Designation: D5110 – 22a

Standard Practice for Calibration of Ozone Monitors and Certification of Ozone Transfer Standards Using Ultraviolet Photometry[1]

This standard is issued under the fixed designation D5110; 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 practice covers a means for calibrating ambient, workplace, or indoor ozone monitors, and for certifying transfer standards to be used for that purpose.

1.2 This practice describes means by which dynamic streams of ozone in air can be designated as primary ozone standards.

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

1.4 *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.* See Section 8 for specific precautionary statements.

1.5 *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

D3195 Practice for Rotameter Calibration

D3249 Practice for General Ambient Air Analyzer Procedures

D3631 Test Methods for Measuring Surface Atmospheric Pressure

D5011 Practices for Calibration of Ozone Monitors Using Transfer Standards

E220 Test Method for Calibration of Thermocouples By Comparison Techniques

E591 Practice for Safety and Health Requirements Relating to Occupational Exposure to Ozone (Withdrawn 1990)[3]

E644 Test Methods for Testing Industrial Resistance Thermometers

3. Terminology

3.1 *Definitions*—For definitions of terms used in this practice, refer to Terminology D1356.

3.2 *Definitions of Terms Specific to This Standard:*

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

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

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

3.2.4 *transfer standard, n*—a type of secondary standard. It is a transportable device or apparatus that, together with operational procedures, is capable of reproducing pollutant concentration or producing acceptable assays of pollutant concentrations.

3.2.5 *zero air, n*—purified air that does not contain ozone, and does not contain any other component that may interfere with the measurement (see 7.1).

4. Summary of Practice

4.1 This practice is based on the photometric assay of ozone (O_3) concentrations in a dynamic flow system. The concentration of O_3 in an absorption cell is determined from a measurement of the amount of 253.7 nm light absorbed by the sample. This determination requires knowledge of (*1*) the absorption coefficient of O_3 at 253.7 nm, (*2*) the optical path length through the sample, (*3*) the transmittance of the sample at a

[1] This practice 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 Sept. 1, 2022. Published September 2022. Originally approved in 1990. Last previous edition approved in 2022 as D5110 – 22. DOI: 10.1520/D5110-22A.

[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] The last approved version of this historical standard is referenced on www.astm.org.

wavelength of 253.7 nm, and (*4*) the temperature and pressure of the sample. The transmittance is defined as the ratio:

$$I/I_o$$

where:

I = the intensity of light that passes through the cell and is sensed by the detector when the cell contains an O_3 sample, and

I_o = the intensity of light that passes through the cell and is sensed by the detector when the cell contains zero air.

It is assumed that all conditions of the system, except for the contents of the absorption cell, are identical during measurements of I and I_o. The quantities defined above are related by the Beer-Lambert absorption law:

$$\text{Transmittance} = I/I_o = e^{-acd} \quad (1)$$

where:

a = absorption coefficient of O_3 at 253.7 nm, $(304.39 \pm 0.94) \times 10^{-6}$ ppm^{-1} cm^{-1} at 0 °C and 101.3 kPa (1 atm) **(1-9)**,[4]

c = O_3 concentration, ppm, and

d = optical path length, cm.

4.1.1 In practice, a stable O_3 generator (see 6.1.4) is used to produce O_3 concentrations over the required range. Each O_3 concentration is determined from the measurement of the transmittance of the sample at 253.7 nm, and is calculated from the equation:

$$c = \frac{-ln\frac{I}{I_o}}{(ad)} \quad (2)$$

The calculated O_3 concentrations must be corrected for O_3 losses, which may occur in the photometer, and for the temperature and pressure of the sample.

5. Significance and Use

5.1 The reactivity and instability of O_3 preclude the storage of O_3 concentration standards for any practical length of time, and precludes direct certification of O_3 concentrations as Standard Reference Materials (SRMs). Moreover, there is no available SRM that can be readily and directly adapted to the generation of O_3 standards analogous to permeation devices and standard gas cylinders for sulfur dioxide and nitrogen oxides. Dynamic generation of O_3 concentrations is relatively easy with a source of ultraviolet (UV) radiation. However, accurately certifying an O_3 concentration as a primary standard requires assay of the concentration by a comprehensively specified analytical procedure, which must be performed every time a standard is needed **(10)**.

5.2 This practice is not designed for the routine calibration of O_3 monitors at remote locations (see Practices D5011).

6. Apparatus

6.1 A typical complete UV calibration system consists of an O_3 generator, an output port or manifold, a photometer, a source of zero air, and other components as necessary. The configuration must provide a stable O_3 concentration at the system output and allow the photometer to assay accurately the output concentration to the precision specified for the photometer. Fig. 1 shows the system, and illustrates the calibration system. Ozone is highly reactive and subject to losses upon contact with surfaces. All components between the O_3 generator and the photometer absorption cell shall be of inert material, such as glass or TFE-fluorocarbon. Lines and interconnections shall be as short as possible, and all surfaces shall be chemically clean. For certification of transfer standards that provide their own source of O_3, the generator and possibly other components shown in Fig. 1 may not be required (see Practices D5011).

6.1.1 *UV Photometer,* consisting of a low-pressure mercury discharge lamp, collimation optics (optional), an absorption cell, a detector, and signal-processing electronics, as shown in Fig. 1. It shall be capable of measuring the transmittance, I/I_o, at a wavelength of 253.7 nm with sufficient precision that the standard deviation of the concentration measurements does not exceed the greater of 0.005 ppm or 3 % of the concentration. It shall incorporate means to assure that no O_3 is generated in the cell by the UV lamp. This is generally accomplished by absorbing the 184.9 nm Hg line with a high silica window, or by isolating the 253.7 nm Hg line with an interference filter. In addition, at least 99.5 % of the radiation sensed by the detector shall be 253.7 nm. This is usually accomplished by using a solar blind photodiode tube. The length of the light path through the absorption cell shall be known with an accuracy of at least 0.5 %. In addition, the cell and associated plumbing shall be designed to minimize loss of O_3 from contact with surfaces **(11)**.

6.1.2 *Air Flow Controller,* capable of regulating air flows as necessary to meet the output stability and photometer precision requirements.

6.1.3 *Flowmeters,* calibrated in accordance with Practice D3195.

6.1.4 *Ozone Generator,* capable of generating stable levels of O_3 over the required concentration range. It shall be stable over short periods to facilitate the sequential photometric measurement of I and I_o, and to allow for stability of the monitor or transfer standard connected to the output manifold. Conventional UV-photolytic type generators may be adequate, but shall have line voltage and temperature regulation.

6.1.5 *Output Manifold,* constructed of glass, TFE-fluorocarbon, or other nonreactive material. It shall be of sufficient diameter to ensure a negligible pressure drop at the photometer connection and other output ports. The output manifold serves the function of providing an interface between the calibration system and other devices and systems that utilize the output O_3 concentrations. It shall have one or more ports for connection of the external instruments or systems, and shall be such that all ports provide the same O_3 concentrations. The vent, which exhausts excess gas flow from the system and insures that the manifold outlet ports are kept at atmospheric pressure for all flowrates, shall be large enough to avoid appreciable pressure drop, and shall be located downstream of

[4] The boldface numbers in parentheses refer to the references listed at the end of this practice.