

Performance of the Proposed New Federal Reference Method for Measuring Ozone Concentrations in Ambient Air

Technical Report

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Executive Summary

The current Federal Reference Method (FRM) for measuring concentrations of ozone in ambient air, described in EPA regulations at 40 CFR Part 50, Appendix D, is based on the dry, gas-phase, chemiluminescence reaction between ethylene and any ozone that may be present in air samples. This methodology is technically sound and has well served its role in ozone monitoring and as an FRM for many years since its establishment in 1971. However, the method now no longer meets the full needs of an FRM because no manufacturer of ozone-monitoring instruments currently offers an FRM analyzer for sale. Existing FRM analyzers are largely obsolete and poorly supported (if supported at all) by their manufacturers, and, consequently, all current ozone monitoring is carried out with other types of monitors (equivalent methods). A new FRM for ozone is needed to meet the needs that the existing FRM can no longer fulfill.

A rather similar measurement method, based on the dry, gas-phase, chemiluminescence reaction between nitric oxide (NO) and any ozone present in ambient samples has been subjected to extensive laboratory and field testing (along with an FRM and other Federal Equivalent Methods [FEMs]) to determine its performance and other attributes relative to those of the existing FRM. This report describes the nature and results of this testing and documents the conclusion that this alternative nitric oxide-chemiluminescence (NO-CL) method has performance as good as or better than the existing FRM. Further, at least two NO-CL ozone-monitoring analyzers are commercially available (from one manufacturer) and have been designated by the U.S. Environmental Protection Agency as FEMs for use in ozone-monitoring networks. Therefore, this alternative method is shown to be well suited as a supplemental FRM for ozone to serve in the FRM role as a practical reference standard for candidate FEMs and for quality assurance of ozone-monitoring data.

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Acronyms/Abbreviations

AIRS	Ambient Air Innovative Research Site	MDA8	maximum daily 8-h average
API	Advanced Pollution Instrumentation	MFC	mass flow controller
AQS	Air Quality System	NAAQS	National Ambient Air Quality Standards
C ₂ H ₄	ethylene	NIST	National Institute of Standards and Technology
CFR	Code of Federal Regulations	NO	nitric oxide
Cal/Dil	calibration/dilution	NO ₂	nitrogen dioxide
Cl ₂	chlorine	NO-CL	nitric oxide-chemiluminescence
CO	carbon monoxide	O ₂	oxygen
CO ₂	carbon dioxide	O ₃	ozone
DC	direct current	OD	outer diameter
DISCOVER-AQ	Deriving Information on Surface Conditions from Column and Vertically Resolved Observations Relevant to Air Quality	Pb	lead
DOAS	differential optical absorption spectroscopy	PM	particulate matter
EPA	U.S. Environmental Protection Agency	PMT	photomultiplier tube
FEM	Federal Equivalent Method	R ²	coefficient of determination
FR	Federal Register	RH	relative humidity
FRM	Federal Reference Method	RMS	root mean square
H ₂ O	water	RTP	Research Triangle Park, NC
H ₂ S	hydrogen sulfide	SLAMS	State and Local Air Monitoring Station
Hg	mercury	SL-UV	scrubberless ultraviolet
hν	photon	SO ₂	sulfur dioxide
IE	interference equivalent	T	temperature
		URL	upper range limit
		UV	ultraviolet
		V	volts
		VOC	volatile organic compound
		x	linear regression independent variable
		y	linear regression dependent variable
		ZAG	zero air generator

1.0

Introduction

Under the Clean Air Act, the U.S. Environmental Protection Agency (EPA) has established National Ambient Air Quality Standards (NAAQS) (i.e., concentration limits) for six air pollutants, known as the criteria air pollutants: (1) carbon monoxide (CO), (2) lead (Pb), (3) nitrogen dioxide (NO₂), (4) sulfur dioxide (SO₂), (5) ozone (O₃), and (6) particulate matter (PM). These NAAQS are set forth in Title 40, Part 50 of the Code of Federal Regulations (40 CFR Part 50). EPA and the States are jointly responsible for monitoring the ambient air for these six criteria pollutants. This monitoring is carried out as part of a national network of approximately 4000 monitoring sites, called the State and Local Air Monitoring Stations (SLAMS). The air quality data obtained from these sites are collected in EPA's Air Quality System (AQS) database, along with other information, and are used for

- determining compliance with the NAAQS,
- assessing effectiveness of State Implementation Plans in addressing NAAQS nonattainment areas,
- characterizing local, State, and national air quality status and trends, and
- associating health and environmental damage with air quality levels and concentrations.

To assure the accuracy, integrity, and uniformity of the SLAMS air quality monitoring data collected, EPA has established one or more Federal Reference Methods (FRMs) for measuring each criteria pollutant. These FRMs are set forth in several appendixes to 40 CFR Part 50 and typically specify a particular measurement technique to be implemented in a commercially produced monitoring instrument. These monitoring instruments must be shown to meet specific performance and other requirements detailed in the EPA regulations at 40 CFR Part 53, in which case the instrument may be designated by EPA as an FRM analyzer.

Also, to encourage innovation and development of new air quality monitoring methods, EPA has provided for Federal Equivalent Methods (FEMs). An FEM is not constrained to the particular measurement technique specified in the corresponding FRM. However, an FEM must meet the same or similar performance requirements as specified for the corresponding FRM, and in addition, it must show a high degree of comparative agreement with collocated FRM measurements at one or more field testing sites. These FEM requirements also are detailed in 40 CFR Part 53, and a monitor that is shown to meet all applicable requirements may be designated by EPA as an FEM monitor.

Section 2.1 of Appendix C to 40 CFR Part 58 mandates the use of either FRMs or FEMs for SLAMS monitoring to determine compliance with the NAAQS. In addition, FRMs are used in assessing the quality of the SLAMS monitoring data and as reference standards of comparison for designation of FEM monitors. The current listing of all designated FRMs and FEMs can be found at <http://www.epa.gov/ttnamti1/files/ambient/criteria/reference-equivalent-methods-list.pdf>.

2.0

Issues of Concern Regarding the Ozone FRM

The current FRM for measuring concentrations of ozone in ambient air, described in EPA regulations at 40 CFR Part 50, Appendix D,^{1,2} is based on the dry, gas-phase, chemiluminescence reaction between ethylene (C_2H_4) and any ozone that may be present in air samples. This method was established in 1971, and, at that time and for many years after, it was widely used for monitoring ozone, as implemented in a variety of ozone analyzers manufactured by several instrument manufacturers. These analyzers proved to provide accurate and reliable monitoring data in the SLAMS for many years. This FRM is specific for ozone and has no significant interferences. It served its role well as an FRM and remains a technically sound method today.

Unfortunately, the method requires a constant supply of ethylene for continuous operation. Ethylene is a gas that is stored in high-pressure gas cylinders and is flammable and explosive. A large gas cylinder is required for extended operation, and the use of such gas cylinders often is restricted to an outdoor location or entirely precluded at some potential monitoring sites, rendering use of the FRM analyzers inconvenient, if not problematic, at least at many potential monitoring sites. Ozone analyzers utilizing an ultraviolet (UV) photometric measurement technique, which became available in the 1980s, do not require a supply of gas or any other reagent and are much more convenient to install and operate. Several UV photometric analyzer models have been designated by EPA as FEMs, and such monitors (along with

a few other types of FEMs) have completely replaced the use of FRM analyzers in SLAMS monitoring. With no demand for FRM analyzers for SLAMS monitoring, instrument manufacturers have stopped producing them. The last ozone FRM analyzer was designated by EPA in 1979.

Although FEMs can fill the need for routine monitoring, FRM analyzers are required for other important purposes, such as quality assurance of monitoring data and for reference measurements for the required FEM comparability qualification. With no manufacturer of ozone-monitoring instruments currently offering an FRM analyzer for sale, the existing FRM can no longer fulfill the needs of an FRM. Previously manufactured FRM analyzers are largely obsolete, poorly supported (if supported at all) by their manufacturers, and likely now to be well beyond their expected operational lifetime. Because of the lack of availability and poor support, they are entirely inadequate for FRM-specific applications. For these reasons, a new FRM is needed.

A similar measurement technique based on the dry, gas-phase chemiluminescence reaction of nitric oxide (NO) with ozone in sampled air has been identified as a potential and advantageous candidate for a new ozone FRM. This report documents the extensive laboratory and field testing and analyses that have been carried out to examine the viability of this nitric oxide-chemiluminescence (NO-CL) method as a proposed new FRM for ozone. In addition, this report documents laboratory and field testing and analysis of additional methodologies that were also evaluated as potential FRMs. The results of this examination support the conclusion that the NO-CL method has the performance characteristics and other attributes necessary and appropriate for a new FRM for ozone.

3.0

Ozone Monitor/Analyzer Types

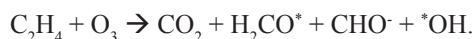
Various types of methods have been developed to monitor ozone concentrations in ambient air, and analyzers using several different methodologies have been designated by EPA as either FRM or FEM monitors. The current ozone FRM is the ethylene-chemiluminescence method, based on the dry, gas-phase reaction between ethylene and ozone as described in 40 CFR Part 50, Appendix D.

Because of the significant limitations of the current ethylene-chemiluminescence type FRM analyzers, other types of ozone-measurement technologies have been examined as possible candidates for a new ozone FRM. The types of ozone methods that have achieved FRM or FEM status are described briefly below, with consideration of the FEMs as possible candidates for a new FRM.

3.1 Ethylene-Chemiluminescence Ozone Analyzers (FRM)

3.1.1. Theory of Operation

These analyzers implement the measurement principle specified for FRM analyzers, described in Appendix D of 40 CFR Part 50. Ethylene-chemiluminescence ozone analyzers measure ozone concentrations by using the dry, gas-phase chemiluminescence reaction of ethylene with ozone in a flowing air sample. The overall reaction mechanism for ethylene-chemiluminescence generally proceeds as follows:



The reaction generates electronically activated formaldehyde that luminesces (which is indicated by an asterisk) in the high UV to visible portion of the spectrum (380 nm to 550 nm) and vibrationally activated hydroxide ions that luminesce in the visible light to low infrared portion of the spectrum (550 nm to 800 nm). The number of photons emitted during the reaction is directly proportional to the amount of ozone present. When air without ozone (zero air) or an air sample containing ozone is introduced into the analyzer mixing chamber/reaction cell, the emitted photons (if any) are counted by a photomultiplier tube (PMT), with its response centered at 440 nm, then the count is converted to ozone concentration by a software-driven algorithm.³ Measurements are referenced to certified ozone concentration standards according to the calibration procedure specified as part of the FRM.

3.1.2. Advantages

The method is largely free of measurement interferences. It has been implemented successfully by several instrument manufacturers in various ozone analyzer models, which (in years past) have proved to provide stable and reliable ozone measurements in monitoring network operation. This method is not impacted by the known interferents (hydrogen sulfide [H₂S], carbon dioxide [CO₂], NO, water [H₂O], meta-xylene, volatile organic compounds [VOCs], mercury [Hg], NO₂, SO₂, and chlorine [Cl₂]), which are found in ambient air and can reduce the operational performance and reliability of the UV-based ozone analyzers. The resulting chemiluminescence from the reaction between ethylene and ozone is specific to ozone (i.e., there are no other atmospheric substances that react with ethylene resulting in chemiluminescence at or near the 440-nm wavelength). The reaction between ethylene and ozone is a flameless one.

3.1.3. Disadvantages

The method requires a constant supply of ethylene, which is a dangerous, flammable, and potentially explosive gas typically stored in high-pressure gas cylinders. The use of such gas cylinders may be inconvenient and is often restricted by building fire codes or other monitoring site limitations. Following the development and availability of other types of ozone monitors (such as those utilizing the UV absorption method) that do not require a supply of reagent gas, use of such alternative methods in ozone-monitoring networks completely supplanted the use of FRM analyzers in virtually all current ozone-monitoring networks. With little or no demand for FRM analyzers, manufacturers no longer produce them. There are no ethylene-chemiluminescence FRM analyzers currently used in EPA's SLAMS network.

3.1.4. Interferences

The chemiluminescence from the reaction between ethylene and ozone is specific to ozone, thus the method is not impacted significantly by typical concentrations of potential interferents (such as H₂S, CO₂, NO, meta-xylene, VOCs, Hg, NO₂, SO₂, and Cl₂) that may occur in ambient air. There are no other atmospheric substances that react with ethylene resulting in chemiluminescence near 440 nm. Some sensitivity to variations in water vapor concentration (because of quenching of the chemiluminescence reaction) generally does not present a significant measurement problem.

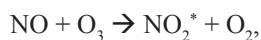
3.1.5. Current Status

There are no ethylene-chemiluminescence analyzers currently in EPA's SLAMS network.

3.2 NO-CL Ozone Analyzers (FEM)

3.2.1. Theory of Operation

This method is quite similar to that of the ethylene-chemiluminescence FRM. NO-CL ozone analyzers measure ozone concentrations by using the fact that the dry, gas-phase reaction between nitric oxide and ozone generates nitrogen dioxide in an activated state (NO_2^*), and oxygen (O_2).^{4,5} As each unstable NO_2^* returns to a lower energy state (NO_2), it emits a photon ($h\nu$). The reaction causes luminescence in a broadband spectrum ranging from visible light to infrared light (approximately 590 nm to 2800 nm). The two-step gas-phase reaction proceeds as follows:



then



The number of photons emitted during the reaction is directly proportional to the amount of ozone present, and the photons are counted by a PMT. The photon count is converted to ozone concentration by a software-driven algorithm.

3.2.2. Advantages

Similar to the FRM, the NO-CL method has no significant interferents. The method behaves in the same manner as the ethylene-chemiluminescence FRM when exposed to the same interferents listed in 40 CFR Part 53, Table B-3 (e.g., H_2S , CO_2 , and H_2O) that are found in ambient air, which may have an effect on the response of the widely-used UV-spectrophotometric ozone methods in certain situations.

The NO-CL method is designated as an FEM. It meets all of the same performance specifications (as specified in 40 CFR Part 53) as the existing FRM and is comparable to the existing FRM from a measurement perspective. In addition, the NO-CL devices currently are in manufacturing production. The method has been implemented successfully by at least one instrument manufacturer, which offers two models that have been designated by EPA as FEMs.

In addition, extensive laboratory and field testing by EPA has shown that the NO-CL method exhibits performance that equals or exceeds that of FRM analyzers and is, thus, a fully qualified candidate for consideration as a proposed new FRM for ozone.

3.2.3. Disadvantages

The method requires a constant supply of nitric oxide gas (approximately 1% [w/w]), which is stored in a high-pressure gas cylinder. Because nitric oxide is not flammable or explosive, monitoring site restrictions on the use of a high-pressure nitric oxide gas cylinder may be less than those for ethylene gas needed for FRM analyzers, but analyzer installation is still somewhat inconvenient. For use in nonmonitoring FRM applications, where shorter

term operation is likely, the use of small, more convenient, compressed-gas cylinders (as opposed to the large cylinders required for long-term operation) is possible. High concentrations of nitric oxide such as those found in the nitric oxide cylinders are toxic (asphyxiant).

3.2.4 Interferences

The NO-CL method is not impacted significantly by typical concentrations of potential interferents (such as H_2S , CO_2 , H_2O , NO, meta-xylene, VOCs, Hg, NO_2 , SO_2 , and Cl_2) that may occur in ambient air. Further testing by EPA has confirmed the lack of any significant interferences from compounds that might be encountered in ambient air monitoring.

3.2.5. Current Status

Currently, one commercial manufacturer has had an NO-CL instrument type (with two different model numbers) designated in 2011 as an FEM.

3.3. UV Photometric Ozone Analyzers (FEM)

3.3.1. Theory of Operation

UV photometric ozone analyzers determine ozone concentrations by quantitatively measuring the attenuation of light due to absorption by ozone present in an absorption cell at the specific wavelength of 254 nm.^{6,7} The ozone concentration generally is determined through a two-step process in which the light intensity passing through the sample air (I) is compared with the light intensity passing through similar sample air from which all ozone is first removed (I_0). The ratio of these two light-intensity values (I/I_0) provides the measure of the light absorbed at 254 nm, and the ozone concentration in the sample then is determined through the use of the Beer-Lambert Law as:

$$I/I_0 = e^{-KLC} \quad (C = 1/KL \ln [I/I_0]),$$

where L is the length of the absorption cell (in centimeters), C is the ozone concentration (in parts per million), and K is the absorption cross section of ozone at 254 nm at standard atmospheric temperature and pressure conditions ($308 \text{ atm}^{-1} \text{ cm}^{-1}$). Some systems have one absorption cell with I and I_0 measured alternately, whereas other systems have two separate absorption cells with I and I_0 measured concurrently. Photometric monitors for ozone generally use mercury lamps as the UV light source, with optical filters to attenuate lamp output at other than the 254 nm wavelength. Zero air for the reference measurement typically is obtained with manganese dioxide, heated silver wool, or nitric oxide gas to “scrub” ozone from the sample air while preserving other substances in the sample air that absorb at 254 nm, so that their effects are cancelled in the differential I/I_0 measurement.

3.3.2. Advantages

UV photometric ozone analyzers require no external gas supply or other reagents and are compact, easy to install, and convenient to operate. Various analyzer models from several instrument manufacturers have been shown to meet FEM performance requirements and have been designated as FEMs by EPA. These UV FEM analyzers currently represent the vast majority of analyzers used in State and local ozone monitoring networks. In general, UV photometric measurements compare very well with those obtained from FRM analyzers. UV ozone analyzers represent more recent measurement technology than the current FRM and would be advantageous for consideration as a new FRM because they currently are in manufacturing production, and their use is widespread.

3.3.3. Disadvantages

The integrity of the ozone zero air scrubber is critical and may enable measurement interferences if it does not perform adequately (see section 3.3.4 Interferences). Similarly, any tendency of the scrubber to fail to effectively remove all ozone from the reference sample will result in a measurement bias. The integrity of the scrubber has been shown to be affected to some extent by changes in sample air humidity. These shortcomings make the method an unlikely candidate for consideration as a new FRM for ozone. The UV photometric method is impacted by known interferences (see section 3.3.4 Interferences) that often are found in ambient air and may reduce the operational performance and reliability of this method.

3.3.4. Interferences

Various substances that may be present at some monitoring sites (including H₂S, CO₂, H₂O, meta-xylene, Hg, and aromatic hydrocarbon compounds) have strong absorbance of light at 254 nm and may cause measurement interferences if the zero air ozone scrubber fails to pass any such substances unattenuated in the zero reference air.

3.3.5. Current Status

UV photometric analyzers are the most widely used methods for ozone compliance measurements. There were 1,367 UV photometric analyzers in EPA's SLAMS network as of June 2014. A newly introduced and recently designated (June 18, 2014, 79 FR 34734) ozone FEM analyzer represents a variation of the UV photometric method, known as the "scrubberless" UV photometric method,⁴ that specifies removal of ozone from the sample air for the zero reference by a gas-phase reaction with nitric oxide rather than via a conventional solid chemical scrubber. The nitric oxide reacts with the ozone much faster than with other potential interfering compounds and is very effective at removing the ozone without affecting other compounds that may be present in the ambient air sample. The differential UV measurement then effectively can eliminate interferences to an insignificant level. EPA currently is evaluating this variation of the UV photometric method for future consideration as an ozone FRM.

3.4 Other Ozone Measurement Methodologies

3.4.1 Open-Path Ozone Monitors

EPA has designated two open-path air analyzers as FEMs. These analyzers operate on the principle of differential optical absorption spectroscopy (DOAS) over an open path of several meters up to 1 kilometer.⁷ The DOAS system analyzes the spectral absorption fingerprint of several ambient air pollutants over a range of visible or near-UV wavelengths. This technology was not evaluated as a potential candidate FRM for ozone because its open-path nature makes it difficult to assess in a laboratory setting.

3.4.2 Sensors

Sensors are small, relatively inexpensive monitoring devices that represent a new class of air pollution measurement devices. These gas-measurement sensors, such as those used to measure ozone, are based on electrochemical, metal oxide, and spectroscopic technologies. Some sensors have undergone preliminary testing in EPA's Office of Research and Development laboratory in Research Triangle Park (RTP), NC.⁸ A number of sensors have been evaluated in the field in Houston (September 2013), and in Denver, CO (July and August 2014). EPA continues its laboratory and field analysis of ozone sensors. Preliminary results will be documented in future technical reports and peer-reviewed scientific journal articles.

4.0

Performance Tests of the NO-CL Method

4.1 Test Analyzer

The NO-CL method—the proposed new FRM—is implemented in two ozone analyzers manufactured by Teledyne Advanced Pollution Instrumentation (API), Inc. (9480 Carroll Park Drive, San Diego, CA 92121-5201, 858-657-9800, www.teledyne-api.com). Both Models 265E and T265 provide user-selectable ozone measurement ranges of 0 to 100 ppb to 0 to 2000 ppb (0 to 2 ppm) and identical performance, with the following manufacturer ratings.

Zero noise	<0.15 ppb (root mean square [RMS])
Span noise	<0.5% of reading (RMS) above 100 ppb
Lower detectable limit	<0.3 ppb
Zero drift	<0.5 ppb/24 h
Span drift	<0.5% of full scale/24 h
Rise and fall time	<20 s to 95% of final reading
Linearity	<1% of full scale
Precision	<0.5% of reading
Sample flow rate	500 cm ³ /min ±10%
The Model T265 features a more advanced user interface than the standard Model 265E.	

4.2 Manufacturer Tests

Both analyzer models were designated by EPA as FEMs (identified as Equivalent Method No. EQOA-0611-199) on October 7, 2011 (76 FR 62402). This designation indicates that a representative Model 265 analyzer was tested in accordance with the FEM test and performance requirements specified in 40 CFR Part 53 and has, to EPA's satisfaction, been shown to meet all such requirements. In laboratory FEM tests, the candidate FEM analyzer is required to show performance equal to or better than the FRM/FEM requirements given in Table B-1 of Part 53. These requirements are listed in Table 1, along with revised performance requirements that EPA intends to propose for new ozone FRM and FEM analyzers.

Table 1 compares the manufacturer's claimed performance for the analyzer (taken from the manufacturer's published specification sheet) with both the existing FRM and FEM performance requirements, as well as the revised and new requirements that EPA intends to propose for new FRM and FEM analyzers. The manufacturer's performance specifications for some of performance parameters defined

Table 1. Comparison of Model T265 and Model 211 Ozone Analyzer's Manufacturer's Performance Specifications with the Existing and Proposed Performance Requirements for Ozone FRM and FEM Analyzers

Performance Parameter	Model T265 Manufacturer's Claimed Performance Specification ¹	Model 211 Manufacturer's Claimed Performance Specification ¹	FRM and FEM Performance Limit Specifications ²	Proposed New FRM and FEM Performance Limit Specifications ³	
				Standard Range	Lower Range
1. Range	0-0.5 ppm (0-0.1 to 0-2.0 available)	0.0005-2.0 ppm	0-0.5 ppm	0-0.5 ppm	0-<0.5 ppm
2. Noise	<0.00015 ppm		0.005 ppm	0.001 ppm	0.0005 ppm
3. Lower detectable limit	<0.0003 ppm	0.001 ppm	0.010 ppm	0.003 ppm	0.001 ppm
4. Interference equivalent					
Each interferent	Not specified	±0.002 ppm	±0.02 ppm	±0.005 ppm	±0.005 ppm
Total, all interferents	Not specified	≤0.007 ppm	0.06 ppm	—	—
5. Zero drift, 12- and 24-h	<0.0005 ppm	<0.001 ppm	±0.02 ppm	±0.004 ppm	±0.002 ppm
6. Span drift, 80% of URL	<0.5% (of 0.5 ppm URL)	<0.8%	±5.0%	±3.0%	±3.0%
7. Lag time	<10 s	1 min	20 min	2 min	2 min
8. Rise time	<20 s	1 min	15 min	2 min	2 min
9. Fall time	<20 s	1 min	15 min	2 min	2 min
10. Precision					
20% URL	<0.5% of reading (0.001 ppm)	<0.4% of reading	0.010 ppm	2% ⁴	2% ⁴
80% URL	<0.5% of reading (0.004 ppm)	<1% of reading	0.010 ppm	2% ⁴	2% ⁴

¹The manufacturer may not specify performance for all of the performance parameters defined by the FRM/FEM requirements or may measure them differently. The manufacturers' specification sheets for Model T265 and Model 211 can be found in references 12 and 13, respectively.

²Current performance specifications taken from Table B-1 to Subpart B of Part 53—Performance Limit Specifications for Automated Methods

³In conjunction with the proposal of a new FRM for O₃, EPA intends to propose revised, more stringent performance specifications, along with new performance specifications applicable to optional lower ranges for O₃ analyzers.

⁴Standard deviation expressed as percent of the URL.

for FRM and FEM analyzers are not given or may be described somewhat differently. As noted above, the designation of the analyzer as an FEM confirms that actual FEM tests of these performance parameters, as carried out by the manufacturer, were examined by EPA, and those test results were found to show that the analyzer met all existing FEM requirements. (These manufacturer-conducted FEM test results are included in a confidential business information claim covering the entire FEM application and, therefore, cannot be presented here.) Table 1 also suggests a high probability that the analyzer would meet the proposed revised and new requirements, as well.

The FEM test requirements also include a field test to compare ozone measurements from the candidate method with concurrent measurements from an FRM analyzer at a suitable field test site (40 CFR Part 53, Subpart C).⁹ Agreement must be shown within 20 to 40 ppb, depending on the concentration level. Again, designation of the Model 265 as an FEM by EPA indicates that such a test was performed by the manufacturer, and that the results were examined by EPA and were determined to meet the FEM test requirements for comparability. (Again, these test results cannot be presented here because they are included in the confidential business information claim for the FEM application.)

4.3 EPA Tests

4.3.1 Background

EPA conducted extensive laboratory and ambient testing of the NO-CL method (Model T265 analyzer) (1) to verify that the method meets all existing requirements for FRM and FEM analyzers and its capability to serve the functions of a reference method and (2) to determine its ability to meet proposed revised and new requirements for FRM and FEM analyzers. The tests also evaluated the analyzer's general performance relative to the FRM (Bendix Model 8002 Ozone Analyzer; Reference Method No. RFOA-0176-007) and several other FEM ozone analyzers, namely Thermo Scientific Model 49i Photometric Ambient Ozone Analyzer (Equivalent Method No. EQOA-0880-047), Ecotech EC9810 Ozone Analyzer (Equivalent Method No. EQOA-0193-091) and 2B Technologies Model 205 (Equivalent Method No. EQOA-1410-190) and Model 211 (Equivalent Method No. EQOA-0514-215). The Bendix Model 8002 is a true

ethylene-chemiluminescence FRM analyzer that has been refurbished to full operational status. These analyzers, operation principle, and designation information are summarized in Table 2.

4.3.2 Approach

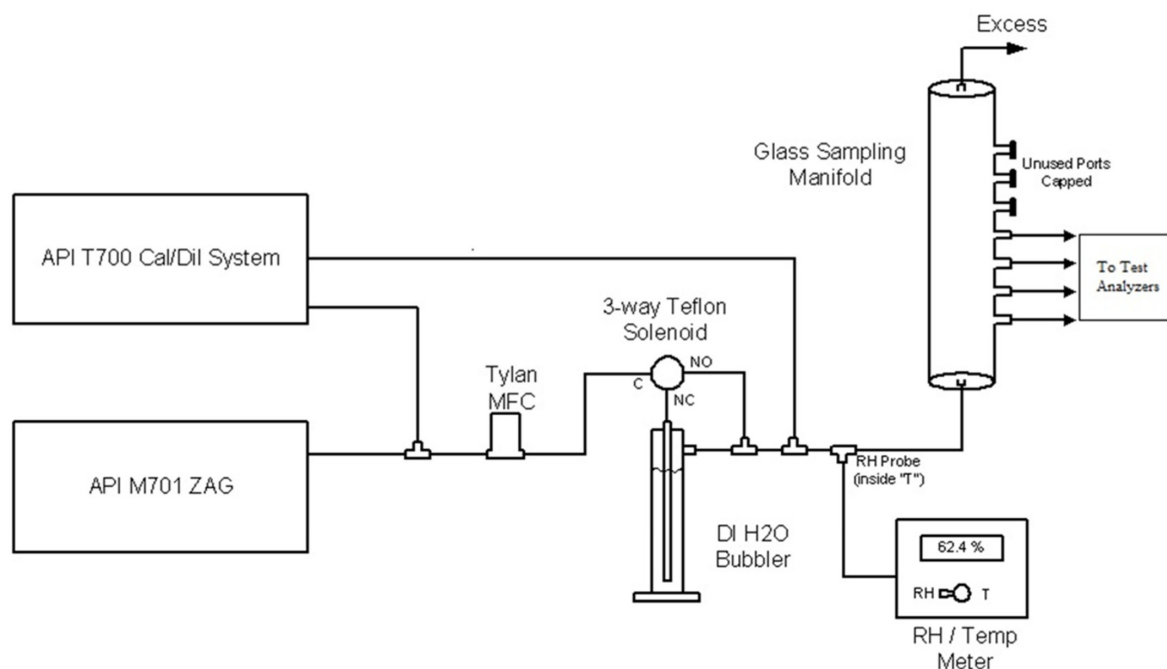
4.3.2.1 Laboratory Tests

The laboratory-based tests were conducted in accordance with the test procedures detailed in Subpart B of 40 CFR Part 53.¹⁰ Prior to laboratory-based testing, all analyzers under evaluation were calibrated according to manufacturers' operation manuals and in accordance with FRM requirements listed in 40 CFR 50, Appendix D. During laboratory testing, all analyzers were connected to a common sampling manifold (Ace Glassware) via 6.4-mm (0.25-in) outer diameter (OD), perfluoroalkoxy Teflon sampling lines. Particulate filters (5- μ m pore size) were fitted to each analyzer's inlet port. Air containing known concentrations of the test atmosphere (ozone) and/or interferent gas was provided to the manifold inlet as needed to conduct the test procedures. An exhaust line was attached to the manifold outlet and placed into the laboratory's 6-in ceiling vent to allow a continuous flow-through-design feature. All calibration gas concentrations and laboratory test atmospheres were established using a National Institute of Standards and Technology (NIST)-traceable and programmable dynamic dilution calibration system (Teledyne API Model T700U). Constituents were delivered to the system from either the T700U enclosed ozone generator (with NIST-traceable photometer) or EPA protocol ($\pm 2\%$ accuracy) reference gas standards. Dilution air that had been scrubbed of all contaminants was delivered to the mixing system to meet test gas dilution needs. Relative humidity (RH) within the system was produced and controlled through the use of a deionized water bubbler. Temperature and RH were measured with a temperature/RH probe consisting of a precision thin-film platinum, 1000- Ω resistive temperature device that employs a linear resistance change with temperature converted to a 0- to 10-V DC output proportional to 0 to 100.0 $^{\circ}$ C. The sensor was calibrated using a NIST-traceable reference thermometer. The RH sensor consists of a HyCal, Inc., IH-3602-C monolithic integrated circuit capacitance sensor that produces a linear voltage proportional to RH (0- to 10-V DC output directly proportional to 0 to 100% RH). The RH sensor was calibrated using saturated

Table 2. FRMs and FEMs for Ozone Used in the Evaluation Study

Manufacturer and Model	Operation Principle	FRM/FEM Designation
Bendix Model 8002 (FRM)	Ethylene-chemiluminescence	Federal Register: Vol. 41, page 5145, 02/04/76
Teledyne API Model T265 (FEM)	NO-CL	Federal Register: Vol. 76, page 62402, 10/07/11
2B Technologies Model 211 (FEM)	"Scrubberless" UV photometric (dual beam)	Federal Register: Vol.79, pages 34734-34735, 06/18/2014
2B Technologies Model 205 (FEM)	UV photometric (dual beam)	Federal Register: Vol.75, pages 22126-22127, 04/27/10
Ecotech EC9810 (FEM)	UV photometric	Federal Register: Vol. 58, page 6964, 02/03/93
Thermo Scientific Model 49i (FEM)	UV photometric	Federal Register: Vol. 45, page 57168, 08/27/1980
Teledyne API Model T700U ¹	Dynamic dilution calibrator	
Teledyne API Model 701 ¹	Zero air generator	

¹Used for calibration and nightly zero and span checks



Solenoid switched by API T 700 Control Output bit

Figure 1. Apparatus for performing laboratory-based evaluations of FRM/FEM analyzers.

salt solutions that have known RH over headspace. The temperature and RH signal response were shown on a liquid crystal display and logged using an in-laboratory data-acquisition system (Envistas Ultimate). A schematic diagram of the apparatus used during the laboratory-based evaluations is given in Figure 1.

4.3.2.2 Ambient Evaluations

Ambient evaluations of the proposed FRM and the various FEM methods were conducted during field-intensive studies at the Ambient Air Innovative Research Site (AIRS) located on the EPA campus in RTP during the springs and summers of 2012 and 2014. Ambient evaluations also were performed as part of the National Aeronautics and Space Administration's Deriving Information on Surface Conditions from Column and Vertically Resolved Observations

Relevant to Air Quality (DISCOVER-AQ) project conducted during July 2011 near Baltimore, MD; September 2013 in Houston (La Porte); and July and August 2014 near Denver. During field-intensive studies, instruments were calibrated according to manufacturers' operation manuals and in accordance with FRM requirements listed in 40 CFR 50, Appendix D. During the ambient evaluation campaigns, nightly automated zero and span checks were performed to monitor the validity of the calibration and to control for drifts or variations in the span or zero response. Both the calibration gas concentrations and the nightly zero and span gas concentrations were delivered using the T700U dynamic dilution calibration system described in section 4.3.2.1. The analyzers were contained within a temperature-controlled shelter during the sampling campaigns. A glass inlet with sampling height located approximately 5 m above ground

Table 3. Ozone Analyzer Inventory Deployed During Each Field Study

Field Deployment (Date)	Ozone Analyzer
Baltimore MD (July 2011)	Teledyne API Model T265 (FEM) Ecotech EC9810 (FEM) Teledyne API Model T700U ¹ Teledyne API Model 701 ¹
AIRS 2012 (June and July 2012)	Teledyne API Model T265 (FEM) 2B Technologies Model 205 (FEM) Bendix Model 8002 (FRM) Thermo Scientific Model 49i (FEM) Teledyne API Model T700U ¹ Teledyne API Model 701 ¹
Houston (LaPorte), TX (September 2013)	Teledyne API Model T265 (FEM) 2B Technologies Model 211 (FEM) Bendix Model 8002 (FRM) Thermo Scientific Model 49i (FEM) Teledyne API Model T700U ¹ Teledyne API Model 701 ¹

Field Deployment (Date)	Ozone Analyzer
AIRS 2014 (April-June 2014)	Teledyne API Model T265 (FEM) 2B Technologies Model 211 (FEM) 2B Technologies Model 205 (FEM) Bendix Model 8002 (FRM) Teledyne API Model T700U ¹ Teledyne API Model 701 ¹
Denver, CO (July and August 2014)	Teledyne API Model T265 (FEM) 2B Technologies Model 211 (FEM)—2 analyzers collocated Bendix Model 8002 (FRM) Teledyne API Model T700U ¹ Teledyne API Model 701 ¹

¹Used for calibration and nightly zero and span checks

level and a subsequent sampling manifold were shared by all instruments. Table 3 summarizes the different ozone analyzers evaluated during each field deployment.

4.3.2.3 Quality Assurance

As previously stated, the laboratory-based tests were conducted in accordance with the test procedures detailed in Subpart B of 40 CFR Part 53.10. Prior to both laboratory-based and ambient testing, all analyzers under evaluation were calibrated according to manufacturers' operation manuals (per FEM designations) and in accordance with FRM requirements listed in 40 CFR 50, Appendix D. In addition, all research detailed in this report was conducted under the EPA approved QAPP-AB-12-02 – Quality Assurance Project Plan: Ambient Air Monitoring Methods Assessment and Development for Criteria Gas National Ambient Air Quality Standards.

4.3.3 Results

4.3.3.1 Laboratory Test Results

The average laboratory test results are summarized in Table 4, which is presented in a format similar to that given in Table B-1 of Subpart B (Part 53). The result of each test trial is compared with the prescribed test limit requirement to determine whether the test result passes or fails. All test results must pass the test criteria to pass the test requirement for that performance parameter. Clearly, the test results

reported in Table 4 show that the Model T265 met all existing and revised proposed performance requirements proposed for new ozone FRM and FEM analyzers for the standard measurement range (0 to 0.5 ppm). Even the test results for total interferences met the existing requirements for these parameters. (This requirement is proposed to be withdrawn in the revised performance requirements and is shown in Table 1 but not in Table 4.)

The laboratory-based tests were carried out with the test analyzer operating with a 0- to 0.5-ppm measurement range, so the test results are not directly comparable with the proposed new, lower range performance requirements for noise, lower detectable limit, span drift, and precision. However, the results given in Table 4 clearly show that the T265 analyzer would meet the proposed lower range performance requirements as well.

In addition, the EPA-performed laboratory test results reported in Table 4 show that other methods, including the Model 211 and Model 49i, met all existing and revised performance requirements proposed for new ozone FRM and FEM analyzers for the standard measurement range (0 to 0.5 ppm). Similar to those for the T265 analyzer, the laboratory-based tests for the other methods were carried out in the 0- to 0.5-ppm analyzer measurement range. The results also clearly suggest that the Model 211 and Model 49i analyzer

Table 4. Comparison of EPA Laboratory Test Results to Existing and Proposed Revised FRM and FEM Performance Requirements

Performance Parameter	Teledyne-API Model T265	2B Technologies Model 211	Thermo Model 49i	FRM and FEM Performance Limit Specifications ¹	Proposed New FRM and FEM Performance Limit Specifications ²	
					Standard Range	Lower Range
1. Range	0-0.1 ppm 0-1.0 ppm	0-2.0 ppm	0-0.5 ppm 0-1.0 ppm	0-0.5 ppm	0-0.5 ppm	0-<0.5 ppm
2. Noise	<0.0005 ppm	<0.0005 ppm	<0.0005 ppm	0.005 ppm	0.001 ppm	0.0005 ppm
3. Lower detectable limit	<0.0006 ppm	<0.001 ppm	<0.001 ppm	0.010 ppm	0.003 ppm	0.001 ppm
4. Interference equivalent - Each interferent	<0.0001 ppm	<0.0002 ppm	<0.0001 ppm 0.01 ppm for water vapor	±0.02 ppm	±0.005 ppm	±0.005ppm
5. Zero drift, 12- and 24-h	<0.0001 ppm	<0.0001 ppm	<0.0002 ppm	±0.02 ppm	±0.004 ppm	±0.002 ppm
6. Span drift, 80% of URL	<0.5%	<0.5%	<0.5%	±5.0%	±3.0%	±3.0%
7. Lag time	<1 min	<1 min	<1 min	20 min	2 min	2 min
8. Rise time	<1 min	<1 min	<2 min	15 min	2 min	2 min
9. Fall time	<1 min	<1 min	<2 min	15 min	2 min	2 min
10. Precision						
20% URL	<0.4%	<0.5%	<0.4%	0.010 ppm	2% ³	2% ³
80% URL	<0.6%	<0.5%	<0.4%	0.010 ppm	2% ³	2% ³

¹ Current performance specifications taken from Table B-1 to Subpart B of Part 53—Performance Limit Specifications for Automated Methods

² In conjunction with the proposal of a new FRM for O₃, EPA intends to propose revised, more stringent performance specifications, along with new performance specifications applicable to optional lower ranges for O₃ analyzers.

³ Standard deviation expressed as percent of the URL.

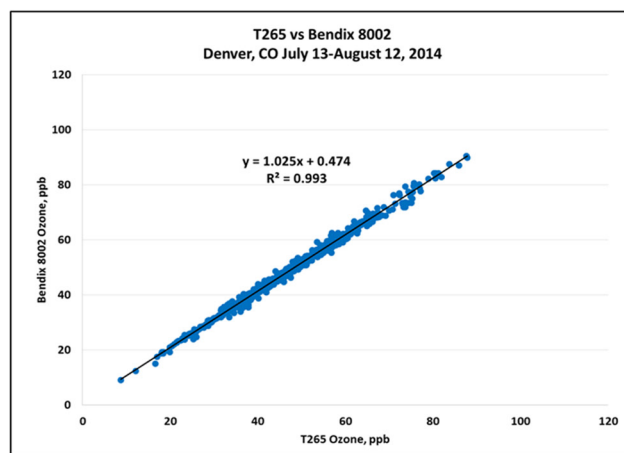
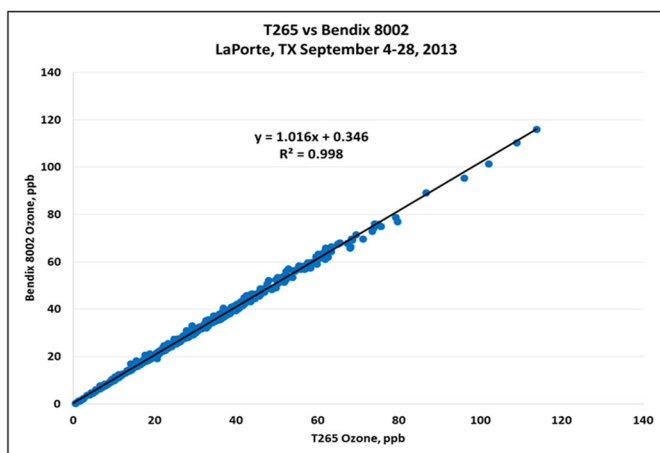


Figure 2. Comparison of the 1-h-average Bendix 8002 (FRM) and T265 (NO-CL) ozone results in ambient air at Houston, TX, during September 2013 (left) and at Denver, CO, during July and August 2014 (right).

likely would meet the proposed lower range performance requirements, with the exception of the water interference result for the Model 49i (see Table 4).

4.3.3.2 Ambient Evaluation Results

Table 5 gives comparisons (linear regressions) of 1-h EPA test results for the NO-CL ozone analyzer (Teledyne API Model T265) collected during the various field deployments. In ambient air evaluations in Houston and Denver, hourly average ozone results from the T265 compared very closely with those from the Bendix 8002 FRM, as shown in Figure 2. Linear regression results for comparison of the T265 with the Bendix 8002 FRM in Houston and Denver give slopes within 2.5% of unity and sub-parts-per-billion intercepts (Table 5, Figure 2). It should be noted that the Bendix 8002 FRM

operated by EPA during the ambient evaluations was quite an old instrument, possibly not performing completely up to original factory specifications. This is evident in comparing the linear regression results of the T265 with the various other analyzers during each of the campaigns (Table 5). Generally, more scatter (lower R2 value) and deviations from a slope of 1.0 are observed when comparing the T265 with the Bendix 8002 (Table 5, Figure 2) than when comparing the T265 with other analyzer types (Table 5, Figures 3 and 4). The exception to this is comparison of the 1-h T265 results with those obtained from the 49i during both the RTP summer 2012 and Houston summer 2013 studies, as shown in Figure 5. The 49i analyzer is a conventional UV photometric method that does not employ a sample conditioning system to

Table 5. Comparison of 1-h EPA Ozone Analyzer Results Collected During the Various Field Deployments

Comparison x vs. y	n	x Average (ppb)	y Average (ppb)	Linear Regression	R2	Comments
Baltimore, MD: July 2011 T265 vs. EC9810	689	42.3	42.4	y=1.002x-0.046	0.997	
AIRS, NC: June and July 2012 T265 vs. Bendix 8002	756	35.3	37.8	y=1.013x-0.817	0.983	Scatter in data attributed to Bendix 8002
AIRS, NC: June and July 2012 T265 vs. Model 205	756	35.3	35.6	y=1.006x+0.123	0.998	
AIRS, NC: June and July 2012 T265 vs. 49i	735	35.3	35.4	y=1.019x+0.121	0.998	
Houston (LaPorte), TX: September 2013 T265 vs. Bendix 8002	564	30.3	31.1	y=1.016x+0.346	0.998	
Houston (LaPorte), TX: September 2013 T265 vs. Model 211	564	30.3	32.4	y=0.998x+2.192	0.999	
Houston (LaPorte), TX: September 2013 T265 vs. Model 205	564	30.3	32.6	y=0.999x+2.574	0.999	
Houston (LaPorte), TX: September 2013 T265 vs. 49i	564	30.3	32.9	y=0.974x+3.444	0.997	
AIRS, NC: April-June 2014 T265 vs. Bendix 8002	924	35.3	36.6	y=1.027x+0.085	0.996	
AIRS, NC: April-June 2014 T265 vs. Model 211	938	35.3	36.4	y=0.996x+1.090	0.999	
AIRS, NC: April-June 2014 T265 vs. Model 205	729	36.1	35.5	y=0.973x-0.180	0.999	
Denver, CO: July and August 2014 T265 vs. Bendix 8002	670	45.7	47.3	y=1.025x+0.424	0.993	
Denver, CO: July and August 2014 T265 vs. Model 211#1	670	45.7	45.9	y=0.989x+0.652	0.999	
Denver, CO: July and August 2014 T265 vs. Model 211#2	665	45.7	45.6	y=0.995x+0.075	0.999	

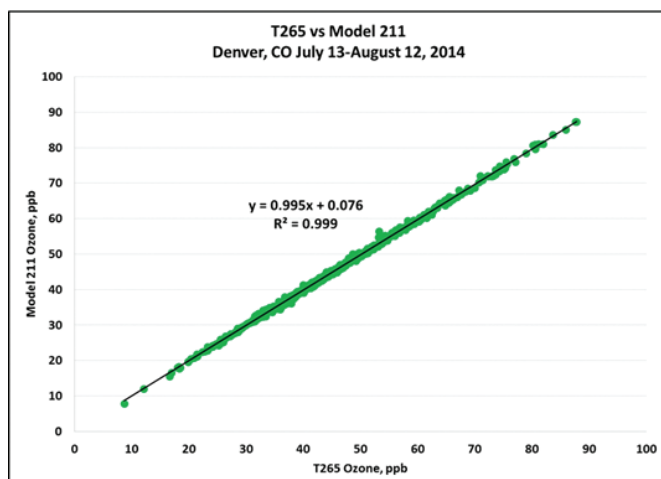
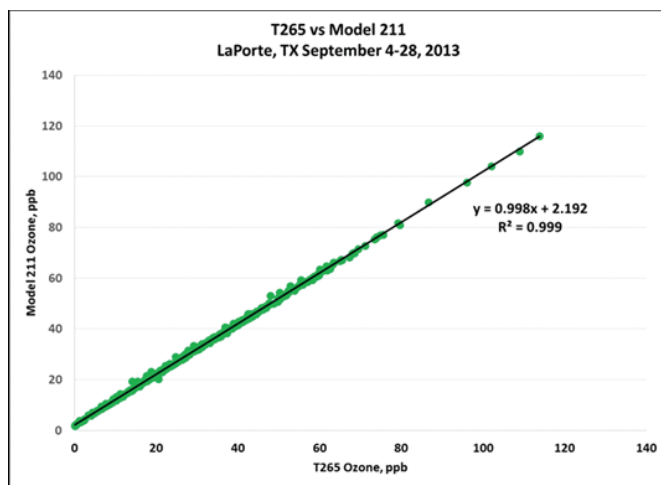


Figure 3. Comparison of the 1-h-average Model 211 (SL-UV) and T265 (NO-CL) ozone results in ambient air at Houston (LaPorte), TX, during September 2013 (top) and at Denver, CO, during July and August 2014 (bottom).

remove water (a known interferent in UV photometric ozone determination, see section 3.3.4) from the sample stream. During the RTP and Houston studies, RH values were high (>85%), possibly resulting in a measurement interference associated with the 49i. The closest agreement was obtained while comparing the T265 results with the Model 211 results during multiple field studies (Table 5, Figure 3). Linear regression results for comparison of the T265 with the Model 211 in Houston, RTP (2014), and Denver give slopes within 1% of unity (Table 5, Figure 3). A slightly elevated offset (~2

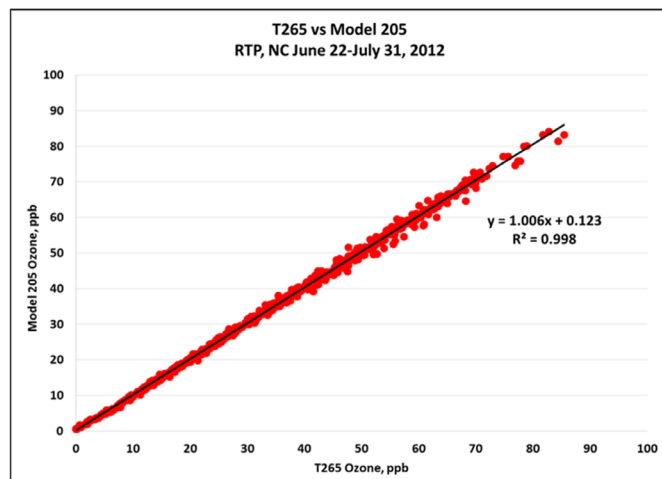
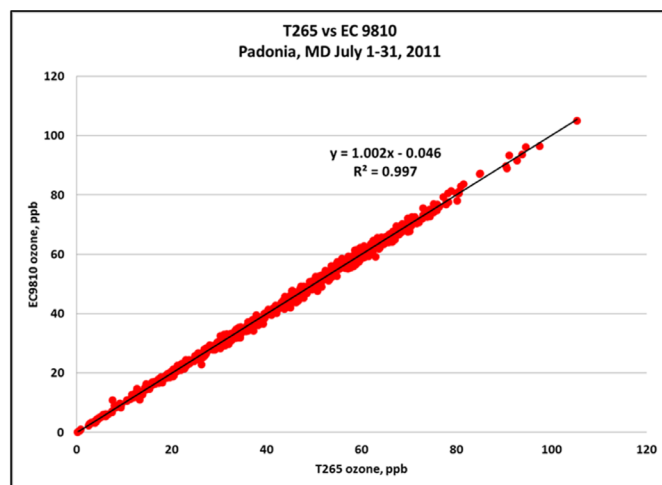


Figure 4. Comparison of the 1-h-average EC9810 and T265 (NO-CL) ozone results in ambient air at Baltimore (Padonia), MD, during July 2011 (top) and comparison of the 1-h-average Model 205 and T265 (NO-CL) ozone results in ambient air at RTP, NC, during June and July 2012 (bottom). Both the EC9810 and the Model 205 employ the UV photometric method and contain sample conditioning systems to remove water from the sample stream.

ppb) was observed during the Houston study. Further analysis of the T265 and Model 211 and Bendix 8002 datasets indicates the offset is associated with the Model 211.

The current NAAQS for ozone is 0.075 ppm (75.0 ppb) in the form of the annual fourth-highest daily maximum 8-h concentration, averaged over 3 years. To enable evaluation of the T265 and other FRM and FEM analyzers' performance with respect to monitoring for the ozone NAAQS, maximum daily 8-h-average (MDA8) ozone concentrations were calculated.¹¹ Table 6 gives a comparison (linear regression) of MDA8 ozone analyzer results collected during the various field deployments. In ambient air evaluations in Houston and

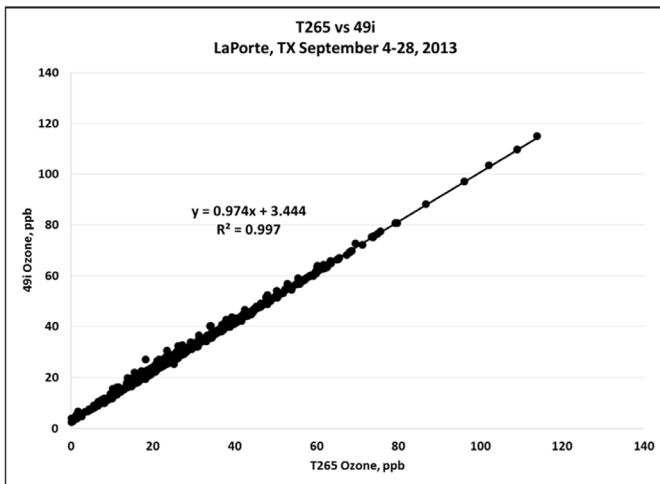
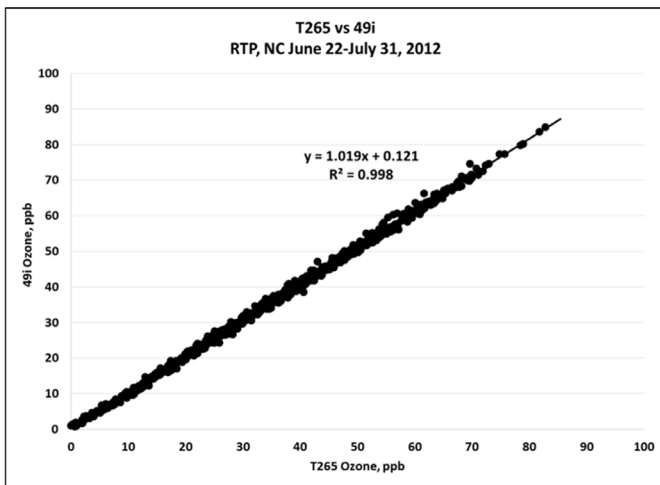


Figure 5. Comparison of the 1-h-average 49i and T265 (NO-CL) ozone results in ambient air at RTP, NC, during June and July 2012 (top) and at Houston (LaPorte), TX, during September 2013 (bottom). The 49i employs the UV photometric method but does not contain a sample conditioning system to remove water from the sample stream.

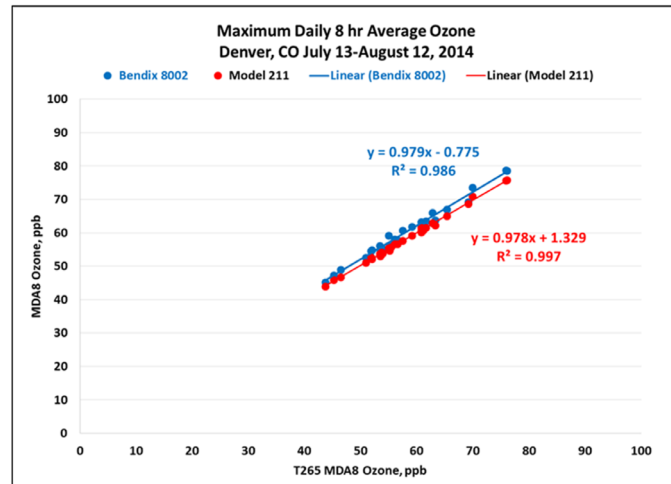
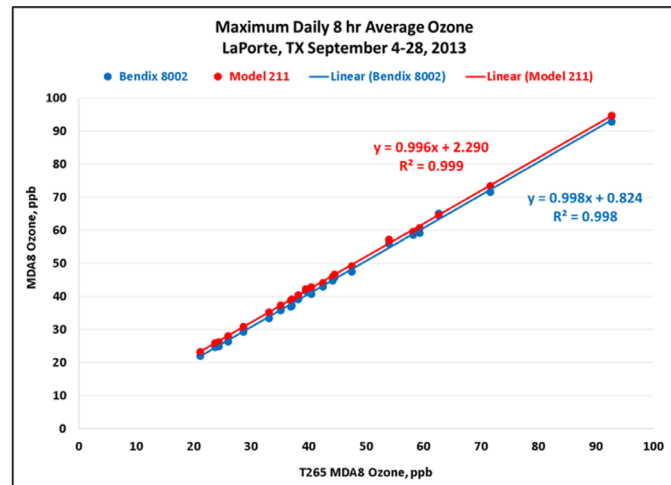


Figure 6. Comparison of the maximum daily 8-h-average (MDA8) ozone results in ambient air at Houston (LaPorte), TX, during September 2013 (top) and at Denver, CO, during July and August 2014 (bottom).

Denver, MDA8 ozone results from the T265 compared very closely with those from the Bendix 8002 FRM and Model 211, as shown in Figure 6.

Clearly and as expected, ambient air measurement performance of the Model T265 is comparable with that of other FRM and FEM analyzers. Operation of the analyzer was very similar to that of the FRM analyzer, and it was straightforward to install, operate, and calibrate, particularly with the advanced user interface of the Model T265. No problems or user difficulties were encountered, and all operational observations indicated that the analyzer could serve well as an FRM analyzer if the proposed NO-CL ozone FRM were to be adopted. According to the manufacturer, Models T265 and 265E have the same specified performance. Therefore, the results of Model T265 testing should apply equally to the Model 265E, notwithstanding some differences in the user interface between the two models.

Table 6. Comparison of Maximum Daily 8-h-Average Ozone Analyzer Results Collected During the Various Field Deployments

Comparison x vs. y	n	x Average (ppb)	Average (ppb)	Linear Regression	R2	Comments
Baltimore, MD: July 2011 T265 vs. EC9810	28	62.9	63.1	$y=0.993x+0.657$	0.984	
AIRS, NC: June and July 2012 T265 vs. Bendix 8002	30	52.1	53.4	$y=1.059x-1.766$	0.974	Scatter in data attributed to Bendix 8002
AIRS, NC: June and July 2012 T265 vs. Model 205	30	52.1	52.6	$y=1.009x-0.001$	0.997	
AIRS, NC: June and July 2012 T265 vs. 49i	30	52.1	53.4	$y=0.992x+1.695$	0.983	
Houston (LaPorte), TX: September 2013 T265 vs. Bendix 8002	24	42.9	43.4	$y=0.998x+0.824$	0.998	
Houston (LaPorte), TX: September 2013 T265 vs. Model 211	24	42.9	44.8	$y=0.996x+2.296$	0.999	
Houston (LaPorte), TX: September 2013 T265 vs. Model 205	24	42.9	44.8	$y=1.004x+2.149$	0.999	
Houston (LaPorte), TX: September 2013 T265 vs. 49i	24	42.9	45.3	$y=0.963x+4.131$	0.998	
AIRS, NC: April-June 2014 T265 vs. Bendix 8002	46	50.5	52.1	$y=0.973x+2.927$	0.976	
AIRS, NC: April-June 2014 T265 vs. Model 211	46	50.5	51.4	$y=0.977x+2.086$	0.996	
Denver CO: July and August 2014 T265 vs. Bendix 8002	29	58.2	60.2	$y=0.979x-0.775$	0.986	
Denver, CO: July and August 2014 T265 vs. Model 211#1	29	58.2	58.2	$y=0.978x+1.329$	0.997	

5.0

Conclusions

Tests of the NO-CL method using the Teledyne API Model T265 analyzer show it to meet all existing performance requirements for candidate ozone FRM and FEM analyzers. It has previously been shown to meet all FEM performance requirements and is listed by EPA as a designated equivalent method (EQOA-0611-199). The tests also show it would meet proposed revised requirements for ozone FRM and FEM analyzers as well. The analyzer is commercially available and is shown to be operationally fully acceptable as an alternative FRM analyzer if the proposed new ozone FRM is adopted as a modification to 40 CFR Part 50, Appendix D. Therefore, the NO-CL method, as represented by the Teledyne API T265 analyzer, is shown to be well suited as an FRM for ozone to serve in the FRM role as a practical reference standard for candidate FEMs and for quality assurance of ozone monitoring data.

6.0

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