Designation: D5149 – 02 (Reapproved 2016)

Standard Test Method for Ozone in the Atmosphere: Continuous Measurement by Ethylene Chemiluminescence[1]

This standard is issued under the fixed designation D5149; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This test method describes the sampling and continuous analysis of the ozone content of the atmosphere at concentrations of 20 to 2000 µg of ozone/m^3 (10 ppb (v) to 1 ppm (v)).

1.2 This test method is limited in application by its sensitivity to interferences as described below. This test method is not suitable for personal sampling because of instrument size and sensitivity to vibration and ambient temperature.

1.3 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.* Some specific precautionary statements are presented in Section 8.

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D1356 Terminology Relating to Sampling and Analysis of Atmospheres

D1357 Practice for Planning the Sampling of the Ambient Atmosphere

D1914 Practice for Conversion Units and Factors Relating to Sampling and Analysis of Atmospheres

D3249 Practice for General Ambient Air Analyzer Procedures

D3670 Guide for Determination of Precision and Bias of Methods of Committee D22

D5011 Practices for Calibration of Ozone Monitors Using Transfer Standards

D5110 Practice for Calibration of Ozone Monitors and Certification of Ozone Transfer Standards Using Ultraviolet Photometry

IEEE/ASTM SI-10 Practice for Use of the International System of Units (SI) (the Modernized Metric System)

2.2 *U.S. Environmental Protection Agency Standards:*[3]

EPA-600/4-79-056 Transfer Standards for Calibration of Air Monitoring Analyzers for Ozone (NTIS: PB80146871)

EPA-600/4-79-057 Technical Assistance Document for the Calibration of Ozone Monitors (NTIS: PB80149552)

EPA-600/4-80-050 Evaluation of Ozone Calibration Techniques (NTIS: PB81118911)

EPA-600/4-83-003 Performance Test Results and Comparative Data for Designated Reference and Equivalent Methods for Ozone (NTIS: PB83166686)

2.3 *Code of Federal Regulations:*[3]

40-CFR-Part 53.20

3. Terminology

3.1 *Definitions*—For definitions of terms used in this test method, refer to Terminology D1356 and Practice D1914. An explanation of units, symbols and conversion factors may be found in Practice IEEE/ASTM SI-10.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *absolute ultra-violet photometer*—a photometer whose design, construction and maintenance is such that it can measure the absorbance caused by ozone mixtures without reference to external absorption standards. Given a value for the absorption coefficient of ozone at 253.7 nm and a reading from the absolute ultraviolet photometer, ozone concentrations can be calculated with accuracy. Measurements by an absolute ultraviolet photometer should be made on prepared ozone mixtures free from interferences.

3.2.2 *primary standard*—a standard directly defined and established by some authority, against which all secondary standards are compared.

3.2.3 *secondary standard*—a standard used as a means of comparison, but checked against a primary standard.

3.2.4 *standard*—an accepted reference sample or device used for establishing measurement of a physical quantity.

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[1] This test method is under the jurisdiction of ASTM Committee D22 on Air Quality and is the direct responsibility of Subcommittee D22.03 on Ambient Atmospheres and Source Emissions.

Current edition approved Oct. 1, 2016. Published October 2016. Originally approved in 1990. Last previous edition approved in 2008 as D5149 – 02 (2008). DOI: 10.1520/D5149-02R16.

[2] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

[3] Available from National Technical Information Service (NTIS), 5285 Port Royal Rd., Springfield, VA 22161, http://www.ntis.gov.

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3.2.5 *transfer standard*—a type of secondary standard. It is a transportable device or apparatus which, together with operational procedures, is capable of reproducing a sample concentration or producing acceptable assays of sample concentrations.

4. Significance and Use

4.1 Air quality standards for ozone have been promulgated by government authorities to protect the health and welfare of the public. Though ozone itself is a toxic material, it is often complex organic compounds that cause the symptoms of *smog* such as tearing and burning eyes. However, ozone is the predominant oxidant and is much more easily monitored than organic species. Since ozone concentrations are also correlated with other photochemical oxidant levels, it is the substance that is specified in air quality standards and regulations.

5. Interferences

5.1 Any aerosol that scatters light or that may deposit on the photomultiplier window constitutes a negative interference to this test method. Particulate matter can be removed with a poly-tetrafluoroethylene (PTFE) membrane filter; however, this filter may become contaminated and scrub ozone. It is important to check the ozone-inertness of these filters periodically. (See Practice D5110.)

5.2 Atmospheric humidity constitutes a positive interference to this test method when calibrations are conducted with dry span gas mixtures. The range of interference reported is tabulated in Annex A2 of this test method.[4]

5.3 Reduced sulfur compounds have not been found to constitute positive interferences to this test method.[5]

6. Measurement Principle

6.1 This measurement principle is based on the photometric detection of the chemiluminescence (light produced by a chemical reaction) resulting from the flameless gas phase reaction of ethylene (C_2H_4) with ozone (O_3). The sample gas containing ozone is mixed with excess ethylene (bottle gas, C.P. or better, supplied to the instrument) to generate excited formaldehyde (HCHO*) molecules. The excited formaldehyde molecules decay immediately to the ground energy state, releasing energy in the form of light in the 300 to 600 nm region, with maximum intensity at 430 nm. The light energy is measured by a photosensor (frequently a photomultiplier tube) that produces an output current proportional to the light intensity. The current, converted to voltage and conditioned as necessary by the electronic circuits, becomes the analyzer's output signal.

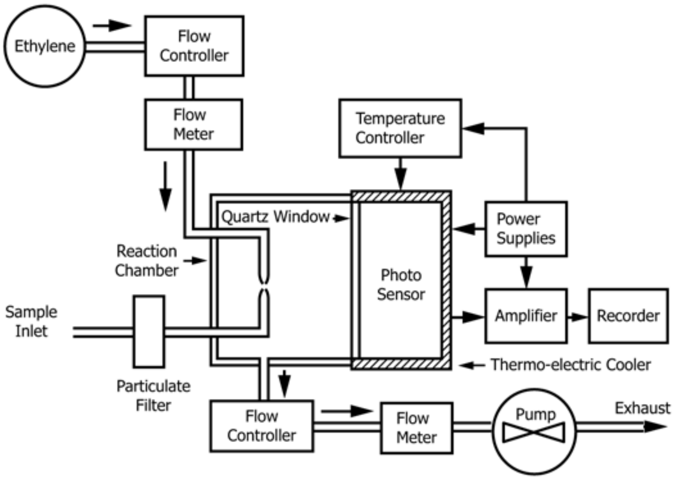

FIG. 1 Schematic Diagram of a Chemiluminescence Ozone Analyzer

7. Apparatus

7.1 A schematic of the instrument is given in Fig. 1. The chemiluminescent reaction cell is constructed of materials inert to ozone, for example, PTFE-coated metal, borosilicate glass, fused silica.

7.2 The input filter is installed in front of the sample line to prevent aerosols or particulate matter from entering the measuring system. PTFE filters with pore sizes between 0.5 and 5.0 µm should be used. The filter should be kept clean since accumulated material on the filter may catalyze the breakdown of ozone into oxygen. Depressed ozone responses have been observed immediately after filter changes for periods up to one hour.

7.3 Internal lines and fittings in the sample stream prior to the reaction call are made of PTFE or other ozone-inert material.

7.4 Due to the flammability of ethylene, some manufacturers suggest the use of ethylene-carbon dioxide blends instead of 100 % ethylene when the monitoring device is to be used in a public facility. This blend is a liquefied, nonflammable mixture of approximately 9 % ethylene and 91 % CO_2. The chemiluminescent reaction is the same; however, gas consumption is considerably higher as a result of the reduced ethylene concentration. The proportions of ethylene and CO_2 supplied by the blend change as the mixture is consumed from the cylinder. Since this changes the sensitivity of the analyzer, the analyzer should be recalibrated periodically. The concentration of ethylene supplied by the blend is also changed by the temperature of the cylinder, which must be maintained constant during use.

8. Safety Hazards

8.1 Beyond the normal precautions necessary when working with any instrument that contains high voltages and flammable gases, this test method raises the need for some special considerations. When calibrating the instrument, vent the excess gas mixture, especially if it contains high concentrations

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[4] Kleindienst, T. E., Hudgens, E. E., Smith, D. F., McElroy, F. F., and Bufalini, J. J., "Comparison of Chemiluminescence and Ultraviolet Ozone Monitor Responses in the Presence of Humidity and Photochemical Pollutants," *Journal of the Air and Waste Management Assoc.*, Vol. 43, 1993, p 213.

[5] Kleindienst, T.C., McIver, C.D., Ollison, W. M., "A Study of Interferences in Ambient Ozone Monitors," VIP-74, *Measurement of Toxic and Related Air Pollutants, Air & Waste Management Association*, Pittsburgh, PA, p. 215.

of ozone, through a charcoal filter. This will avoid contamination of the work area around the instrument with ozone, which at the concentrations likely to be encountered in this test method, can induce headaches and occasionally nausea.

9. Sampling

9.1 Sampling the atmosphere should be done in accordance with the guidelines in Practices D1357 and D3249. These practices point out the need to avoid sites which are closer than 50 m distance from traffic which could give rise to transient hydrocarbon and nitrogen oxides effects on ambient ozone levels.

9.2 The sampling lines shall be made of PTFE, with an inside diameter between 4 and 7 mm. The sampling line shall be short and direct, preferably not more than 5 m long to avoid a net loss of ozone by reaction with ambient nitric oxide under reduced light.[6]

9.3 Ozone in ambient air is created and destroyed in a series of interacting chemical reactions of varying speeds, driven by sunlight in the presence of nitrogen oxides and hydrocarbon gases. Consequently, the ambient ozone concentration found in a shady location under calm air conditions can be different from that found only a few yards away in bright sunshine.

9.4 A PTFE particle filter shall be included in the sampling line.

9.5 Where the outside ambient air is hot and humid, the sample or its path through the instrument shall not be cooled to the point where condensation occurs since ozone is both soluble in, and possibly destroyed by, condensate. However, Kleindienst et al.[4] report little effect of sampling line condensate in laboratory tests on chemiluminescence instruments.

9.6 Since ethylene scavenges ozone, excess ethylene from the instrument output shall be vented or scrubbed in a manner so as not to affect the ozone levels near the sampling probe.

10. Calibration and Standardization

10.1 The calibration of ozone monitors and the certification of transfer standards using an absolute ultraviolet photometer is described in 2.2 and in Practice D5110. The use of transfer standards thus certified is described in Practices D5011.

10.2 During calibration of ozone analyzers an *overshoot* condition is sometimes encountered. Overshoot refers to a peculiar response when ozone input is changed from low to high levels; the initial response may exceed the high span concentration by up to 10 %. An overshoot, which relaxes to the high span level over a few hours, may appear when the analyzer samples dry span gas for extended periods and seems to predominate in instruments operating on ethylene/CO_2 mixtures. (See 2.2 and 7.4.)

10.3 The response of the chemiluminescent analyzer is affected by the oxygen content of the sample gas. Thus, if synthetic zero air is used, its oxygen content shall closely match the normal atmospheric concentrations. (See 2.2.)

11. Procedures

11.1 Site the monitor with consideration of Practice D1357.

11.2 Sample the atmosphere with a probe having nonreactive inside walls, PTFE or glass for example. The probe shall be kept clean and shall be leak-tested. The sample flow into the instrument shall be free of particulate matter and the PTFE filter, which is used to achieve this, shall be kept clean. The degree to which the concentration of ozone in the sample atmosphere is changed by the probe and filter shall be checked by passing calibration gases to the monitor directly and then via the probe and filter and observing the difference in response.

11.3 Avoid situations where the analyzer will be exposed to rapid and frequent changes of ambient temperature. Where, for example, the monitor is operated in a small sampling station which is cooled or heated by a high-capacity system, it shall be shielded from direct air flow from the system. Many instruments are well compensated for slow changes in ambient temperature, but do not respond well to the rapid changes often found in small air monitoring stations, which may exceed 1°C/min.

11.4 Choose a data recording system that matches the output of the monitor. In the case of a data logger or telemetry system, the sampling interval and data analysis method shall detect and report instrument malfunctions such as excessive variability in the output, *spikes* and so forth, and shall not merely average them away. The dynamic range and precision of the recorder or data logger shall be wide enough to accommodate the range of concentrations anticipated. In the case of ozone in the ambient atmosphere, the peak levels can be ten times higher than typical summer day levels. Automatic multi-ranging may help to retain accuracy at low levels while allowing for occasional high levels to be measured and recorded.

11.4.1 All recording or data logging devices shall positively identify calibration values. This can be achieved as simply as using a chart recording and writing the information on the chart. An automatic data logger shall include a status signal recorded along with the instrument output information which labels calibration points as different from ambient measurements.

11.5 See Practice D3249 for general guidelines on operating ambient air analyzers.

12. Precision and Bias

12.1 The median precision at 20 % and 80 % of the upper range limit for six instruments is reported as ±0.001 ppm (v) O_3 in Annex A1. Interferent bias reported in Annex A2 ranges up to +18 % at high absolute humidity for some instruments calibrated with dry span gases. Calibrations with wet span gas at typical ambient humidities may be used to reduce this bias.[5,7]

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[6] Butcher, S., and Ruff, R., "Effect of Residence Time on Analysis of Atmospheric Nitrogen Oxides and Ozone," *Anal. Chem.*, Vol. 43, p. 1890, 1971.

[7] Parrish, D. D., Fehsenfeld, F. C., "Methods for Gas-Phase Measurements of Ozone, Ozone Precursors, and Aerosol Precursors," *Atmospheric Environment*, Vol. 34, 2000, pp. 1921–1957.

13. Keywords

13.1 chemiluminescent; continuous analyzer; ethylene; ozone

ANNEXES

(Mandatory Information)

A1. PERFORMANCE SPECIFICATIONS

TABLE A1.1 Performance Specifications for Ethylene Chemiluminescent Ozone Monitor (40 CFR Part 53.20)[A]

Parameters	EPA Specification	Manufacturers Test[B]			EPA Retest[C]		
		Instrument Number	Range	Median	Instrument Number[D]	Range	Median
Noise 0 % URL[E]	0.005 ppm	6	<0.001–0.001	0.000	5	0.000–0.001	0.000
80 % URL	0.005 ppm	6	0.001–0.002	0.002	5	0.001–0.003	0.002
LDL[E]	0.01 ppm	6	0.009–0.011	0.010	5	0.011–0.013	0.012
H_2O Interference[F]	+0.02 ppm	6	<0.001–0.002	0.001	5	<0.001–0.001	0.000
H_2S Interference[F]	+0.02 ppm	6	<0.001–<0.001	0.000	5	–0.001–0.001	0.000
CO_2 Interference	+0.02 ppm	6	<0.001–0.006	0.000	5	0.000–<0.001	0.000
Total interference[A]	<0.06 ppm	6	0.001–0.007	0.002	5	<0.001–0.002	<0.001
Zero drift[A] 12 h	+0.02 ppm	6	<0.001–0.004	0.001	5	0.001–0.004	0.001
24 h	+0.02 ppm	6	<0.001–0.003	0.001	5	0.001	0.001
Span drift[A] 20 % URL	+20 %	6	0.48–3.41	2.36	5	2.3–6.96	2.8
80 % URL	+5 %	6	1.21–2.87	1.33	5	1.62–3.36	2.17
Lag time	20 min	6	<0.1–<1.0	0.2	5	0.1–0.2	0.2
Rise time	15 min	6	0.2–2.0	<1.0	5	0.8–1.2	1.1
Fall time	15 min	6	0.3–2.0	<1.0	5	1.3–2.0	1.5
Precision 20 % URL	0.01 ppm	6	<0.001–0.002	0.001	5	0.000–0.001	0.001
80 % URL	0.01 ppm	6	0.001–0.002	0.001	5	0.001–0.006	0.001

[A] Average of absolute values.

[B] Average values for each instrument model from manufacturer's application for equivalency determination.

[C] Average values for each instrument model from EPA post designation tests.

[D] Individual instrument testing is recommended; four of the five instruments purchased through normal procurement procedures required component replacement before retest program could be completed.

[E] Upper Range Limit; Lower Detection Limit.

[F] Tested in the absence of ozone; see Annex A2 for the effects of water vapor in the presence of ozone.

A2. HUMIDITY INTERFERENCE

TABLE A2.1 Reported Humidity Interference

Approximate Absolute Humidity (ppm)	Equivalent Temperature at 50 % RH (°C)	Wet/Dry Ratio[A] of Chemiluminescent Response		
		Number of Instruments	Range of Ratios	Median Ratio
5 000	7	7	1.01–1.04	1.03
10 000	18	7	1.03–1.07	1.04
15 000	24	9	1.07–1.12	1.08
20 000	29	7	1.06–1.12	1.08
25 000	33	5	1.07–1.15	1.12
30 000	37	4	1.10–1.18	1.11

[A] Linear Regression of all data: Ratio (Wet/Dry) = 1.0105 + 3.975 × 10^{-6} [ppm H_2O] r^2 = 0.71. Source: "Water Vapor Effect on Ozone Reference Methods," 29 December 1980 Memorandum to T. R. Hauser from M. E. Beard and K. A. Rehme, USEPA. Research Triangle Park, NC.

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