



Designation: D5156 – 22

Standard Test Methods for Continuous Measurement of Ozone in Ambient, Workplace, and Indoor Atmospheres (Ultraviolet Absorption)¹

This standard is issued under the fixed designation D5156; 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 ozone (O_3) in the atmosphere at concentrations ranging from 10 to 2000 $\mu\text{g}/\text{m}^3$ of O_3 in air (5 ppb(v) to 1 ppm(v)).

1.1.1 The test method is limited to applications by its sensitivity to interferences as described in Section 6. The interference sensitivities may limit its use for ambient and workplace atmospheres.

1.2 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

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, health, and environmental practices and determine the applicability of regulatory limitations prior to use.*

1.4 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

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

¹ These test methods are 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 Sept. 1, 2022. Published September 2022. Originally approved in 1991. Last previous edition approved in 2016 as D5156 – 02 (2016). DOI: 10.1520/D5156-22.

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.

D3249 Practice for General Ambient Air Analyzer Procedures

D3631 Test Methods for Measuring Surface Atmospheric Pressure

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 Other Documents:

EPA-600/4-76-005 *Quality Assurance Handbook for Air Pollution Measurement Systems*, Vol I, "Principles"³

EPA-600/4-77-027a *Quality Assurance Handbook for Air Pollution Measurement Systems*, Vol II, "Ambient Air Specific Methods"³

3. Terminology

3.1 *Definitions*—For definitions of terms used in this test method, refer to Terminology **D1356**. 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 ultraviolet photometer*—a photometer whose design, construction, and maintenance is such that it can measure the absorbance caused by O_3 mixtures without reference to external absorption standards. Given a value for the absorption coefficient of O_3 at 253.7 nm and a reading from the absolute ultraviolet photometer, O_3 concentrations can be calculated with accuracy. An absolute ultraviolet photometer is used only on prepared O_3 mixtures free from interferences, as in calibration activity.

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

³ Available from National Technical Information Service (NTIS), 5301 Shawnee Rd., Alexandria, VA 22312, <http://www.ntis.gov>.

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 the measurement of a physical quantity.

3.2.5 *transfer standard*—a type of secondary standard; it is a transportable device or apparatus that, together with operational procedures, is capable of reproducing pollutant concentrations or producing acceptable assays of pollutant concentrations.

4. Summary of Test Method

4.1 This test method is based on the absorption of ultraviolet radiation at 253.7-nm wavelength by O₃ and the use of an ozone-specific scrubber to generate a reference air stream with only O₃ scrubbed from it. A single-cell ultraviolet absorption photometer is used, with the cell filled alternately with ambient and O₃-scrubbed ambient air. The absorption to be measured at the lower part of the operating range is extremely small. Special precautions and designs must be used to obtain accurate results.

4.2 The absorption of radiation at 253.7 nm by O₃ at very low concentrations follows the Beer-Lambert Law. Namely, for a cell of length d , assuming a constant input ultraviolet intensity, the ratio of the emerging intensities for the cell filled with sample air, I_s , and with O₃-scrubbed air, I_o , is:

$$\frac{I_s}{I_o} = e^{-(cad)} \quad (1)$$

where:

c = the concentration of O₃, ppm (v),

d = the length of the cell, cm, and

a = the absorption coefficient of O₃ per length unit of d and per concentration unit of c .

4.3 When (cad) is $\ll 1$, as is the case for O₃ at 253.7 nm in the concentration range specified for this test method, the approximation

$$e^{-x} \approx (1 - x) \quad (2)$$

can be used to simplify the signal processing electronics, so that

$$I_s \approx I_o (1 - cad) \quad (3)$$

and thus

$$c \approx \frac{(I_o - I_s)}{I_o ad} \quad (4)$$

4.4 At 1 ppm (v), the high end of the recommended range, and a path length of 50 cm, the error resulting from application of the above approximation is approximately 1 part in 10 000.

4.5 Thus, the concentration of O₃ can be obtained from the difference between the signal from the photosensor (often a vacuum photodiode) when the contents of the absorption cell contain sample air from which O₃ has been scrubbed, and when it contains sample air containing O₃.

4.6 At 5 ppb (v) with a 50-cm path length, the absorption is $304.39 \times 0.005 \times 50 \times 10^{-6}$ or $\times 10^{-5}$ **(1-5)**.⁴

4.7 The instrument is calibrated by methods given in Practices **D5011** and **D5110**, which describe the use of an absolute ultraviolet photometer as a primary standard and the qualification and use of transfer standards.

5. Significance and Use

5.1 Standards for O₃ in the atmosphere have been promulgated by government authorities to protect the health and welfare of the public **(6)** and also for the protection of industrial workers **(7)**.

5.2 Although O₃ itself is a toxic material, in ambient air it is primarily the photochemical oxidants formed along with O₃ in polluted air exposed to sunlight that cause smog symptoms such as lachrymation and burning eyes. Ozone is much more easily monitored than these photochemical oxidants and provides a good indication of their concentrations, and it is therefore the substance that is specified in air quality standards and regulations.

6. Interferences

6.1 Any aerosol or gas that absorbs or scatters ultraviolet radiation at 253.7 nm, and that is removed by the O₃-specific scrubber, constitutes an interferent **(8)** to this test method **(9)**. Particulate matter can be removed with a polytetrafluoroethylene (PTFE) membrane filter. Any type of filter can, however, become contaminated and may then scrub O₃. It is important to check the O₃-inertness of such devices frequently.

6.2 Some reported positively interfering organic species for a manganese dioxide scrubber are tabulated in **Annex A2** of this test method. In general, if interferences are suspected, it is preferable to use another test method rather than to try to scrub out the interfering agent, since the instability of O₃ makes the testing and proving of additional interferant scrubbers particularly difficult.

6.3 Water vapor may constitute either a positive or negative interferant in instruments calibrated with dry span gas **(10-13)**.

6.3.1 Improperly polished absorption cell windows may lead to increased signal noise and apparent ozone increases in instruments subject to rapidly changing humidity, such as at a coastal site where instruments may be exposed to frequent shifts between relatively dry terrestrial and moist oceanic air parcels **(9)**.

6.3.2 A negative water vapor interference, due to humidity dependent changes in elution rates of interferences from the ozone scrubber may develop in manganese dioxide scrubbers exposed to ambient air **(11, 13, 14)**. This phenomenon is described in **7.2.6**.

⁴ The boldface numbers in parentheses refer to the list of references at the end of this test method.