



Standard Practices for Calibration of Ozone Monitors Using Transfer Standards¹

This standard is issued under the fixed designation D5011; 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 These practices describe means for calibrating ambient, workplace or indoor ozone monitors, using transfer standards.

1.2 These practices describe five types of transfer standards:

(A) Analytical instruments

(B) Boric acid potassium iodide (BAKI) manual analytical procedure

(C) Gas phase titration with excess nitric oxide

(D) Gas phase titration with excess ozone

(E) Ozone generator device.

1.3 These practices describe procedures to establish the authority of transfer standards: qualification, certification, and periodic recertification.

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 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:*²

[D1071 Test Methods for Volumetric Measurement of Gaseous Fuel Samples](#)

[D1193 Specification for Reagent Water](#)

[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](#)

[D5110 Practice for Calibration of Ozone Monitors and](#)

¹ These practices are under the jurisdiction of ASTM Committee D22 on Air Quality and are the direct responsibility of Subcommittee D22.03 on Ambient Atmospheres and Source Emissions.

Current edition approved March 1, 2009. Published March 2009. Originally approved in 1989. Last previous edition approved in 2003 as D5011 – 92 (2003). DOI: 10.1520/D5011-92R09.

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.

[Certification of Ozone Transfer Standards Using Ultraviolet Photometry](#)

[E591 Practice for Safety and Health Requirements Relating to Occupational Exposure to Ozone \(Withdrawn 1990\)](#)³

2.2 *Other Documents:*

[40 CFR Part 50, Environmental Protection Agency Regulations on Ambient Air Monitoring Reference Methods](#)⁴

3. Terminology

3.1 For definitions of terms used in this standard, see Terminology [D1356](#).

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, which, 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](#).

3.3 *Symbols:*

b = Spectrophotometer cell path length, cm. See [Annex A2](#).

d_{avg} = Average of discrete single point comparisons. See [Annex A1](#).

d_i = Single point comparison. See [Annex A1](#).

F_D = Diluent air flow, mL/min.

F_D' = New diluent air flow, mL/min.

F_{NO} = NO flow, mL/min.

³ The last approved version of this historical standard is referenced on www.astm.org.

⁴ Available from U.S. Government Printing Office Superintendent of Documents, 732 N. Capitol St., NW, Mail Stop: SDE, Washington, DC 20401, <http://www.access.gpo.gov>.

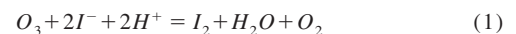
F_O	= Flow through the O ₃ generator, mL/min.	s_d	= Standard deviation of single point comparisons. See Annex A1 .
F_R	= Flowrate corrected to reference conditions (25°C and 101.3 kPa), mL/min. See Annex A2 .	s_i	= Relative standard deviation of the six intercepts. See Annex A1 .
F_S	= Flowrate at sampling conditions, mL/min. See Annex A2 .	s_m	= Relative standard deviation of the six slopes. See Annex A1 .
F_T	= The total flow required at the output manifold (monitors demand plus 10 to 50 % excess), mL/min.	t_R	= Residence time in reaction chamber, min.
I	= The intensity of light which passes through the photometer absorption cell and is sensed by the detector when the cell contains an O ₃ sample. See Annex A4 .	t_s	= Sampling time, min. See Annex A2 .
$[I_2]_i$	= Concentration of each I ₂ standard, mol I ₂ /L. See Annex A2 .	T_S	= Temperature at sampling conditions, °C. See Annex A2 .
I_{avg}	= Average intercept. See Annex A1 .	URL	= Upper range limit of O ₃ or NO monitor, ppm.
I_i	= Individual intercepts. See Annex A1 .	V_i	= Volume of I ₂ solution, mL. See Annex A2 .
I_O	= The intensity of light which passes through the photometer absorption cell and is sensed by the detector when the cell contains zero air. See Annex A4 .	V_{O_3}	= Volume of O ₃ absorbed, µL. See Annex A2 .
m_{avg}	= Average slope. See Annex A1 .	V_R	= Volume of air sampled, corrected to 25°C and 101.3 kPa (1 atm), mL. See Annex A2 .
m_i	= Individual slopes. See Annex A1 .	V_{RC}	= Volume of the reaction chamber, mL.
$mol\ I_2$	= I ₂ released, mols. See Annex A2 .	y_i	= O ₃ concentration indicated by the transfer standard, ppm. See 10.6.2 .
N_{KIO_3}	= Normality of KIO ₃ , equivalent/L. See Annex A2 .	Z	= Recorder response with zero air, % scale.
$[NO]$	= Diluted NO concentration, ppm. See Annex A4 .		
$[NO]_{ORIG}$	= Original NO concentration, ppm. See Annex A3 .		
$[NO]_{OUT}$	= Highest NO concentration required at the output manifold, ppm. It is approximately equal to 90 % of the upper range limit of the O ₃ concentration to be determined. See Annex A3 .		
$[NO]_{RC}$	= NO concentration (approximate) in the reaction chamber, ppm. See Annex A3 .		
$[NO]_{REM}$	= NO concentration remaining after addition of O ₃ , ppm. See Annex A3 .		
$[NO]_{STD}$	= Concentration of the undiluted NO standard, ppm.		
n	= Number of comparisons. See Eq 4 .		
$[O_3]_{CERT}$	= Certified O ₃ concentration, ppm.		
$[O_3]_{CERT}$	= Diluted certified O ₃ concentration, ppm.		
$[O_3]_{GEN}$	= O ₃ concentration produced by the O ₃ generator, ppm. See Annex A4 .		
$[O_3]_{OUT}$	= Indicated O ₃ concentration, ppm. See Annex A2 .		
$[O_3]_{OUT}$	= Diluted O ₃ concentration, ppm.		
$[O_3]_{RC}$	= O ₃ concentration (approximate) at the output manifold, ppm.		
P_{H_2O}	= Vapor pressure of H ₂ O at T_S , kPa, wet volume standard. (For a dry standard, $P_{H_2O} = 0$.) (See Test Method D4230 for tables of saturation vapor pressure of water.) See Annex A2 .		
P_R	= Dynamic specification, determined empirically, to ensure complete reaction of O ₃ or NO, ppm/min.		
P_S	= Barometric pressure at sampling conditions, kPa. See Annex A2 .		
S_c	= Slope of KI calibration curve, mL/mol/cm. See Annex A2 .		

4. Summary of Practices

4.1 These practices describe the procedures necessary to establish the authority of ozone transfer standards: qualification, certification, and periodic recertification. Qualification consists of demonstrating that a candidate transfer standard is sufficiently stable (repeatable) to be useful as a transfer standard. Repeatability is necessary over a range of variables (such as temperature, line voltage, barometric pressure, elapsed time, operator adjustments, relocation, etc.), any of which may be encountered during use of the transfer standard. Tests and possible compensation techniques for several such common variables are described. Detailed certification procedures are provided, and the quantitative specifications necessary to maintain continuous certification of the transfer standard are also provided.

4.2 *Method A*—A dedicated ozone monitor is tested as described in [4.1](#) to demonstrate its authority as a transfer standard.

4.3 *Method B*—This method **(1)**⁵ is based on the reaction between ozone (O₃) and potassium iodide (KI) to release iodine (I₂) in accordance with the following stoichiometric equation **(2)**:



The stoichiometry is such that the amount of I₂ released is equal to the amount of O₃ absorbed. Ozone is absorbed in a 0.1 N boric acid solution containing 1 % KI, and the I₂ released reacts with excess iodide ion (I⁻) to form triiodide ion (I₃⁻), which is measured spectrophotometrically at a wavelength of 352 nm. The output of a stable O₃ generator is assayed in this manner, and the O₃ generator is immediately used to calibrate the O₃ monitor.

4.4 *Method C*—This procedure is based on the rapid gas phase reaction between nitric oxide (NO) and O₃, as described by the following equation **(3)**:

⁵ The boldface numbers in parentheses refer to the references at the end of these practices.



When O₃ is added to excess NO in a dynamic system, the decrease in NO response is equivalent to the concentration of O₃ added. The NO is obtained from a standard NO cylinder, and the O₃ is produced by a stable O₃ generator. A chemiluminescence NO analyzer is used to measure the change in NO concentration. The concentration of O₃ added may be varied to obtain calibration concentrations over the range desired. The dynamic system is designed to produce locally high concentrations of NO and O₃ in the reaction chamber, with subsequent dilution, to effect complete O₃ reaction with relatively small chamber volumes.

4.5 *Method D*—This procedure is based on the rapid gas phase reaction between O₃ and nitric oxide (NO) as described by the following equation (3):



When NO is added to excess O₃ in a dynamic system, the decrease in O₃ response observed on an uncalibrated O₃ monitor is equivalent to the concentration of NO added. By measuring this decrease in response and the initial response, the O₃ concentration can be determined. Additional O₃ concentrations are generated by dilution. The gas phase titration (GPT) system is used under predetermined flow conditions to insure that the reaction of NO is complete and that further reaction of the resultant nitrogen dioxide (NO₂) with residual O₃ is negligible.

4.6 *Method E*—A dedicated ozone generator is tested as described in 4.1 to demonstrate its authority as a transfer standard.

5. Significance and Use

5.1 The reactivity and instability of O₃ precludes the storage of O₃ concentration standards for any practical length of time, and precludes direct certification of O₃ concentrations as SRM's. Moreover, there is no available SRM that can be readily and directly adapted to the generation of O₃ standards analogous to permeation devices and standard gas cylinders for sulfur dioxide and nitrogen oxides. Dynamic generation of O₃ concentrations is relatively easy with a source of ultraviolet (UV) radiation. However, accurately certifying an O₃ 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.

5.2 The primary UV standard photometers, which are usually used at a fixed location under controlled conditions, are used to certify transfer standards that are then transported to the field sites where the ambient ozone monitors are being used. See Practice D5110.

5.3 The advantages of this procedure are:

- 5.3.1 All O₃ monitors in a given network or region may be traced to a single primary standard.
- 5.3.2 The primary standard is used at only one location, under controlled conditions.
- 5.3.3 Transfer standards are more rugged and more easily portable than primary standards.
- 5.3.4 Transfer standards may be used to intercompare various primary standards.

6. Apparatus

6.1 *Apparatus Common to Methods A Through E:*

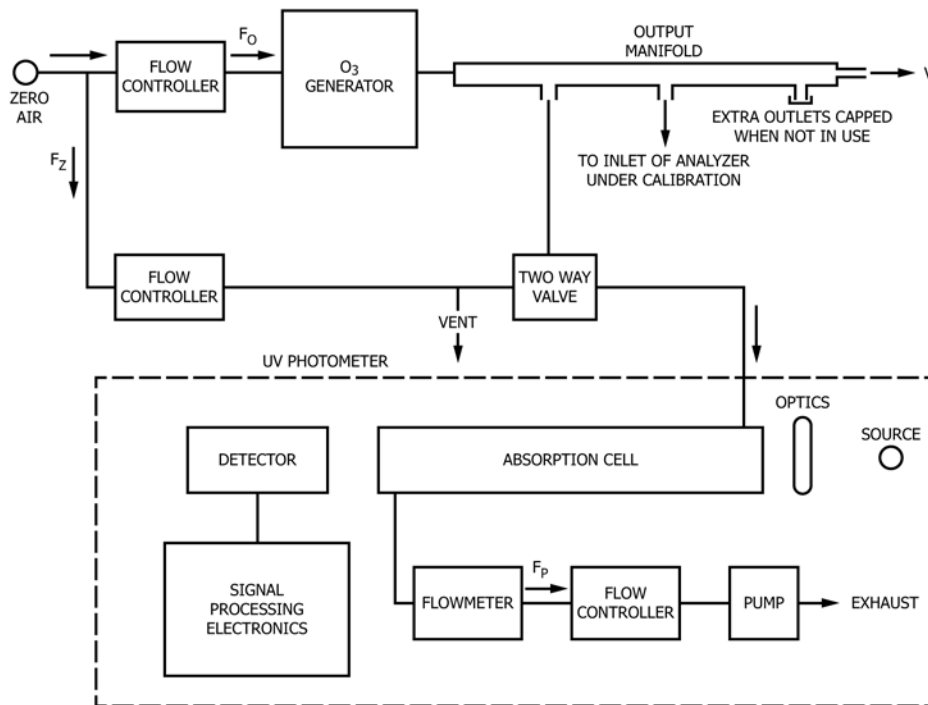


FIG. 1 Schematic Diagram of a Typical UV Photometric Calibration System

6.1.1 UV Photometric calibration system, as shown in Fig. 1, consisting of the following:

6.1.1.1 *Primary Ozone Standard*—a UV photometer, consisting of a low-pressure mercury discharge lamp, collimation optics (optional), an absorption cell, a detector, and signal-processing electronics. It shall be capable of measuring the transmittance, I/I_0 , 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 filtering out the 184.9 nm Hg line with a high silica 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 within at least 99.5 %. In addition the cell and associated plumbing shall be designed to minimize loss of O_3 from contact with surfaces (4). See Practice D5110.

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

6.1.1.3 *Flowmeters*—calibrated in accordance with Practice D3195.

6.1.1.4 *Ozone Generator*—capable of generating stable levels of O_3 over the required concentration range. It shall be stable over short periods to 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.

6.1.1.5 *Output Manifold*—constructed of glass, TFE-fluorocarbon, or other relatively inert material. It shall be of sufficient diameter to cause 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 maintained 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 insure that no ambient air enters the manifold due to eddy currents, back diffusion, etc.

6.1.1.6 *Temperature Indicator*—accurate to $\pm 1^\circ C$. This indicator is needed to measure the temperature of the gas in the photometric cell in order 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 temperature.

6.1.1.7 *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 in order 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 than the local barometric pressure, some means of accurately measuring the cell pressure (manometer, pressure gage, or pressure transducer) is required. This device shall be calibrated against a suitable pressure standard, in accordance with Test Methods D3631.

6.1.2 *Output Indicating Device, such as Continuous Strip Chart Recorder or Digital Volt Meter*—If a recorder is used, it shall have the following specifications:

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

6.1.2.1 If a digital voltmeter is used, it shall have an accuracy of ± 0.25 % of range.

6.1.2.2 Method A output indicating device shall be considered as part of the transfer standard, and employed during qualification, certification, and use.

6.1.2.3 Methods C, D, and E require two output indicating devices.

6.1.3 *Variable Autotransformer*.

6.1.4 *AC Voltmeter*—Accurate to ± 1 %.

6.2 *Apparatus Common to Methods A and D:*

6.2.1 *Ozone Monitor*

6.2.1.1 Method A: An ozone monitor used as a transfer standard shall receive special treatment consistent with its authoritative status: that is, careful handling and storage, frequent maintenance, a QA program, operation by a competent and trained technician. In particular, it shall not be used for ambient monitoring between uses as a transfer standard, as dust and dirt will affect its accuracy.

6.3 *Apparatus Common to Methods C and D—Fig. 2, a*

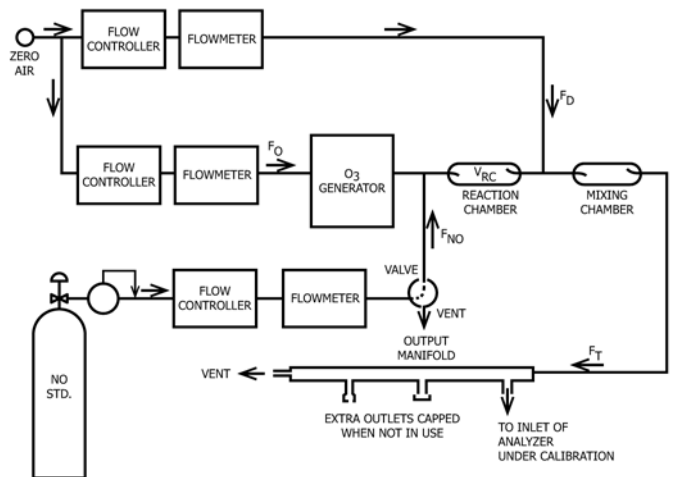


FIG. 2 Schematic Diagram of a Typical GPT System

schematic of a typical GPT apparatus, shows the suggested configuration listed below. All connections shall be glass or TFE-fluorocarbon. See Ref 5 for additional information regarding the assembly and use of the GPT calibration apparatus (5).

6.3.1 *Nitric Oxide Flow Controller*—A device capable of maintaining constant NO flow within $\pm 2\%$. Component parts in contact with NO shall be of a non-reactive material.

6.3.2 *Nitric Oxide Flowmeter*—A flowmeter capable of measuring NO flows within $\pm 2\%$, and shall be calibrated according to Practice D3195. (**Warning**—Rotameters have been reported to operate unreliably when measuring low NO flows, and are not recommended.)

6.3.3 *NO Cylinder Pressure Regulator*—This regulator shall have non-reactive internal components, and shall include a purge port.

6.3.4 *Reaction Chamber*—A glass chamber for the quantitative reaction between O₃ and NO. It shall be of sufficient volume that the reaction time is less than two minutes.

6.3.5 *Mixing Chamber*—A glass chamber to provide for mixing of reaction products and dilution air.

6.4 *Apparatus for Method B Alone:*

6.4.1 *Sampling Train*—(see Fig. 3), consisting of:

6.4.1.1 *Glass Midget Impingers*—Two impingers connected in series.

6.4.1.2 *Air Pump and Flow Controller*—Any air pump and flow controller capable of maintaining a constant flow of 0.4 to 0.6 L/min through the impingers. A critical orifice, as described

by Lodge et al (6), is recommended. The orifice shall be protected from moisture and particulate matter with a membrane filter or trap containing Drierite, silica gel, and glass wool. The air pump shall be capable of maintaining a pressure differential of at least 60 to 70 kPa (0.6 to 0.7 atm) across the critical orifice.

6.4.2 *Spectrophotometer*—Capable of measuring absorbance at 352 nm with an absolute accuracy of $\pm 1\%$, and with a linear response over the range of 0 to 1.0 absorbance units. The accuracy shall be verified using optical glass filters with certified absorbance values at specified wavelengths. Matched 10-mm or 20-mm cells shall be used.

6.4.3 *pH meter*—with a resolution of ± 0.1 pH units.

6.5 *Apparatus for Method C Alone:*

6.5.1 *Chemiluminescence Nitric Oxide Monitor*—The NO channel of a chemiluminescence NO/NO₂/NO_x monitor shall meet the requirements of Method D3824 or the performance requirements for Reference Methods for NO₂ monitors in 40 CFR Part 50.

6.6 *Apparatus for Method D Alone:*

6.6.1 *Ozone Generator*—The generator shall be of the UV lamp type, with means to adjust the O₃ concentration over a convenient range without changing the flowrate. It shall have an output manifold similar to that described in 6.1.1.5, and a zero air supply as described in 7.1.1.1.

7. Reagents and Materials

7.1 *Reagents Common to Methods A Through E:*

7.1.1 *Zero Air*—free of O₃ and any substance that might react with O₃ or undergo photolysis (for example, NO, NO₂, ethylene or other hydrocarbons, 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, etc.

7.1.1.1 A system which has been used successfully is described as follows: 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 O₃ to convert NO to NO₂, and passed through a column of activated charcoal (6 to 14 mesh) to remove NO₂, O₃, hydrocarbons, and various other substances, and is followed by a column of molecular sieve (6 to 16 mesh, type 4A), and a final particulate filter (2 micron) to remove particulate matter.

7.1.1.2 If a chemiluminescent O₃ monitor is being calibrated, the interference by high humidity shall be checked.

7.2 *Reagents and Materials for Method B Only:*

7.2.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. All reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society where such specifications are available.⁶ Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

⁶ "Reagent Chemicals, American Chemical Society Specifications," Am. Chemical Soc., Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see "Analytical Standards for Laboratory U.K. Chemicals," BDH Ltd., Poole, Dorset, and the "United States Pharmacopeia."

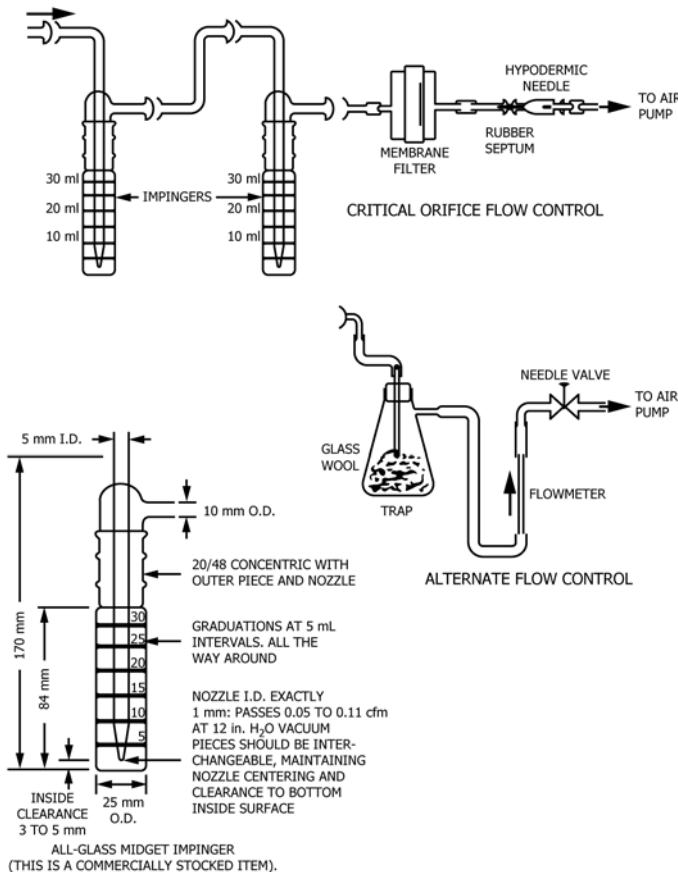


FIG. 3 Components of a KI Sampling Train

7.2.2 *Purity of Water*—References to water shall mean reagent water as defined by Type 2 of Specification **D1193**.

7.2.3 *Absorbing Reagent*—Dissolve 6.2 g of boric acid (H_3BO_3) in 750 mL of water in an amber 1000 mL volumetric flask. The flask may be heated gently to speed dissolution of the boric acid, but the solution must be cooled to room temperature or below before proceeding. (While the boric acid solution is cooling, prepare the H_2O_2 solution (7.2.6).) When cooled, add 10 g of KI to the H_3BO_3 and dissolve. Add 1 mL of H_2O_2 (7.2.6) solution and mix. Within 5 minutes after adding the H_2O_2 , dilute to volume with water, mix, and determine the absorbance of this BAKI solution at 352 nm against water as the reference. The pH of the BAKI solution shall be 5.1 ± 0.02 .

7.2.3.1 Set the absorbing solution aside for two hours, and redetermine the absorbance at 352 nm against water as the reference. If the resulting absorbance from the second determination is at least 0.008 absorbance units/cm greater than the first determination, the solution is ready for use. If no increase or an increase of less than 0.008 absorbance units/cm is observed, the KI reagent probably contains an excessive amount of a reducing contaminant, and must be discarded. If an unacceptable absorbing reagent results from different lots of KI, test the possibility of contamination in the H_3BO_3 by using a different numbered lot of H_3BO_3 .

7.2.4 *Boric Acid* (H_3BO_3).

7.2.5 *Hydrogen Peroxide* (H_2O_2)—3 % or 30 %.

7.2.6 *Hydrogen Peroxide Solution* (0.0021 %)—Using a graduated pipet, add 0.7 mL of 30 % or 7.0 mL of 3 % H_2O_2 (7.2.5) to 200 mL of water in a 500 mL volumetric flask, dilute to volume with water, and mix. Pipet 5 mL of the above solution into 50 mL of water in a 100 mL volumetric flask, dilute to volume with water, and mix. Both solutions must be prepared fresh every time a fresh batch of absorbing solution is prepared.

7.2.7 *Potassium Iodide* (KI).

7.2.8 *Potassium Iodate* (KIO_3)—certified 0.1 N.

7.2.9 *Sulfuric Acid* (H_2SO_4)—95 to 98 %.

7.2.10 *Sulfuric Acid* (1N)—Dilute 28 mL of concentrated H_2SO_4 (7.2.9) to volume in a 1 L volumetric flask by adding the water to the water.

7.2.11 *Standard Solutions*:

7.2.11.1 Pipet 10 mL of 0.1 N KIO_3 solution (7.2.8) into a 100 mL volumetric flask containing 50 mL of water. Add 1 g KI (7.2.7) and 5 mL of 1 N H_2SO_4 (7.2.10), dilute to volume with water, and mix.

7.2.11.2 Immediately before use, pipet 10 mL of the I_2 solution (7.2.11.1) into a 100 mL volumetric flask, and dilute to volume with water. Then pipet 10 mL of this solution into a 200 mL volumetric flask, and dilute to volume with absorbing reagent (7.2.3).

7.2.11.3 In turn, pipet 5, 10, 15, 20, and 25 mL aliquots of the final solution (7.2.11.2) into 25 mL volumetric flasks. Dilute to volume with absorbing reagent (7.2.3), and mix. To prevent loss of I_2 by volatilization, the flasks shall remain stoppered until absorbance measurements are made. Absorbance measurements shall be made within 20 minutes after preparation of the I_2 standards (See **A2.4**).

7.3 *Reagents and Materials for Methods C Only*:

7.3.1 *Nitric Oxide Concentration Standard*—Compressed gas cylinder containing 50 to 100 ppm NO in N_2 . This need not be NBS traceable, but a useful check of the transfer standard's accuracy is obtained if the NO standard is traceable to an NIST Standard Reference Material (SRM 1629). With a traceable NO standard, the transfer standard's indicated O_3 concentration shall agree with the UV standard within -5% to $+15\%$ (most GPT-NO systems have a positive bias). If it does not agree within this envelope, a problem with either the transfer standard or the primary standard is indicated, and standards shall be established using new sources.

7.4 *Reagents and Materials for Method D Only*:

7.4.1 *Nitric Oxide Concentration Standard*—Compressed gas cylinder containing 50 to 100 ppm NO in N_2 , traceable to an NIST Standard Reference Material (SRM 1629 or SRM 1684) or NO_2 Standard Reference Material (SRM 1629). The cylinder shall be recertified on a regular basis as determined by a quality control program.

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 material. 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. Measures must be taken to avoid a back pressure in the cell and manifold, and in the monitor or transfer standard being calibrated.

9. Establishing the Authority of Transfer Standards

9.1 The primary purpose of an O_3 transfer standard is to transfer the authority of a primary O_3 standard from one time and place to another. Since a transfer standard has no authority of its own, its authority must be first established by confirming a high probability or confidence that O_3 concentration standards obtained, under a variety of operating conditions, are very nearly as accurate as primary O_3 standard. This confidence is first established by determining that the transfer standard has adequate reproducibility to qualify it as a transfer standard, then by certifying the transfer standard by relating it to a primary standard, and finally by periodically recertifying it by reverifying its accuracy and stability.

9.2 *Comparing Transfer Standards to Primary Ozone Standard*—Basic to the qualification and certification of an O_3 transfer standard is the need to compare the output (either a concentration determination or an O_3 concentration) of the transfer standard to the primary standard, so that relationships can be determined.

9.2.1 *Assay-Type Transfer Standards*—For transfer standards that provide an assay of an externally generated O_3 concentration (Methods A and B), the transfer standard is connected to the output manifold shown in **Fig. 1** and **Fig. 4**. There shall be sufficient flow of ozonized air for both the primary and secondary standards. The output of the transfer

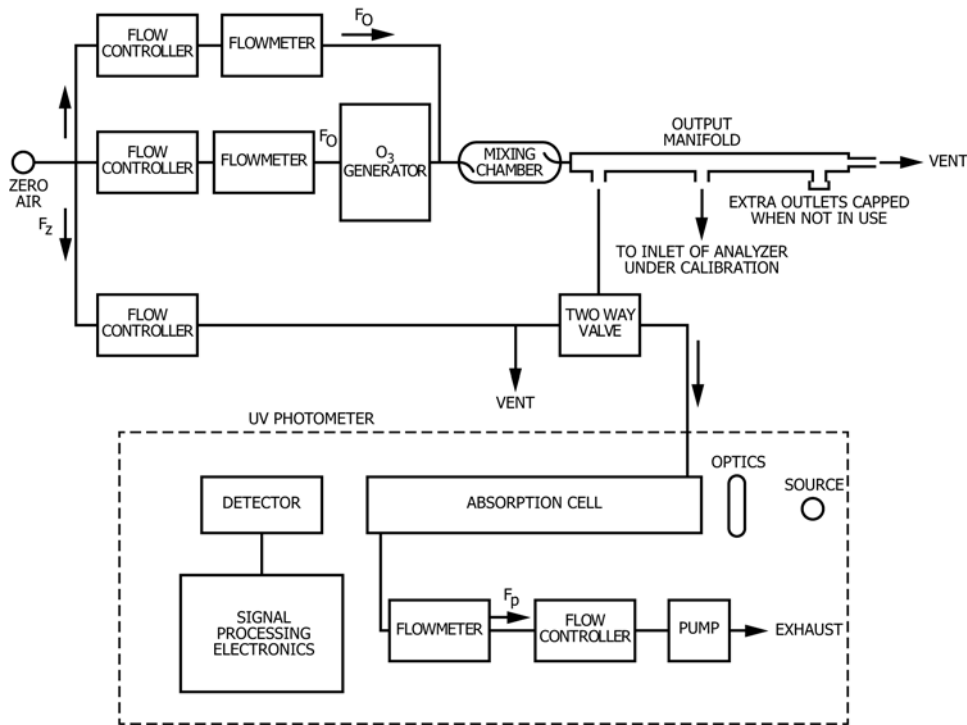


FIG. 4 Schematic Diagram of a Typical UV Photometric Calibration System (Option 1)

standard is an indicated concentration, which is compared directly to the primary standard concentration obtained from the primary standard.

9.2.2 *Ozone-Generation Type Transfer Standards*—Transfer standards that generate O₃ concentrations themselves include O₃ generators (Method E) and may include those assay procedures that have an integral source of O₃ (Methods C and D). Three procedures that may be used to compare the transfer standard to the primary standard are described in Annex A5. They are presented in order of preference.

9.3 *Qualification*—The first step in establishing the authority of a candidate transfer standard is to prove that it qualifies for use as a transfer standard. It must be demonstrated that the output of the transfer standard is reproducible and repeatable under the changing conditions that might be encountered in field use. A transfer standard must be assumed unacceptable until it can be conclusively demonstrated to be acceptable.

9.3.1 The primary requirement of a transfer standard is repeatability under the stress of variable conditions that may change between certification in the laboratory and use in the field. A candidate transfer standard is qualified by proving that it is repeatable over an appropriate range for each variable likely to change between the time and place of certification, and the time and place of use. According to the specifications in Annex A1, the repeatability must be between ±4 % or ±4 ppb, whichever is greater, for each condition or variable that may change between the point of certification and the point of use.

9.3.2 Selecting the conditions that are likely to vary and may affect the repeatability is largely a matter of intelligent informed judgment. It is the user's responsibility to determine all of the conditions to be considered in the demonstration of

repeatability, and to document the choices, and the reasons for them. Common conditions likely to affect a wide variety of transfer standards include ambient temperature, line voltage and frequency, barometric pressure, elapsed time, physical shock, and relocation. Conditions not likely to affect the transfer standard can be usually eliminated from consideration. The user, however, must be constantly alert for the unusual situation where an unexpected condition is present.

9.3.3 It should be noted that a transfer standard does not necessarily need to be constant with respect to the variables, but only repeatable or predictable. Demonstration of repeatability for a candidate transfer standard normally requires testing for each condition that could or may affect it. Typical tests for common conditions are discussed in Section 10. For qualification of procedural candidates such as Methods B, C, or D, testing may be minimal, provided the user is adequately trained, uses good laboratory technique, and uses a specific apparatus and set of supplies. For commercially available transfer standards, some or all of the testing may have been carried out by the manufacturer. In some cases it may be possible to judiciously substitute design rationale for actual testing. For example, a device whose power supply is designed to be highly regulated may not require specific line voltage tests. However, such situations should be viewed with considerable skepticism because of the possibility of failure of a component.

9.3.4 This brings up the further question of whether candidate transfer standards must be tested individually or whether they can be qualified by type, model, or user. In the case of procedural candidates such as Methods B, C, or D, each user must qualify them in the laboratory/use situation in which it will be used, since the procedures have a number of potential

variables. Commercial transfer standards are designed and manufactured to be identical. The manufacturer could carry out the necessary qualification tests on representative samples under this concept. It shall be appropriate to require that the manufacturer guarantee that each unit meet appropriate performance specifications, and provide documentation accordingly. Again, the user should assume a skeptical attitude, and at least carry out some minimal tests to verify that each unit is acceptable.

10. Qualification Tests

Some of the more common conditions likely to be encountered or to change while using transfer standards, and that may affect the repeatability of the device are discussed below. The exact conditions or variables that must be considered depend on the specific nature of the transfer standard or procedure. The user (or manufacturer) shall determine the conditions for each case on an intelligent judgment basis derived from a complete understanding of the operation of the device or procedure and supported by appropriate rationale.

10.1 Once the conditions to be considered have been determined, the objective of the qualification tests is either [10.1.1](#) or [10.1.2](#):

10.1.1 To determine that the candidate transfer standard's output is not affected by more than $\pm 4\%$ or ± 4 ppb (whichever is greater) by the condition over the range likely to be encountered during use of the transfer standard.

10.1.2 To demonstrate the candidate transfer standard's output is repeatable within $\pm 4\%$ or ± 4 ppb (whichever is greater) as the variable is changed over the range likely to be encountered during use, and to quantify the relationship between the output and the variable.

10.2 *Temperature*—Changes in ambient temperature are likely to occur from place to place and from one time to another. Temperature changes are likely to affect almost all types of transfer standards unless appropriate means are used to avoid adverse effects. Temperature affects transfer standards in many ways: changes in action of components, changes in chemical reactions or rates of reaction, volume changes of gases, electronic drift, variable warm-up time, etc. The most important effects are changes in the output of generation devices, changes in the sensitivity of O_3 assay systems, and changes in the volume of air flows which must be measured accurately.

10.2.1 Temperature effects may be minimized in several ways. The easiest way is to restrict the use of the transfer standard to a temperature range over which the effects are within the specification. This restriction may be the only practical approach for some candidate transfer standards, but it may preclude use of such a transfer standard in too many situations. Transfer standard devices may be insensitive to temperature changes by design, such as thermostatic regulation of sensitive components or of the entire device, or by temperature compensation.

10.2.2 Temperature effects on flow measurements may be minimized by the use of mass flowmeters, which do not measure volume, or by the regulation of gas temperature.

Alternately, ideal-gas-law corrections may be made to adjust measured values. See Practice [D3195](#) for appropriate formulas for corrections.

10.2.3 Testing a candidate transfer standard for sensitivity to temperature is facilitated by use of a controlled temperature chamber. However, temperature tests may be carried out in many ordinary laboratories where the temperature may be manually controlled by adjusting thermostats, blocking air vents or outlets, opening doors or windows, or using supplemental heaters or air conditioners. A reasonable temperature range is 20° to 30°C [68° to 86°F]. Broader temperature ranges could be used if necessary for special situations.

10.2.4 The candidate transfer standard is tested by comparing its output to a stable concentration reference, which shall be an UV photometer system. See Practice [D5110](#). The reference may also be another transfer standard known to be repeatable and, in particular, insensitive to temperature changes. However, it would be better to locate the reference outside of the variable temperature area. The candidate transfer standard shall be tested at several different points over the temperature range, including the extremes, and at several different concentrations. Sufficient time shall be allowed for all components of the calibration system to equilibrate each time the temperature is changed. The test results shall be plotted as shown in [Fig. 5](#).

10.2.5 If the candidate transfer standard has a significant temperature dependence, additional test points at various concentrations and temperature shall be taken to define the relationship between output and temperature accurately. Furthermore, if the candidate transfer standard has a dependence on more than one variable, tests shall be carried out over the range of both variables simultaneously to determine any interdependence between the two variables. Once the test data are acquired, they shall be analyzed to determine if some general formula or curve can be derived (either analytically or empirically) to predict the correct O_3 concentration at any temperature in the range (see [Fig. 6](#)). The correction formula or curve shall be accurate within $\pm 4\%$ or ± 4 ppb, whichever is greater. If two or more variables are involved, a family of curves may be required; unless the relationship is simple, this situation may prove impractical in actual use.

10.3 *Line Voltage*—Line voltage may vary from place to place, and from one time to another. Good electrical or electronic design of the transfer standard shall avoid sensitivity to line voltage variations, but poorly designed equipment may easily be affected. In addition, line voltage sensitivity may appear only as a long time thermal drift, which is a subtle effect.

10.3.1 Aside from adequate design, line voltage effects may be minimized by the addition of a line voltage regulator. However, such devices may distort the line voltage waveform, thereby adversely affecting some types of transfer standards. If such regulators are used, it is important the same regulator is used both during certification and use of the transfer standards. Restriction of the transfer standards to a line voltage range in which effects are insignificant is another alternative, but requires monitoring the voltage during use, and may preclude use at some sites.

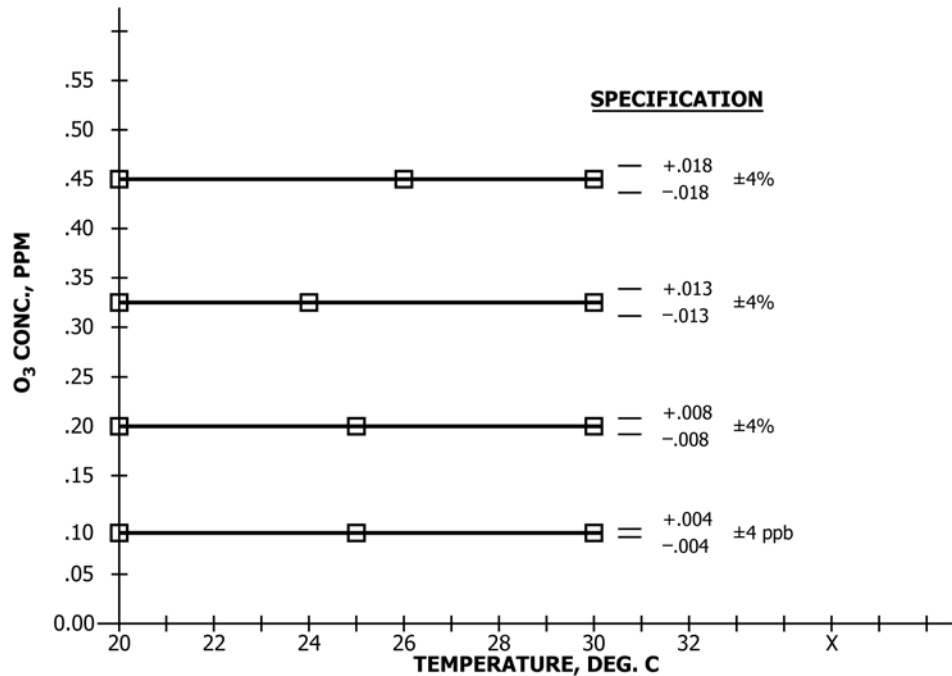


FIG. 5 Example of Temperature Qualification Test Results Showing no Dependence on Temperature

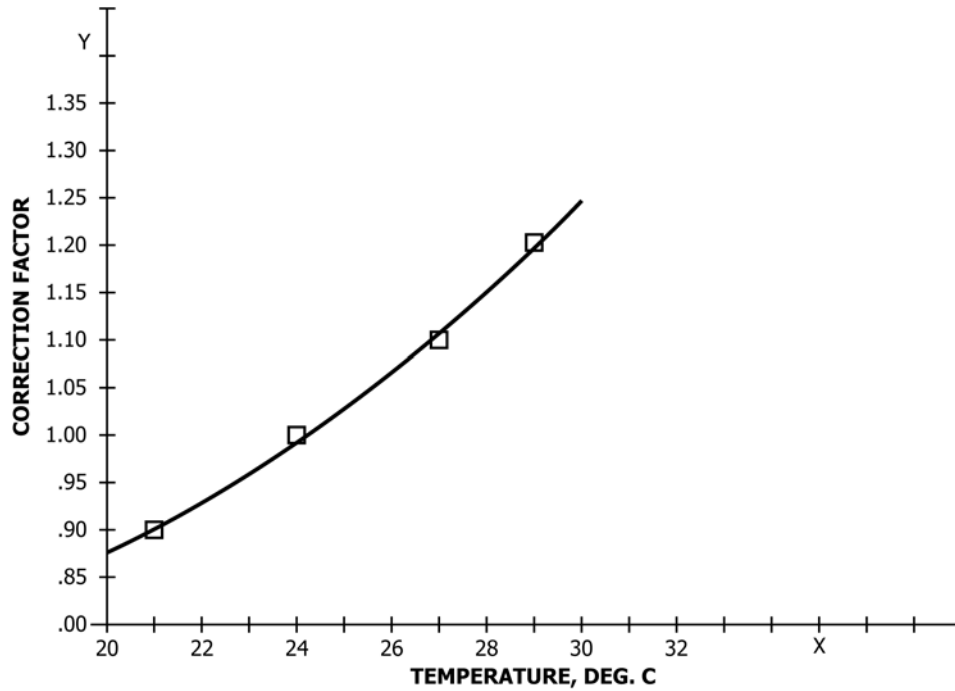


FIG. 6 Example of a Temperature Dependence Quantitatively Defined as a Correction Factor

10.3.2 Testing for line voltage sensitivity may be conducted along the same lines as described for temperature testing. The line voltage may be varied by means of a variable autotransformer and measured by an accurate ac voltmeter. Do not use

electronic “dimmer” controls which operate on a delayed-conduction principle, as such devices cause drastic waveform distortions.

10.3.3 A line voltage range of 105 to 125 V should adequately cover the majority of line voltages available.

10.3.4 If the transfer standard is used when power is from a small power generator, the frequency variation shall be checked.

10.4 *Barometric Pressure/Altitude*—Since O₃ concentrations are gaseous, all transfer standards will have some basic or inherent sensitivity to changes in barometric pressure. It is difficult to minimize pressure effects by design. Air pressure can be regulated mechanically against an absolute reference, but most such schemes are not practical when working with O₃ concentrations because of restrictions to inert material such as glass or TFE-fluorocarbon. With Methods B, C, and D, the effect is limited primarily to the measurements of flowrates, which were discussed in 10.2, and are applicable to barometric pressure changes as well. At a constant altitude, normal day-to-day variations in barometric pressure is only a few percent. If the use of the transfer standards can be restricted to altitudes within a hundred meters of the certification altitude, it may be acceptable to neglect the barometric effect. However, if the use of the transfer standard is necessary at altitudes different than the certification altitude, then pressure effects may not be ignored.

10.4.1 Although not preventable, pressure effects are likely to be repeatable. As a result, barometric pressure may be the variable most likely to be handled by a defined relationship. The technique is similar to that used to determine a temperature relationship; a unique quantitative relationship will result. (**Warning**—In any work with O₃ concentrations at altitudes significantly above sea level, the concentration units must be clearly understood. The volume ratio concentration units (ppm, ppb, etc.) are independent of pressure, while density units such as µg/m³ are related to pressure. The µg/m³ unit defined and used by EPA is “corrected” to 101.3 kPa (1 atm) and 25°C, and is therefore related to ppm by a constant.)

10.4.2 Testing barometric pressure effects may be difficult. The use of a variable pressure chamber is the best approach, but few laboratories have access to one. It is conceivable that various pressures may be obtained in a manifold setup, but construction of such an apparatus is difficult, and of questionable validity. The use of a mobile laboratory which may be driven to several altitudes to conduct tests may offer the best solution. Some types of transfer standards may not require pressure tests because their pressure variations are well known. For Methods B, C, and D, the flow measurement problem constitutes the only pressure effect. Assay-types such as Method A are directly related to gas density, and the ideal-gas law correction may be used. (See Practice D3195 for correction equations.) Pressure tests are not needed for these types. For commercially-available devices, the manufacturer is expected to perform the required qualification tests and to provide documentation.

10.5 *Elapsed Time*—As the elapsed time between certification and use increases, the confidence in the repeatability decreases. As a result, periodic recertification is required. Some types of O₃ generation devices have a definite loss of output (decay) with time. This decay is usually associated with use-time or on-time rather than with total elapsed time. Since

the decay rate tends to be quantifiable, it may be accommodated with the defined relationship mechanism discussed in connection with temperature effects: the transfer standard is equipped with an hours meter, and a series of tests over a sufficient time period may then be used to determine the decay rate. During use, a correction to the output is applied based on the number of hours of on-time since the last certification.

10.5.1 Alternately, the transfer standard may be recertified often enough so the error due to decay never exceeds the specifications in Annex A1.

10.6 *Variability*—The preciseness of the relationship between a transfer standard and a primary O₃ standard is dependent on the variability of the transfer standard. Variability reduces confidence in the accuracy of a certified transfer standard. A high degree of variability may be the cause for disqualifying a device or procedure for use as a transfer standard, or for selecting one with lower variability. Although the certification procedure in Section 11 includes a test for variability, more extensive tests for variability may be necessary to qualify a transfer standard because the certification test is for variability in the slope of the certification relationship and not for individual point variability. Furthermore, variability may be due to changes in conditions not encountered during certification.

10.6.1 Different types of transfer standards may have excessive variability for a variety of reasons. Qualification variability testing is most needed to test for the effect of a variety of non-specific or non-quantitative variables that cannot be tested individually. For example, qualification variability tests for Methods B, C, and D may include the use of various operators, various sources of chemicals and water, minor variations or substitutions of apparatus and components, etc. These tests may be conveniently combined with tests for relocation and operator adjustments described below. Whenever increased variability may be assigned to a specific cause, corrective actions or restrictions may be applied to reduce the variability.

10.6.2 Qualification testing for individual-point variability, unlike the certification variability test, shall be carried out on a single-point basis. A series of at least 6 single-point comparisons shall be made between the candidate transfer standard and the primary O₃ standard at each of at least two fixed concentrations—one low (less than 0.1 ppm) and one high (over 80 % of the upper range limit (URL)). These comparisons shall be made over a variety of conditions and situations and over a number of days. For each concentration, verify that all O₃ concentration measurements determined by the UV primary standard are very nearly equal. Then calculate the average of the 6 (or more) concentrations indicated by the transfer standard, using the following equation:

$$\text{Avg} = 1/n \sum_{i=1}^n y_i \quad (4)$$

10.6.3 Determine the differences between each concentration shown by each transfer standard and the average concentration ($y_i - \text{Avg}$). Each difference must be less than ±5 % of the average (for concentrations over 0.1 ppm) or less than ±5 ppb (for concentrations less than 0.1 ppm). For this test, the acceptable limits are ±5 % or ±5 ppb rather than ±4 % or ±4

ppb, because the test is for general variability, which may derive from a number of non-identifiable causes. Under these circumstances, slightly wider limits than those allowed for the other qualifications tests are allowed.

10.6.4 One technique that may reduce variability and improve accuracy is repetition and averaging. For example, the variability of assay procedures may be reduced by assaying each concentration several times, and averaging the results. Of course, if this technique is used, it becomes a necessary part of the transfer standard procedure and shall be carried out each time the transfer standard is used and certified.

10.7 *Relocation*—A transfer standard needs to maintain repeatability after being moved and encountering mechanical shocks, jolts, and stress. Any electrical or thermal stress incident to turning the device or equipment on and off frequently is also of concern, as is consideration of orientation and set-up factors.

10.7.1 Tests for these conditions, while perhaps not particularly quantitative, shall also include actually moving the candidate transfer standard to different locations and comparing the output every time it is returned to the primary standard. Tests may also include mild shock and drop tests, and tests for set-up factors that can be specifically identified, e.g., physical orientation, removal of covers, etc. Any cause-and-effect-relationship discovered shall be investigated completely, and documented. The tests may be conveniently combined or included with those tested previously for variability.

10.8 *Operator Adjustments*—Those transfer standards whose outputs will be related to an operator adjustment (such as an adjustable O₃ generator) shall be tested for repeatability with respect to the adjustment. Mechanical adjustments may need to be tested for play, backlash, hysteresis, slippage, and resolution. Other types of adjustments may require tests for analogous aspects. If possible, specific tests shall be used. For example, approaching a given setting from both above and below the setting may be appropriate for testing play or hysteresis. If specific tests cannot be designed, then simple repeatability tests at several different settings shall be conducted.

10.9 *Malfunctions*—The usefulness of a transfer standard is dependent on the degree of confidence that may be put on its ability to reproduce O₃ standards. While any device is subject to occasional malfunctions, frequent malfunctions would certainly compromise the purpose of a transfer standard. Of particular concern are non-obvious type malfunctions that may cause a significant error of which the operator is unaware. While no specific tests for malfunctions are normally used, the tests described above, used with an extensive quality control program, will minimize malfunctions, and contribute to their identification. After a malfunction has been corrected, the transfer standard shall be recertified.

10.10 *Other Conditions*—Any other conditions that might affect a candidate transfer standard or might cause change between the point of certification and point of use shall be corrected.

11. Procedure for Certification

11.1 The accuracy of a transfer standard is established by relating the output to a primary O₃ standard, and demonstrating that the repeatability of the transfer standard is within the limits specified in **Annex A1**.

11.1.1 An acceptable transfer standard is precisely repeatable. Its accuracy, however, is relative and depends entirely on its certification to the primary O₃ standard. Certification establishes a precise quantitative relationship between the output of the transfer standard and a series of primary O₃ concentrations. The primary O₃ concentrations shall be obtained by means of the UV calibration procedure. After a transfer standard has been shown to meet the qualification requirements discussed in Section 10, it shall be certified before it may be used. The prescribed certification procedure and specifications are shown in **Annex A1**, but are discussed in more detail in the remainder of this section. See Practice **D5110**.

11.2 *Certification:*

11.2.1 Certification requires the averaging of at least 6 comparisons between the transfer standard and a primary O₃ standard system. Each comparison shall cover the full range of O₃ concentrations and shall be conducted on a different day.

11.2.2 Each comparison shall consist of 6 or more individual comparison points, including 0 and (90 ± 5 %) of the URL of the transfer standard. The other points shall be approximately evenly spaced between these points. For each comparison, the slope and intercept is computed by a least square linear regression. The result shall be similar to **Fig. 7**. Most assay-type transfer standards (Methods B, C, and D) will be linear, and the linear regression can be calculated directly. However, for non-linear transfer standards or generation type standards (Method E) where the output is related to a control setting or an adjustable parameter, a preliminary calibration relationship such as shown in **Fig. 8** is required. Note that the curve in **Fig. 8** may have a considerable zero offset, and may be nonlinear. This preliminary calibration should also contain any necessary correction formulas for defined variables. A smooth curve fitting the points in **Fig. 8** shall be developed. There are no specific requirements on the form, number of points, linearity, or frequency of repetition for this preliminary calculation. However, excessive inaccuracy in this relationship will appear as variability in the certification comparison, and may cause failure of the certification specifications. During the certification comparisons, the preliminary calculation relationship (see **Fig. 8**) is used to obtain the indicated O₃ concentration used in the linear regression calculations of **Fig. 7**. (Note that **Fig. 7** should be linear even though **Fig. 8** is nonlinear.)

11.2.3 When 6 comparisons as shown in **Fig. 7** have been completed, compute the average slope (m_{AVG}) from the 6 individual slopes (m_i), and the average intercept (I_{AVG}) from the 6 individual intercepts (I_i).

11.2.4 Compute the relative standard deviation (s_m) of the 6 slopes (m_i) and the quantity S_I as shown in **A1.3.4**.

11.2.5 Compare s_m to the 3.7 % specification, and compare s_I to the 1.5 % specification. If either of the specifications is exceeded, it indicates the transfer standard has too much variability, and corrective action shall be taken to reduce the

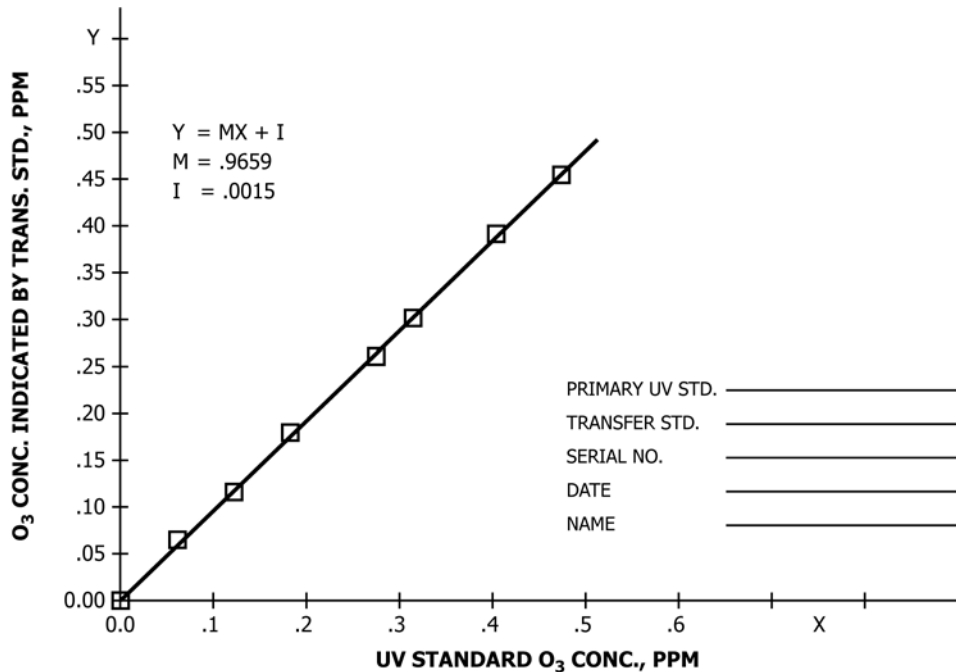


FIG. 7 Example of a Comparison (Regression Slope and Intercept) of a Transfer Standard to a Primary O₃ Standard

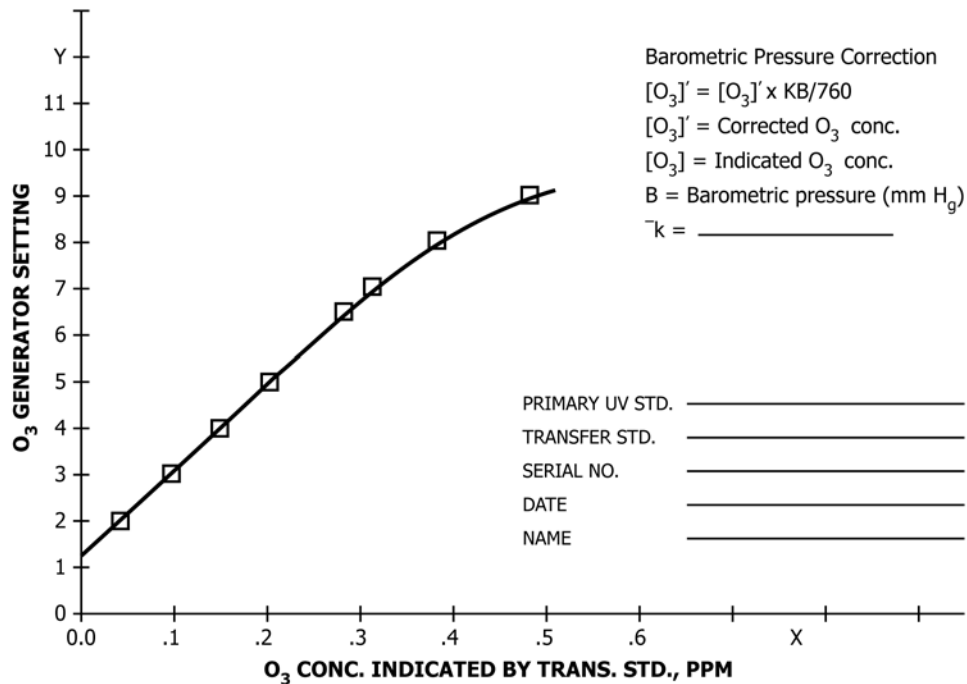


FIG. 8 Example of a Preliminary Calibration Relationship for an Adjustable O₃ Device

variability before the transfer standard may be certified. (Excessive variability in the UV primary standard is possible, although much less likely.)

11.2.6 If the specifications are met, the certification relationship for the transfer standard consists of the average slope (m_{AVG}) average intercept (I_{AVG}) and may be plotted as shown in Fig. 9. Note the qualification restrictions shall also be included with the certification relationship and shall be shown

on a plot of the certification relationship as shown in Fig. 9. When the transfer standard is subsequently used, the standard O₃ concentration is calculated as shown in A1.3.6.

11.3 *Transfer Standards Having a Defined Dependence on Some Variable*—Certification of transfer standards having a defined relationship on a variable such as barometric pressure or temperature is complicated by the need to take the variable

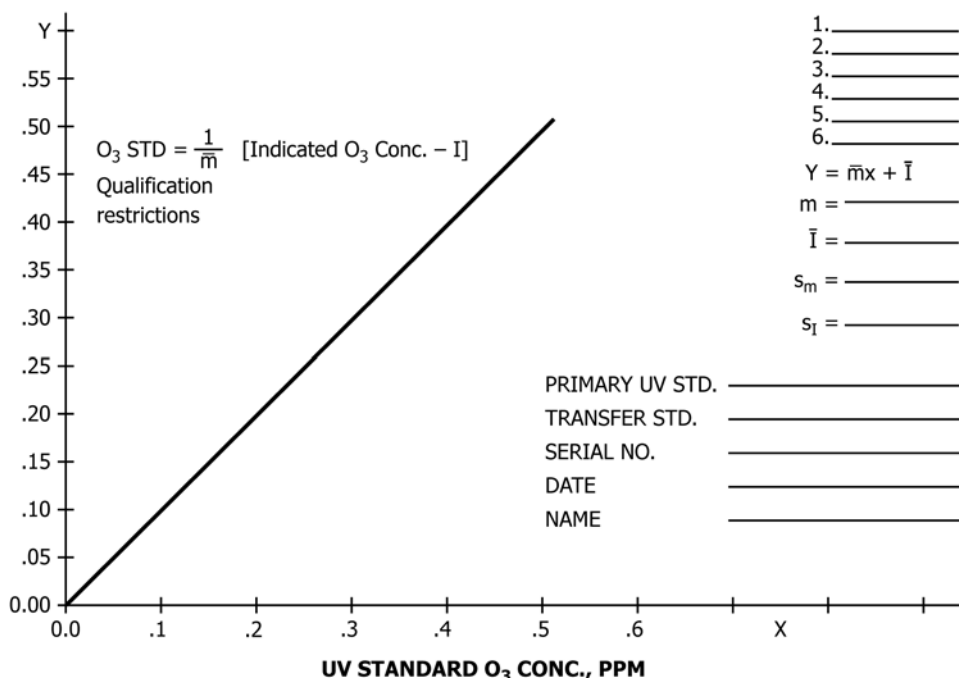


FIG. 9 Example of a Transfer Standard Certification Relationship (Average of 6 Comparisons)

into account. During certification, the variable must be measured accurately, ideally with the same measuring instrument that will be used during subsequent use of the transfer standard. A correction for effects of the variable must then be included, by way of the preliminary calibration, during the certification comparisons. The final certification relationship must also clearly identify the applicable calibration and correction associated with the transfer standard.

11.3.1 If the effect of the variable is limited to the measurement of the gaseous flow rates, the appropriate corrections shall be applied to the flowrates during the certification comparisons, and an ordinary comparison similar to Fig. 7 or Fig. 8 will result. Where a simple linear dependence on a variable exists, a suitable reference level shall be defined (for example, 101.3 kPa or barometric pressure); then the appropriate mathematical correction to correct the output from the reference level to any other level within a reasonable range shall be specified. An *inverse* correction is applied to the transfer standard output during establishment of the preliminary calibration curve (see Fig. 8) to normalize the output to the reference level. The preliminary calibration relationship is then plotted with the normalized data.

11.3.2 Other approaches may also be used. For example, if the linearity of the transfer standard is not affected by the variable, then the certification relationship can include a “correction factor” relationship as shown in Fig. 6 and Fig. 10. Such correction factor relationships may be determined either by changing the variable during the preliminary calibrations, or by calculation based on data obtained during qualification tests. Another technique is to use a preliminary calibration consisting of a family of curves, as shown in Fig. 11. Here, interpolation

may be used to obtain the defined O₃ concentrations at values of the variable falling between the lines.

11.3.3 In any case, the technique used shall be completely described in writing, verified to make sure it is accurate, and clearly understood by all users of the transfer standard.

11.4 *Use*—After certification, when the transfer standard is used to reproduce O₃ standards, the certification relationship (such as illustrated in Fig. 9) shall be used to determine the certified O₃ concentration from the concentration defined by assay or variable setting. In using transfer standards, it is good practice to try to minimize any changes in variables even though the transfer standard may be insensitive to them. This insensitivity is particularly true of transfer standards where there are numerous variables that may not have been included in qualification tests. Special effort shall be made to use the same standards, reagents, apparatus, technique, etc. to the greatest possible extent during certification and use. Of course, for any transfer standard which has a defined relationship to some variable, that variable shall be accurately measured and the output of the transfer standard corrected.

11.5 *Traceability*—Ozone standards obtained from a transfer standard will always be somewhat less accurate than primary O₃ standards because of the inevitable variability in the certification process. Consequently, it is good practice to always certify a transfer standard directly against primary O₃ standards obtained by the UV calibration procedure. See Practice D5110. Certification of a transfer standard against another transfer standard is discouraged, but could be appropriate for some limited purposes if the variability of both

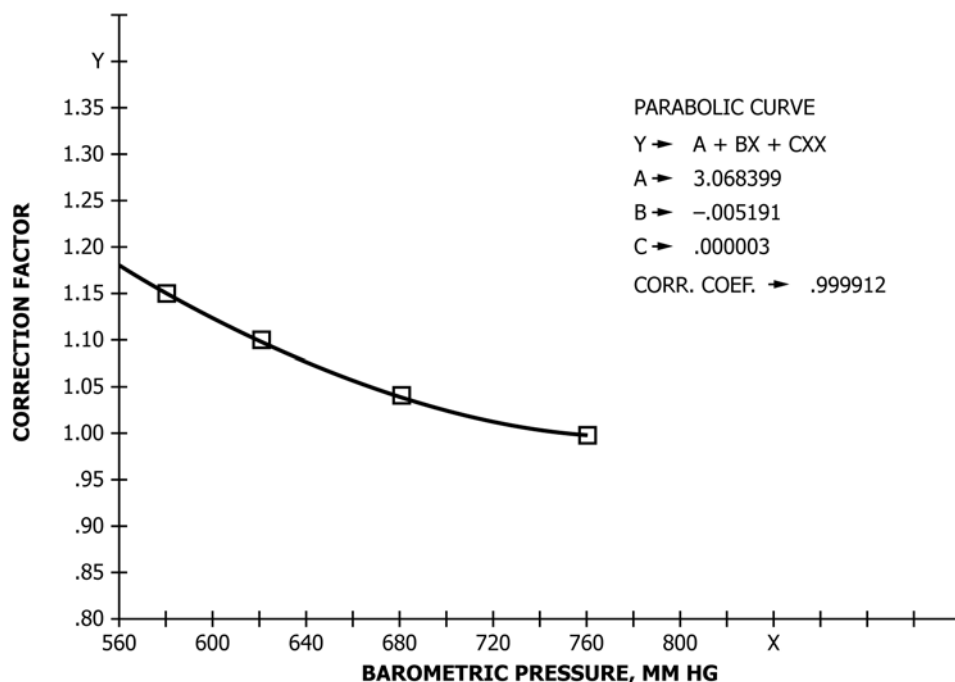


FIG. 10 Example of a Defined Barometric Pressure Dependence

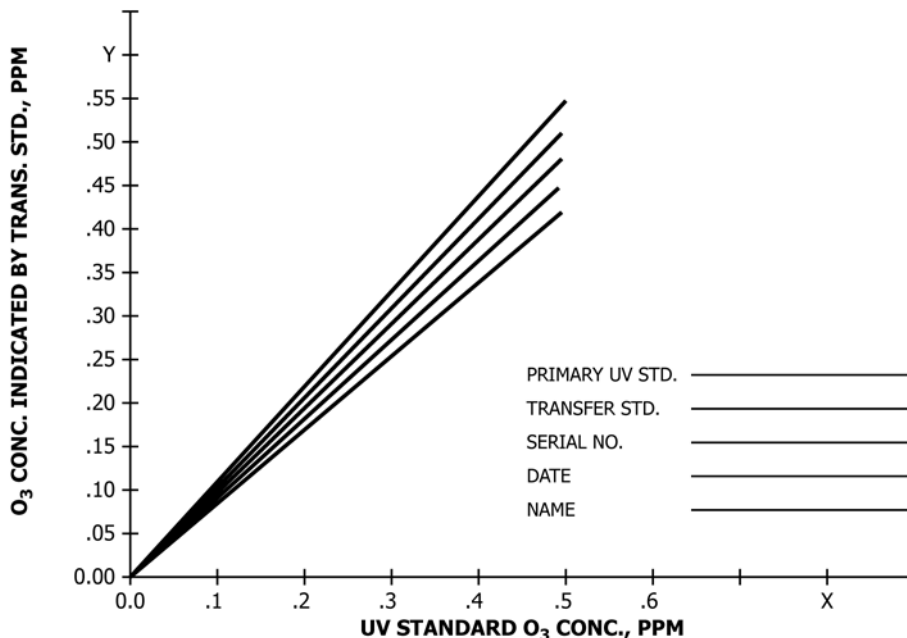


FIG. 11 A "Family" of Preliminary Calibration Curves

transfer standards is very low. The use of more than one intermediate transfer standard shall be avoided.

12. Recertification

12.1 While the accuracy of a transfer standard is established during certification, the confidence in that accuracy is maintained by continual reverification to demonstrate stability. The objective is to show, to the greatest extent possible, that the

transfer standard does not change between certification and use. However, if the UV primary standard is located in a laboratory, the recertification process may always occur under nearly identical conditions (temperature, line voltage, barometric pressure, etc.). Therefore, occasional repetition of the qualification tests is an important supplement to recertification.

12.1.1 The procedures and specifications are described in the Annexes, but are explained in more detail below.

12.2 Procedure for Recertification—A certified transfer standard shall be recertified at least twice per calendar quarter to maintain continuous certification. A transfer standard which loses its certification may cause the loss of ambient O₃ measurements made with the ambient monitors that were calibrated with the transfer standard. Consequently, a more frequent recertification schedule will reduce the magnitude and risk of such loss. More frequent recertification may also provide better accuracy, particularly for transfer standards that show slow but steady drift over long periods of time.

12.2.1 The first step in the recertification procedure is to carry out a comparison to a UV primary standard, as described in A1.3.2 (see Fig. 7).

12.2.2 The linear regression slope of the new comparison (m) shall be between $\pm 5\%$ of the average slope (m_{AVG}) current certification relationship (that is, the average slope of the last six comparisons) to maintain certification. Thus, m shall be within the interval $0.95 m_{AVG} \leq m \leq 1.05 m_{AVG}$. A more convenient way to monitor the performance of a transfer standard is to plot each new slope on a chart format as shown in Fig. 12.

12.2.3 If the new slope is within the $\pm 5\%$ specification, then a new average slope (m_{AVG}) and a new average intercept (I_{AVG}) are calculated using the new comparison and the five most recent comparisons. Thus the average slope and intercept are running averages always based on the five most recent previous comparisons. The new average slope and the new $\pm 5\%$ limits can also be plotted on the chart as shown in Fig. 12.

12.2.4 New values for the relative standard deviation of the slopes (s_m) and the quantity (s_I) are calculated based on the new comparison and the five most recent previous comparisons, as shown in A1.3.4. These parameters can also be monitored with a chart format shown in Fig. 13.

12.2.5 The new s_m and s_I must again meet the respective 3.7% and 1.5% specifications given in A1.3.5. If all specifications are met, then a new certification relationship (based on the updated average slope (m_{AVG}) and average intercept (I_{AVG})) is established according to A1.3.6, and illustrated by Fig. 9.

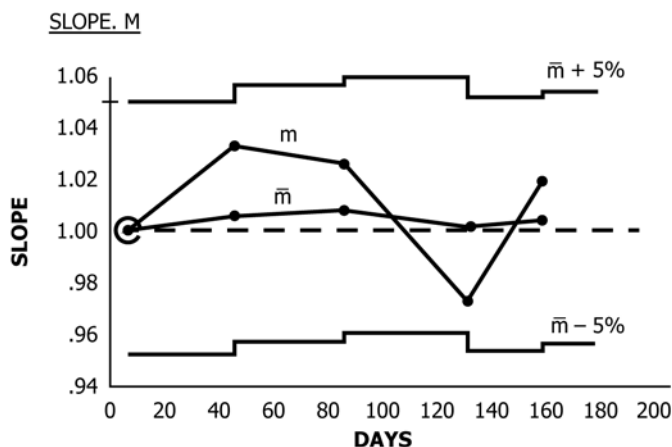


FIG. 12 Example of a Chart Showing Recertification Slope Data for a Transfer Standard

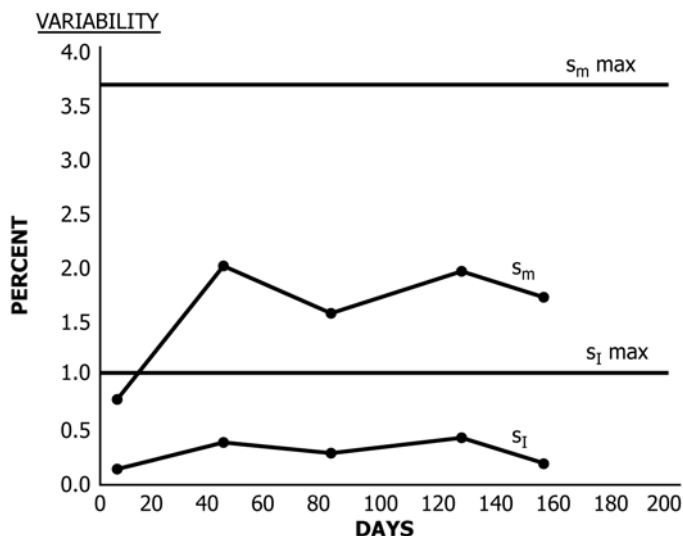


FIG. 13 Example of a Chart showing Recertification Variability of Slope and Intercept for a Transfer Standard

12.2.6 If a certified transfer standard fails to meet one of the recertification specifications, it loses its certification. Recertification then requires six new comparisons according to the entire certification procedure, starting at A1.3.1. This failure could be due to malfunction, which obviously must be corrected before repeating the certification procedure. If a transfer standard has been repaired or serviced in a way which could affect its output, the complete certification procedure must also be repeated. Another possible cause for failure of the recertification specifications might be a change in the preliminary calibration (Fig. 8), which shall then be reestablished before the certification is repeated.

12.3 Cross Checks—Frequently, an assay-type transfer standard (Methods B, C, or D) is used with an O₃ generator for which a preliminary calibration such as shown in Fig. 8 is available (even though the O₃ generator is not certified as a transfer standard). In which case, any large discrepancy between the two could serve as a warning that the transfer standard may require recertification.

12.4 Recertification Tests—Normally the characteristics of a transfer standard would not be expected to change profoundly or suddenly. For example, a transfer standard that is not initially sensitive to line voltage changes is not likely to become so after a period of use. However, malfunctions are a major exception: malfunctions in line voltage regulation or temperature regulation, or any other variable control components can easily render a transfer standard sensitive to a variable at any time. Furthermore, the malfunction may not be obvious to the operator, and could go undetected for some time. Even a recertification may not disclose such a malfunction. In consequence, some of the qualification tests shall be repeated on some periodic basis, depending on the system quality assurance plan. Such tests may be more cursory than the original tests, but are nevertheless important. Other techniques include warning lights or operation indicators on components that are critical to regulatory functions and that

might otherwise provide no indication of malfunction. A user should always be somewhat skeptical that a transfer standard is operating properly.

13. Keywords

13.1 boric acid titration; gas phase titration; ozone; primary standard; transfer standard

ANNEXES

(Mandatory Information)

A1. SPECIFICATION FOR OZONE TRANSFER STANDARDS

A1.1 **Documentation**—The following comprehensive documentation of an O₃ transfer standard is required:

A1.1.1 A complete listing and description of all equipment, materials, and supplies necessary or incidental to the use of the transfer standard.

A1.1.2 A complete and detailed operational procedure for using the transfer standard, including all operational steps, specifications, quality control checks.

A1.1.3 Test data, rationale, evidence, and other information confirming the transfer standard meets the qualification requirements.

A1.1.4 The current certification relationship (slope and intercept) as described in A1.3.6 and applicable to current use of the transfer standard, with any other corrections or restrictions in the operating conditions (temperature, line voltage, barometric pressure, etc.).

A1.1.5 A logbook including a complete chronological record of all certification and recertification data, as well as all O₃ monitor calibrations conducted with the transfer standard.

A1.2 **Qualification**—An O₃ transfer standard shall meet the following general requirements for qualification:

A1.2.1 The transfer standard output shall not vary by more than ±4 % or ±4 ppb (whichever is greater) from its stated value over a designated range of any of the conditions to which it might be sensitive. Documentation of conformance to this requirement shall be provided as shown in A1.1.

A1.3 **Certification**—Prior to use, an O₃ transfer standard shall be certified by establishing a quantitative certification relationship between the transfer standard and the primary O₃ concentrations. The certification procedure is as follows (see Practice D5110):

A1.3.1 The certification relationship shall consist of the average of 6 individual comparisons of the transfer standard to the primary O₃ standard system. Each comparison shall be performed on a different day.

A1.3.2 Each comparison shall consist of at least six comparison points at concentrations evenly spaced over the concentration range of the transfer standard, including zero and

(90 ± 5 %) of the URL. For the six or more comparison points of each comparison, compute the slope and intercept by the least squares regression of the transfer standard output (either a generated O₃ concentration or a concentration assay) and the UV primary O₃ standard.

A1.3.3 For the 6 comparisons, compute the average slope (m_{avg}) as follows:

$$m_{\text{avg}} = 1/6 \sum_{i=1}^6 m_i \quad (\text{A1.1})$$

and the average intercept (I_{avg}):

$$I_{\text{avg}} = 1/6 \sum_{i=1}^6 I_i \quad (\text{A1.2})$$

where m_i and I_i are the individual slopes and intercepts, respectively, of each comparison regression.

A1.3.4 Compute the relative standard deviation of the 6 slopes, (s_m):

$$s_m = \frac{100}{m_{\text{avg}}} \sqrt{\frac{1}{5} \left[\sum_{i=1}^6 (m_i)^2 - \frac{1}{6} \left(\sum_{i=1}^6 m_i \right)^2 \right]} \% \quad (\text{A1.3})$$

and the quantity s_I for the 6 intercepts:

$$s_I = \frac{100}{I_{\text{avg}}} \sqrt{\frac{1}{5} \left[\sum_{i=1}^6 (I_i)^2 - \frac{1}{6} \left(\sum_{i=1}^6 I_i \right)^2 \right]} \% \quad (\text{A1.4})$$

A1.3.5 The value of s_m shall be ≤3.7 %, and s_I shall be ≤1.5 %.

A1.3.6 If the transfer standards meets the specifications of A1.3.5, compute the certification relationship:

$$\text{Std. O}_3 \text{ conc.} = 1/m_{\text{avg}} (\text{Indicated O}_3 \text{ conc.} - I_{\text{avg}}). \quad (\text{A1.5})$$

A1.4 Recertification

A1.4.1 O₃ transfer standards shall be recertified as follows to maintain continuous certification as follows. In general, O₃ transfer standards shall be recertified at least twice per calendar quarter; a transfer standard which remains at a fixed monitoring site may be recertified only once per quarter if it is sufficiently stable to avoid loss of certification over that time period (See A1.4.6).

A1.4.2 Carry out a comparison of the transfer standard to the UV primary standard at the time of certification as prescribed in A1.3.2.

A1.4.3 The slope of the new comparison shall be within the interval $m_{avg} \pm 0.05 m_{avg}$.

A1.4.4 Compute a new m_{avg} and a new I_{avg} as prescribed in A1.3.3, using the 6 most recent comparisons (running averages) if the transfer standard meets the specifications in A1.4.2.

A1.4.5 Compute a new s_m and s_I as prescribed in A1.3.4, using the 6 most recent comparisons.

A1.4.6 Compute a new certification relationship as shown in A1.3.6, using the updated m_{avg} and I_{avg} if the new s_m and s_I meet the specifications given in A1.3.5.

A1.4.7 If the transfer standard fails its certification, repeat all the certification steps (A1.3 – A1.3.6).

A1.5 Transfer Standards Having Fewer Than Five Discrete Outputs

A1.5.1 Generation-type transfer standards having discrete or fixed outputs that are too few in number to meet the requirements of A1.3.2 shall be certified as defined in A1.5.1.1 or A1.5.1.2.

A1.5.1.1 Any calibrated transfer standard must incorporate an integral dilution system to provide capability for at least six calibration concentrations (including zero). The complete transfer standard system, including the dilution system, shall then be certified as specified in A1.3 and A1.4.

A1.5.1.2 Any transfer standard used for purposes other than calibration where discrete outputs are acceptable (for example, audits, span checks), may be certified at each discrete output by substituting single point comparison, d_i , for the slopes m_i , and ignoring all steps pertaining to intercepts. Calculate d_{avg} :

$$d_{avg} = 1/6 \sum_{i=1}^6 d_i, \tag{A1.6}$$

and s_d :

$$s_d = \frac{100}{d_{avg}} \sqrt{\frac{1}{5} \left[\sum_{i=1}^6 (d_i)^2 - \frac{1}{6} \left(\sum_{i=1}^6 d_i \right)^2 \right]} \% \tag{A1.7}$$

If s_d is $\leq 3.7\%$, compute the certified discrete output as:

$$\text{Std. O}_3 \text{ conc.} = 1/d_{avg} (\text{Indicated O}_3 \text{ conc.}). \tag{A1.8}$$

Recertification shall be carried out similarly.

A2. CERTIFICATION OF THE BORIC ACID POTASSIUM IODIDE PROCEDURE AS A TRANSFER STANDARD

A2.1 Assemble an O₃ generation system such as shown in Fig. A2.1.

A2.2 Assemble the KI sampling train as shown in Fig. 3. All connections between the various components shall be leak tight, and shall be made using grease-free ball joint fittings,

heat shrinkable TFE-fluorocarbon tubing or TFE-fluorocarbon tube fittings. The connections to the O₃ output manifold shall be made with 6 mm (1/4 in.) TFE-fluorocarbon tubing, not to exceed 1.5 meters in length.

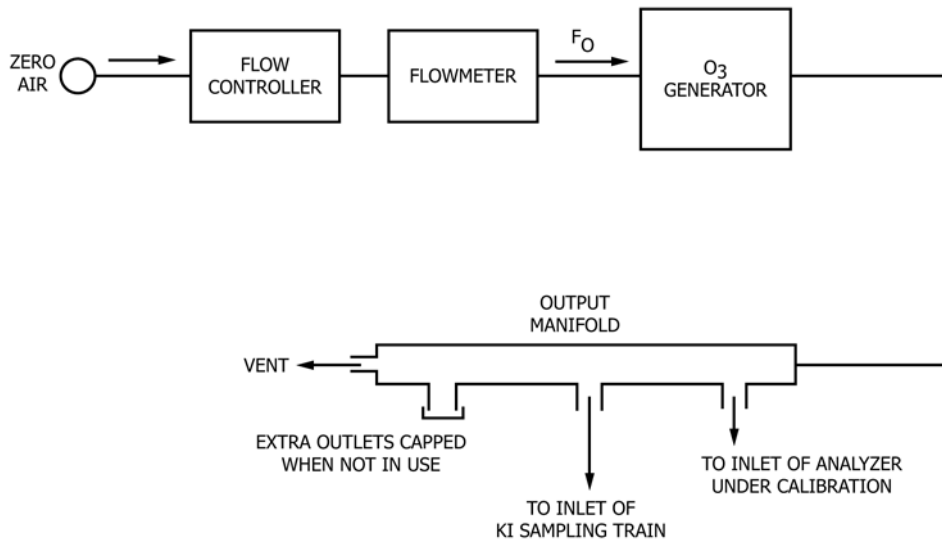


FIG. A2.1 Schematic Diagram of a Typical BAKI Calibration System

A2.3 Calibrate all flowmeters and critical orifices under the conditions of use to standards traceable to the NBS (See Practice [D3195](#) and Test Methods [D1071](#)). Correct all volumetric flowrates to 25°C and 101.3 kPa (1 atm) as follows:

$$F_R = F_S \frac{P_S - P_{H_2O}}{101.3} \frac{298}{T_s + 273} \quad (\text{A2.1})$$

A2.4 Potassium Iodide Calibration Curve

A2.4.1 Prepare iodine standards, fresh when required, as described in [7.2.11](#).

A2.4.2 Determine the absorbance of each I_2 standard at 352 nm. Measure the absorbance of a sample of unexposed absorbing reagent ([7.2.3](#)). Determine the net absorbance of each I_2 standard as:

$$\text{Net absorbance} = \text{sample absorbance} \quad (\text{A2.2})$$

– unexposed absorbing reagent.

A2.4.3 For each I_2 standard, calculate the net absorbance/cm as:

$$\text{Net absorbance/cm} = \text{net absorbance/b} \quad (\text{A2.3})$$

A2.4.4 For each I_2 standard, calculate the I_2 concentration in mol/L, as follows:

$$[I_2]_i = N_{KIO_3} \times V_i \times 10^{-5} \quad (\text{A2.4})$$

A2.4.5 Plot net absorbance/cm (y-axis) versus the mol I_2 (x-axis) for each I_2 standard, and determine the KI calibration curve, using the method of least squares. Calculate the slope of the curve in $\text{L/mol}^{-1}\text{cm}^{-1}$, and record it as S_c . The value of the slope shall be $26\,000 \pm 780$. If the slope is not within this range, and the photometric accuracy of the spectrophotometer meets the specifications given in [6.4.3](#), repeat the procedure using freshly prepared I_2 standards. If the slope is still not within the specified range, repeat the procedure using a different lot of certified 0.1 N KIO_3 to prepare the I_2 standards.

NOTE A2.1—Preparation of a new KI calibration curve may not be necessary each time the BAKI procedure is used, if adequate repeatability can be established with less frequent KI calibration.

A2.5 Calibration of the O_3 Generator

A2.5.1 Adjust the air flow through the O_3 generator to the desired flowrate, and record it as F_O . At all times the air flow through the generator shall be greater than the total flow required by the sampling system, to assure exhaust flow at the vent.

A2.5.2 With the O_3 generator off, flush the system with zero air for at least 15 min to remove residual O_3 . Pipet 10 mL of absorbing reagent ([7.2.3](#)) into each of two impingers, and connect them into the sampling train, as shown in [Fig. 3](#). Draw air from the output manifold of the O_3 calibration system through the sampling train at 0.4 to 0.6 L/min for 10 min. Immediately transfer the exposed solutions to clean spectrophotometer cells. Determine the net absorbance (sample – unexposed reagent) of each solution, at 352 nm, within 3 min. Add the net absorbance of the two solutions to obtain the total net absorbance. Calculate the indicated O_3 concentration (system blank) as equivalent O_3 concentration according to [A2.5.4](#).

If the system blank is greater than 0.005 ppm O_3 , continue flushing the O_3 generator system for an additional 30 minutes, and then redetermine the system blank. If the system blank is still greater than 0.005 ppm O_3 , the zero air probably contains traces of an oxidizing contaminant, and the activated charcoal and molecular sieve (see [7.1.1](#)) shall be replaced.

A2.5.3 Adjust the O_3 generator to generate an O_3 concentration in the range of interest, and allow the system to equilibrate for about 15 min. The uncalibrated O_3 monitor to be calibrated can conveniently be used to indicate the stability of the O_3 generator output. When the O_3 generator output has become stabilized, pipet 10 mL of absorbing reagent ([7.2.3](#)) into each impinger. Draw O_3 from the output manifold of the O_3 calibration system through the sampling train at 0.4 to 0.6 L/min. Use a sample time of between 10 and 30 min so that a total net absorbance of between 0.1 and 1.0 absorbance units is obtained. (At an O_3 concentration of 0.1 ppm and a sampling rate of 0.5 L/min, a total net absorbance of 0.1 absorbance units should be obtained if a sampling time of 20 min and 10-mm spectrophotometer cells are used.) Immediately after collection, transfer the exposed solutions to clean spectrophotometer cells. Determine the net absorbance (sample – unexposed reagent) for each solution, at 352 nm, within 3 min. Add the net absorbance of the two solutions to obtain the total net absorbance.

A2.5.4 Calculation of Indicated O_3 Concentration

A2.5.4.1 Calculate the total volume of air sampled, corrected to 25°C and 101.3 kPa (1 atm) as follows:

$$V_R = F_R \times t_s \quad (\text{A2.5})$$

A2.5.4.2 Calculate the I_2 released, in moles, as:

$$\text{mole } I_2 = \frac{\text{total net absorbance}}{S_c \times b} \times 0.01 \quad (\text{A2.6})$$

where:

total net absorbance = sum of net absorbance for the 2 solutions,
0.01 = volume of absorbing reagent in each impinger, L.

A2.5.4.3 Calculate the volume of O_3 absorbed in μL :

$$V_{O_3} = \text{mol } I_2 \times 24.47 \times 10^6 \quad (\text{A2.7})$$

A2.5.4.4 Calculate the indicated O_3 concentration in ppm as:

$$[O_3]_{OUT} = \frac{V_{O_3}}{V_R} 10^{-3} \quad (\text{A2.8})$$

A2.5.4.5 Repeat steps [A2.5.3](#) and [A2.5.4](#) at least one more time at the same O_3 generator setting. Average the determinations, and record the average and the O_3 generator setting.

A2.5.4.6 Adjust the O_3 generator to obtain a minimum of five other O_3 concentrations over the desired range. Determine each indicated O_3 concentration as above. Plot the indicated O_3 concentrations versus the corresponding O_3 generator settings, and determine the calibration curve, using the method of least squares.

A2.6 Certification as a Transfer Standard

A2.6.1 Carry out qualification tests as described in Section 10.

A2.6.2 Certify the procedure against a primary O₃ standard as described in Sections 9 – 12. See Practice D5110. Prepare a certification relationship curve relating indicated O₃ concentrations to the primary standard O₃ concentrations, similar to Fig. 9.

A2.6.3 Recertify the procedure as appropriate in accordance with Sections 9 – 11.

A2.7 Calibration of the O₃ Monitor

A2.7.1 Allow sufficient time for the O₃ monitor to warm up and stabilize.

A2.7.2 Allow the O₃ monitor to sample zero air until a stable response is obtained, and adjust the zero control to + 5 % of scale. Record the zero air response as Z.

A2.7.3 Using the O₃ generator, the same F_O, the same O₃ generator calibration curve, and the certification relationship obtained in A2.6.2, generate a certified O₃ concentration near 80 % of the URL of the O₃ monitor.

A2.7.4 Allow the O₃ monitor to sample this O₃ concentration until a stable response is obtained. Adjust the monitor span control to obtain a convenient recorder response as noted below:

$$\text{Recorder response (\% scale)} = \frac{([O_3]_{CERT} \times 100)}{URL} + Z \quad (A2.9)$$

Record the certified O₃ concentration and the monitor response. If substantial adjustment of the span control is

necessary, recheck the zero and span adjustments by repeating steps A2.7.1 through A2.7.4.

A2.7.5 Generate several other O₃ concentrations (at least five) over the range of the O₃ monitor by adjusting the O₃ generator settings (preferably the same settings used in A2.5.4.5 or by A2.7.7). For each O₃ concentration, allow for a stable monitor response, then record the response and the corresponding certified O₃ concentration from the certification relationship.

A2.7.6 Plot the O₃ monitor response versus the corresponding certified O₃ concentrations, and develop the calibration curve using the method of least squares.

A2.7.7 *Optional Method*—The various O₃ concentrations required in A2.6.5 may be obtained by dilution of the certified O₃ concentration generated in A2.6. With this option, accurate flowrate measurements are required. The dynamic calibration system shall be modified as shown in Fig. 4 to allow for dilution air to be metered in downstream of the O₃ generator. A mixing chamber between the O₃ generator and the output manifold is also required. The flowrate through the O₃ generator (F_O) and the dilution air flowrate (F_D) are measured with flowmeters traceable to NBS. The highest O₃ concentration standard (80 % URL) is assayed according to A2.4. Each dilution O₃ concentration is calculated from:

$$[O_3]_{CERT}' = [O_3]_{CERT} \times \frac{F_O}{F_O + F_D} \quad (A2.10)$$

NOTE A2.2—Direct calibration of the O₃ generator may also be accomplished by assaying the O₃ concentrations using the procedure in A2.4 while simultaneously measuring the corresponding O₃ monitor responses as described in A2.6.

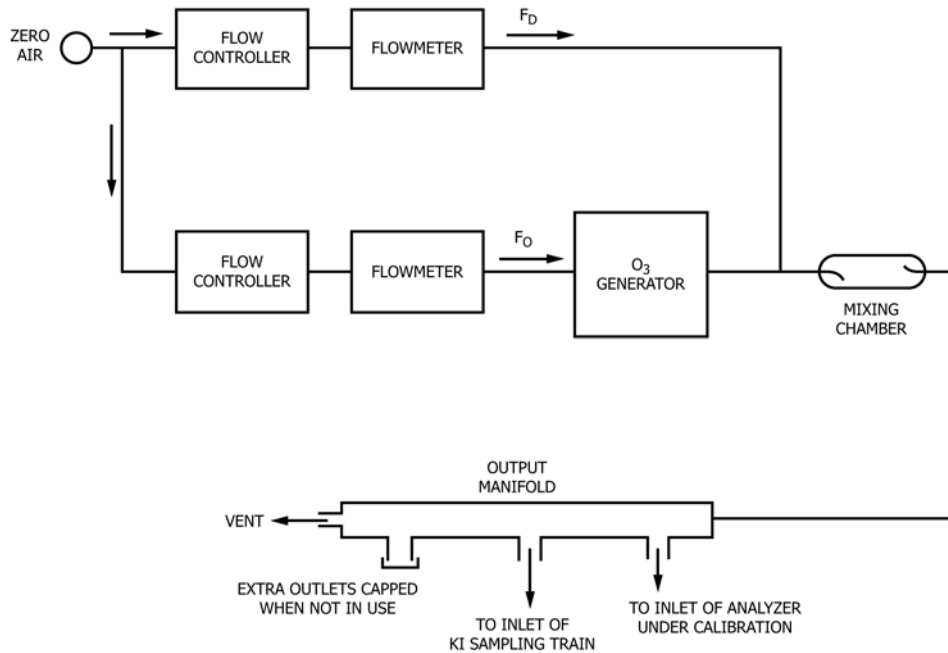


FIG. A2.2 Schematic Diagram of a Typical BAKI Calibration System (Option 1)

A3. CERTIFICATION OF THE GAS PHASE TITRATION WITH EXCESS NITRIC OXIDE PROCEDURE AS A TRANSFER STANDARD

A3.1 Dynamic Parameter Specifications

A3.1.1 The residence time (t_R) in the reaction chamber and the gas flows (F_O and F_{NO}) must be adjusted according to the following:

$$P_R = t_R[NO]_{RC} \geq 3.75 \text{ ppm} \cdot \text{min} \quad (\text{A3.1})$$

$$[NO]_{RC} = [NO]_{STD} \frac{F_{NO}}{F_O + F_{NO}} \quad (\text{A3.2})$$

$$t_R = \frac{V_{RC}}{F_O + F_{NO}} < 2 \text{ min} \quad (\text{A3.3})$$

A3.1.2 These parameters shall be selected as follows:

A3.1.2.1 Determine F_T , the total flow required at the output manifold ($F_T = \text{monitor(s) demand plus 10 to 50 \% excess}$).

A3.1.2.2 Establish $[NO]_{out}$ as the highest NO concentration (ppm) which will be required at the output manifold. $[NO]_{OUT}$ shall be approximately equivalent to 90 % of the URL of the O_3 concentration to be determined.

A3.1.2.3 Determine F_{NO} as:

$$F_{NO} = \frac{[NO]_{OUT}}{[NO]_{STD}} \times F_T \quad (\text{A3.4})$$

A3.1.2.4 Select a convenient or available reaction chamber volume. Initially, a trial V_{RC} may be selected in the range of approximately 200 to 500 mL.

A3.1.2.5 Compute F_O as:

$$F_O = \sqrt{\frac{([NO]_{STD} \times F_{NO} \times V_{RC})}{3.75}} - F_{NO} \quad (\text{A3.5})$$

A3.1.2.6 Compute t_R as:

$$t_R = \frac{V_{RC}}{F_O + F_{NO}} \quad (\text{A3.6})$$

Verify that $t_R > 2$ min. If not, select a reaction chamber with a smaller V_{RC} .

A3.1.2.7 Compute F_D as:

$$F_D = F_T - F_O - F_{NO} \quad (\text{A3.7})$$

A3.1.2.8 If F_O is impractical for the desired system, select a reaction chamber with a different V_{RC} and recompute F_O and F_D . For a more detailed discussion of these requirements, and other related considerations, as well as sample calculations, see Ellis (5).

A3.2 Procedure

A3.2.1 Assemble a dynamic transfer standard system such as shown in Fig. 2.

A3.2.2 Establish the dynamic parameters as shown in A3.1.

A3.2.3 Insure that all flowmeters are calibrated. (See Practice D3195 or Test Methods D1071.) All volumetric flowrates shall be corrected to 25°C and 101.3 kPa (1 atm).

A3.2.4 Care shall be taken to remove O_2 and other contaminants from the NO pressure regulator and delivery system prior to the start of the calibration to avoid any conversion of standard NO to NO_2 . (**Warning**—Failure to do so will cause significant errors in the calibration.)

This may be minimized by (1) carefully evacuating the regulator after it has been connected to the cylinder and before opening the cylinder valve, using the purge port; (2) thoroughly flushing the regulator and delivery system with NO after opening the cylinder valve; and (3) not removing the regulator from the cylinder between calibrations unless necessary.

A3.2.5 Adjust the diluent air and O₃ generator air flows to obtain the flows determined in A3.1.2. The total air flow shall exceed the total demand of the monitor(s) or any UV certification photometer connected to the output manifold to insure that no ambient air is pulled into the manifold vent. Record F_O , F_D , and F_{NO} used during certification and use approximately the same values during field use.

A3.3 Calibration of the NO Monitor

A3.3.1 Allow sufficient time for the NO monitor to warm up and stabilize.

A3.3.2 Allow the NO monitor to sample zero air until a stable NO response is obtained, and make the necessary zero control adjustments.

A3.3.3 Adjust F_{NO} to obtain an NO output concentration of approximately 80 % of the URL of the NO range. The exact concentration is calculated from:

$$[NO]_{OUT} = \frac{F_{NO} \times [NO]_{STD}}{F_{NO} + F_O + F_D} \quad (A3.8)$$

Sample this NO concentration until the NO monitor response has stabilized. Adjust the NO span control to obtain a convenient recorder response as indicated below:

$$\text{Recorder response (\% scale)} = \frac{[NO]_{OUT}}{URL} \times 100 \quad (A3.9)$$

Record the NO concentration and the monitor response. The NO monitor shall be spanned to the same value as that of the O₃ monitor to be calibrated. If subsequent adjustments of the span control are required, recheck the zero and span controls by repeating steps A3.3.2 and A3.3.3.

A3.3.4 Generate several additional NO concentrations (at least 5) by decreasing F_{NO} or increasing F_D . For each NO concentration, calculate the exact NO concentration as described in A3.3.3 and record the monitor response. Plot the monitor response versus the calculated NO concentration, and develop the NO calibration curve, using the method of least squares. This plot should be linear. For subsequent calibrations, this curve may be verified with a two-point calibration.

A3.4 Calibration of the O₃ Generator

A3.4.1 Adjust F_O , F_{NO} , and F_D as determined in A3.1.2 and used in A3.2.5; generate an NO concentration near 90 % of the URL of the NO range. Using the NO monitor and calibration curve obtained in A3.3.4, measure and record this NO concentration as $[NO]_{ORIG}$.

A3.4.2 Adjust the O₃ generator to generate sufficient O₃ to produce a decrease in NO concentration equivalent to approximately 80 % of the URL. The O₃ concentration shall not exceed 90 % of the available NO concentration.

A3.4.3 Calculate the indicated O₃ concentration as:

$$[O_3]_{OUT} = ([NO]_{ORIG} - [NO]_{REM}) \times \frac{(F_O + F_{NO} + F_D)}{F_O + F_D} \quad (A3.10)$$

Record $[O_3]_{OUT}$ and the corresponding generator settings.

A3.4.4 Adjust the O₃ generator settings to obtain other O₃ concentrations over the desired range, and calculate the indicated O₃ concentrations as shown in A3.4.3. At least five O₃ concentrations are required. Plot the indicated concentrations versus the O₃ generator settings, and define the calibration curve, using the method of least squares. Record the O₃ generator settings used during certification, and use approximately the same settings during field use. The O₃ generator calibration curve should replicate fairly closely each time the transfer standard is used; substantial deviations may indicate a problem with the transfer standard.

A3.5 Certification as a Transfer Standard

A3.5.1 Carry out appropriate qualification tests as discussed in Section 10.

A3.5.2 Certify the procedure against the primary UV O₃ standard. See Practice D5110.

Prepare a certification relationship curve relating indicated O₃ concentrations to the primary O₃ standard concentrations, similar to Fig. 9.

A3.5.3 Recertify the procedure as appropriate in accordance with A3.2 and A3.3.

A3.6 Calibration of the O₃ Monitor

A3.6.1 Allow sufficient time for the O₃ monitor to warm-up and stabilize.

A3.6.2 Allow the O₃ monitor to sample zero air until a stable response is obtained, and adjust the O₃ monitor's zero control to read + 5 % of scale to facilitate observing negative drift. Record the stable zero air response as "Z."

A3.6.3 Using the O₃ generator as calibrated in A3.4, generate a certified concentration near 80 % of the URL of the O₃ monitor. F_O , F_D , F_{NO} , and the O₃ generator settings shall be as close as possible to their values used during certification. Use the O₃ generator calibration curve and the certification relationship curve from A3.5.2 to establish the certified concentration, $[O_3]_{CERT}$.

A3.6.4 Allow the O₃ monitor to sample this O₃ concentration until a stable response is obtained. Adjust the monitor's span control to obtain a convenient recorder response as shown by:

$$\text{Recorder response (\% scale)} = \frac{([O_3]_{CERT} \times 100)}{URL} + Z \quad (A3.11)$$

Record the certified O₃ concentration and the monitor response. If substantial adjustment of the span control (more than ±15 %) is necessary, recheck the zero and span adjustments by repeating steps A3.5.1 – A3.5.3.

A3.6.5 Generate several other O₃ concentrations (at least five) over the range of the O₃ monitor by adjusting the O₃ generator settings (preferably the same settings used in

A3.4.4). For each O₃ concentration, allow for a stable monitor response, then record the response and the corresponding O₃ certified O₃ concentration from the certification relationship.

A3.6.6 Plot the O₃ monitor response versus the corresponding certified O₃ concentrations, and develop the calibration curve using the method of least squares.

A3.7 Options

NOTE A3.1—**Warning:** If either of the options in A3.7 are elected, the same procedure must be used during qualification, certification, and field use.

A3.7.1 Option 1

A3.7.1.1 The various O₃ concentrations required in A3.6.5 may be obtained by dilution of the certified O₃ concentrations generated in A3.6.3. In this case, F_D is increased to various values to decrease the O₃ output concentration, which is calculated as:

$$[O_3]_{OUT}' = [O_3]_{OUT} \times \frac{F_O + F_D}{F_O + F_D'} \quad (\text{A3.12})$$

Since only one O₃ generator setting is used, the generator need be qualified at only that setting. $[O_3]_{OUT}$ may also be obtained from A3.4.3 and the certification relationship without actually calibrating the O₃ generator, if the settings are not changed from A3.4.2 and A3.4.3. Because F_D must be increased substantially to obtain low O₃ concentrations, the original F_D shall be as small as possible (consistent with A3.2.5).

A3.7.2 Option 2—

A3.7.2.1 The O₃ monitor may be calibrated “directly” by GPT-NO without intermediate calibration of the O₃ generator and without changing F_D . Under this option, the various O₃ concentrations required for calibration in A3.6.4 and A3.6.5 are obtained by adjusting the O₃ generator settings. For each such adjustment, the certified O₃ concentration is first established by GPT-NO using A3.4.3 and the certification relationship. Then the NO flow is diverted to allow the O₃ to be delivered to the output manifold and sampled by the O₃ monitor.

A4. CERTIFICATION OF THE GAS PHASE TITRATION WITH EXCESS OZONE PROCEDURE AS A TRANSFER STANDARD

A4.1 Dynamic Parameter Specifications

A4.1.1 Prior to qualification and certification of the apparatus and procedure, the residence time (t_R) in the reaction chamber, and the gas flows (F_O and F_{NO} , see Fig. 2) must be optimized. Initially, they shall be adjusted according to the following relationship:

$$PR = [O_3]_{RC} \times t_R = 2.0 \text{ ppm} - \text{min} \quad (\text{A4.1})$$

$$[O_3]_{RC} = [O_3]_{OUT} \times \frac{F_T}{F_O + F_{NO}} \quad (\text{A4.2})$$

$$t_R = \frac{V_{RC}}{F_O + F_{NO}} \quad (\text{A4.3})$$

A4.2 These parameters shall be selected as follows:

A4.2.1 Determine F_T , the total flow required at the output manifold (F_T equals output demand plus 10 to 50 % excess).

A4.2.2 Determine $[O_3]_{OUT}$ as the 80 % URL concentration required at the output manifold.

A4.2.3 Determine F_{NO} as:

$$F_{NO} = 0.8 \frac{[O_3]_{OUT}}{[NO]_{STD}} \times F_T \quad (\text{A4.4})$$

A4.2.4 Select a convenient or available reaction chamber volume. Initially, a trial V_{RC} may be selected in the range of approximately 300 to 1500 mL.

A4.2.5 Compute F_O as:

$$F_O = \sqrt{\frac{[O_3]_{OUT} \times F_T \times V_{RC}}{2}} \times F_{NO} \quad (\text{A4.5})$$

A4.2.6 Compute t_r as:

$$t_r = \frac{V_{RC}}{F_O + F_{NO}} \quad (\text{A4.6})$$

A4.2.7 Compute F_D as:

$$F_D = F_T - F_O - F_{NO} \quad (\text{A4.7})$$

A4.2.8 If F_O turns out to be impractical for the desired system, select a reaction chamber with a different V_{RC} and recompute F_O and F_D .

A4.2.9 Determine the final system flowrates as follows:

A4.2.9.1 Using the GPT-O₃ system and the gas flows determined above, generate an 80 % URL O₃ concentration as measured by the primary standard UV photometer. See Practice D5110. Measure this same O₃ concentration using the GPT-O₃ procedure (steps A4.3.6.1 – A4.3.6.6). Calculate the ratio of the two measurements, $[O_3]_{GPT}/[O_3]_{UV}$. For most GPT-O₃ systems, this ratio shall be between 0.95 and 1.15 when using a dynamic parameter specification of 2.0. (Most GPT-O₃ systems have a positive bias.) Ratios greater than 1.05 are indicative of incomplete NO reaction (which can be verified by using an NO monitor to detect any unreacted NO in the output). Ratios less than 1.05 are indicative of reaction of resultant NO₂ with residual O₃ (excessive residence time). When ratios outside this range are obtained or when a ratio close to 1.00 is desired, the gas flows shall be adjusted and new comparative measurements obtained. This procedure is most easily accomplished by varying F_O and F_D while maintaining F_{NO} and F_T constant. Decreasing F_O should decrease the comparative ratio; likewise increasing F_O should increase the ratio. Once an acceptable value (0.95 to 1.15) is obtained, record F_O , F_D , and F_{NO} . These flow conditions shall then be used during qualification, certification, and subsequent use of the GPT-O₃ procedure as a transfer standard. (**Warning**—The

$[O_3]_{GPT}/[O_3]_{UV}$ ratio can also be affected by an inaccurate NO cylinder standard, inaccurate flow measurements, leaks, and possibly other factors. These possible errors must be eliminated before the flows are adjusted based on that ratio. If possible, measurements with an NO/NO₂ monitor should be used to establish optimum flowrates to avoid both incomplete NO reaction and secondary reaction of NO₂ with O₃.

A4.3 Procedure

A4.3.1 Assemble a dynamic transfer standard system such as shown in Fig. 2.

A4.3.2 Establish the dynamic flow conditions as shown in A4.2.

A4.3.3 Ensure that all flowmeters are calibrated (see Practice D3195 or Test Methods D1071). All volumetric flowrates shall be corrected to 25°C and 101.3 kPa (1 atm).

A4.3.4 Care must be taken to remove O₂ and other contaminants from the NO pressure regulator and delivery system prior to the start of the calibration to avoid any conversion of standard NO to NO₂. Failure to do so will cause significant errors in the calibration. This may be minimized by (1) carefully evacuating the regulator after it has been connected to the cylinder and before opening the cylinder valve, using the purge port; (2) thoroughly flushing the regulator and delivery system with NO after opening the cylinder valve; and (3) not removing the regulator from the cylinder between calibrations unless necessary.

A4.3.5 Certification as a Transfer Standard

A4.3.5.1 Complete appropriate qualification tests as discussed in 10, using the indicated O₃ concentration ($[O_3]_{OUT}$) from A4.3.6.6 for the qualification tests.

A4.3.5.2 Certify the procedure against the primary UV O₃ standard. See Practice D5110. Prepare a certification relationship curve relating indicated O₃ concentrations ($[O_3]_{OUT}$ from A4.3.6.6) to the primary O₃ standard concentrations, similar to Fig. 8. Record the gas flowrates (F_O , F_D , and F_{NO}), and the O₃ generator setting required for the 80 % URL O₃ concentration.

A4.3.5.3 Recertify the procedure as appropriate in accordance with Section 9.

A4.3.6 Calibration of the O₃ Monitor

A4.3.6.1 Allow the O₃ monitor to warm-up and stabilize. Adjust the diluent air and O₃ generator air flows to the same values as used during certification. To ensure that no ambient air is pulled into the manifold vent, the total air flow must exceed the demand of the monitor under calibration and the UV certification photometer connected to the output manifold. Allow the O₃ monitor to sample zero air until a stable response is obtained and adjust the O₃ monitor's zero control to +5 % of scale to facilitate observing negative zero drift. Record the stable zero air response as "Z."

A4.3.6.2 Adjust the O₃ generator to deliver an O₃ concentration of approximately 80 % of the URL, using the same

generator setting as during certification. When the response has stabilized, record the response as I_O . If the monitor response is offscale, adjust the diluent air flow (F_D) until an onscale response is obtained, and record the new flow.

A4.3.6.3 Turn the NO flow on, and adjust to the same value as used during certification. Provided the O₃ generator output has not changed significantly, the O₃ monitor response should decrease by 75 to 80 % of its original value. When the resultant response has stabilized, record response as (I).

A4.3.6.4 Measure the NO flow, and record as F_{NO} .

A4.3.6.5 Calculate the exact NO concentration from:

$$[NO] = \frac{F_{NO} \times [NO]_{STD}}{F_{NO} + F_O + F_D} \quad (A4.8)$$

A4.3.6.6 Calculate the indicated O₃ concentration from:

$$[O_3]_{OUT} = \frac{I_O - Z}{(I_O - Z) \left(\frac{F_O + F_D}{F_{NO} + F_O + F_D} \right) - (I - Z)} \times [NO] \quad (A4.9)$$

A4.3.6.7 Remove the NO flow. The O₃ monitor response should return to its original value.

A4.3.6.8 Determine the certified O₃ concentration from the certification relationship obtained in A4.3.5.2 and adjust the O₃ monitor's span control to obtain a convenient recorder response as indicated below:

$$\text{Recorder response (\% scale)} = \frac{([O_3]_{CERT} \times 100)}{URL} + Z \quad (A4.10)$$

If substantial adjustment of the span control (more than ±15 %) is necessary, make the span adjustment and repeat steps A4.3.6.1 – A4.3.6.8. If F_D had to be adjusted to give an on-scale O₃ monitor response, readjust to the initial value prior to repeating these steps. After the final span adjustment, record the certified O₃ concentration and the recorder response.

A4.3.6.9 Calculate the indicated O₃ concentration produced by the O₃ generator from:

$$[O_3]_{GEN} = [O_3]_{OUT} \times \frac{F_O + F_D}{F_O} \quad (A4.11)$$

A4.3.6.10 Generate several other O₃ concentrations (at least five) by increasing F_D , the diluent air flow. Calculate the diluted O₃ concentrations from:

$$[O_3]_{OUT}' = [O_3]_{GEN} \times \frac{F_O}{F_O + F_D'} \quad (A4.12)$$

A4.3.6.11 Allow the O₃ monitor to sample each diluted O₃ concentration until a stable response is obtained. For each concentration, determine the certified O₃ concentration from the certification relationship and record the monitor response and the corresponding O₃ concentration.

A4.3.6.12 Plot the O₃ monitor response versus the corresponding certified O₃ concentration, and develop the calibration curve using the method of least squares.

A5. ALTERNATE PROCEDURES TO COMPARE A GENERATION-TYPE TRANSFER STANDARD TO A UV PRIMARY OZONE STANDARD

A5.1 Assay by Ultraviolet—The UV procedure for obtaining primary O₃ standards is basically an alternate technique using a UV photometer. See Practice D5110. The photometer may be used to assay the output concentration of a generation-type transfer standard. To do this, the photometer shall be disconnected from its own O₃ generator and output system and connected to the transfer standard output, as shown in Fig. A5.1. Care must be exercised to disturb the photometer as little as possible from its normal configuration, and to ensure the output flow of the transfer standard exceeds the flow demand of the photometer. (**Warning**—A significant problem arises with this procedure, however. In order to accurately measure I_o for the transmittance (I/I_o) measurement, the photometer must be able to sample zero air from the same source as that used for the generation of the O₃ concentration. If the zero air supply of the transfer standard (or GPT system) is capable of providing sufficient additional zero air for the photometer, it must be tapped and connected to the two-way valve as shown in Fig. 1. Care must be taken in the process to ensure that the transfer standard is not adversely affected. If the zero air supply cannot provide sufficient zero air, or cannot be readily tapped, this procedure shall not be used, and the alternate procedures in A5.2 or A5.3 shall be followed.)

A5.2 Comparison by Calibrated Ozone Monitor —In its normal configuration, the UV primary O₃ standard system produces assayed O₃ concentration standards. Such standards may be used to calibrate an ordinary ambient O₃ monitor. See

Practice D5110. The calibrated O₃ monitor is then immediately used to assay the output concentration of the generator-type transfer standard, as shown in Fig. A5.2. In this situation, the O₃ monitor may be used as a temporary or short time transfer standard without the otherwise required qualification tests described in 10, since the O₃ monitor is used immediately after calibration. Accordingly, it is used under the same conditions as those during calibration, and is not shut down or moved between calibration and use. Nevertheless, it is important the monitor be stable between calibration and subsequent use to assay the transfer standard output. The monitor calibration shall therefore be rechecked at several concentrations against the primary standard after the transfer standard is certified. Also, the entire process of calibration, use and calibration recheck of the O₃ monitor shall be repeated each time a generation type transfer standard is certified or recertified.

A5.3 Comparison by Uncalibrated Ozone Monitor—It is possible to avoid the calibration and calibration recheck steps described in A5.2 by using an uncalibrated O₃ monitor to compare the transfer standard to a primary standard. The primary O₃ standard, the transfer standard output, or both, are adjusted until each is producing exactly the same output concentration. This equivalent point is determined by switching an uncalibrated O₃ monitor back and forth between the primary standard and the transfer standard as shown in Fig. A5.2. The O₃ monitor must not drift or change its sensitivity during the process. Sufficient time must be allowed for stable

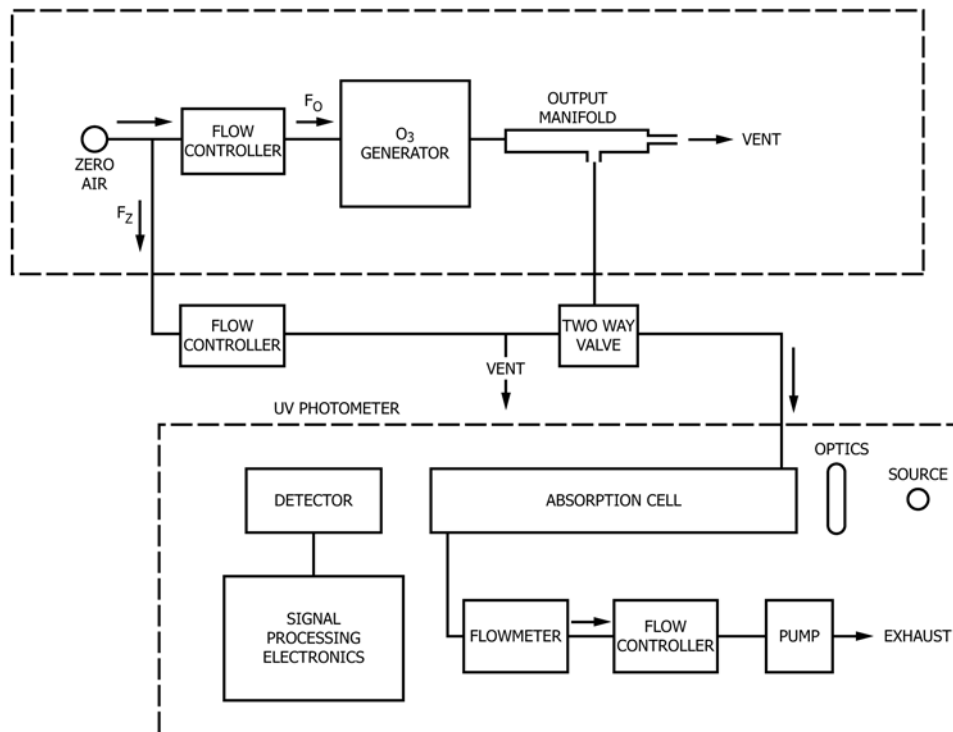


FIG. A5.1 Sample Comparison Set-up of an O₃ Generation-type Transfer Standard to a UV Primary Standard (Procedure 1)

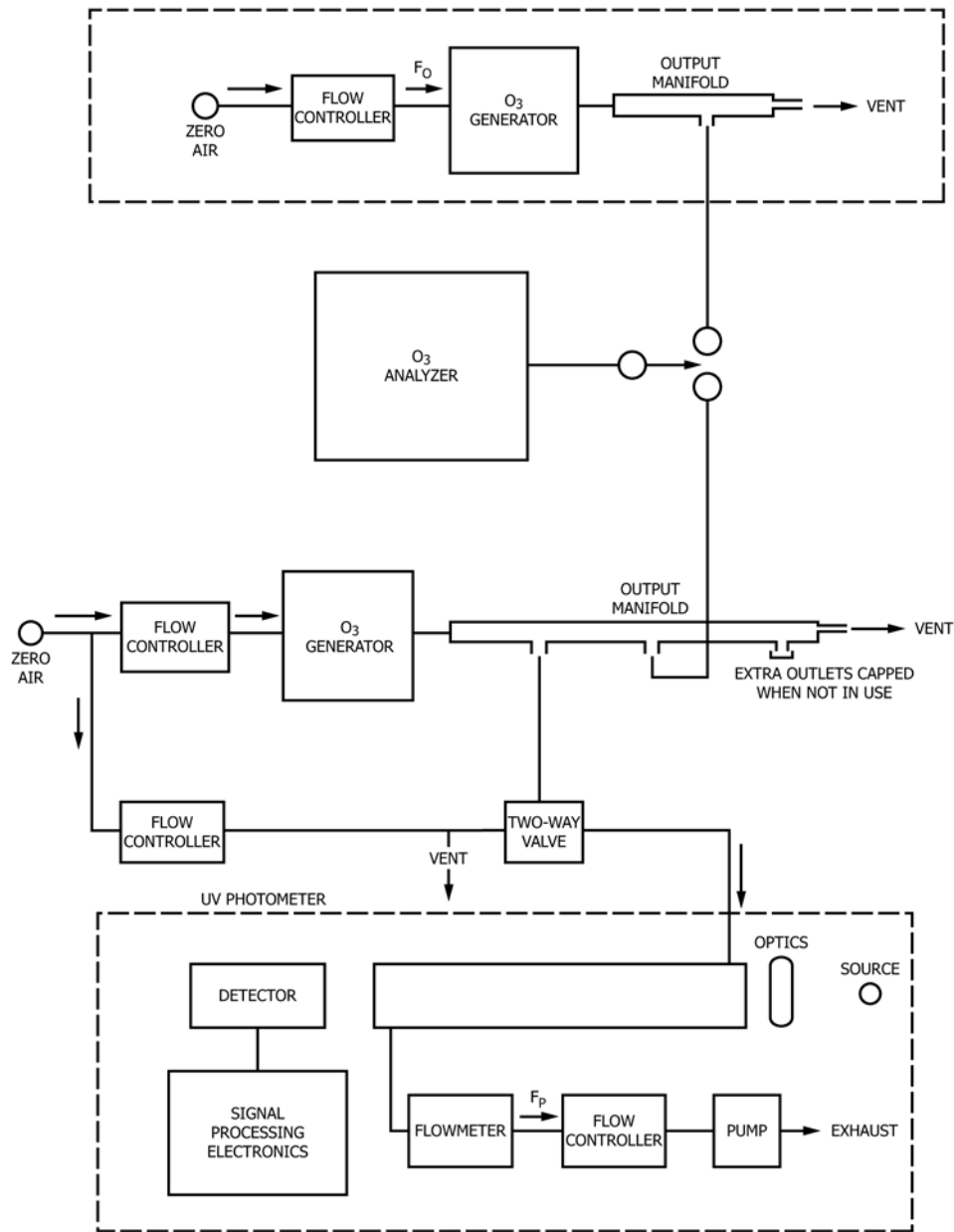


FIG. A5.2 Sample Comparison Set-up of an O₃ Generation-type Transfer Standard to a UV Primary Standard (Procedure 2 and 3)

readings on each source. When the monitor response is exactly the same for both the primary standard and the transfer standard, the transfer standard output is comparable to the UV primary standard at that concentration. This procedure shall be repeated for each concentration at which the transfer standard is to be compared.

A5.3.1 This procedure is of obvious advantage for transfer standards which have only a single or a few fixed outputs. It could also be used to rapidly verify the accuracy of transfer standards between their periodic recertification.

A6. CERTIFICATION OF AN OZONE MONITOR AS A TRANSFER STANDARD

A6.1 The O₃ monitor to be certified as a transfer standard does not have to be a UV photometric monitor. However, the UV type monitors may be more readily portable or have practical advantages over other types of O₃ monitors.

A6.2 Preliminary Requirements

A6.2.1 A stable source of O₃ to be assayed by the monitor/transfer standard, and an attendant source of zero air for the O₃ generator are required. Some monitors have internal or associated O₃ generators that may be used; otherwise an O₃ generator/zero air system must be provided by the user at each site where the transfer standard will be used.

A6.2.2 Review any operator instructions provided by the manufacturer of the O₃ monitor to become familiar with its use.

A6.3 Qualification

A6.3.1 The next step is to qualify the transfer standard by demonstrating it is repeatable to within the specifications given in [Annex A1](#). The variables likely to affect an O₃ monitor are normally the same as those discussed in Sections 9 – 12. Unless otherwise discussed in this section, see Sections 9 – 12 for certification procedures.

A6.3.2 Generally, a preliminary calibration relationship as shown in [Fig. 8](#) is not necessary, as most O₃ monitors are linear and provide a direct output indication of concentration. The zero and span of the monitor shall be adjusted for approximate calibration (with respect to the UV standard) over the desired concentration relationship. The final “calibration” of the monitor is the certification relationship.

A6.4 Qualification Tests

A6.4.1 Temperature

A6.4.1.1 Select an O₃ monitor that has a good temperature regulation (or compensation), preferably one with a temperature indicator or other warning device to indicate whether the temperature regulator is working properly. Keep in mind that temperature regulation systems require a warm-up period before the temperature stabilizes.

A6.4.1.2 Select a temperature range over which the O₃ monitor is to be qualified, such as 20° to 30°C [68° to 86°F] may be appropriate, or possibly 15° to 30°C [59° to 86°F]. Test the monitor over this range at several O₃ concentrations as shown by [Fig. 5](#) which shows how the indicated output of the monitor varies as the temperature changes. Be sure that (1) the proper temperature and pressure corrections are made to the UV standard, (2) the O₃ monitor is allowed to equilibrate each time the temperature is changed, and (3) the O₃ monitor’s span is not adjusted between each temperature (adjustment of other parameters to nominal values is permitted). If the manufacturer has tested the O₃ monitor (or one like it), only enough tests are needed to show that the monitor is operating properly and meets the specifications.

A6.4.1.3 If the O₃ monitor’s indicated concentration does not vary more than ±4 % or ±4 ppb over the entire tempera-

ture range, then it is qualified over that temperature range. If it does not meet the specifications, the following options are available:

(a) determine the monitor has a malfunction or inadequacy, attempt to correct it, and retest it;

(b) reduce the temperature to a range over which the monitor does meet the specification (this may inconveniently reduce the subsequent use of the monitor); or

(c) attempt to determine, either analytically or empirically, the temperature-output relationship such as illustrated in [Fig. 6](#). When this relationship is used to calculate a “corrected” indicated reading, the monitor should meet the specifications. If so, this correction formula becomes a necessary and integral part of the transfer standard and must be included with the ultimate certification relationship (see [Fig. 9](#)).

A6.4.2 *Line Voltage*—See [10.3](#). A well-designed O₃ monitor should show little or no sensitivity to line voltage changes over this range. If the monitor does not meet the specifications, it should be rejected.

A6.4.3 *Barometric Pressure/Altitude*—See [10.4](#). An O₃ monitor may be sensitive to pressure changes unless it is specifically designed to compensate for pressure effects. If the use of the transfer standard can be restricted to altitudes within a range of about 100 meters (300 feet), the range of pressure variations is only about 2 or 3 % (about 1 % for altitude variations and about 1 to 2 % for normal barometric pressure changes). Under these conditions, an uncompensated O₃ monitor which operates at ambient pressure could be expected to meet the qualification specifications. However, the monitor shall be tested over a normal range of barometric pressures, by testing it on various days when the barometric pressure is different, and plot the results as shown in [Fig. 5](#).

A6.4.3.1 When a larger altitude range is needed (or for applications requiring more accuracy) the monitor may be tested in a pressure chamber or by moving it to various altitudes, as described in [10.4](#). If so, the O₃ monitor’s sensitivity to pressure changes may have to be compensated, either by design or by defining the pressure-output relationship and developing a correction formula as shown in [Fig. 10](#). In doing this, be sure (1) the proper temperature and pressure corrections are made to the primary standard, (2) the O₃ monitor is not adjusted between each different pressure, and (3) the other variables (temperature, line voltage, etc.) are controlled so they do not affect the monitor. Determine a correction formula from the test data, and include it with the certification relationship.

A6.4.4 *Elapsed Time*—See [10.5](#). The specified recertification frequency shall be sufficient to compensate for any long-time response changes in the monitor.

A6.4.5 *Variability*—See [10.6](#). Variability is not likely to be a factor, but if any of the other qualification tests show variability not strongly correlated with a specific variable, then a test for general variability will be required.

A6.4.6 *Relocation*—See 10.7. During the relocation tests make sure that the zero, span, and other controls are locked so they don't change when the monitor is moved.

A6.4.7 *Operator Adjustments*—See 10.8. Test the monitor for repeatability with respect to any operator settings such as flow or gas pressure. Note if a stabilization period is required after an adjustment.

A6.4.8 *Malfunctions*—See 10.9.

A6.5 Certification

A6.5.1 Before conducting the certification tests, make any zero, span, or any other adjustments to the monitor as necessary so that the monitor readings are close to the O₃ concentrations obtained from the primary standard.

A6.5.2 When the adjustments are complete, secure the controls, record their values, and proceed to certify the transfer

standard as specified in Annex A1. See also Section 11. If any correction formulas are required, use them during the certification process and clearly specify the conditions at the time of certification relationship. Be certain the specified correction formulas are accurate. Note any special operating instructions, limits or other pertinent information. It is very important to complete the documentation requirements specified in A1.1 .

A6.6 *Use*—In using the O₃ monitor as a transfer standard, review the guidance in 11.4. Make any zero, flow, or other adjustments *except span adjustments* to the values recorded at the time of certification. Recertify the transfer standard as required in Section 12 and Annex A1. Perform occasional cross checks to other O₃ standards, and occasionally repeat the qualification tests to be certain the transfer standard is maintaining adequate reliability.

A7. CERTIFICATION OF AN OZONE GENERATOR AS A TRANSFER STANDARD

A7.1 Preliminary Requirements

A7.1.1 Review the three alternate procedures for comparing the output of an O₃-generator-type-transfer-standard described in Annex A1, and decide which one to use.

A7.1.2 Review any operator instructions provided by the manufacturer of the O₃ monitor to become familiar with its use.

A7.2 Qualification

A7.2.1 The next step is to qualify the transfer standard by demonstrating that it is repeatable to within the specifications given in Annex A1. The variables likely to affect an O₃ generator are normally the same as those discussed in Sections 9 – 12.

A7.2.2 Before starting qualification tests, first prepare a tentative preliminary calibration relationship as shown in Fig. 8, where the O₃ output concentration is related to the O₃ adjustment setting. Although a more complete preliminary calibration relationship will be required after certification, this tentative relationship is necessary to carry out the qualification tests. Prepare the relationship as shown in Fig. 8 by plotting the O₃ generator's output concentrations as measured with the UV reference system (6.1.1) at various O₃ settings as discussed in 9.2. Note the temperature, barometric pressure, line voltage, and other pertinent conditions. During the qualification tests, use this preliminary relationship to determine each "indicated output" from the O₃ for a given setting of the concentration adjustment (that is, sleeve setting or current setting).

A7.3 Qualification Tests

A7.3.1 Temperature

A7.3.1.1 Select an O₃ generator that has a good temperature regulation (or compensation), preferably one with a temperature indicator or other warning device to indicate whether the

temperature regulator is working properly. Keep in mind that temperature regulation systems require a warm-up period before the temperature stabilizes.

A7.3.1.2 Select a temperature range over which the O₃ generator is to be qualified, such as 20° to 30°C [68° to 86°F] or 15° to 30°C. Test the generator over this range at several O₃ concentrations as shown by Fig. 5, which shows how the indicated output of the generator varies as the temperature changes. Be sure (1) the proper temperature and pressure corrections are made to the UV standard, (2) the O₃ generator is allowed to equilibrate each time the temperature is changed, and (3) the O₃ setting is repeated precisely for each different temperature. If the manufacturer has tested the O₃ generator (or one like it), only enough tests are needed to show the generator is operating properly, and meets the specifications.

A7.3.1.3 If the O₃ generator's actual output concentration does not vary more than ±4 % over the entire temperature range, then it is qualified over that temperature range. If it does not meet the specifications, the following options are available:

(a) determine the generator has a malfunction or inadequacy, attempt to correct it, and retest it;

(b) reduce the temperature range to a range over which the generator does meet the specification (this may inconveniently reduce the subsequent use of the generator); or

(c) attempt to determine, either analytically or empirically, the temperature-output relationship such as illustrated in Fig. 6. When this relationship is used to calculate a "corrected" indicated reading, the generator shall meet the specifications. If so, this correction formula becomes a necessary and integral part of the transfer standard and must be included with the ultimate certification relationship (see Fig. 7).

A7.3.2 *Line Voltage*—See 10.3. A well-designed O₃ generator should show little or no sensitivity to line voltage changes over this range. If the generator does not meet the

specifications, the same three options as with temperature are available, plus the fourth of adding an external voltage regulator.

A7.3.3 Barometric Pressure/Altitude—See 10.4. An O₃ generator may be sensitive to pressure changes unless it is specifically designed to compensate for pressure effects. If the use of the transfer standard can be restricted to altitudes within a range of about 100 metres [300 feet], the range of pressure variations is only about 2 or 3 % (about 1 % for altitude variations and about 1 to 2 % for normal barometric pressure changes). Under these conditions, an uncompensated O₃ generator which operates at ambient pressure could be expected to meet the qualification specifications. Pressure changes can then be ignored, and no tests would be necessary.

A7.3.3.1 When a larger altitude range is required (or for applications demanding more accuracy) the generator may be tested in a pressure chamber or by moving it to various altitudes, as described in 10.4. If so, the O₃ generator's sensitivity to pressure changes may have to be compensated, either by design or by defining the pressure-output relationship and developing a correction formula as shown in Fig. 10. In doing this, be sure (1) the proper temperature and pressure corrections are made to the primary standard, (2) the O₃ setting is repeated precisely for each different pressure, and (3) the other variables (temperature, line voltage, etc.) are controlled so they do not affect the generator. Determine a correction formula from the test data, and include it with the certification relationship.

A7.3.4 Elapsed Time—See 10.5. The output of an O₃ generator is expected to decrease somewhat with time. Comparisons with the primary standard over a period of time are necessary to determine the rate of decay. Then, either the transfer standard may be recertified often enough so that it stays within specification between certifications, or a correction factor based on elapsed time can be determined and used with the preliminary calibration relationship.

A7.3.5 Variability—See 10.6. Variability is not likely to be a factor. If any of the other qualification tests show variability not strongly correlated with a specific variable, then a test for general variability would be needed. If the generator meets the specifications for other tests, no specific test for general variability is required.

A7.3.6 Relocation—See 10.7.

A7.3.7 Operator Adjustments—See 10.8. Test the O₃ generator for repeatability of O₃ concentration settings. Check each of several setting repeatedly, approaching sometimes from a higher setting, and sometimes from a lower setting. Intersperse the various settings. Note if a stabilization period is required for each new setting, or if any other observable peculiarities are evident. A well-designed O₃ generator is not likely to fail this test, but the information obtained will help to achieve better precision.

A7.3.8 Malfunctions—See 10.9.

A7.4 Certification

A7.4.1 Before conducting the certification tests, decide if a new preliminary calibration relationship should be prepared, as shown in Fig. 8. This will be necessary if:

- (a) the transfer standard needs one or more correction formulas for the defined-relationship variables;
- (b) the original relationship was rough, inaccurate, or incomplete;
- (c) the original relationship indicates output concentrations more than 30 % different than the primary standard; or
- (d) the qualification tests provided other information to suggest that a new relationship should be prepared.

A7.4.2 If a new calibration relationship is needed, prepare it carefully and accurately, including enough points to define it precisely over the entire operating range. Ozone generators that are non-linear or have appreciable variability need additional comparisons to define the relationship precisely. If any correction formulas are needed, clearly specify the conditions at the time of certification relationship. Be sure the specified correction formulas are accurate. If necessary, various qualification tests shall be repeated to verify the conditions are accurate. Note any special operating instructions, operating instructions, limits, or other pertinent information.

A7.4.3 When the preliminary calibration relationship has been prepared, proceed to certify the transfer standard as specified in Annex A1. See also Section 11. It is very important to complete the documentation requirements specified in A1.1.

A7.5 Use—In using the O₃ generator as a transfer standard, review the guidance in 11.4. Recertify the transfer standard as required in Section 12 and Annex A1. Perform occasional cross checks to other O₃ standards, and occasionally repeat the qualification tests to verify the transfer standard is maintaining adequate reliability.

REFERENCES

- (1) Flamm, D. L. "Analysis of Ozone at Low Concentrations with Boric Acid Buffered Potassium Iodide." *Environmental Science and Technology*, 10, 978 (1977).
- (2) Saltzman, and Gilbert, N. "Iodometric Microdetermination of Organic Oxidants and Ozone." *Analytical Chemistry*, 31, 1914 (1959).
- (3) Rehme, K. A., Matrin, B. E., and Hodgeson, J. A. "Tentative Method for the Calibration of Nitric Oxide, Nitrogen Dioxide, and Ozone Monitors by Gas Phase Titration." EPA-R2-73-246, U.S. Environmental Protection Agency, Research Triangle Park, NC. March, 1974. pp. 17.
- (4) Paur, R. J., and McElroy, F. F. "Technical Assistance Document for the Calibration of Ambient Ozone Monitors." EPA-600/4-79-057.
- (5) Ellis, E. C. "Technical Assistance Document for the Chemiluminescence Measurement of Nitrogen Dioxide." EPA-600/4-75-003, U.S. Environmental Protection Agency, Research Triangle Park, NC.
- (6) Lodge, J. P., Pate, J. B., Ammons, B. E., and Swanson, G. A. "The use of Hypodermic Needles as Critical Orifices in Air Sampling." *Air Pollution Control Association*, 16, 197 (1966).

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). Permission rights to photocopy the standard may also be secured from the Copyright Clearance Center, 222 Rosewood Drive, Danvers, MA 01923, Tel: (978) 646-2600; <http://www.copyright.com/>