

Designation: D 5110 - 98

# Standard Practice for Calibration of Ozone Monitors and Certification of Ozone Transfer Standards Using Ultraviolet Photometry<sup>1,2</sup>

This standard is issued under the fixed designation D 5110; 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 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. See Section 8 for specific precautionary statements.

#### 2. Referenced Documents

- 2.1 ASTM Standards:
- D 1356 Terminology Relating to Sampling and Analysis of Atmospheres<sup>3</sup>
- D 3195 Practice for Rotameter Calibration<sup>3</sup>
- D 3249 Practice for General Ambient Air Analyzer Procedures<sup>3</sup>
- D 3631 Test Methods for Measuring Surface Atmospheric Pressure<sup>3</sup>
- D 5011 Practices for Calibration of Ozone Monitors Using Transfer Standards<sup>3</sup>
- E 220 Method for Calibration of Thermocouples By Comparison Techniques<sup>4</sup>
- E 591 Practice for Safety and Health Requirements Relating to Occupational Exposure to Ozone<sup>5</sup>
- E 644 Test Methods for Testing Industrial Resistance Thermometers<sup>6</sup>

# 3. Terminology

- 3.1 For definitions of terms used in this practice, refer to Terminology D 1356.
  - 3.2 Definitions of Terms Specific to This Standard:
- 3.2.1 *primary standard*—a standard directly defined and established by some authority, against which all secondary standards are compared.
- 3.2.2 *secondary standard*—a standard used as a means of comparison, but checked against a primary standard.
- 3.2.3 *standard*—an accepted reference sample or device used for establishing measurement of a physical quantity.
- 3.2.4 transfer standard—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*—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

where:

- = the intensity of light that passes through the cell and is sensed by the detector when the cell contains an O<sub>3</sub> 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:

<sup>&</sup>lt;sup>1</sup> This practice is under the jurisdiction of ASTM Committee D-22 on Sampling and Analysis of Atmospheres, and is the direct responsibility of Subcommittee D22.03 on Ambient Atmospheres and Source Emissions.

Current edition approved Oct. 10, 1998. Published December 1998. Originally published as D 5110 - 90. Last previous edition D 5110 - 94.

<sup>&</sup>lt;sup>2</sup> This practice is adapted from EPA-600/4-79-057, September 1979; "Technical Assistance Document for the Calibration of Ambient Ozone Monitors", by R. J. Paur and F. F. McElroy. Available from the National Technical Information Service, Springfield, VA 22161.

<sup>&</sup>lt;sup>3</sup> Annual Book of ASTM Standards, Vol 11.03.

<sup>&</sup>lt;sup>4</sup> Discontinued; see 1994 Annual Book of ASTM Standards, Vol 14.03.

<sup>&</sup>lt;sup>5</sup> Discontinued; see 1990 Annual Book of ASTM Standards, Vol 11.03.

<sup>&</sup>lt;sup>6</sup> Annual Book of ASTM Standards, Vol 14.03.

Transmittance=
$$I/I_0 = e^{-acd}$$
 (1)

where:

 $c = O_3$  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:

$$c = \frac{-lI}{(ad)}$$

$$c = \frac{-lI}{(ad)}$$
(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 (SRM's). 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<sub>3</sub> monitors at remote locations (see Practices D 5011).

# 6. Apparatus

6.1 A typical complete UV calibration system consists of an O<sub>3</sub> 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<sub>3</sub> 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<sub>3</sub> 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<sub>3</sub>, the generator and possibly other components shown in Fig. 1 may not be required (see Practices D 5011).

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<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 D 3195.

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<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  $I_o$  measurement) to manifold gas (for the I measurement).

6.1.7 Temperature Indicator, accurate to  $\pm 1^{\circ}$ 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

<sup>&</sup>lt;sup>7</sup> The boldface numbers in parentheses refer to the references listed at the end of this practice.

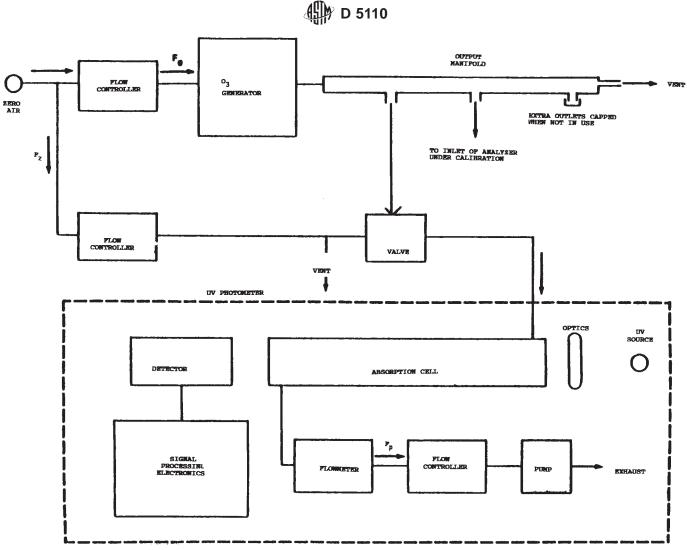


FIG. 1 Schematic Diagram of a Typical UV Photometric Calibration System

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 Method E 220 or Test Methods E 644 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 trans-

ducer) is required. This device shall be calibrated against a suitable pressure standard, in accordance with Test Methods D 3631.

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:

 $\begin{array}{lll} \mbox{Accuracy} & \pm 0.25 \mbox{ \% of span} \\ \mbox{Chart width} & \mbox{no less than 150 mm} \end{array}$ 

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  $O_3$  and any substance that by itself or whose decomposition products from the ozonizer might react with  $O_3$ , absorb 255.7 nm light, or undergo photolysis (for example NO, NO<sub>2</sub>, 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, followed by a column of indicating silica gel. The air is irradiated with a UV lamp to generate  $O_3$ , to convert NO to  $NO_2$  and then passed through a column of activated charcoal (6 to 14 mesh) to remove  $NO_2$ ,  $O_3$ , hydrocarbons, and various other substances, a column of molecular sieve (6 to 16 mesh, type 4A), and a final particulate filter (2  $\mu$ m) to remove particulate matter.

Note 1—Caution: —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  $O_3$ . 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  $O_3$  generator transfer standards that have their own source of zero air or  $O_3$ (see Practices D 5011). The zero air produced in 7.1.1 is very dry. The  $O_3$  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 D 3249 for safety precautions on the use of monitors and electronic equipment.
- 8.1.1 Ozone is a toxic gaseous substance. See Practice E 591 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  $O_3$  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 O<sub>3</sub> losses and will give erratic readings. Reserving the photometer for use as a primary standard, where only clean, dry, filtered gas passes through the cell, will minimize loss of accuracy. A photometer used as a transfer standard will be subjected to environmental conditions, which may have an effect on its output.

- 9.3 *Photometer Verifications*—Since the accuracy of the calibration standards obtained by this practice depends entirely on the accuracy of the photometer, it is important to ensure that the photometer is operating properly and accurately.
- 9.3.1 A well designed and properly built photometer is a precision instrument; once shown to operate adequately, it is likely to continue to do so for some time, particularly if it is held stationary and used intermittently under laboratory conditions. Therefore, the performance checks may not necessarily have to be conducted every time the photometer is used. The actual frequency of the checks is a trade-off between confidence in the photometer performance and the cost and effort to conduct the checks. This is a matter of judgment, subject to the laboratory quality control checks (11). One reasonable approach is to perform the checks very frequently with a new photometer, keeping a chronological record of each performance check, using the QA control chart, and to reduce the frequency as experience dictates. Even where the record shows excellent stability, the checks shall be performed at some minimum frequency (for example, once every 2 or 3 weeks) because the possibility of malfunction is always present. A regular schedule of checks will avoid the risk of losing long periods of data due to photometer malfunction.
- 9.4 *Instrument Manual*—If the photometer is commercially manufactured, it shall have been provided with an operation/instruction manual. The manual shall be studied thoroughly and its recommendations followed carefully and completely.
- 9.5 System check—A visual inspection of the photometer system shall be conducted to verify that the system is in order. The configuration and plumbing connections shall be compared to the flow diagram. All connections shall be verified as being sound, and not restricting the flow. Any leaks shall be corrected. Cleanliness of cell, manifold, and lines shall be checked. A thorough leak check is performed by blocking the output ports and measuring the inlet and exhaust flow rates with an external flowmeter. An alternate procedure is to measure the outlet flowrate and compare the reading against the system flowmeter reading. This procedure also checks the system flowmeter. The three-way valve shall be leak checked. Flowrates and vents shall be checked for lack of back pressure. The zero air supply components shall be checked to determine if the consumables require replacing.
- 9.6 Linearity Test—A linearity check is an indication of accuracy because the photometric measurement is a direct ratio measurement. The photometer operates over a very narrow range of absorbance, so nonlinearity is normally not a problem with properly functioning apparatus.
- 9.6.1 The linearity test is conducted by first generating and assaying an  $O_3$  concentration near the upper range limit of the system. Then the concentration is diluted with a configuration similar to that shown in Fig. 2. A flow of zero air is added to the original generated concentration, and the mixture is passed through a mixing chamber to produce a homogeneous concentration at the output manifold. The dilution ratio shall be accurately known; hence the original and dilution flowrates shall be measured to  $\pm 2$  %. To ensure sufficiently precise measurements of the ratio, the two flowmeters shall be of the

<sup>&</sup>lt;sup>8</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.



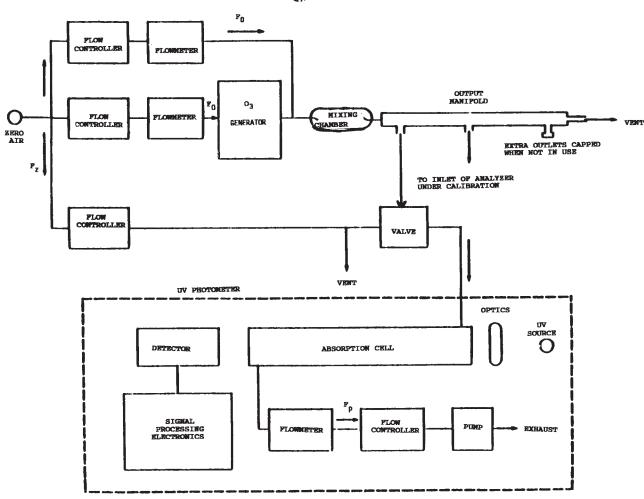


FIG. 2 Schematic Diagram of a Typical UV Photometric Calibration System (Option)

same general type, and one shall be calibrated against the other. The dilution ratio is calculated as follows:

$$R = \frac{F_O}{(F_D + F_O)} \tag{3}$$

where:

R = dilution ratio,

 $F_O$  = flow of original concentration, and

 $F_D$  = dilution flow.

9.6.2 When the dilution flow has been adjusted and the dilution ratio has been calculated, the diluted concentration is measured with the photometer. The diluted concentration is then compared to the original undiluted concentration by calculating the percent linearity error in accordance with the following:

$$E = \frac{(A_1 - A_2/R)}{A_1} 100 \tag{4}$$

where:

E = linearity error, %

 $A_I$  = original concentration, ppm  $A_2$  = diluted concentration, ppm, and R = dilution ratio, from 9.6.1.

9.6.3 The linearity error shall be less than 5 %. It should be noted, however, that the result may not be a true linearity test

because it includes possible errors in the flow measurements. If the error is greater than 5 % or exceeds previous determinations, the accuracy of the flow dilution shall be verified.

9.6.4 The linearity test shall be performed for at least five dilution ratios, and the mean linearity error calculated.

9.6.5 If the linearity error is excessive and is not due to flow measurement inaccuracy, the photometer system shall be checked for the following:

Dirty or contaminated cell, lines or manifold Inadequate system conditioning Leaking three-way valve or system Contaminated zero air Nonlinear photometer detectors Faulty photometer electronics

9.7 Intercomparison—A good check on the overall accuracy of a photometer calibration system is an occasional comparison with O<sub>3</sub> standards from other (independent) organizations. Such comparisons can best be made with transfer standards (see Practices D 5011). If both standards agree, it is likely that both are accurate; if they disagree, it is evident that one of them is inaccurate, and further investigations are necessary.

9.8 Ozone losses—In spite of scrupulous cleaning and preconditioning, some O<sub>3</sub> may inevitably be lost upon contact

with photometer cell walls and gas handling components. Any significant  $O_3$  loss must be quantitatively determined and used to correct the output concentration assay accordingly.  $O_3$  loss shall not exceed 3 % and shall be constant.

9.8.1 To determine  $O_3$  loss, first calibrate a stable photometer with the UV calibration system, assuming no  $O_3$  loss. An  $O_3$  concentration is then generated and measured with the monitor as close as possible to the actual inlet of the photometer cell. Then the concentration is measured as closely as possible to the outlet of the cell. Each measurement shall be repeated several times, and at several  $O_3$  concentrations, to obtain a reliable average. The concentrations at the output manifold shall also be measured. Some commercial photometers have access fittings permanently installed to facilitate frequent loss checks.

9.8.2 Since a continuous  $O_3$  flow through the photometer system is required when making these loss checks, the three-way valve shall be in the "sample" mode. In making these measurements, it is important to avoid shock or damage to the photometer, and to reassemble the fittings and check for leaks if permanent fittings are not available. Also, any pressure differences at the measurement points may cause inaccurate measurements if the monitor is affected by pressure changes.

9.8.3 For the system in Fig. 1, the percent  $O_3$  loss is calculated as follows:

Percent O<sub>3</sub> loss equals 
$$\frac{c_m - \frac{(c_{in} + c_{out})}{2}}{c_m} 100$$
 (5)

where:

 $c_{in} = O_3$  concentration at the cell inlet,

 $c_{out} = O_3$  concentration at the cell outlet, and

 $c_m = O_3$  concentration at the output manifold.

9.8.4 The O<sub>3</sub> loss correction factor is then calculated as:

$$L=1-(0.01) \text{ (Percent O}_3 \text{ loss)}$$

where:

 $L = O_3$  loss correction factor

# 10. Procedure

- 10.1 Allow the photometer to reach equilibrium, and condition it according to 9.1.
- 10.2 Verify that the flowrate through the photometer cell allows the cell to be flushed in a reasonably short period of time (for a cell volume of 30 mL, 2 L/min is adequate). The precision of the measurements is inversely related to the time required for flushing since the photometer drift error increases with time.
- 10.3 The flowrate into the output manifold shall be at least 1 L/min greater than the flowrate required by the photometer and all monitors and transfer standards connected to the output manifold.
- 10.4 The flowrate of zero air shall be at least 1 L/min greater than the flowrate required by the photometer.
- 10.5 With zero air flowing into the output manifold, actuate the three-way valve to allow the photometer to sample first the manifold zero air  $(F_O)$  (see Fig. 1), then the by-pass air  $(F_z)$ . The two readings must be equal  $(I = I_O)$ .

Note 2—In some commercial photometers, the operation of the three-

way valve and various other operations may be carried out automatically by the photometer.

- 10.6 Adjust the  $O_3$  generator to produce an  $O_3$  concentration at 90 % of the upper range limit.
- 10.6.1 Allow the  $O_3$  generator to stabilize at this setting, and allow the entire system to condition to this  $O_3$  concentration.
- 10.7 Actuate the three-way valve to allow the photometer to sample zero air until the absorption cell is thoroughly flushed, and record the stable measured value as  $I_{o}$ .
- 10.8 Actuate the three-way valve to allow the photometer to sample the  $O_3$  concentration until the cell is thoroughly flushed, and record the stable measured value of I.
- 10.9 Record the temperature and pressure of the gas in the absorption cell.
- 10.10 Calculate the  $O_3$  concentration as shown in Section 13. Repeat the determination several times to provide better precision.

Note 3—Some commercial photometers may automatically evaluate the pressure, temperature, or both, of the gas in the absorption cell, and it will not then be necessary to follow 10.9. Some commercial photometers determine the concentration using a linear approximation of the Beer-Lambert Law. In these cases, a manual correction shall be required at higher  $O_3$  concentrations. See the photometer instruction manual and Ref (10) for guidance.

10.11 Generate a minimum of five additional  $O_3$  concentration standards equally spaced over the range of the photometer, and repeat 10.6 through 10.10. Prepare a calibration curve by the method of least squares.

#### 11. Certification of Transfer Standards

11.1 Transfer standards shall be certified by relating the output of the transfer standard to the photometer as determined in Section 10. The exact procedure will vary depending on the design of the transfer standard (see Practices D 5011).

# 12. Calibration of Ozone Monitors

- 12.1 Ozone monitors shall be calibrated as follows, using  $O_3$  standards obtained directly according to Section 10 (or by transfer standards) (see Practices D 5011).
- 12.1.1 Allow the  $O_3$  monitor and the photometer to reach equilibrium conditions.
- 12.1.2 Allow the  $O_3$  monitor to sample zero air until a stable response is obtained. Adjust the monitor zero control to +5 % of scale. Record the stable zero air response as Z.
- 12.1.3 Generate an  $O_3$  concentration standard of approximately 80 % of the upper range limit of the  $O_3$  monitor. Allow the  $O_3$  monitor to sample this concentration until a stable response is obtained.
- 12.1.4 Adjust the  $O_3$  monitor span control to obtain a convenient response, as noted:

Recorder Response = 
$$\frac{(C \times 100)}{URL} + Z$$
 (7)

where:

 $= O_3$  concentration, ppm,

URL = upper range limit of the  $O_3$  monitor, ppm, and Z = instrument response with zero air, % scale.



- 12.1.5 Record the  $O_3$  concentration and the corresponding monitor response. If substantial adjustment of the span control is required, recheck the zero and span adjustments by repeating 12.1.2 to 12.1.4.
- 12.1.6 Generate a minimum of five other  $O_3$  concentrations equally spaced over the range of the  $O_3$  monitor by adjusting the ozone generator or by following the procedure in Annex A1.
- 12.1.7 Plot the  $O_3$  monitor response versus the corresponding  $O_3$  concentrations, and develop the  $O_3$  monitor calibration curve by the method of least squares.

# 13. Calculation

13.1 Calculate the  $O_3$  concentrations for each determination in Section 10, 11, or 12 by using the following equation:

$$c = \frac{(-1)}{(ad)} \frac{(T+273)}{(273)} \frac{(101.3)}{P} \frac{(1)}{L} \ln(II_o)$$
 (8)

where:

 $c = O_3$  concentration, ppm

a = absorption coefficient of  $O_3$  at 253.7  $nm = (308 \pm 4) \times 10^{-6} \text{ ppm}^{-1} \text{ cm}^{-1} \text{ at } 0^{\circ}\text{C} \text{ and } 101.3$ 

kPa (1 atm)

d = optical path length, cm  $T = \text{sample temperature, } ^{\circ}\text{C}$ P = sample pressure, kPa, and

 $L = O_3$  loss correction factor, from 9.8.4.

## 14. Keywords

14.1 ambient atmospheres; calibration; indoor atmospheres; monitoring; ozone calibration; primary ozone standard; primary standard; transfer standard; ultraviolet photometry; workplace atmospheres

#### **ANNEX**

(Mandatory Information)

# A1. OPTIONAL METHOD OF GENERATING OZONE CONCENTRATIONS

A1.1 The various  $O_3$  concentrations required in 10.11 and 11.5 may be obtained by dilution of the  $O_3$  concentrations generated in 10.6 and 12.1.3. With this option, accurate flow measurements are required. The dynamic calibration system shown in Fig. 1 may be modified as shown in Fig. 2 to allow for dilution air to be metered in downstream of the  $O_3$  generator. A mixing chamber between the  $O_3$  generator and the output manifold is also required. Both the flowrate through the  $O_3$  generator and the dilution air flowrate are measured with a flow or volume standard calibrated according to Practice D 3195. Each  $O_3$  concentration generated is calculated from:

$$[O_3]_{out} = c \frac{F_O}{(F_O + F_D)}$$
 (A1.1)

where:

 $[O_3]_{out}$  = diluted  $O_3$  concentration, ppm, c =  $O_3$  output of ozone generator, ppm

 $F_O$  = flowrate through the  $O_3$  generator, L/min,

 $F_D$  = diluent air flowrate, L/min

#### REFERENCES

- (1) Inn, E. C. Y., and Tanaka, Y., "Absorption Coefficient of Ozone in the Ultraviolet and Visible Regions," *Journal of the Optical Society of America*, Vol 43, p. 870 (1953).
- (2) Hearn, A. G., "Absorption of Ozone in the Ultraviolet and Visible Regions of the Spectrum," *Proceedings of the Physical Society* (London), Vol 78, 932 (1961).
- (3) DeMore, W. B. and Raper, O., "Hartley Band Extinction Coefficients of Ozone in the Gas Phase and in Liquid Nitrogen, Carbon Monoxide, and Argon," *Journal of Physical Chemistry*, Vol 68, p. 412 (1964).
- (4) Griggs, M., "Absorption Coefficients of Ozone in the Ultraviolet and Visible Regions," *Journal of Chemical Physics*, Vol 49, p. 857 (1968).
- (5) Becker, K. H., Schurath, U., and Seitz, H., "Ozone Olefin Reactions in the Gas Phase." *International Journal of Chemical Kinetics*, VI, p. 725, (1974).
- (6) Clyne, M. A. A., and Coxon, J. A., "Kinetic Studies of OxoHalogen

- Radical System," *Proceedings of the Royal Society of London, A303*, p. 207 (1968).
- (7) Simons, J. W., Paur, R. J., Webster, H. A., and Bair, E. J., "Ozone Ultraviolet Photolysis," VI. The Ultraviolet Spectrum," *Journal of Chemical Physics*, Vol 59, p. 1203 (1973).
- (8) Hampson, R. F. (ed.). "Survey of Photochemical and Rate Data for Twenty-eight Reactions of Interest in Atmospheric Chemistry," *Journal of Physical Chemistry Reference Data*, Vol 2, p. 267 (1973).
- (9) McElroy, F. F., "Transfer Standards for Calibration of Ambient Air Monitoring Analyzers for Ozone," EPA-600/4-79-056.
- (10) Paur, J. P., and McElroy, F. F., "Technical Assistance Document for the Calibration of Ambient Ozone Analyzers," EPA-600/4-79-057.
- (11) Taylor, J. K., "Quality Assurance of Chemical Measurements," Lewis Publishers, Inc., 1987.



ASTM International takes no position respecting the validity of any patent rights asserted in connection with any item mentioned in this standard. Users of this standard are expressly advised that determination of the validity of any such patent rights, and the risk of infringement of such rights, are entirely their own responsibility.

This standard is subject to revision at any time by the responsible technical committee and must be reviewed every five years and if not revised, either reapproved or withdrawn. Your comments are invited either for revision of this standard or for additional standards and should be addressed to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee, which you may attend. If you feel that your comments have not received a fair hearing you should make your views known to the ASTM Committee on Standards, at the address shown below.

This standard is copyrighted by ASTM International, 100 Barr Harbor Drive, PO Box C700, West Conshohocken, PA 19428-2959, United States. Individual reprints (single or multiple copies) of this standard may be obtained by contacting ASTM at the above address or at 610-832-9585 (phone), 610-832-9555 (fax), or service@astm.org (e-mail); or through the ASTM website (www.astm.org).