



Designation: D3824 – 20

Standard Test Methods for Continuous Measurement of Oxides of Nitrogen in the Ambient or Workplace Atmosphere by Chemiluminescence¹

This standard is issued under the fixed designation D3824; 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 test methods cover procedures for the continuous determination of total nitrogen dioxide (NO₂) and nitric oxide (NO) as NO_x, or nitric oxide (NO) alone or nitrogen dioxide (NO₂) alone, in the ranges shown in the following table:

Approximate Range of Concentration
(25°C and 101.3 kPa (1 atm))

Gas	Ambient Atmosphere μg/m ³ (ppm)	Workplace Atmosphere mg/m ³ (ppm)
NO	10 to 600 (0.01 to 0.5)	0.6 to 30 (0.5 to 25)
(NO + NO ₂) = NO _x	20 to 1000 (0.01 to 0.05)	1 to 50 (0.5 to 25)
NO ₂	20 to 1000 (0.01 to 0.5)	1 to 50 (0.5 to 25)

1.2 The test methods are based on the chemiluminescent reaction between nitric oxide and ozone.

1.3 The values stated in SI units are to be regarded as standard. The values given in parentheses after SI units are provided for information only and are not considered standard.

1.4 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety, health, and environmental practices and determine the applicability of regulatory limitations prior to use. For specific precautionary statements, see Section 9.*

1.5 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

2. Referenced Documents

2.1 ASTM Standards:²

¹ These test methods 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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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.

- D1356 Terminology Relating to Sampling and Analysis of Atmospheres
- D1357 Practice for Planning the Sampling of the Ambient Atmosphere
- D1914 Practice for Conversion Units and Factors Relating to Sampling and Analysis of Atmospheres
- D3195/D3195M Practice for Rotameter Calibration
- D3249 Practice for General Ambient Air Analyzer Procedures
- D3609 Practice for Calibration Techniques Using Permeation Tubes
- D3631 Test Methods for Measuring Surface Atmospheric Pressure

2.2 Other Documents:

- 29 CFR Part 1910, Occupational Safety and Health Standards³
- 40 CFR Parts 50 and 53, Environmental Protection Agency Regulations on Ambient Air Monitoring Reference and Equivalent Methods³

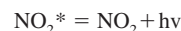
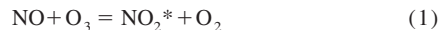
3. Terminology

3.1 Definitions:

3.1.1 Four definitions of terms used in these test methods, refer to Terminology D1356 and Practice D3249.

4. Summary of Test Methods

4.1 The principle of the methodology is based upon the chemiluminescence, or the emission of light, resulting from the homogeneous gas phase reaction of nitric oxide and ozone (1).⁴ The equation is as follows:



In the presence of excess ozone, the intensity of the light emission is directly proportional to the nitric oxide concentration.

³ Available from U.S. Government Printing Office, Superintendent of Documents, 732 N. Capitol St., NW, Washington, DC 20401-0001, http://www.access.gpo.gov.

⁴ The boldface numbers in parentheses refer to a list of references at the end of this standard.

4.2 To measure nitric oxide concentrations, the gas sample being analyzed is blended with ozone in a flow reactor. The resulting light emissions are monitored by a photomultiplier tube.

4.3 To measure total oxides of nitrogen ($\text{NO}_x = \text{NO} + \text{NO}_2$), the gas sample is diverted through a NO_2 to NO converter before being admitted to the flow reactor.

4.4 To measure nitrogen dioxide (NO_2), the gas sample is intermittently diverted through the converter, and the NO signal subtracted from the NO_x signal. Some instruments utilize a dual stream principle with two reaction chambers.

5. Significance and Use

5.1 Most oxides of nitrogen are formed during high-temperature combustion. The U.S. Environmental Protection Agency (EPA) has set primary and secondary air quality standards for NO_2 that are designed to protect the public health and the public welfare (40 CFR, Part 50).

5.2 Oxides of nitrogen are generated by many industrial processes that can result in employee exposures. These are regulated by the Occupational Safety and Health Administration (OSHA), which has promulgated exposure limits for the industrial working environment (29 CFR, Part 1910).

5.3 These test methods have been found to be satisfactory for measuring oxides of nitrogen in ambient and workplace atmospheres over the ranges shown in 1.1.

6. Interferences

6.1 The chemiluminescent detection of NO with ozone is not subject to interference from any of the common air pollutants, such as O_3 , NO_2 , CO , NH_3 , and SO_x , normally found in the atmosphere (1). The possible interference of hydrocarbons is eliminated by means of a red sharp-cut optical filter.

6.2 The chemiluminescent detection of NO with O_3 is subject to positive interference from olefins (for example 2-butene) and organic sulfur compounds (for example methane thiol) (2, 3).

6.2.1 Negative interference approaching 10 % may occur at high humidities for instruments that have been calibrated with dry span gas (4).

6.3 When the instrument is operated in the NO_2 or NO_x modes, any nitrogen compound decomposing to NO in the converter or yielding products capable of generating atomic hydrogen or chlorine in the ozonator will produce a positive interference (2, 5, 6).

6.3.1 Reported interferences are presented in Annex A8. Note that some organic sulfur species will positively interfere in the NO mode, and negatively in the NO_2 mode.

7. Apparatus

7.1 Commercially available analyzers of oxides of nitrogen shall be installed on location and their acceptable performance demonstrated by the manufacturer. Minimum performance specifications are shown in Annex A1. The manufacturers shall verify that the instrument meets the specifications as determined by the test methods in 40 CFR, Part 53 or applicable regional or international regulations.

7.2 A simplified schematic of the analyzer used in the method is shown in Fig. 1. The principal components are as follows:

7.2.1 NO_x Converter—A device to reduce NO_2 to NO . This usually utilizes a stainless steel, molybdenum, or molybdenum-coated stainless steel coil at elevated temperatures. Conversion efficiency shall be at least 96 %.

7.2.2 Ozonator—A device that produces ozone for the chemiluminescent reaction.

7.2.3 Reactor—The reaction chamber in which nitric oxide and ozone undergo the gas phase chemiluminescent reaction.

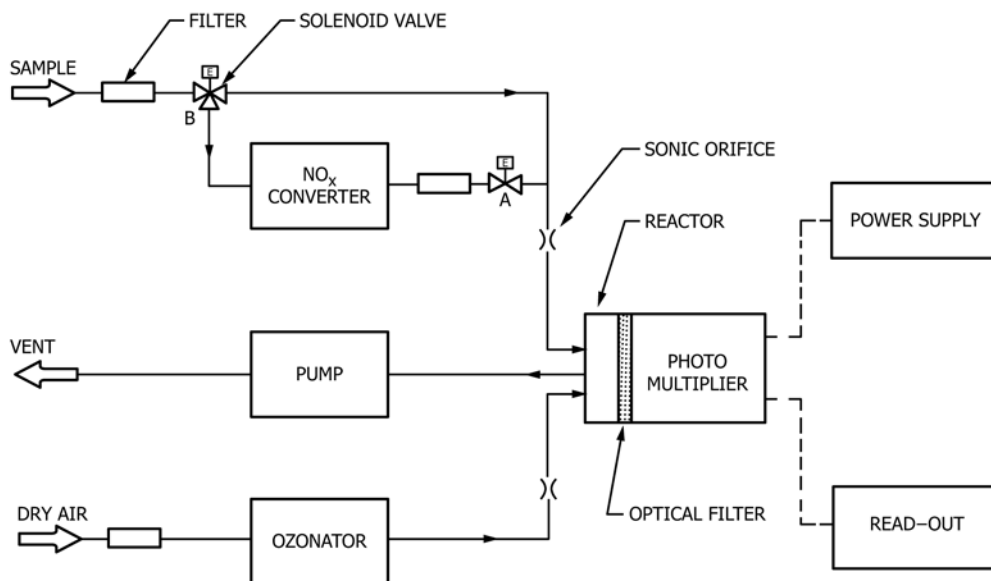


FIG. 1 Schematic of NO- NO_x Chemiluminescence Monitor

7.2.4 Photomultiplier—A device used in conjunction with a red sharp-cut optical filter (600 nm) (1) for measuring the light output of the reaction between nitric oxide and ozone. (**Warning**—The photomultiplier tube may become permanently damaged if it is exposed to ambient light while the high voltage is on.)

7.2.5 Pump—A device to provide a flow of gas (sample and ozone) through the reaction chamber and to set the reactor operating pressure for a given flow rate.

7.2.6 Pressure Regulator for Standard NO Cylinder—A two-stage regulator to fit the NO cylinder, having internal parts of stainless steel with a tetrafluoroethylene (TFE)-fluorocarbon or polychlorotrifluoroethylene seat and a delivery pressure of 200 kPa (30 psi). It shall contain a purge port or purge assembly to flush the regulator and delivery systems after connecting the regulators to the NO cylinder, but before the cylinder valve is opened.

7.3 Zero and Span Calibrator, containing an NO₂ permeation device (see Practice D3609), a means of controlling the temperature of the permeation device to $\pm 0.1^\circ\text{C}$, flow controllers, flowmeters, and an air pump. It shall include means of continually flushing the permeation device with pure nitrogen gas that has been passed through a drying tube containing a mixture of molecular sieve and indicating calcium sulfate.

NOTE 1—In some applications, permeation device accuracy may be too low for span calibrations meeting data quality objectives but these devices can still be used to check responses or track drift in these cases. As an alternative, compressed NO₂ gas standards certified to $\pm 1\%$ analytic uncertainty can be used instead of permeate.

7.4 Gas Phase Titration Apparatus:

7.4.1 General—The apparatus consists of flow controllers, flowmeters, ozone generator, reaction chamber, and mixing chamber (see Fig. 2). All interconnections in the gas phase

titrator shall be made with glass and TFE-fluorocarbon.

NOTE 2—Recent advances in technology have produced systems that have only one reaction chamber and no mixing chamber, or dilute high NO concentration to a lower value prior to mixing with O₃ in the reaction chamber.

7.4.2 Air Flowmeters, capable of measuring air flows between 0 to 10 L/min with an accuracy of $\pm 2\%$.

7.4.3 Nitric Oxide Flowmeters, capable of measuring nitric oxide flow between 0 to 100 mL/min with an accuracy of $\pm 2\%$.

7.4.4 Soap Bubble Flowmeter, for calibrating the NO flowmeter with an accuracy of $\pm 2\%$.

7.4.5 Ozone Generator, consisting of a quartz tube fixed adjacent to a low-pressure mercury vapor lamp capable of emitting ultraviolet light of 185 nm. Alternatively, an ozone generation using an UV lamp, electrode, or corona discharge module can be used. The concentration of ozone is controlled by adjusting the generator as specified by the manufacturer.

7.4.6 Reaction Chamber—A borosilicate glass bulb (a Kjeldahl bulb is satisfactory) (see Annex A2 for choosing size).

7.4.7 Mixing Chamber—Similar 7.4.6; a borosilicate glass bulb (a Kjeldahl bulb is satisfactory) (see Annex A2 for choosing size).

7.5 Air Purifier, to purify ambient air for use in the zero and span calibrator and in the gas phase titration apparatus. It consists of an indicating silica gel trap to remove moisture, an ozone generator to convert nitric oxide to nitrogen dioxide, and a trap containing activated coconut charcoal and molecular sieve. The purifier shall deliver air containing no more than 2.5 $\mu\text{g}/\text{m}^3$ of NO (0.002 ppm), 4 $\mu\text{g}/\text{m}^3$ of NO₂ (0.002 ppm), and 4 $\mu\text{g}/\text{m}^3$ of O₃ (0.002 ppm).

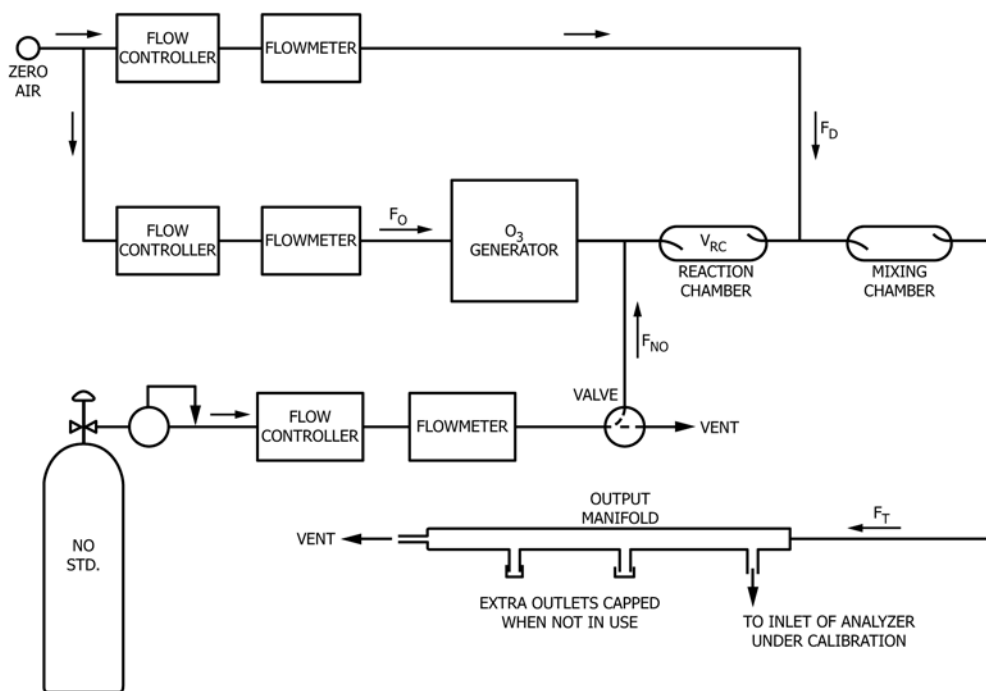


FIG. 2 Schematic Diagram of a Typical GPT Calibration System

7.6 *Temperature Sensor to Measure Ambient Temperature*—Temperature measuring devices such as RTDs (resistance temperature devices), thermistors, and organic liquid-in-glass thermometers meeting the requirements of specific applications may be used.

7.7 *Barograph or Barometer*, capable of measuring atmospheric pressure to ± 0.5 kPa (see Test Methods [D3631](#)).

7.8 *Ozone Analyzer*, chemiluminescent or ultraviolet, meeting the requirements of 40 CFR, Part 50.

7.9 *Recorders*, strip chart recorders (three) or electronic/computer-based data recording for use during calibration.

8. Reagents and Materials

8.1 *Primary Standard* (either [8.1.1](#) or [8.1.2](#) is satisfactory):

8.1.1 *Nitric Oxide Standard Cylinder*, traceable to National Institute of Standards and Technology (NIST) Reference Material SRM-1683 cylinder containing 60 mg/m³ (50 ppm) of NO in N₂, or SRM-1684a cylinder containing 120 mg/m³ (100 ppm) of NO in N₂.

8.1.2 *Nitrogen Dioxide Standard Permeation Device*, traceable to NIST Reference Material SRM-1629.

8.2 *Nitric Oxide Working Cylinder*, containing from 60 to 120 mg/m³ (50 to 100 ppm) NO in oxygen-free nitrogen and less than 2 mg/m³ (1 ppm) of NO₂.

8.3 *Nitrogen Dioxide Permeation Device*, for use in zero and span calibration.

8.4 *Nitrogen*, ultra high purity nitrogen, oxygen-free, containing less than 10 µg/m³ of NO or 20 µg/m³ of NO₂ (0.01 ppm).

8.5 *Molecular Sieve*, type 4E, 3.36 to 1.41 mm (6 to 14 mesh).

8.6 *Calcium Sulfate*, indicating.

8.7 *Activated Coconut Charcoal*, 3.36 to 1.41 mm (6 to 14 mesh).

8.8 *Silica Gel*, indicating, 3.36 to 1.41 mm (6 to 14 mesh).

NOTE 3—Mesh sizes are not SI standard but are included to facilitate use of this standard in regions where material sizes are sold using this non-SI units of measure.

9. Precautions

9.1 The handling and storage of compressed gas cylinders and the installation and use of the analyzer shall follow Practice [D3249](#). Cylinders shall not be exposed to direct sunlight.

9.2 The exhaust from the analyzer may contain high concentrations of ozone if the internal scrubber of the analyzer fails or becomes exhausted. For this reason, vent the exhaust from the vicinity of the analyzer and work area.

9.3 Vent excess gases from calibrations outside the work area and downwind of the sample probe.

9.4 Purge the NO cylinder regulators with nitrogen using the purge port or assembly before opening the NO cylinder valve.

9.5 The NO and NO₂ SRMs are not indefinitely stable with time; the stated concentration will change. They shall not be used for a longer period of time than that recommended in their certificate.

10. Sampling

10.1 *General*—For planning sampling programs, refer to Practices [D1357](#) and [D3249](#).

10.2 When sampling the outside ambient atmosphere from an enclosure with an ambient monitor, utilize a TFE-fluorocarbon or borosilicate probe or sampling line. Extend the probe at least 1 m (3 ft) from the building and protect it against the entry of precipitation. Utilize a TFE-fluorocarbon in-line filter of 0.5-mm pore size to remove particulates from the air stream. Heat the portion of the probe inside the building above the highest ambient outdoor temperature encountered at the sampling location to prevent condensation.

11. Calibration and Standardization

11.1 *Analyzer*:

11.1.1 For calibration procedures, refer to [Annex A2](#) and [Annex A3](#).

11.1.2 *Frequency of Calibration*—Perform a complete calibration at least once a month.

11.2 *Flowmeters*:

11.2.1 Calibrate the flowmeters of the zero and span calibrator and the gas phase titration apparatus in accordance with Practice [D3195/D3195M](#).

11.2.2 Calibrate any flow orifice with a flowmeter that has been calibrated in accordance with Practice [D3195/D3195M](#).

11.2.3 Perform the calibrations in [11.2.1](#) when the flowmeters are received, when they are cleaned, and when they show signs of erratic behavior.

11.2.4 Perform the calibration in [11.2.2](#) when the analyzers are received and when the orifices are cleaned or replaced.

11.3 *Zero and Span Calibrator*:

11.3.1 Calibrate the zero and span calibrator in accordance with [Annex A4](#).

11.3.2 Perform the calibration when the nitrogen dioxide permeation device is received and at least every month thereafter.

11.4 *Certification of NO Cylinder*—Procedures for certifying NO working cylinder against a primary standard traceable to standard reference material. (See [Annex A7](#).)

12. Procedure

12.1 After proper calibration has been established, activate the analyzer system to sample the atmosphere to be tested.

12.2 Take the recorder electronic device, or computer output and determine the concentration of NO, NO_x, or NO₂ directly from the calibration curves in desired units of parts per million.

12.3 Check the NO₂ converter efficiency at least every month in accordance with [Annex A5](#).

12.4 Perform a zero and span check daily in accordance with [Annex A6](#).