.EPA, 2013).

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

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

25
26 In addition to the NO-CL method, ORD should continue to consider and vigorously evaluate the
27 Ultraviolet-Scrubberless Method (UV-SL) as an additional O₃ FRM, since UV-SL monitors based on
28 light absorption have been shown to not have the level of interference problems that exist in the current
29 light absorbance FEM monitors. It is likely that the SL-UV method may be acceptable as a third FRM if
30 the 2 ppb zero offset present in the ORD tests is resolved. As described further below, the 2B Tech
31 Model 211 light absorption UV-SL O₃ monitor is commercially available and has been shown through
32 research and publications to not have the level of interference problems that exist in current light
33 absorbance FEM monitors. The 2B Tech Model 211 is manufactured by 2B Technologies Inc. (an
34 InDevR Company) and is described in their patent (Birks et al., 2013). If ORD eventually proposes to
35 make the UV-SL method an FRM, ORD should develop additional detail similar to what is included
36 within EPA’s Federal Register Notice for the Ultraviolet Fluorescence Method for SO₂ within Appendix
37 D-1 to 40 CFR Part 50 for the UV-SL method and discussed in the response to Charge Question 2.

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39 There are other measurement methods available to measure O₃ including quantum cascade laser based
40 tunable multi-pass IR absorption spectroscopy, as well as cavity ring down spectroscopy (CRDS) and
41 cavity attenuated phase shift spectroscopy (CAPS) methods. The CRDS and CAPS methods measure
42 O₃ indirectly via absorption of NO₂ from reacting O₃ with NO. However, monitors using these methods
43 are relatively expensive and more complex in comparison to monitors using the UV-SL or NO-CL
44 methods, and are not broadly in use throughout state agencies, and thus are not practical at this time for
45 consideration as FRMs.

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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 sensor-based monitors are probably not sufficiently developed to be considered as FRMs at this time.

2B Tech Model 211 Instrument: The 2B Tech Model 211 monitor has been used by Ollison et al. (2014) and Johnson et al. (2014). This method uses gas-phase scrubber technology with NO added to the sampled air to quantitatively react with O₃ and remove it from the sample to generate O₃-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 O₃ can be calculated directly from Beer's Law (a general spectrophotometry equation which relates the absorption of light to the properties of the material through which the light is traveling). The 2B Tech Model 211 monitor has a moisture compensation and control system that removes water interference, although that control system has not been well described in the manufacturer's literature. 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). Thus this improved version of their O₃ monitor appears to be a strong candidate for designation as an FRM if the offset issue noted above can be resolved.

CASAC also concludes that, in principle, light-absorption measurement techniques which utilize ozone-free sample air for the ambient reference channel (as done in the UV-SL method) are inherently superior to traditional UV O₃ methods in correcting for measurement interferences. In laboratory studies, the 2B Tech Model 211 UV-SL monitor reported higher but negligible interference (0.2 ppb) from water vapor (when tested in zero air) than NO-CL (0.0 ppb); the level of interference is at least an order of magnitude lower than the proposed specification of 5 ppb in 40 CFR Part 53. It should be noted that, 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.

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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)?

Reference methods are relatively expensive to operate and are not likely to be deployed at locations that are not specifically tied to a regulatory monitoring requirement. Non-regulatory air quality monitoring can be achieved with low cost monitoring technologies (“sensors”) where FRM/FEM monitors are either not cost effective or not practical.

Low-cost sensors are well suited for developing micro scale and personal exposure estimates that can augment neighborhood or urban scale regulatory monitors. Their portability and low power requirements make them ideal 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 are also well suited 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.

Current low-cost sensors are not well suited to the measurement of secondary pollutants such as O₃ in rural areas where spatial concentration gradients are small. Rural measurements often require more accurate and precise instruments than measurements in urban settings with larger spatial variation. In many cases, the difference between a regulatory and sensor measurement would exceed the actual rural spatial variation of O₃.

Low-cost sensors do not need to meet the same performance specifications as regulatory monitors. However, in order to aid the interpretation of their data, sensor-based monitors need to be well characterized (precision, bias, interferences) and also evaluated though co-location with regulatory

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1 monitors. It is unlikely that current sensor-based monitors would be appropriate as an additional (or
2 replacement) O₃ FRM.

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1 **REFERENCES**

2
3 Bart, M., Williams, D.E., Ainslie, B., McKendry, I., Salmond, J., Grange, S.K., Alavi-Shoshtari, M.,
4 Steyn, D., and Henshaw, G.S. 2014. High density ozone monitoring using gas sensitive semi-conductor
5 sensors in the Lower Fraser Valley, British Columbia. *Environ. Sci. Technol.* 48(7):3970-7. doi:
6 10.1021/es404610t. Epub 2014 Mar 13.

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

10
11 Johnson, T., Capel, J., and Ollison, W. 2014. Measurement of microenvironmental ozone
12 concentrations in Durham, North Carolina, using a 2B Technologies 205 Federal Equivalent Method
13 monitor and an interference-free 2B Technologies 211 monitor. *Journal of the Air & Waste*
14 *Management Association* 64:360-371.

15
16 Ollison, W.M., Crow, W., and Spicer, C.W. 2014. Field testing of new-technology ambient air ozone
17 monitors. *Journal of the Air & Waste Management Association* 64: 855-863.

18
19 U.S. EPA. 2013. Transfer standards for calibration of air monitoring analyzers for ozone: Technical
20 assistance document. Report Number EPA-454/B-13-004; prepared by U.S. Environmental Protection
21 Agency, Research Triangle Park, NC,
22 <http://www.epa.gov/ttnamti1/files/ambient/qaqc/OzoneTransferStandardGuidance.pdf>.

23
24 White, W.H. Considerations in the use of ozone and PM_{2.5} data for exposure assessment. 2009. *Air*
25 *Qual. Atmos. Health* 2:223–230.

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

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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

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2
3 *Charge Question 1. What is the AMMS view on adding an additional O₃ FRM (as Appendix D-1 of the*
4 *40 CFR Part 50 Federal Regulation) for the purpose of establishing a new FRM that is implemented in*
5 *analyzers currently in production status? This new O₃ FRM will serve as an additional FRM to*
6 *supplement the current Ethylene-Chemiluminescence method, which is no longer being produced or*
7 *supported.*

8
9 Response: Good idea since the Ethylene method is out of date and as long as the NO method shows that
10 it's the same or better than the FRM and it's not more prone to interferences and is easy to
11 implement/practical for routine monitoring.
12

13
14 *Charge Question 2. What is the AMMS views on establishing the Nitric Oxide-Chemiluminescence (NO-*
15 *CL) method (currently an FEM) as the new, additional O₃ FRM?*

16
17 Response: Is it really worth the effort to make the NO FEM method an FRM method?
18

19
20 *Charge Question 3. Do any other ozone measurement methods exist that the AMMS recommends for*
21 *consideration of possible promulgation as a new (additional) O₃ FRM?*

22
23 Response: UV method?
24

25
26 *Charge Question 4. What is the AMMS views on the use of low-cost sensor technology to supplement*
27 *regulatory ozone monitoring (i.e., in rural areas)?*

28
29 Response:

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

31 Would measurements be used for designation purposes?

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

2
3 *Charge Question 1. What is the AMMS view on adding an additional O₃ FRM (as Appendix D-1 of the*
4 *40 CFR Part 50 Federal Regulation) for the purpose of establishing a new FRM that is implemented in*
5 *analyzers currently in production status? This new O₃ FRM will serve as an additional FRM to*
6 *supplement the current Ethylene-Chemiluminescence method, which is no longer being produced or*
7 *supported.*

8
9 Response:

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

18
19 EPA should consider specifying FRM performance criteria (Chow, 1995; Watson et al., 1995) rather
20 than specifying a measurement method or instrument design, such as the NO-CL. Such performance
21 criteria should include specifications and tolerances for: 1) baseline stability; 2) span stability; 3)
22 response linearity; 4) minimum detectable limits; 5) tolerance of known interfering species at normal
23 ambient and extreme ambient concentrations; 6) response time; 7) flow control; and 8) sensitivity to
24 environmental extremes (temperature, humidity, precipitation). The specifications should be the ideal,
25 with tolerances that can be achieved with current technology. Tolerances could be reduced as future
26 technologies allow. As noted above, the current FEM tolerances (Code of Federal Regulations, 2010)
27 may have been appropriate for 1980s measurement technology, but they are much too loose for current
28 technology. Any measurement principle or instrument design that meets these criteria would qualify as a
29 FRM.

30
31 *Charge Question 2. What is the AMMS views on establishing the Nitric Oxide-Chemiluminescence (NO-*
32 *CL) method (currently an FEM) as the new, additional O₃ FRM?*

33
34 Response:

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

1 wavelength while Stedman et al. (Stedman et al., 1972) cite 648 nm. It appears that detectors sensitive
2 to the red to near-IR part of the spectrum are used in most method implementations (Minarro et al.,
3 2011; Ray et al., 1986; Ulanovsky et al., 2001; Zahn et al., 2012; Zhang et al., 2010). The NO-CL
4 method has the advantage over the ethylene-chemiluminescence method since it has faster reaction rates,
5 higher signal to noise (m/z) ratio, the ability to work under vacuum, requires a smaller reaction volume,
6 and accommodates flexible operating conditions (Pearson and Stedman, 1980; Ridley et al., 1992).

7
8 Many compounds emit light upon reaction with O_3 (Hansen et al., 1977; Mihalatos and Calokerinos,
9 1995; Toda and Dasgupta, 2008; Zhang et al., 2010; Zhang et al., 1999), including ethylene which is the
10 basis for the current CL FRM (Code of Federal Regulations, 1997). Light from these reactions is
11 typically broad-band and extends from the UV to IR regions of the spectrum. These reactions do not
12 appear to affect light from the NO- O_3 reaction (Figure 2 from Clough and Thrush, 1967) when it is
13 assumed that such reactions have already taken place in the atmosphere prior to entering the sensing
14 zone.

15
16 When the NO reactant concentration is much higher than ambient levels, the effect of ambient NO
17 appears to be negligible. Interferences from water vapor (Pearson, 1990) are eliminated by sample
18 drying at the inlet (Wilson and Birks, 2006) and reaction-quenching by changes in the atmospheric
19 composition appear to be negligible. Improved sensitivity and specificity of the NO-CL method has
20 been recognized (Parrish and Fehsenfeld, 2000), but its linear response to O_3 must be externally
21 calibrated. A few comparisons between UV absorption and NO- or ethylene-chemiluminescence
22 methods were examined (Arshinov et al., 2002; Ryerson et al., 1998; Williams et al., 2006). Good
23 correlations were found by Ryerson et al. (1998) based on five field measurements of urban plume, but
24 NO-CL method reported ~5% systematically low measurements from aircraft as compared to UV
25 absorption. The disagreement between NO-CL and UV measurements was attributed to the deficiency
26 in photon counting efficiency of the NO-CL.

27
28 There have been limited comparisons of the NO-CL method with UV absorption methods (Ollison et al.,
29 2013; Williams et al., 2006) that are in more common use. The most recent, and interesting results, are
30 summarized in Figures 3 and 8 of Ollison et al. (2013), demonstrating good agreement with one UV
31 absorption system and poorer agreement with another. The disagreement was attributed to UV
32 interferences rather than NO-CL interferences in an environment known to have high VOC levels.

33
34 Although the concept is good, the proposed revision to Appendix D-1 of Part 50 needs additional work.
35 It is a small modification to the current O_3 FRM specification (Code of Federal Regulations, 1997),
36 which is itself sketchy on the design and performance standards needed to specify a FRM. For example,
37 UV light-emitting diodes (LEDs) and photodiode detectors are now available (Fowles and Wayne, 1981;
38 SETI, 2014; Sglux, 2014) that might mitigate some of the temperature dependence of the mercury lamp.
39 Modern methods of linear regression that consider errors in both variables should be considered for
40 calculating slopes and intercepts of calibration curves (York, 1966). More modern measurements of O_3
41 UV absorption efficiencies and their variation with temperature should be evaluated (Barnes and
42 Mauersberger, 1987; Bass and Paur, 1981; Malicet et al., 1995; Mauersberger et al., 1987; Voigt et al.,
43 2001). The statement in Section 3 of Appendix D-1 that "...the NO-CL measurement system is
44 relatively free of significant interferences from other pollutant substances that may be present in ambient
45 air" needs to be tested under a wider variety of conditions than have been reported to date. Spicer et al.

1 (2010) provide a good example of an array of ambient and laboratory tests that would be useful. Figures
2 1 and 2 of Appendix D-1 also need to be revised to specify the optics and source. Reference 8, “Transfer
3 standards for calibration of Ambient Air Monitoring Analyzers for Ozone” dated 2010 should be
4 replaced with the October 2013 version (U.S.EPA, 2013b) at the same website.
5

6 EPA’s May 5, 2014 PowerPoint presentation (Long et al., 2014) provides insufficient documentation to
7 arrive at the conclusion that “based upon the work that has been done to date and this subsequent data
8 analysis, ORD is confident that the NO-CL method meets and exceeds all requirements for proposal of a
9 new FRM for ozone.” A full technical report, of which there are several examples (Holowecky et al.,
10 2008; Leston, 2014; Spicer et al., 2010; U.S.EPA, 1979; U.S.EPA, 1998; U.S.EPA, 2013b), which
11 includes: 1) specification of performance criteria (see above); 2) literature review; 3) explanation of
12 measurement principles, interferences, and currently available instruments; 4) laboratory tests; 5) field
13 tests (including site selection to evaluate interferences and environmental effects); 6) data analysis; and
14 7) recommendations. Slides 5 and 6 show that the “FRM” is inferior to the collocated FEMs, although it
15 is unclear why this is the case; nor is it clear what specific instruments were tested, how old they were,
16 or how they were maintained. Slides 8, 10, and 17 show that the NO-CL and UV instruments measure
17 well within reasonable performance criteria, and there is no reason to select one method over the other
18 as a FRM.
19

20 *Charge Question 3. Do any other ozone measurement methods exist that the AMMS recommends for*
21 *consideration of possible promulgation as a new (additional) O₃ FRM?*
22

23 Response:

24 Spectrophotometric determination of atmospheric O₃ also has a long history (Bravo and Lodge, 1964;
25 Grosjean and Harrison, 1985; Stair, 1959). An additional O₃ FRM by UV absorption should be
26 considered, as most O₃ monitoring networks in the U.S. (i.e., federal, state, local, and tribal) use a UV
27 photometric FEM. Switching from ethylene-CL to the UV absorption method apparently reduced
28 operational costs and improved safety by eliminating the compressed flammable ethylene gas.
29 Appendix D-1 uses this principle as the transfer standard that is in turn related to UV primary standards
30 (Norris et al., 2013; Viallon et al., 2006). These units are mostly based on the 254 nm emission line
31 from a low pressure mercury (Hg) discharge lamp as the UV light source (Leston et al., 2005). The
32 major objection to them as FRMs has been the potential absorption interferences at this wavelength from
33 certain VOCs, water vapor, and mercury. As indicated in Figure 8 of Ollison et al., 2013, it appears that
34 it is possible to compensate for these with appropriate sample pre-treatment and parallel absorbance
35 cells.
36

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

1 MnO₂, heated silver wool, or optimal heated metal scrubber) and interference by ultrafine particles in
2 UV O₃ systems need to be further tested prior to consideration as an additional O₃ FRM.

3
4 *Charge Question 4. What is the AMMS views on the use of low-cost sensor technology to supplement*
5 *regulatory ozone monitoring (i.e., in rural areas)?*

6
7 Response:

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

11
12 Early O₃ measurements monitored the cracks in a piece of bent rubber (Beatty and Juve, 1955; Bradley
13 and Haagen-Smit, 1951; Soret, 1853), and these were indicative of different levels. More recently,
14 passive samplers have been used for long-term averages and exposure studies, although variable
15 diffusion rates increase concentration uncertainty (Bhangar et al., 2013; Cox, 2003; Geyh et al., 2000;
16 Grosjean and Hisham, 1992; Manning et al., 1996; Monn and Hangartner, 1990; Plaisance et al., 2007;
17 Varns et al., 2001). Ozonesondes (Brewer and Milford, 1960; Hogrefe et al., 1998; Johnson et al., 2008;
18 Komhyr, 1969; Liu et al., 2006; Newchurch et al., 2003; Shiotani et al., 2002; Vomel and Diaz, 2010)
19 use a buffered potassium iodide (KI) reaction (Byers and Saltzman, 1958; Hodgeson et al., 1971;
20 Kopczynski and Bufalini, 1971) with coulometric or colorimetric detection. The disadvantage of this
21 method is that it responds to all oxidants, not just O₃, and it has a limited capacity. Longer-lived
22 electrochemical detectors are being developed (Knake and Hauser, 2002; Williams et al., 2013).

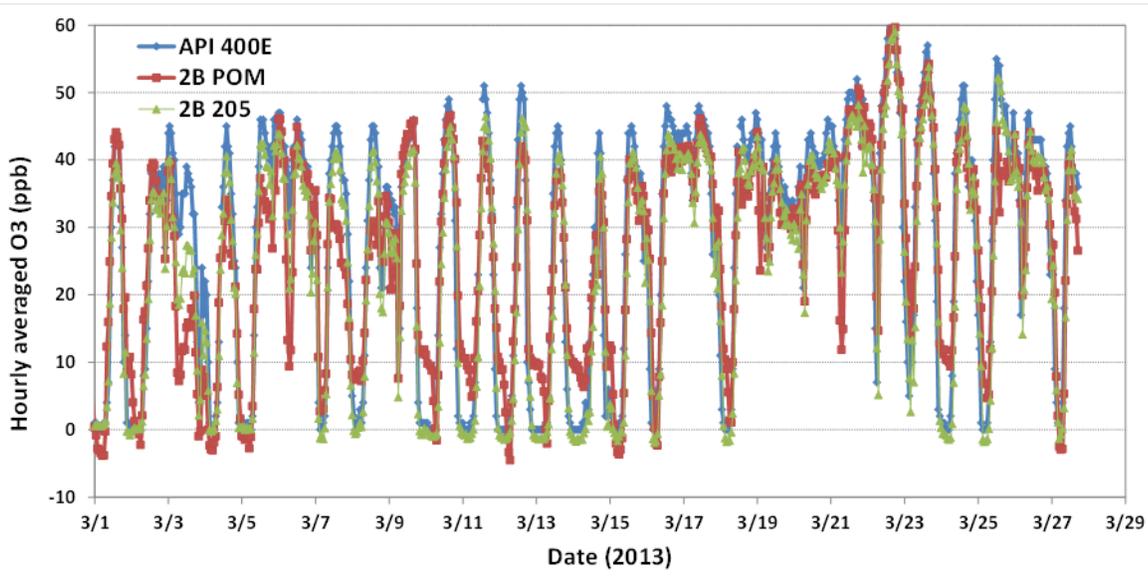
23
24 For remote environments, continuous monitors must be small, lightweight, low power, and easy to
25 operate. Hints et al. (2004) tested two O₃ sensors (i.e., Physical Science Inc. [PSI; Andover, MA] and
26 2B Technologies [Golden, CO]) for O₃ monitoring at ocean buoys and towers. These sensors reported
27 good precision (~1–1.5 ppm) and accuracy (~2%) with 4–4.5 Watts power required. The 2B
28 Technologies O₃ monitor has been applied in the National Park Service network
29 (<http://www.nature.nps.gov/air/Studies/portO3.cfm>), and a modified 2B Model 202 was also found to
30 sustain low temperature (<-60 °C) in the Antarctic (Bauguitte et al., 2011).

31
32 2B Technology Personal Ozone Monitor (POM) with a 0.34 Kg weight and 3 Watt power requirement
33 can be considered as a low-cost sensor (~\$5,000 vs. ~\$9,000–13,000 for a conventional O₃ monitor). An
34 example of collocated comparisons at Sparks, NV, the monitoring site operated by the Washoe County
35 Health Department, is shown in Figure 1 for a collocated comparison among three UV absorption O₃
36 monitors: 1) Teledyne API Model 400E; 2) 2B Technology Personal Ozone Monitor (POM); and 3) 2B
37 Technology Model 205 for the period of 3/1–29/13 at Sparks, NV (Green et al., 2013)

38
39 The Sparks site is known to be affected by residential wood burning during cold nights (Chow et al.,
40 1988). The effect of wood smoke VOCs (Huntzicker and Johnson, 1979) can be seen on the POM
41 results for several nights in a higher concentration. These also seem to correspond to lower
42 concentrations during the daytime. The three monitors tracked well, with correlations (R²) of 0.82–0.93;
43 larger intercepts (4.87 ppb) were found between the 2B Model POM and API 400E and between the 2B
44 Models POM and 205 (intercept of 5.32 ppb) as shown in Figure 2. (Green et al., 2013)

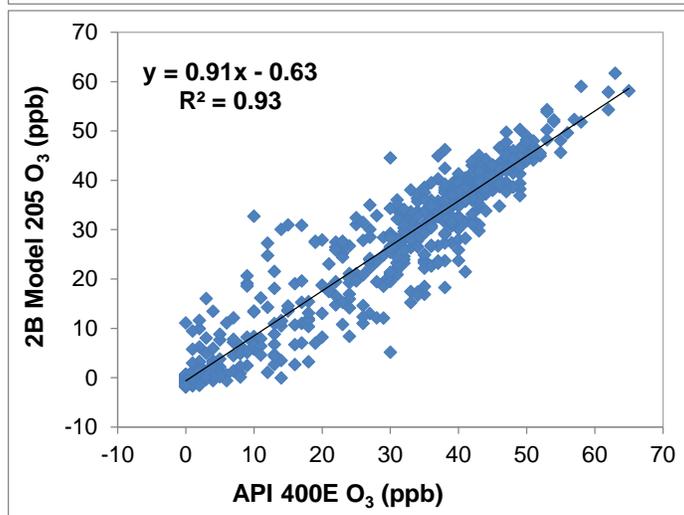
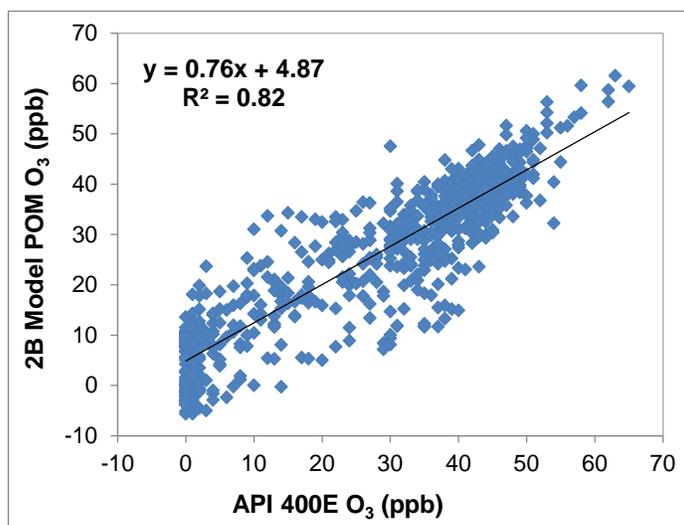
1 O’Keeffe and Lewis (2007) used an optical fiber sensor to measure O₃ at both UV (254 nm) and visible
2 (603 nm) absorption spectra. The sensitivity of optical fiber sensors is proportional to the path length of
3 the gas cells. Optical fiber sensors minimize chemical and electromagnetic interference with relatively
4 low cost.
5

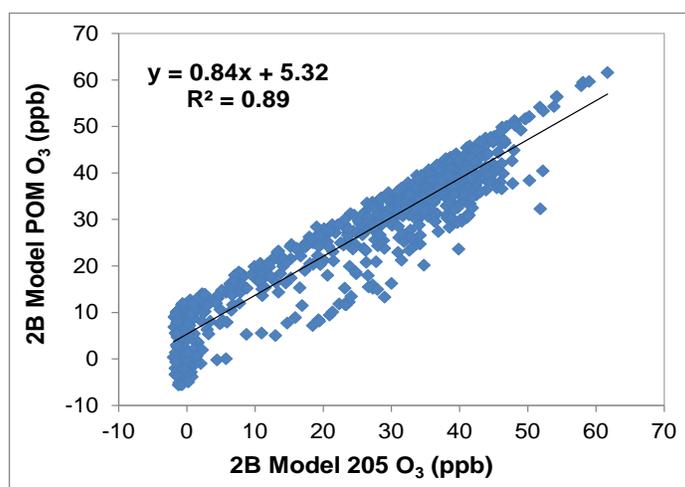
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Figure 1. Collocated comparison among three UV absorption O₃ monitors: 1) Teledyne API Model 400E; 2) 2B Technology Personal Ozone Monitor (POM); and 3) 2B Technology Model 205 for the period of 3/1–29/13 at Sparks, NV (Green et al., 2013). The Sparks 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.





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

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

14
15 Darby et al. (2012) combined cavity-enhanced absorption spectroscopy (CEAS) with a low pressure
16 mercury lamp to achieve low detection limit (8.4 ppb) for O₃. Gomez and Rosen (2013) reported a fast-
17 response cavity-enhanced O₃ monitor based on incoherent broadband CEAS (IBB-CEAS) with ~1 ppb
18 sensitivity at 0.1 s integration time. Gao et al. (2012) documented the development and testing of the
19 NOAA-2 O₃ monitor using the polarized UV beam in the absorption cells to reduce cell length and a
20 capillary mercury lamp to increase UV intensity. A chemiluminescence O₃ detector for airborne
21 applications is also presented by Zahn et al. (2012).

22
23 Other techniques, including photoacoustic (Veres et al., 2005), solid state (Korotcenkov et al., 2007a;
24 2007b; 2009; 2014; Korotcenkov and Cho, 2012), and electrochemical cells cited above need to be
25 further tested. The performance of several O₃ monitors employing several different operation principles
26 is shown in Table 1 of Gomez and Rosen (2013). These low-cost, lightweight O₃ monitors need to be
27 collocated with proven O₃ monitors (e.g., FRM or FEM) to assure their equivalence and comparability
28 during O₃ measurements. Bowman (2013) calls attention to the need of an international O₃ air quality
29 monitoring system that integrates a continuum of observations from local to global scale, including both

Clean Air Scientific Advisory Committee (CASAC) Draft Report (7/1/14) for Quality Review -- Do not Cite or Quote --This draft has not been reviewed or approved by the chartered CASAC and does not represent EPA policy.

1 ground- and satellite-based observations of O₃. Tests of low-cost O₃microsensors should be part of the
2 EPA tasks to verify the emerging technology.

3

4

References

- 1
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3 Arshinov, M.Y.; Belan, B.D.; Fofonov, A.V.; Krasnov, O.A.; Kovalevskii, V.K.; Pirogov, V.A.;
4 Tolmachev, G.N. (2002). Comparison of ultraviolet and chemiluminescent ozonometers. *Atmospheric*
5 *and Oceanic Optics*, **15**:656-658.
- 6 Barnes, J.; Mauersberger, K. (1987). Temperature-dependence of the ozone absorption cross-section at
7 the 2537 nm mercury line. *Journal of Geophysical Research-Atmospheres*, **92**(D12):14861-14864.
- 8 Bass, A.M.; Paur, R.J. (1981). UV absorption cross-sections for ozone - the temperature dependence.
9 *Journal of Photochemistry*, **17**(1-2):141.
- 10 Bauguitte, S.J.B.; Brough, N.; Frey, M.M.; Jones, A.E.; Maxfield, D.J.; Roscoe, H.K.; Rose, M.C.;
11 Wolff, E.W. (2011). A network of autonomous surface ozone monitors in Antarctica: technical
12 description and first results. *Atmos. Meas. Tech.*, **4**(4):645-658. [http://www.atmos-meas-](http://www.atmos-meas-tech.net/4/645/2011/amt-4-645-2011.pdf)
13 [tech.net/4/645/2011/amt-4-645-2011.pdf](http://www.atmos-meas-tech.net/4/645/2011/amt-4-645-2011.pdf).
- 14 Beatty, J.R.; Juve, A.E. (1955). A simple objective method for estimating low concentrations of ozone
15 in air. *Rubber Chemistry and Technology*, **28**(2):608-622.
- 16 Bhangar, S.; Singer, B.C.; Nazaroff, W.W. (2013). Calibration of the Ogawa passive ozone sampler for
17 aircraft cabins. *Atmos. Environ.*, **65**:21-24.
- 18 Bowman, K.W. (2013). Toward the next generation of air quality monitoring: Ozone. *Atmos. Environ.*,
19 **80**:571-583.
- 20 Bradley, C.E.; Haagen-Smit, A.J. (1951). The application of rubber in the quantitative determination of
21 ozone. *Rubber Chemistry and Technology*, **24**(4):750-755.
- 22 Bravo, H.A.; Lodge, J.P. (1964). Specific Spectrophotometric Determination of Ozone in the
23 Atmosphere
24 BRAVO1964. *Anal. Chem.*, **36**(3):671-673. <http://dx.doi.org/10.1021/ac60209a040>.
- 25 Brewer, A.W.; Milford, J.R. (1960). The Oxford-Kew ozone sonde. *Proc. Roy. Soc. Lond.*, **256A**:470-
26 495.
- 27 Byers, D.H.; Saltzman, B.E. (1958). Determination of ozone in air by neutral and alkaline iodide
28 procedures. *AIHA Journal*, **19**:251-257.
- 29 Chow, J.C.; Watson, J.G.; Egami, R.T.; Frazier, C.A.; Goodrich, A.; Ralph, C. (1988). PM₁₀ source
30 apportionment in Reno and Sparks, Nevada for state implementation plan development: Chemical
31 mass balance results. Report Number DRI 8086.1F2; prepared by Desert Research Institute, Reno,
32 NV, for State of Nevada, Carson City, NV.
- 33 Chow, J.C. (1995). Critical review: Measurement methods to determine compliance with ambient air
34 quality standards for suspended particles. *J. Air Waste Manage. Assoc.*, **45**(5):320-
35 382. <http://www.tandfonline.com/doi/pdf/10.1080/10473289.1995.10467369>.
- 36 Clough, P.N.; Thrush, B.A. (1967). Mechanism of chemiluminescent reaction between nitric oxide and
37 ozone. *Trans. Faraday Soc.*, **63**:915.
- 38 Code of Federal Regulations (1983). Appendix F to Part 50-Measurement principle and calibration
39 procedure for the measurement of nitrogen dioxide in the atmosphere (gas phase
40 chemiluminescence). *CFR*, **40**(50):26-38. [http://www.ecfr.gov/cgi-bin/text-](http://www.ecfr.gov/cgi-bin/text-idx?SID=2497f5e7ef364619527718c988923dc0&node=40:2.0.1.1.0.1.19.7&rgn=div9)
41 [idx?SID=2497f5e7ef364619527718c988923dc0&node=40:2.0.1.1.0.1.19.7&rgn=div9](http://www.ecfr.gov/cgi-bin/text-idx?SID=2497f5e7ef364619527718c988923dc0&node=40:2.0.1.1.0.1.19.7&rgn=div9).
- 42 Code of Federal Regulations (1997). Appendix D to Part 50-Measurement principle and calibration
43 procedure for the measurement of ozone in the atmosphere. *CFR*, **40**(50):26-38.
44 [http://www.ecfr.gov/cgi-bin/text-](http://www.ecfr.gov/cgi-bin/text-idx?SID=317c84d3fd074ff5d462bc9c8539784c&node=40:2.0.1.1.0.1.19.5&rgn=div9)
45 [idx?SID=317c84d3fd074ff5d462bc9c8539784c&node=40:2.0.1.1.0.1.19.5&rgn=div9](http://www.ecfr.gov/cgi-bin/text-idx?SID=317c84d3fd074ff5d462bc9c8539784c&node=40:2.0.1.1.0.1.19.5&rgn=div9).

- 1 Code of Federal Regulations (2010). Test procedures for methods for SO₂, CO, O₃, and NO₂. *CFR*,
2 **40**(53.32)[http://www.ecfr.gov/cgi-bin/text-](http://www.ecfr.gov/cgi-bin/text-idx?SID=fe69264994c290cd218f61eddf2a1c4e&node=40:6.0.1.1.1.3.1.3&rgn=div8)
3 [idx?SID=fe69264994c290cd218f61eddf2a1c4e&node=40:6.0.1.1.1.3.1.3&rgn=div8](http://www.ecfr.gov/cgi-bin/text-idx?SID=fe69264994c290cd218f61eddf2a1c4e&node=40:6.0.1.1.1.3.1.3&rgn=div8).
- 4 Cox, R.M. (2003). The use of passive sampling to monitor forest exposure to O₃, NO₂ and SO₂: A
5 review and some case studies. *Environ. Poll.*, **126**(3):301-311.
- 6 Darby, S.B.; Smith, P.D.; Venables, D.S. (2012). Cavity-enhanced absorption using an atomic line
7 source: application to deep-UV measurements. *Analyst*, **137**:2318-2321.
- 8 Dunlea, E.J.; Herndon, S.C.; Nelson, D.D.; Volkamer, R.M.; Lamb, B.K.; Allwine, E.J.; Grutter, M.;
9 Villegas, C.R.R.; Marquez, C.; Blanco, S.; Cardenas, B.; Kolb, C.E.; Molina, L.T.; Molina, M.J.
10 (2006). Technical note: Evaluation of standard ultraviolet absorption ozone monitors in a polluted
11 urban environment. *Atmos. Chem. Phys.*, **6**:3163-3180. [http://www.atmos-chem-](http://www.atmos-chem-phys.net/6/3163/2006/acp-6-3163-2006.pdf)
12 [phys.net/6/3163/2006/acp-6-3163-2006.pdf](http://www.atmos-chem-phys.net/6/3163/2006/acp-6-3163-2006.pdf).
- 13 Dunlea, E.J.; Herndon, S.C.; Nelson, D.D.; Volkamer, R.M.; San Martini, F.; Sheehy, P.M.; Zahniser,
14 M.S.; Shorter, J.H.; Wormhoudt, J.C.; Lamb, B.K.; Allwine, E.J.; Gaffney, J.S.; Marley, N.A.;
15 Grutter, M.; Marquez, C.; Blanco, S.; Cardenas, B.; Retama, A.; Villegas, C.R.R.; Kolb, C.E.;
16 Molina, L.T.; Molina, M.J. (2007). Evaluation of nitrogen dioxide chemiluminescence monitors in a
17 polluted urban environment. *Atmos. Chem. Phys.*, **7**(10):2691-2704.
- 18 Fowles, M.; Wayne, R.P. (1981). Ozone monitor using an LED source. *J. Phys. E: Sci. Instrum.*,
19 **14**:1143-1145.
- 20 Gao, R.S.; Ballard, J.; Watts, L.A.; Thornberry, T.D.; Ciciora, S.J.; McLaughlin, R.J.; Fahey, D.W.
21 (2012). A compact, fast UV photometer for measurement of ozone from research aircraft. *Atmos.*
22 *Meas. Tech.*, **5**(9):2201-2210.
- 23 Geyh, A.S.; Xue, J.P.; Ozkaynak, H.; Spengler, J.D. (2000). The Harvard Southern California chronic
24 ozone exposure study: Assessing ozone exposure of grade-school-age children in two Southern
25 California communities. *Environ. Health Perspect.*, **108**(3):265-270.
- 26 Gomez, A.L.; Rosen, E.P. (2013). Fast response cavity enhanced ozone monitor. *Atmos. Meas. Tech.*,
27 **6**(2):487-494. <http://www.atmos-meas-tech.net/6/487/2013/amt-6-487-2013.pdf>.
- 28 Green, M.C.; Wang, X.L.; Watson, J.G.; Chow, J.C.; Kohl, S.D. (2013). Spatial distribution of
29 wintertime PM_{2.5} in Sparks, NV: Analysis of air quality and meteorological data. prepared by Desert
30 Research Institute, Reno, NV.
- 31 Grosjean, D.; Harrison, J.F. (1985). Response of chemiluminescence NO_x analyzers and ultraviolet
32 ozone analyzers to organic air pollutants. *Environ. Sci. Technol.*, **19**(9):862-865.
- 33 Grosjean, D.; Hisham, M.W.M. (1992). A passive sampler for atmospheric ozone. *J. Air Waste Manage.*
34 *Assoc.*, **42**(2):169-173.
- 35 Gubarev, S.P.; Opaleva, G.P.; Taran, V.S.; Zolototrubova, M.I. (2013). Devices for ozone concentration
36 monitoring. *Problems of Atomic Science and Technology*, (1):234-236.
37 http://vant.kipt.kharkov.ua/ARTICLE/VANT_2013_1/article_2013_1_234.pdf.
- 38 Hansen, D.A.; Atkinson, R.; Pitts, J.N. (1977). Structural effects on chemiluminescence from reaction of
39 ozone with selected organic compounds. *Journal of Photochemistry*, **7**(6):379-404.
- 40 Hints, E.J.; Allsup, G.P.; Eck, C.F.; Hosom, D.S.; Purcell, M.J.; Roberts, A.A.; Scott, D.R.; Sholkovitz,
41 E.R.; Rawlins, W.T.; Mulhall, P.A.; Lightner, K.; McMillan, W.W.; Song, J.; Newchurch, M.J.
42 (2004). New ozone measurement systems for autonomous operation on ocean buoys and towers. *J.*
43 *Atmos. Oceanic Technol.*, **21**(7):1007-1016. [http://journals.ametsoc.org/doi/pdf/10.1175/1520-](http://journals.ametsoc.org/doi/pdf/10.1175/1520-0426(2004)021%3C1007%3ANOMSFA%3E2.0.CO%3B2)
44 [0426\(2004\)021%3C1007%3ANOMSFA%3E2.0.CO%3B2](http://journals.ametsoc.org/doi/pdf/10.1175/1520-0426(2004)021%3C1007%3ANOMSFA%3E2.0.CO%3B2).

- 1 Hodgeson, J.A.; Baumgardner, R.E.; Martin, B.E.; Rehme, K.A. (1971). Stoichiometry in the neutral
2 iodometric procedure for ozone by gas-phase titration with nitric oxide. *Anal. Chem.*, **43**(8):1123-
3 1126. <http://dx.doi.org/10.1021/ac60303a026>.
- 4 Hogrefe, C.; Rao, S.T.; Zurbenko, I.G. (1998). Detecting trends and biases in time series of ozonesonde
5 data. *Atmos. Environ.*, **32**(14/15):2569-2586.
- 6 Huntzicker, J.J.; Johnson, R.L. (1979). Investigation of an ambient interference in the measurement of
7 ozone by ultraviolet absorption photometry. *Environ. Sci. Technol.*, **13**(11):1414-1416.
- 8 Johnson, B.J.; Helmig, D.; Oltmans, S.J. (2008). Evaluation of ozone measurements from a tethered
9 balloon-sampling platform at South Pole Station in December 2003. *Atmos. Environ.*, **42**(12):2780-
10 2787.
- 11 Johnson, T.; Capel, J.; Ollison, W. (2014). Measurement of microenvironmental ozone concentrations in
12 Durham, North Carolina, using a 2B Technologies 205 Federal Equivalent Method monitor and an
13 interference-free 2B Technologies 211 monitor. *J. Air Waste Manage. Assoc.*, **64**(3):360-371.
- 14 Kalnajs, L.E.; Avallone, L.M. (2010). A novel lightweight low-power dual-beam ozone photometer
15 utilizing solid-state optoelectronics. *J. Atmos. Oceanic Technol.*, **27**:869-880.
- 16 Knake, R.; Hauser, P.C. (2002). Sensitive electrochemical detection of ozone. *Anal. Chim. Acta.*,
17 **459**(2):199-207.
- 18 Komhyr, W.D. (1969). Electrochemical concentration cells for gas analysis. *Ann. Geophysicae*, **25**:203.
- 19 Kopczynski, S.L.; Bufalini, J.J. (1971). Stoichiometry of iodometric analyses of ozone at pH 7.0. *Anal.*
20 *Chem.*, **43**(8):1126-1127. <http://dx.doi.org/10.1021/ac60303a024>.
- 21 Korotcenkov, G.; Blinov, I.; Ivanov, M.; Stetter, J.R. (2007a). Ozone sensors on the base of SnO₂ films
22 deposited by spray pyrolysis. *Sensors and Actuators B-Chemical*, **120**(2):679-686.
- 23 Korotcenkov, G.; Blinov, I.; Brinzari, V.; Stetter, J.R. (2007b). Effect of air humidity on gas response of
24 SnO₂ thin film ozone sensors. *Sensors and Actuators B-Chemical*, **122**(2):519-526.
- 25 Korotcenkov, G.; Cho, B.K.; Gulina, L.; Tolstoy, V. (2009). Ozone sensors based on SnO(2) films
26 modified by SnO(2)-Au nanocomposites synthesized by the SILD method. *Sensors and Actuators B-*
27 *Chemical*, **138**(2):512-517.
- 28 Korotcenkov, G.; Cho, B.K. (2012). Ozone measuring: What can limit application of SnO₂-based
29 conductometric gas sensors? *Sensors and Actuators B-Chemical*, **161**(1):28-44.
- 30 Korotcenkov, G.; Cho, B.K.; Brinzari, V.; Gulina, L.B.; Tolstoy, V.P. (2014). Catalytically active filters
31 deposited by SILD method for inhibiting sensitivity to ozone of SnO₂-based conductometric gas
32 sensors. *Ferroelectrics*, **459**(1):46-51.
- 33 Leston, A.R.; Ollison, W.M.; Spicer, C.W.; Satola, J. (2005). Potential interference bias in ozone
34 standard compliance monitoring. *J. Air Waste Manage. Assoc.*, **55**(10):1464-1472.
- 35 Liu, X.; Chance, K.; Sioris, C.E.; Kurosu, T.P.; Newchurch, M.J. (2006). Intercomparison of GOME,
36 ozonesonde, and SAGE II measurements of ozone: Demonstration of the need to homogenize
37 available ozonesonde data sets. *J. Geophys Res. - Atmospheres*, **111**(D14)ISI:000239579100003.
- 38 Malicet, J.; Daumont, D.; Charbonnier, J.; Parrisé, C.; Chakir, A.; Brion, J. (1995). Ozone UV
39 spectroscopy 2. Absorption cross-sections and temperature-dependence. *Journal of Atmospheric*
40 *Chemistry*, **21**(3):263-273.
- 41 Manning, W.J.; Krupa, S.V.; Bergweiler, C.J.; Nelson, K.I. (1996). Ambient ozone (O₃) in three Class I
42 wilderness areas in the northeastern USA: Measurements with Ogawa passive samplers. *Environ.*
43 *Poll.*, **91**(3):399-403.

- 1 Mauersberger, K.; Hanson, D.; Barnes, J.; Morton, J. (1987). Ozone vapor-pressure and absorption
2 cross-section measurements - Introduction of an ozone standard. *Journal of Geophysical Research-*
3 *Atmospheres*, **92**(D7):8480-8482.
- 4 Mihalatos, A.M.; Calokerinos, A.C. (1995). Ozone chemiluminescence in environmental analysis. *Anal.*
5 *Chim. Acta.*, **303**(1):127-135.
- 6 Minarro, M.D.; Ferradas, E.G.; Rico, J.B.; Alonso, F.D.; Martinez, F.J.M.; Trigueros, C.R. (2011).
7 Study of the uncertainty in NO₂ chemiluminescence measurements due to the NO-O₃ reaction in
8 sampling lines. *Environmental Science and Pollution Research*, **18**(3):436-445.
- 9 Monn, C.; Hangartner, M. (1990). Passive sampling of ozone. *J. Air Waste Manage. Assoc.*, **40**(3):357-
10 358.
- 11 Newchurch, M.J.; Ayoub, M.A.; Oltmans, S.; Johnson, B.; Schmidlin, F.J. (2003). Vertical distribution
12 of ozone at four sites in the United States. *J. Geophys. Res.*, **108**(D1):ACH 9-1-ACH 9-17. doi:
13 10.1029/2002JD002059.
- 14 Norris, J.E.; Choquette, S.J.; Viallon, J.; Moussay, P.; Wielgosz, R.; Guenther, F.R. (2013). Temperature
15 measurement and optical path-length bias improvement modifications to National Institute of
16 Standards and Technology ozone reference standards. *J. Air Waste Manage. Assoc.*, **63**(5):565-574.
- 17 O'Keeffe, S.; Fitzpatrick, C.; Lewis, E. (2007). An optical fibre based ultra violet and visible absorption
18 spectroscopy system for ozone concentration monitoring. *Sensors and Actuators B-Chemical*,
19 **125**(2):372-378.
- 20 Ollison, W.M.; Crow, W.; Spicer, C.W. (2013). Field testing of new-technology ambient air ozone
21 monitors. *J. Air Waste Manage. Assoc.*, **63**(7):855-863.
22 <http://www.tandfonline.com/doi/pdf/10.1080/10962247.2013.796898>.
- 23 Parrish, D.D.; Fehsenfeld, F.C. (2000). Methods for gas-phase measurements of ozone, ozone precursors
24 and aerosol precursors. *Atmos. Environ.*, **34**(12-14):1921-1957.
- 25 Pearson, R.; Stedman, D. (1980). Instrumentation for fast-response ozone measurements from aircraft
26 PEARSON1980. *Atmospheric Technology*, **12**:51-54.
- 27 Pearson, R. (1990). Measuring ambient ozone with high sensitivity and bandwidth
28 PEARSON1990. *Rev. Sci. Instrum.*, **61**(2):907-916.
- 29 Plaisance, H.; Gerboles, M.; Piechocki, A.; Detimmerman, F.; De Saeger, E. (2007). Radial diffusive
30 sampler for the determination of 8-h ambient ozone concentrations. *Environ. Poll.*, **148**(1):1-9.
- 31 Proffitt, M.H.; McLaughlin, R.J. (1983). Fast-response dual-beam UV-absorption ozone photometer
32 suitable for use on stratospheric balloons. *Rev. Sci. Instrum.*, **54**(12):1719-1728.
- 33 Ray, J.D.; Stedman, D.H.; Wendel, G.J. (1986). Fast chemiluminescent method for measurement of
34 ambient ozone. *Anal. Chem.*, **58**(3):598-600.
- 35 Ridley, B.A.; Grahek, F.E.; Walega, J.G. (1992). A small, high-sensitivity, medium-response ozone
36 detector suitable for measurements from light aircraft. *J. Atmos. Oceanic Technol.*, **9**(2):142-148.
- 37 Ryerson, T.B.; Buhr, M.P.; Frost, G.J.; Goldan, P.D.; Holloway, J.S.; Hubler, G.; Jobson, B.T.; Kuster,
38 W.C.; McKeen, S.A.; Parrish, D.D.; Roberts, J.M.; Sueper, D.T.; Trainer, M.; Williams, J.;
39 Fehsenfeld, F.C. (1998). Emissions lifetimes and ozone formation in power plant plumes. *J. Geophys*
40 *Res. - Atmospheres*, **103**(D17):22569-22583.
- 41 Saltzman, B.E.; Byers, D.H.; Hyslop, F.L. (1956). Nitrogen oxide impurities in ozone. *Industrial &*
42 *Engineering Chemistry*, **48**(1):115-118.
- 43 Saltzman, B.E.; Gilbert, N. (1959). Iodometric microdetermination of organic oxidants and ozone.
44 Resolution of mixtures by kinetic colorimetry. *Anal. Chem.*, **31**(11):1914-1920.

- 1 SETI (2014). Rethinking UV light sources. prepared by Sensor Electronic Technology Inc., Columbia,
2 SC, <http://www.s-et.com/>.
- 3 Sglux (2014). sglux: The UV experts. prepared by sglux SolGel Technologies GmbH, Berlin, Germany,
4 <http://www.sglux.com/Start.1.0.html?&L=1>.
- 5 Shiotani, M.; Fujiwara, M.; Hasebe, F.; Hashizume, H.; Vomel, H.; Oltmans, S.J.; Watanabe, T. (2002).
6 Ozonesonde observations in the equatorial eastern Pacific - the Shoyo-Maruru survey. *J. Meteorol. Soc.*
7 *Japan*, **80**(4B):897-909. ISI:000179235300010.
- 8 Soret, J.L. (1853). Note sur la prodction de l'ozone par la decomposition del'eau a de basses
9 temperatures. *C. R. Hebd. Seances Adad. Sci. Ser. C.*, **38**:445-448.
- 10 Spicer, C.W.; Joseph, D.W.; Ollison, W.M. (2010). A re-examination of ambient air ozone monitor
11 interferences. *J. Air Waste Manage. Assoc.*, **60**(11):1353-1364.
12 <http://www.tandfonline.com/doi/pdf/10.3155/1047-3289.60.11.1353>.
- 13 Stair, R. (1959). Measurement of Ozone in Terms of Its Optical Absorption
14 STAIR1959. In *Ozone Chemistry and Technology*, 21; American Chemical Society: 269-285.
15 <http://dx.doi.org/10.1021/ba-1959-0021.ch038>
- 16 Stedman, D.H.; Daby, E.E.; Stuhl, F.; Niki, H. (1972). Analysis of ozone and nitric oxide by a
17 chemiluminescent method in laboratory and atmospheric studies of photochemical smog. *J. Air Poll.*
18 *Control Assoc.*, **22**(4):260-263.
- 19 Teledyne API (2011). Model 265E chemiluminescence ozone analyzer. prepared by Teledyne Advanced
20 Pollution Instrumentation, San Diego, CA, [http://www.teledyne-](http://www.teledyne-api.com/manuals/06626B_265E_Addendum.pdf)
21 [api.com/manuals/06626B_265E_Addendum.pdf](http://www.teledyne-api.com/manuals/06626B_265E_Addendum.pdf).
- 22 Toda, K.; Dasgupta, P.K. (2008). New applications of chemiluminescence for selective gas analysis.
23 *Chemical Engineering Communications*, **195**(2):82-97.
- 24 U.S.EPA (2013a). Integrated science assessment for ozone and related photochemical oxidants. Report
25 Number EPA 600/R-10/076F; prepared by Office of Research and Development, National Center for
26 Environmental Assessment - RTP Division, U.S. Environmental Protection Agency, Research
27 Triangle Park, NC.
- 28 U.S.EPA (2013b). Transfer standards for calibration of air monitoring analyzers for ozone: Technical
29 assistance document. Report Number EPA-454/B-13-004; prepared by U.S. Environmental
30 Protection Agency, Research Triangle Park, NC,
31 <http://www.epa.gov/ttnamti1/files/ambient/gaqc/OzoneTransferStandardGuidance.pdf>.
- 32 Ulanovsky, A.E.; Yushkov, V.A.; Sitnikov, N.M.; Ravengnani, F. (2001). The FOZAN-II fast-response
33 chemiluminescent airborne ozone analyzer. *Instruments and Experimental Techniques*, **44**:249-256.
- 34 Varns, J.L.; Mulik, J.D.; Sather, M.E.; Glen, G.; Smith, L.; Stallings, C. (2001). Passive ozone network
35 of Dallas: A modeling opportunity with community involvement. 1. *Environ. Sci. Technol.*,
36 **35**(5):845-855.
- 37 Veres, A.H.; Sarlos, F.; Varga, A.; Szabo, G.; Bozoki, Z.; Motika, G.; Gyapjas, J. (2005). Nd : YAG
38 laser-based photoacoustic detection of ozone: Comparison of pulsed and quasicontinuous wave
39 operation and field tests. *Spectroscopy Letters*, **38**(3):377-388.
- 40 Viallon, J.; Moussay, P.; Norris, J.E.; Guenther, F.R.; Wielgosz, R.I. (2006). A study of systematic
41 biases and measurement uncertainties in ozone mole fraction measurements with the NIST Standard
42 Reference Photometer. *Metrologia*, **43**(5):441-450.
- 43 Villena, G.; Bejan, I.; Kurtenbach, R.; Wiesen, P.; Kleffmann, J. (2012). Interferences of commercial
44 NO₂ instruments in the urban atmosphere and in a smog chamber. *Atmos. Meas. Tech.*, **5**(1):149-159.
45 <http://www.atmos-meas-tech.net/5/149/2012/amt-5-149-2012.pdf>.

- 1 Voigt, S.; Orphal, J.; Bogumil, K.; Burrows, J.P. (2001). The temperature dependence (203-293 K) of
2 the absorption cross sections of O₃ in the 230-850 nm region measured by Fourier-transform
3 spectroscopy. *Journal of Photochemistry and Photobiology A-Chemistry*, **143**(1):1-9.
- 4 Vomel, H.; Diaz, K. (2010). Ozone sonde cell current measurements and implications for observations
5 of near-zero ozone concentrations in the tropical upper troposphere. *Atmos. Meas. Tech.*, **3**(2):495-
6 505.
- 7 Washenfelder, R.A.; Wagner, N.L.; Dube, W.P.; Brown, S.S. (2011). *Environ.Sci.Technol.***45**(7):2938-
8 2944.
- 9 Watson, J.G.; Thurston, G.D.; Frank, N.H.; Lodge, J.P.; Wiener, R.W.; McElroy, F.F.; Kleinman, M.T.;
10 Mueller, P.K.; Schmidt, A.C.; Lipfert, F.W.; Thompson, R.J.; Dasgupta, P.K.; Marrack, D.; Michaels,
11 R.A.; Moore, T.; Penkala, S.; Tombach, I.H.; Vestman, L.; Hauser, T.; Chow, J.C. (1995).
12 Measurement methods to determine compliance with ambient air quality standards for suspended
13 particles: Critical review discussion. *J. Air Waste Manage. Assoc.*, **45**(9):666-684.
14 <http://www.tandfonline.com/doi/pdf/10.1080/10473289.1995.10467395>.
- 15 Williams, D.E.; Henshaw, G.S.; Bart, M.; Laing, G.; Wagner, J.; Naisbitt, S.; Salmond, J.A. (2013).
16 Validation of low-cost ozone measurement instruments suitable for use in an air-quality monitoring
17 network. *Measurement Science & Technology*, **24**(6)[http://iopscience.iop.org/0957-](http://iopscience.iop.org/0957-0233/24/6/065803/pdf/0957-0233_24_6_065803.pdf)
18 [0233/24/6/065803/pdf/0957-0233_24_6_065803.pdf](http://iopscience.iop.org/0957-0233/24_6_065803.pdf).
- 19 Williams, E.J.; Fehsenfeld, F.C.; Jobson, B.T.; Kuster, W.C.; Goldan, P.D.; Stutz, J.; McCleanny, W.A.
20 (2006). Comparison of ultraviolet absorbance, chemiluminescence, and DOAS instruments for
21 ambient ozone monitoring. *Environ. Sci. Technol.*, **40**(18):5755-5762.
- 22 Wilson, K.L.; Birks, J.W. (2006). Mechanism and elimination of a water vapor interference in the
23 measurement of ozone by UV absorbance. *Environ. Sci. Technol.*, **40**(20):6361-6367.
- 24 Winer, A.M.; Peters, J.W.; Smith, J.P.; Pitts, J.N., Jr. (1974). Response of commercial
25 chemiluminescence NO-NO₂ analyzers to other nitrogen-containing compounds. *Environ. Sci.*
26 *Technol.*, **8**:1118-1121.
- 27 Xu, Z.; Wang, T.; Xue, L.K.; Louie, P.K.K.; Luk, C.W.Y.; Gao, J.; Wang, S.L.; Chai, F.H.; Wang, W.X.
28 (2013). Evaluating the uncertainties of thermal catalytic conversion in measuring atmospheric
29 nitrogen dioxide at four differently polluted sites in China. *Atmos. Environ.*, **76**:221-226.
- 30 York, D. (1966). Least-squares fitting of a straight line. *Canadian J. Phys.*, **44**:1079-1086.
- 31 Zahn, A.; Weppner, J.; Widmann, H.; Schlote-Holubek, K.; Burger, B.; Kuhner, T.; Franke, H. (2012).
32 A fast and precise chemiluminescence ozone detector for eddy flux and airborne application. *Atmos.*
33 *Meas. Tech.*, **5**(2):363-375.
- 34 Zhang, L.C.; Hu, J.; Lv, Y.; Hou, X.D. (2010). Recent progress in chemiluminescence for gas analysis.
35 *Applied Spectroscopy Reviews*, **45**(6):474-489.
- 36 Zhang, X.R.; Baeyens, W.R.G.; Garcia-Campana, A.M.; Ouyang, J. (1999). Recent developments in
37 chemiluminescence sensors. *Trac-Trends in Analytical Chemistry*, **18**(6):384-391.
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4 **Dr. Kenneth Demerjian**

5

6 *Charge Question 1. What is the AMMS view on adding an additional O₃ FRM (as Appendix D-1 of the*
7 *40 CFR Part 50 Federal Regulation) for the purpose of establishing a new FRM that is implemented in*
8 *analyzers currently in production status? This new O₃ FRM will serve as an additional FRM to*
9 *supplement the current Ethylene-Chemiluminescence method, which is no longer being produced or*
10 *supported.*

11

12 Response:

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

18

19

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

22

23 Response:

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

1 N₂O is a potential source of OH (via O(¹D) reaction with H₂O) which is highly reactive with other
2 compounds (e.g., VOCs) forming oxidized products with uv absorbing properties in 254nm region.
3 Reported SL-UV interferences (e.g. xylene, SO₂, NO₂, H₂O) are low and do not seem likely to account
4 for the zero offset. ORD may want to consider performing systematic zeroing (e.g., hourly) to see if this
5 reduces the offset.

6
7 *Charge Question 3. Do any other ozone measurement methods exist that the AMMS recommends for*
8 *consideration of possible promulgation as a new (additional) O₃ FRM?*

9
10 Response:

11
12 Based on the results presented in ORD intercomparison of the SL-UV method as discussed above, I
13 would support its consideration as an additional O₃ FRM. Other techniques available for O₃ FRM
14 status but rather expensive include Quantum Cascade Laser based tunable multi-pass IR absorption
15 spectroscopy; cavity ring down spectroscopy (CRDS) and cavity attenuated phase shiftspectroscopy
16 (CAPS) both of the latter techniques measure ozone indirectly via NO₂ from reacting O₃ with NO.

17
18 The JSC Optec 3.02 P-A chemiluminescent ozone analyzer looks like a promising FEM

19
20 Regarding Guidance/Opinion on Emerging Measurement Methodologies: Recent application of an O₃
21 semiconductor gas sensor array network reported by Bart et al., 2014 is an interesting example of an
22 emerging measurement methodology. Such techniques show promise in providing expansive spatial
23 coverage and resolution of ozone concentrations at relatively low cost with some caveats (see response
24 to CQ#4).

25
26
27 *Charge Question 4. What is the AMMS views on the use of low-cost sensor technology to supplement*
28 *regulatory ozone monitoring (i.e., in rural areas)?*

29
30 Response:

31
32 Deployment of low-cost sensor technology to improve spatial coverage of relative ozone concentrations
33 is a useful strategy, if it is backed-up with selective placement of O₃ FEM(s) to support the absolute
34 ozone calibration of the sensor array.

35 36 References

37
38 Bart, M., D. E. Williams, B. Ainslie, I. McKendry, J. Salmond, S. K. Grange, M. Alavi-Shoshtari, D.
39 Steyn, and G. S. Henshaw, 2014: High density ozone monitoring using gas sensitive semi-conductor
40 sensors in the Lower Fraser Valley, British Columbia, *Environmental Science & Technology*, 48 (7),
41 3970-3977.

42
43 Drummond, J. W., A. Volz, D. H. Ehhalt, 1985: An optimized chemiluminescence detector for
44 tropospheric NO measurements. *J. Atmos Chemistry*, Volume 2, Issue 3, pp 287-306

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Ridley, B. A., F. E. Grahek, 1990: A small, low flow, high sensitivity reaction vessel for no chemiluminescence detectors. *J. Atmos. Oceanic Technol.*, 7, 307–311.

Fehsenfeld, F. C., et al. (1990), Intercomparison of NO₂ measurement techniques, *J. Geophys. Res.*, 95(D4), 3579–3597, doi:10.1029/JD095iD04p03579.

Williams, E. J., et al. (1998), Intercomparison of ground-based NO_y measurement techniques, *J. Geophys. Res.*, 103(D17), 22261–22280, doi:10.1029/98JD00074.

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

U.S. Environmental Protection Agency. Environmental Technology Verification Report: JSC Optec 3.02 P-A Chemiluminescent Ozone Analyzer. Prepared by Battelle, through Cooperative Agreement with USEPA. February 2008.

1 **Mr. Eric S. Edgerton**

2
3 *Charge Question 1. What is the AMMS view on adding an additional O₃ FRM (as Appendix D-1 of the*
4 *40 CFR Part 50 Federal Regulation) for the purpose of establishing a new FRM that is implemented in*
5 *analyzers currently in production status? This new O₃ FRM will serve as an additional FRM to*
6 *supplement the current Ethylene-Chemiluminescence method, which is no longer being produced or*
7 *supported.*

8
9 Response: This makes sense, given the status of the of the ethylene-chemiluminescence method.

10
11
12 *Charge Question #2: What is the AMMS views on establishing the Nitric Oxide-Chemiluminescence*
13 *(NO-CL) method (currently an FEM) as the new, additional O₃ FRM?*

14
15 Response: NO-CL is a good choice for a new FRM. The reaction has long been used to measure NO
16 and other components of NO_y at sub-ppb concentrations with minimal interference and good linearity
17 over a broad dynamic range. Field tests performed by ORD show excellent agreement with the O₃
18 FRM, when data from both analyzers are corrected for zero and span response. In addition, the NO-CL
19 method exhibits greater zero and span stability than the current O₃ FRM and the UV FEM. The one
20 significant issue with NO-CL is variable water vapor (quenching). Boylan et al., 2014 show that water
21 vapor interference is on the order of 4.2% per 10,000 ppm H₂O. This can be very significant, given that
22 summertime H₂O concentrations can approach 40,000 ppm in the southeastern U.S. I believe the
23 instrument design reduces this effect by drying sample air upstream of the reaction chamber. In
24 practice, it may be advisable to verify dryer performance on a periodic basis. It might also be
25 worthwhile revisiting the interference equivalent test procedure specified in 40 CFR Part 53. My
26 interpretation of Table B-3, is that water vapor interference testing for the ethylene chemiluminescence
27 (ET-CL) O₃ FRM is performed in zero air (i.e., no pollutant). This may be appropriate for ET-CL, but
28 this is not the case for NO-CL.

29
30 Boylan, P., Helmig, D., and Park, J.H. Characterization and mitigation of water vapor effects in
31 the measurement of ozone by chemiluminescence with nitric oxide. 2014. Atmos. Meas. Tech.
32 7: 1231-1244. doi:10.5194/amt-7-1231-2014, 2014.

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34
35 *Charge Question #3: Do any other ozone measurement methods exist that the AMMS recommends for*
36 *consideration of possible promulgation as a new (additional) O₃ FRM?*

37
38 Response: The scrubberless-UV (SL-UV) method tested by ORD shows great promise and easily
39 exceeds current and proposed specifications for FRM status in 40 CFR Part 53. Field tests are
40 somewhat limited to date. Further evaluation is strongly encouraged. It should be noted, however, that
41 the commercially available SL-UV method as of May 2014 requires an external source of compressed
42 N₂O, and that this imposes cost, space and safety considerations on those who operate the method.
43 Other chemical and spectroscopic methods exist for the measurement of ozone, such as cavity ringdown,
44 but I see no reason to designate these FRM as opposed to FEM.

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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.

1 **Mr. Henry (Dirk) Felton**

2
3 *Charge Question 1: What is the AMMS view on adding an additional O₃ FRM (as Appendix D-1 of the*
4 *40 CFR Part 50 Federal Regulation) for the purpose of establishing a new FRM that is implemented in*
5 *analyzers currently in production status? This new O₃ FRM will serve as an additional FRM to*
6 *supplement the current Ethylene-Chemiluminescence method, which is no longer being produced or*
7 *supported.*

8
9 Response:

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

16
17 FRMs are also necessary to provide data for areas where inadequacies in FEMs may cause their
18 data to be questioned. Monitoring agencies may want to deploy an FRM to obtain data that in
19 the context of the NAAQS are free from biases or interferences.

20
21 It is important that an FRM be available for every criteria pollutant even if it is not routinely
22 deployed by regulatory agencies. The existing Ethylene-Chemiluminescence method should be
23 revoked because it is not commercially available, it is not a method that can easily be assembled
24 as needed and there are no vendors providing service for the few remaining instruments in
25 existence. The existing FEMs that were approved based on comparisons to the Ethylene-
26 Chemiluminescence should keep their approved status until a new FRM is approved that
27 demonstrates a significant improvement over the prior method.

28
29
30 *Charge Question 2: What is the AMMS views on establishing the Nitric Oxide-Chemiluminescence*
31 *(NO-CL) method (currently an FEM) as the new, additional O₃ FRM?*

32
33 Response:

34
35 After consideration of ORD's follow-up data analysis it is evident that the NO-CL method is an
36 acceptable FRM for Ozone. The variability (imprecision) in the initial data report was explained
37 by inconsistencies in the operation of the ET-CL FRM and not the NO-CL instrument. ORD's
38 evaluation of several other Ozone methods is very interesting. It is likely that the SL-UV
39 method may be acceptable as a second FRM once the noise and zero offset issues are resolved.

40
41 One disadvantage of the ET-CL and NO-CL method is the requirement for a reagent. The
42 currently available NO-CL instrument requires a 10,000 ppm cylinder of NO in order to operate.
43 This concentration of NO combined with the size of most cylinders for these applications
44 represent a safety issue for personnel in the buildings where these instruments are located. In
45 regulatory monitoring networks, instruments are sometimes located in schools or other public

1 facilities where gasses with concentrations above safety thresholds are not permitted. This
2 should not preclude the instrument from consideration as an FRM although it may limit where it
3 can be deployed.
4

5 *Charge Question 4: What is the AMMS views on the use of low-cost sensor technology to supplement*
6 *regulatory ozone monitoring (i.e., in rural areas)?*
7

8 Response:

9 Low cost sensors are not well suited to the measurement of regional secondary pollutants that do
10 not vary significantly over wide regions in ambient air. Taking meaningful measurements in
11 rural areas often requires instruments that are more accurate and precise than instruments that are
12 used to measure concentrations that are closer to ambient standards. The variability between a
13 regulatory measurement and a sensor reading in many cases would overwhelm the spatial
14 differences between Ozone measured at two different ambient locations within the same region.
15

16 Low cost sensors are well suited for use in developing personal exposure estimates that can be
17 compared to data collected at neighborhood scale regulatory monitors. Sensors are often
18 inexpensive, portable and operate with low power requirements which make them ideal for
19 measuring air quality throughout a person's day no matter where they are. Actual exposure
20 information is important because ambient standards are generally based on outdoor
21 neighborhood scale exposures which are not representative of actual exposures for a majority of
22 the population. This is especially true for reactive pollutants such as Ozone which typically have
23 very different indoor and outdoor concentrations. Sensor accuracy and precision issues can be
24 resolved with careful study design and collocation with regulatory monitors.
25

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

2
3 *Charge Question 1. What is the AMMS view on adding an additional O₃ FRM (as Appendix D-1 of the*
4 *40 CFR Part 50 Federal Regulation) for the purpose of establishing a new FRM that is implemented in*
5 *analyzers currently in production status? This new O₃ FRM will serve as an additional FRM to*
6 *supplement the current Ethylene-Chemiluminescence method, which is no longer being produced or*
7 *supported.*

8
9 Response: It is critically important that there be an ozone FRM that is commercially available from one
10 or more manufacturers. Potential future ozone FEMs will need to demonstrate equivalency using an
11 FRM, and the FRM should be readily available, affordable, and easy to use.

12
13
14 *Charge Question 2. What is the AMMS views on establishing the Nitric Oxide-Chemiluminescence*
15 *(NO-CL) method (currently an FEM) as the new, additional O₃ FRM?*

16
17 Response: Given the timeframe of the upcoming ozone NAAQs regulation, I can support the
18 designation of this method as an FRM. However, if there is time to explore other methods that may
19 have better performance, and look deeper into the source of error of the NO-CL comparison data, then
20 perhaps other methods may emerge as better FRM candidates (See below).

21
22
23 *Charge Question 3. Do any other ozone measurement methods exist that the AMMS recommends for*
24 *consideration of possible promulgation as a new (additional) O₃ FRM?*

25
26 Response: While other methods are more prevalent in ambient networks (i.e the UV photometric ozone
27 FEM) there may not be a pressing need for additional FRMs if the current one under consideration is
28 approved. But as shown in the EPA presentation, the new UV scrubberless method may show better
29 performance than the NO-CL method. If there is time to further test this new method and it proves
30 superior to the NO-CL method, then I recommend strong consideration as an FRM instead of the NO-
31 CL method. I don't see a need for multiple new FRMs going forward, given that the FEM designation
32 provides an adequate option for other regulatory monitoring methods.

33
34
35 *Charge Question 4. What is the AMMS views on the use of low-cost sensor technology to supplement*
36 *regulatory ozone monitoring (i.e., in rural areas)?*

37
38 Response: Since the typical ozone measurement technologies are relatively expensive to operate,
39 maintain, and calibrate, lower cost sensors for ozone or other ozone related-pollutants could prove very
40 useful in assessing the spatial extent of ozone issues, especially in rural areas. However, before such
41 technology is used for regulatory monitoring, or even as a supplement to regulatory monitoring, the
42 sensor performance must be fully characterized in order to properly interpret the generated data. Sensor
43 testing should include evaluations for accuracy, precision, interferences, sensitivity, longevity, drift, and
44 calibration procedures.

1 **Dr. Philip Hopke**

2
3 *Charge Question 3. Do any other ozone measurement methods exist that the AMMS recommends for*
4 *consideration of possible promulgation as a new (additional) O₃ FRM?*

5
6 Response:

7
8 Light absorption

9
10 There are systems based on light absorption that do not have the level of interference problems that exist in
11 the current light absorbance FEM monitors. This commercially available system, the 2B Tech model 211, is
12 described in their patent (Birks et al., 2013) and has been used by Ollison et al. (2014) and Johnson et al.
13 (2014). It has a water vapor control system although that has not been well described in their literature. This
14 system uses gas-phase scrubber technology with NO added to the sampled air to quantitatively react with
15 ozone and remove it from the sample. A low concentration of NO is added to the sample to generate ozone-
16 free, reference air. The light intensity is measured in the reference and sample modes with a dual beam
17 optical system so that the concentration of ozone can be calculated directly from Beer's Law. Nitric oxide
18 can be supplied from an external NO cylinder and will provide over a year of gas supply. Alternatively, nitric
19 oxide can be generated inside the instrument using an optional photolytic NO generator through photolysis of
20 nitrous oxide (N₂O) that would also supplied by an external cylinder. They also have a moisture
21 compensation system that removes any water issues. The prior versions of the 2B Tech ozone monitors had
22 been given FEM status so this improved unit would appear to be a strong candidate to be an FRM. They
23 have submitted the material needed to qualify the Model 211 as an FEM. In the data presented by EPA, the
24 Model 211 provided a tighter fit to the ethylene chemiluminescence data than does the NO-CL system so in
25 terms of being the best replacement for the current FRM, it represents superior performance relative to the
26 proposed NO-CL system.

27
28 The Birks et al. (2013) patent also includes bromine atoms as another gas phase ozone scrubber. Although
29 normally one does not want to designate a patented technology as an FRM, this system does appear to
30 provide a good system for ozone measurement that is worth consideration.

31
32 Electrochemical

33
34 An electrochemical ozone sensor uses a porous membrane that allows ozone gas to diffuse into a cell
35 containing electrolyte and electrodes. When ozone comes into contact with the electrolyte, a change in
36 electrochemical potential occurs between the electrodes causing electrons to flow. Korotcenkov and
37 Cho (2012) provide a review of a major class of these sensors.

38
39 In zero air, little or no electron flow occurs. As the presence of ozone increases, the electrical signal
40 increases proportionally. The monitor interprets this signal and displays the ozone concentration in PPM
41 (parts per million).
42

1 Advantages

2

3 Linear Response

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

9

10 Disadvantages

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

15

16 Semiconductor-Based Ozone Sensors:

17

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

19

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

25

26 Advantages

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

31

32 Disadvantages

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

39

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

1 References

2
3 Birks, J.W., Anderson, C., Williford, J. (2013) Ozone Monitor with Gas-Phase Ozone Scrubber, Patent
4 No.: US 8,395,776 B2.

5
6 Johnson, T., Capel. J., Ollison, W. (2014) Measurement of microenvironmental ozone concentrations in
7 Durham, North Carolina, using a 2B Technologies 205 Federal Equivalent Method monitor and an
8 interference-free 2B Technologies 211 monitor, Journal of the Air & Waste Management Association,
9 64:360-371.

10
11 Korotcenkov, G., Cho, B.K. (2012) Ozone measuring: What can limit application of SnO₂-based
12 conductometric gas sensors? Sensors and Actuators B: Chemical 161:28–44.

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14 Ollison, W.M., Crow, W., Spicer, C.W. (2014) Field testing of new-technology ambient air ozone
15 monitors, Journal of the Air & Waste Management Association, 64: 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

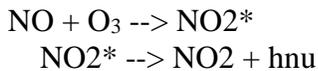
Charge Question 1: What is the AMMS view on adding an additional O₃ FRM (as Appendix D-1 of the 40 CFR Part 50 Federal Regulation) for the purpose of establishing a new FRM that is implemented in analyzers currently in production status? This new O₃ FRM will serve as an additional FRM to supplement the 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.

1 *Charge Question 4: Guidance/Opinion on Emerging Measurement Methodologies:*

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

4
5 Response: A low cost-sensor is potentially attractive to enhance the O₃ monitoring network. The key
6 question is performance. These lower cost sensors do not have the performance of the more expensive
7 FRM type sensors. Therefore EPA needs to carefully think about and clearly specify the required
8 performance specifications. This seems especially important in more rural areas which may have lower
9 O₃ levels, which may require improved performance. One can overcome some of the performance
10 limitations of an individual sensor by deploying networks, but that will erode some of the cost savings.

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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.

1 **5. Comments on the additional data provided by ORD.**

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

4

Dr. Jay Turner

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3 *Charge Question 1. What is the AMMS view on adding an additional O₃ FRM (as Appendix D-1 of the*
4 *40 CFR Part 50 Federal Regulation) for the purpose of establishing a new FRM that is implemented in*
5 *analyzers currently in production status? This new O₃ FRM will serve as an additional FRM to*
6 *supplement the current Ethylene-Chemiluminescence method, which is no longer being produced or*
7 *supported.*

8
9 Response: The proposal to establish an additional O₃ FRM is strongly supported. As clearly articulated
10 in the supporting materials provided to the committee, instruments that conform to the existing FRM
11 method are no longer commercially available. While it might seem convoluted to keep the obsolete
12 FRM (Ethylene-Chemiluminescence method, hereafter simply called the “FRM”), the point was made
13 that existing FEM designations were made by benchmarking against the Ethylene-Chemiluminescence
14 method and thus it would be necessary to redesignate all of the existing FEM methods if the existing
15 FRM was revoked. While revocation of the existing FRM would be a cleaner approach, the effort
16 needed to redesignate the existing FRM methods is understandably difficult to justify. A migration to
17 performance-based criteria would be a long-term solution.

18
19
20 *Charge Question 2: What is the AMMS views on establishing the Nitric Oxide-Chemiluminescence (NO-*
21 *CL) method (currently an FEM) as the new, additional O₃ FRM?*

22
23 Response: As discussed by the committee on April 3, the EPA performance evaluation (presentation
24 materials from Russell Long *et al.*) demonstrates the Nitric Oxide-Chemiluminescence (NO-CL) method
25 fared well in the laboratory evaluation (slide 9). The field data evaluated to date (slides 6-7)
26 demonstrate small bias but considerable scatter between the methods for hourly data. Supplemental
27 material dated May 5 made a compelling case that the major contributor to this scatter was from the
28 FRM (RTP/AIRS study) and from initially not correcting the NO-CL and FRM data for variations in the
29 night span check values (LaPorte/Houston study). Additional measurements conducted at RTP/AIRS in
30 April/May 2014 demonstrate tight relationships between the NO-CL and FRM after correcting the latter
31 for variations in nightly span check values.

32
33 Additional statistical measures of the scatter in the field evaluations data would be helpful. Scattergrams
34 were provided for hourly data and it would be helpful to see the results for 8-hour average data. I
35 presume the regressions in the evaluations are ordinary least squares (OLS) regressions. If so, the FRM
36 measurement is being treated as absolute (no error) and it might be preferred to also use approaches that
37 consider error in both the FRM and candidate measurements. Deming regression and orthogonal
38 regression are examples of suitable approaches and the lead discussant for this charge question (Eric
39 Edgerton) has previously published on their use. Regardless, confidence intervals should be provided
40 for the regression slopes and intercepts.

41
42
43 *Charge Question 3: Do any other ozone measurement methods exist that the AMMS recommends for*
44 *consideration of possible promulgation as a new (additional) O₃ FRM?*

45
46 Response: The UV method scrubberless ozone monitor (UV-SL) laboratory and field data appear quite
47 promising. Based on the laboratory evaluation (slide 12), water vapor remains an interferent but at

1 ~0.2 ppb equivalent is well below the current and proposed 40 CFR Part 53 specifications. The May 5
2 supplemental material further supports that high data quality can be achieved with the UV-SL method.
3 EPA provided a reasonable explanation for proceeding at this time with the NO-CL designation as an
4 FRM and possibly designating the UV-SL method as an FRM after additional testing.

5
6 I do not have access to ISO 13964:1998 (Air quality -- Determination of ozone in ambient air --
7 Ultraviolet photometric method) and am curious whether there are performance criteria in this
8 document.

9
10
11 *Charge Question 4: What is the AMMS views on the use of low-cost sensor technology to supplement*
12 *regulatory ozone monitoring (i.e., in rural areas)?*

13
14 **Charge Question 4: Guidance/Opinion on Emerging Measurement Methodologies:** What is the
15 AMMS views on the use of low-cost sensor technology to supplement regulatory ozone monitoring (i.e.,
16 in rural areas)?

17
18 There is currently some activity to develop low-cost O₃ sensor technologies. While they might not meet
19 the specifications of an FEM, they could play a vital role if their performance is adequately evaluated.
20 Next generation sensors for O₃ were showcased at the EPA-sponsored Air Sensors 2013 Workshop and
21 are briefly discussed in a recent paper by Piedrahita *et al.* (*Atmos. Meas. Tech. Discuss.*, **7**, 2425–2457,
22 2014).

1 **Dr. Yousheng Zeng**

2
3 In review of the materials provided to the AMMS committee members and the current FRM for ozone
4 (Appendix D to 40 CFR 50), some observations are made that have influenced my comments. These
5 observations are first discussed below, and they are followed by my comments.

6
7 **Observations:**

- 8
9 1. Although this rulemaking effort is presented as adding the NO-CL as a new FRM for ozone, the
10 draft rule (proposed Appendix D-1 to 40 CFR 50) has little to do with NO-CL. Other than
11 mentioning the name of the method (NO-CL) in the beginning of the proposed Appendix D-1,
12 there is no technical substance specific to the NO-CL measurement method. The technical
13 substance is about how to accurately generate ozone standard for calibration of the NO-CL
14 analyzer.
15 2. Similarly the existing FRM for ozone (Appendix D to 40 CFR 50) only mentions the ethylene-
16 CL method in the beginning, and the rest of FRM is about how to accurately generate ozone
17 standard to calibrate the ethylene-CL analyzer.
18 3. The core technical substance (i.e., procedures to generate calibration standard) of the existing
19 FRM and the proposed new FRM is essentially same. The difference is that the proposed new
20 FRM includes Sections 1 (Applicability), 2 (Principle), 3 (Interferences), and 5 (Frequency of
21 Calibrations). These new sections do not add technical specifications to the reference method.
22

23 **My Comments:**

24
25 Based on the above observations, I do not see a need to re-designate the current FRM as Appendix D-2
26 and add a new FRM as Appendix D-1. Instead, it makes more sense to revise the current FRM and keep
27 it in current designation of Appendix D, i.e., maintain only one FRM and keep it in Appendix D. The
28 revisions will include:

- 29
30 1. Adding Section 1 (Applicability). However, do not limit it to the NO-CL method. Make it
31 applicable to the ethylene-CL method, NO-CL method, or other methods that meet the
32 requirements of this FRM and quality assurance procedures and guidance provided in 40 CFR
33 58.
34 2. Adding Section 2 (Principle) as proposed except removing Subsection 2.1 (or making it more
35 generic and not limiting to NO-CL), and making Subsections 2.3 and 2.4 more generic and not
36 limiting to NO-CL.
37 3. Adding Section 3 (Interferences) as proposed except making it more generic and not limiting to
38 NO-CL.
39 4. Adding Section 5 (Frequency of Calibration) as proposed.
40

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

1
2 The advantages of revising the current FRM to allow both ethylene-CL and NO-CL based analyzer
3 include:

- 4
- 5 1. Avoid unnecessary regulations.
- 6 2. The FRM for ozone will be more streamlined. It resolves the issue associated with obsolete
7 ethylene-CL based analyzers and related legacy issues. At same time, it achieves the objective of
8 promoting the NO-CL based method to the FRM status. It will be less disruptive to operations of
9 monitoring agencies because this is what they have been doing for many years as FEM. It will be
10 designated as FRM without significant substantive changes.
- 11 3. If worded properly, it may also allow other methods, including emerging methods, to be
12 qualified as FRM, making the rule more adaptive for technological advancement.
- 13

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

- 16
- 17 • Specific descriptions of the NO-CL method, making it distinguishable from the ethylene-CL
18 method in Appendix D-2 (which also means that Appendix D-2 needs to be expanded in the
19 same fashion), and
- 20 • Typical specifications for an analyzer such as detection limit, linearity range, precision,
21 accuracy, zero and calibration drift, response time, etc.
- 22

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

27

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