



# Standard Practices for Calibration of Ozone Monitors Using Transfer Standards<sup>1</sup>

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 ( $\epsilon$ ) 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:*<sup>2</sup>

[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](#)

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

[E591 Practice for Safety and Health Requirements Relating to Occupational Exposure to Ozone \(Withdrawn 1990\)](#)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

2.2 *Other Documents:*

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

## 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.

<sup>1</sup> 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.

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

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

<sup>4</sup> 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>.

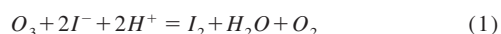
$F_O$	= Flow through the O <sub>3</sub> generator, mL/min.	$s_d$	= Standard deviation of single point comparisons. See <a href="#">Annex A1</a> .
$F_R$	= Flowrate corrected to reference conditions (25°C and 101.3 kPa), mL/min. See <a href="#">Annex A2</a> .	$s_i$	= Relative standard deviation of the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

#### 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)<sup>5</sup> is based on the reaction between ozone (O<sub>3</sub>) and potassium iodide (KI) to release iodine (I<sub>2</sub>) in accordance with the following stoichiometric equation (2):



The stoichiometry is such that the amount of I<sub>2</sub> released is equal to the amount of O<sub>3</sub> absorbed. Ozone is absorbed in a 0.1 N boric acid solution containing 1 % KI, and the I<sub>2</sub> released reacts with excess iodide ion (I<sup>-</sup>) to form triiodide ion (I<sub>3</sub><sup>-</sup>), which is measured spectrophotometrically at a wavelength of 352 nm. The output of a stable O<sub>3</sub> generator is assayed in this manner, and the O<sub>3</sub> generator is immediately used to calibrate the O<sub>3</sub> monitor.

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

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



When  $O_3$  is added to excess  $NO$  in a dynamic system, the decrease in  $NO$  response is equivalent to the concentration of  $O_3$  added. The  $NO$  is obtained from a standard  $NO$  cylinder, and the  $O_3$  is produced by a stable  $O_3$  generator. A chemiluminescence  $NO$  analyzer is used to measure the change in  $NO$  concentration. The concentration of  $O_3$  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  $O_3$  in the reaction chamber, with subsequent dilution, to effect complete  $O_3$  reaction with relatively small chamber volumes.

4.5 *Method D*—This procedure is based on the rapid gas phase reaction between  $O_3$  and nitric oxide ( $NO$ ) as described by the following equation (3):



When  $NO$  is added to excess  $O_3$  in a dynamic system, the decrease in  $O_3$  response observed on an uncalibrated  $O_3$  monitor is equivalent to the concentration of  $NO$  added. By measuring this decrease in response and the initial response, the  $O_3$  concentration can be determined. Additional  $O_3$  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 ( $NO_2$ ) with residual  $O_3$  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  $O_3$  precludes the storage of  $O_3$  concentration standards for any practical length of time, and precludes direct certification of  $O_3$  concentrations as SRM's. Moreover, there is no available SRM that can be readily and directly adapted to the generation of  $O_3$  standards analogous to permeation devices and standard gas cylinders for sulfur dioxide and nitrogen oxides. Dynamic generation of  $O_3$  concentrations is relatively easy with a source of ultraviolet (UV) radiation. However, accurately certifying an  $O_3$  concentration as a primary standard requires assay of the concentration by a comprehensively specified analytical procedure, which must be performed every time a standard is needed.

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  $O_3$  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:*

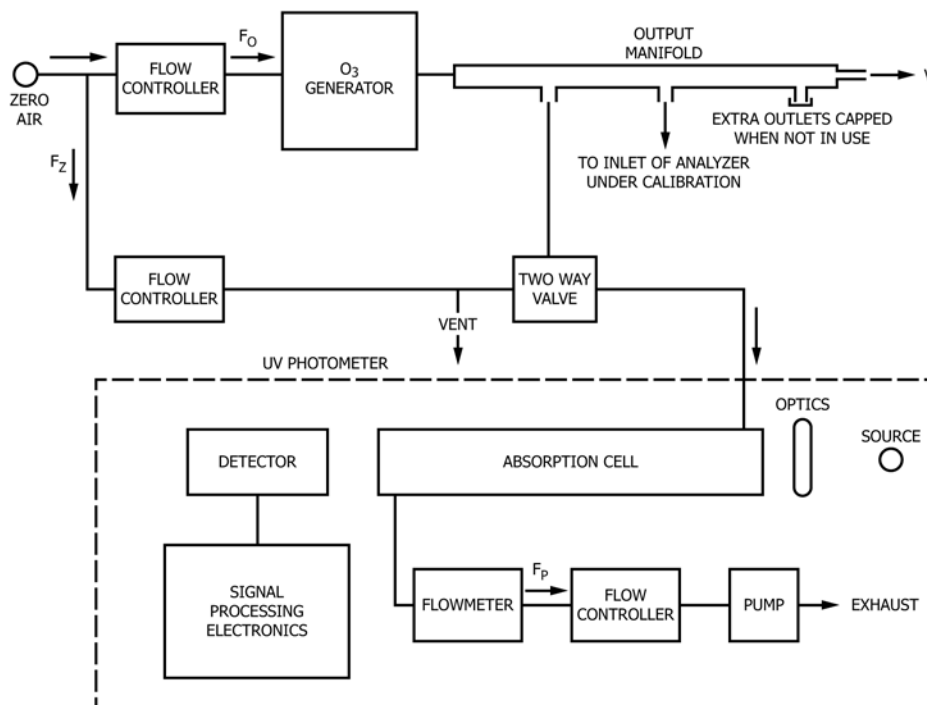


FIG. 1 Schematic Diagram of a Typical UV Photometric Calibration System