



## Designation: ~~D5110–98 (Reapproved 2010)~~ D5110 – 98 (Reapproved 2017)

# Standard Practice for Calibration of Ozone Monitors and Certification of Ozone Transfer Standards Using Ultraviolet Photometry<sup>1</sup>

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 ( $\epsilon$ ) 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~~ safety, health, and ~~health~~ 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:*<sup>2</sup>

[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[E591 Practice for Safety and Health Requirements Relating to Occupational Exposure to Ozone \(Withdrawn 1990\)](#)<sup>3</sup>

[E644 Test Methods for Testing Industrial Resistance Thermometers](#) -4594-bb22-77fd60024036/astm-d5110-982017

## 3. Terminology

3.1 ~~Definitions:~~ *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~~ *standard, n*—a standard directly defined and established by some authority, against which all secondary standards are compared.

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

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

3.2.4 ~~transfer standard~~ *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.

<sup>1</sup> 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.

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

<sup>3</sup> The last approved version of this historical standard is referenced on [www.astm.org](http://www.astm.org).

3.2.5 *zero air*—*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 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,  $(308 \pm 4) \times 10^{-6} \text{ ppm}^{-1} \text{ cm}^{-1}$  at 0°C and 101.3 kPa (1 atm) (1, 2, 3, 4, 5, 6, 7, 8)<sup>4</sup>  
 $a$  = absorption coefficient of  $O_3$  at 253.7 nm,  $(308 \pm 4) \times 10^{-6} \text{ ppm}^{-1} \text{ cm}^{-1}$  at 0°C and 101.3 kPa (1 atm) (1-8),<sup>4</sup>  
 $c$  =  $O_3$  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 (9).

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

<sup>4</sup> The boldface numbers in parentheses refer to the references listed at the end of this practice.

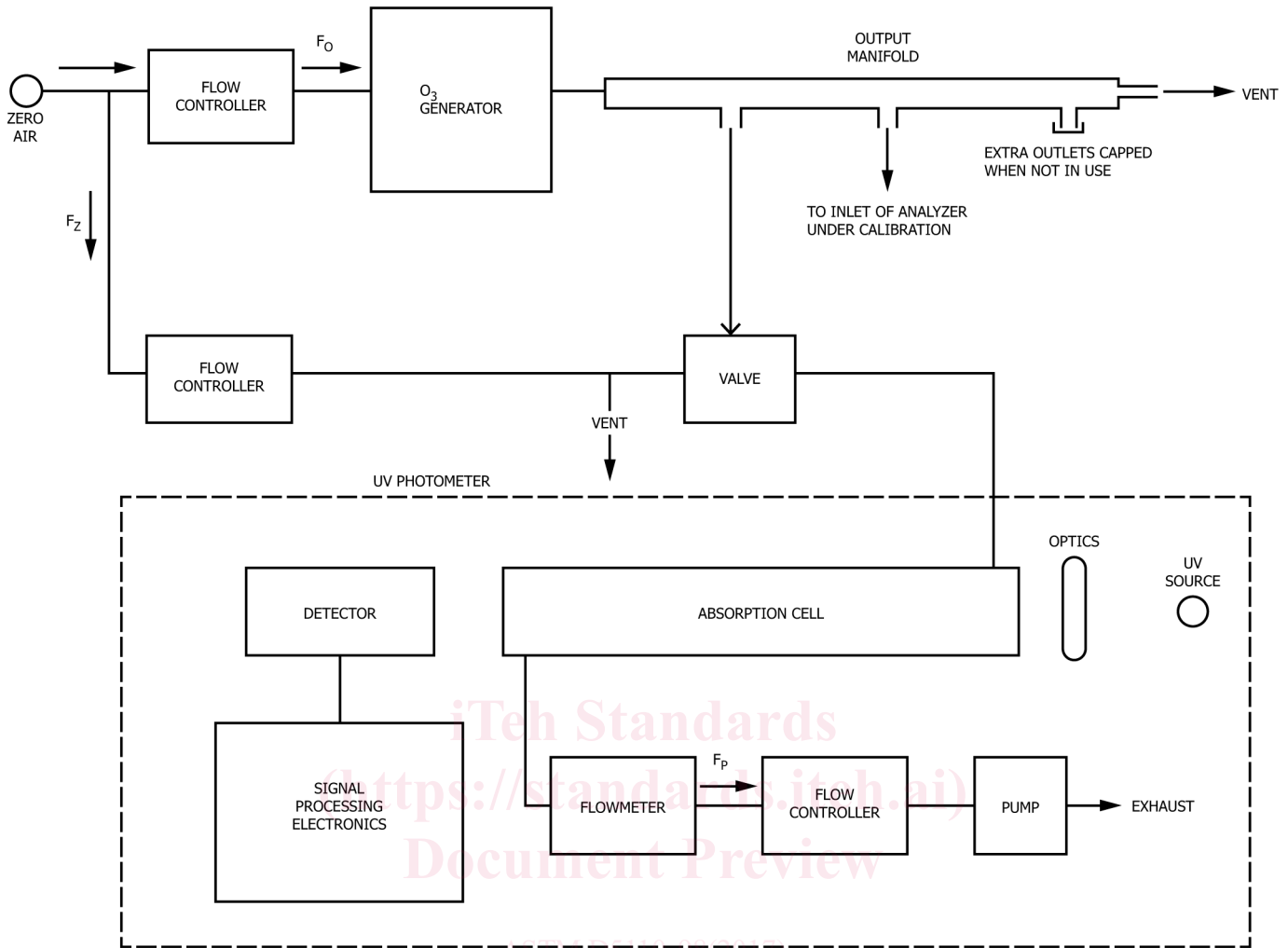


FIG. 1 Schematic Diagram of a Typical UV Photometric Calibration System

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<sub>3</sub> 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<sub>3</sub> from contact with surfaces (10).

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<sub>3</sub> over the required concentration range. It shall be stable over short periods to facilitate the sequential photometric measurement of  $I$  and  $I_0$ , 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<sub>3</sub> 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<sub>3</sub> 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 the output ports to ensure that no ambient air enters the manifold due to eddy currents, back diffusion, and so forth.

6.1.6 *Three-Way Valve*, constructed of TFE-fluorocarbon, to switch the flow through the absorption cell from zero air (for the  $I_0$  measurement) to manifold gas (for the  $I$  measurement).

6.1.7 *Temperature Indicator*, accurate to  $\pm 1^\circ\text{C}$ . This indicator is needed to measure the temperature of the gas in the photometric cell to calculate a temperature correction. In most photometers, particularly those whose cell is enclosed inside a case or housing with other electrical or electronic components, the cell operates at a temperature somewhat above ambient room temperature. Therefore, it is important to measure the temperature of the gas inside the cell, and not room temperature. A small thermocouple or thermistor, connected to an external readout device, may be attached to the cell wall or inserted through the cell wall to measure internal cell temperature. The point of temperature sensing shall be representative of the average cell temperature. The temperature sensing device shall be calibrated against a NIST certified thermometer initially, and at periodic intervals, subject to the laboratory quality control checks (11). See *Test Method E220* or *Test Methods E644* for calibration procedures.

6.1.8 *Barometer or Pressure Indicator*, accurate to 250 Pa (2 torr). The barometer or pressure indicator is used to measure the pressure of the gas in the cell to calculate a pressure correction. Most photometer cells operate at atmospheric pressure. If there are no restrictions between the cell and the output manifold, the cell pressure should be very nearly the same as the local barometric pressure. A certified local barometric pressure reading can then be used for the pressure correction. If the cell pressure is different from the local barometric pressure, some means of accurately measuring the cell pressure (manometer, pressure gauge, or pressure transducer) is required. This device shall be calibrated against a suitable pressure standard, in accordance with *Test Methods D3631*.

6.1.9 *Output Indicating Device*, such as continuous strip chart recorder or digital volt meter.

6.1.9.1 If a recorder is used, it shall have the following specifications:

Accuracy	$\pm 0.25\%$ of span
Chart width	no less than 150 mm
Time for full-scale travel	1 s

6.1.9.2 If a digital volt meter is used, it shall have an accuracy of  $\pm 0.25\%$  of range.

## 7. Reagents and Materials

7.1 *Zero Air*—Free of  $\text{O}_3$  and any substance that by itself or whose decomposition products from the ozonizer might react with  $\text{O}_3$ , absorb 255.7 nm light, or undergo photolysis (for example  $\text{NO}$ ,  $\text{NO}_2$ , ethylene, and particulate matter). The air shall be purified to remove such substances. Dirty air shall be precleaned to remove particulate matter, oil mist, liquid water, and so forth.

7.1.1 The following describes a system that has been used successfully: The air is dried with a membrane type dryer,<sup>5</sup> followed by a column of indicating silica gel. The air is irradiated with a UV lamp to generate  $\text{O}_3$ , to convert  $\text{NO}$  to  $\text{NO}_2$  and then passed through a column of activated charcoal (6 to 14 mesh) to remove  $\text{NO}_2$ ,  $\text{O}_3$ , hydrocarbons, and various other substances, a column of molecular sieve (6 to 16 mesh, type 4A), and a final particulate filter (2  $\mu\text{m}$ ) to remove particulate matter. (**Warning**—An important requirement in photometer operation is that the zero air supplied to the photometer during the  $I_o$  measurement is from the same source as that used for the generation of  $\text{O}_3$ . The impurities present in zero air from different sources can significantly affect the transmittance of an air sample. This requirement presents no problem if the configuration shown in *Fig. 1* is used. However, there may be a problem in certifying  $\text{O}_3$  generator transfer standards that have their own source of zero air or  $\text{O}_3$  (see *Practices D5011*). The zero air produced in 7.1.1 is very dry. The  $\text{O}_3$  response of some measurement methods (for example, ethylene chemiluminescence, KI bubblers) is affected by changes in relative humidity. This dependence should be taken into account when reporting results.)

## 8. Hazards

8.1 *Safety Hazards*—See *Practice D3249* for safety precautions on the use of monitors and electronic equipment.

8.1.1 Ozone is a toxic gaseous substance. See *Practice E591* for biological effects, and for safety and health requirements.

8.1.2 The manifold vents and photometer and monitor exhausts must be vented to remove exhaust gases from the workplace. Care shall be taken to avoid a back pressure in the cell and manifold, and in the monitor or transfer standard being calibrated.

## 9. Preparation of Apparatus

9.1 *Conditioning*—The system shall be conditioned by flowing  $\text{O}_3$  at maximum concentration for 10 to 30 min initially, and after periods of time while the system was not used, prior to reuse.

9.2 *General Operation*—A photometer used as a primary standard shall be dedicated exclusively to calibration service and specifically not used for ambient monitoring or as a transfer standard. The reason for this requirement is that the photometer must be intrinsically accurate and not exposed to outside effects. If it is used for other purposes, it will eventually become dirty and will be prone to  $\text{O}_3$  losses and will give erratic readings. Reserving the photometer for use as a primary standard, where only clean,

<sup>5</sup> The sole source of supply of the apparatus known to the committee at this time is Perma Pure Inc., 8 Executive Drive, P.O. Box 2105, Toms River, NJ 08754. If you are aware of alternative suppliers, please provide this information to ASTM Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee, which you may attend.