Designation: D3824 – 12

Standard Test Methods for Continuous Measurement of Oxides of Nitrogen in the Ambient or Workplace Atmosphere by the Chemiluminescent Method[1]

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 (NO_2) and nitric oxide (NO) as NO_x, or nitric oxide (NO) alone or nitrogen dioxide (NO_2) alone, in the ranges shown in the following table:

Gas	Range of Concentration	
	Ambient Atmosphere	Workplace Atmosphere
	µg/m³ (ppm) (Note 1)	mg/m³ (ppm) (Note 1)
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)

NOTE 1—Approximate range: 25°C and 101.3 kPa (1 atm).

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. No other units of measurement are included in this standard.

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

2. Referenced Documents

2.1 *ASTM Standards:*[2]

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 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 Standards[3]

40 CFR, Parts 50 and 53, Environmental Protection Agency Regulations on Ambient Air Monitoring Reference and Equivalent Methods[3]

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 Method

4.1 The principle 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:

$$NO + O_3 = NO_2^* + O_2 \quad (1)$$

$$NO_2^* = NO_2 + h\nu$$

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

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.

[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.

[3] Available from Superintendent of Documents, U.S. Printing Office, Washington, DC 20402.

[4] The boldface numbers in parentheses refer to the list of references at the end of these test methods.

4.3 To measure total oxides of nitrogen (NO_x = NO + 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 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 methods have been found satisfactory for measuring oxides of nitrogen in the ambient and workplace atmosphere 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 oxides of nitrogen analyzers shall be installed on location and 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.

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.

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.

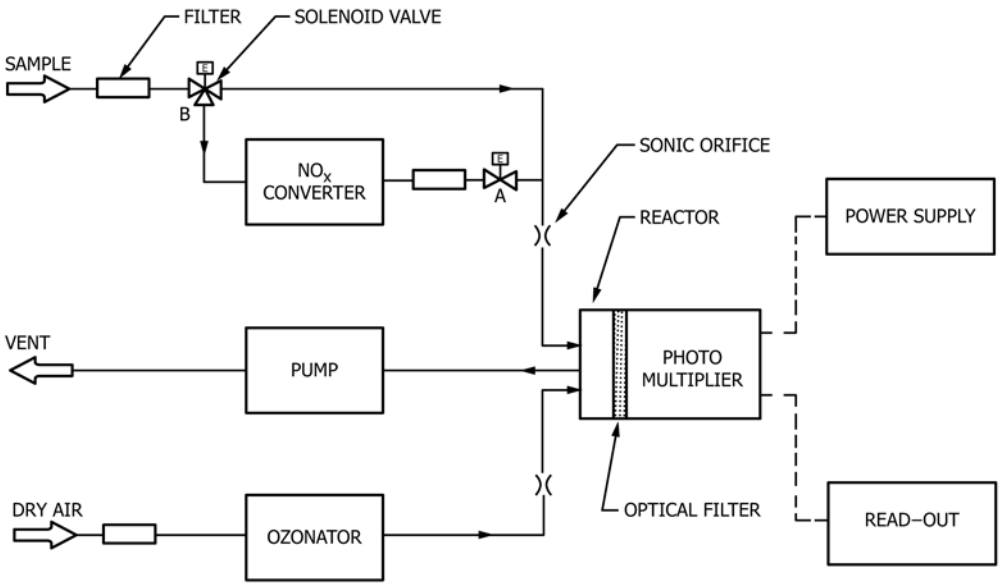

FIG. 1 Schematic of NO-NO_x Chemiluminescence Monitor

(**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 TFE-fluorocarbon or polychlorotrifluorethylene 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 NO_2 permeation device (see Practice D3609), a means of controlling the temperature of the permeation device to ±0.1°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.

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).

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

7.4.3 *Nitric Oxide Flowmeters,* capable of measuring nitric oxide flow between 0 to 100 mL/min.

7.4.4 *Soap Bubble Flowmeter,* for calibrating the NO flowmeter with an accuracy of ±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. 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 All interconnections in the gas phase titrator shall be made with glass and TFE-fluorocarbon.

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 $\mu g/m^3$ of NO (0.002 ppm), 4 $\mu g/m^3$ of NO_2 (0.002 ppm), and 4 $\mu g/m^3$ of O_3 (0.002 ppm).

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 *Strip Chart Recorders,* three, for use during calibration.

8. Reagents and Materials

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

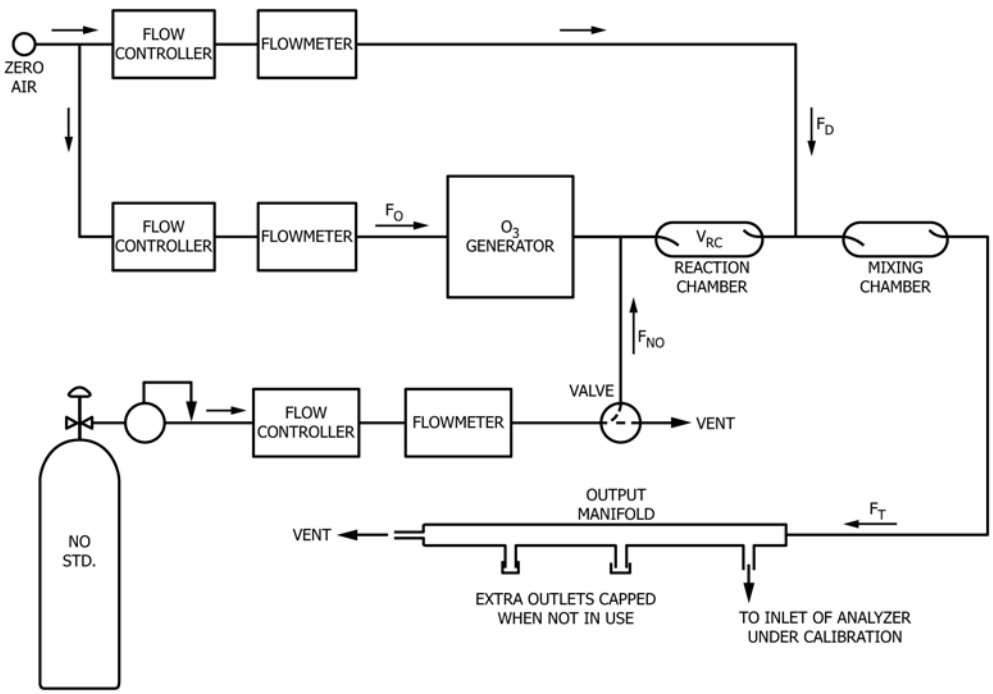

FIG. 2 Schematic Diagram of a Typical GPT Calibration System