Designation: D 3824 – 95 (Reapproved 2000)

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 D 3824; 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 $\mu g/m^3$(ppm) (Note 1)	Workplace Atmosphere mg/m^3(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 *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:*

D 1356 Terminology Relating to Sampling and Analysis of Atmospheres[2]

D 1357 Practice for Planning the Sampling of the Ambient Atmosphere[2]

D 1914 Practice for Conversion Units and Factors Relating to Sampling and Analysis of Atmospheres[2]

D 3195 Practice for Rotameter Calibration[2]

D 3249 Practice for General Ambient Air Analyzer Procedures[2]

D 3609 Practice for Calibration Techniques Using Permeation Tubes[2]

D 3631 Test Methods for Measuring Surface Atmospheric Pressure[2]

E 1 Specification for ASTM Thermometers[3]

2.2 *Other Documents:*

29 CFR, Part 1910, Occupational Safety and Health Standards[4]

40 CFR, Parts 50 and 53, Environmental Protection Agency Regulations on Ambient Air Monitoring Reference and Equivalent Methods[4]

3. Terminology

3.1 *Definitions*:

3.1.1 Four definitions of terms used in these test methods refer to Terminology D 1356 and Practice D 3249.

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)**.[5] The equation is as follows:

$$NO + O_3 = NO_2{}^* + O_2 \qquad (1)$$
$$NO_2{}^* = NO_2 + h\nu$$

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.

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

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[1] These test methods are under the jurisdiction of ASTM Committee D22 on Sampling and Analysis of Atmosphere, and are the direct responsibility of Subcommittee D 22.03 on Ambient Atmospheres and Source Emissions.

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[2] *Annual Book of ASTM Standards*, Vol 11.03.

[3] *Annual Book of ASTM Standards*, Vol 14.03.

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

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

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.

NOTE 2—**Caution:** 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

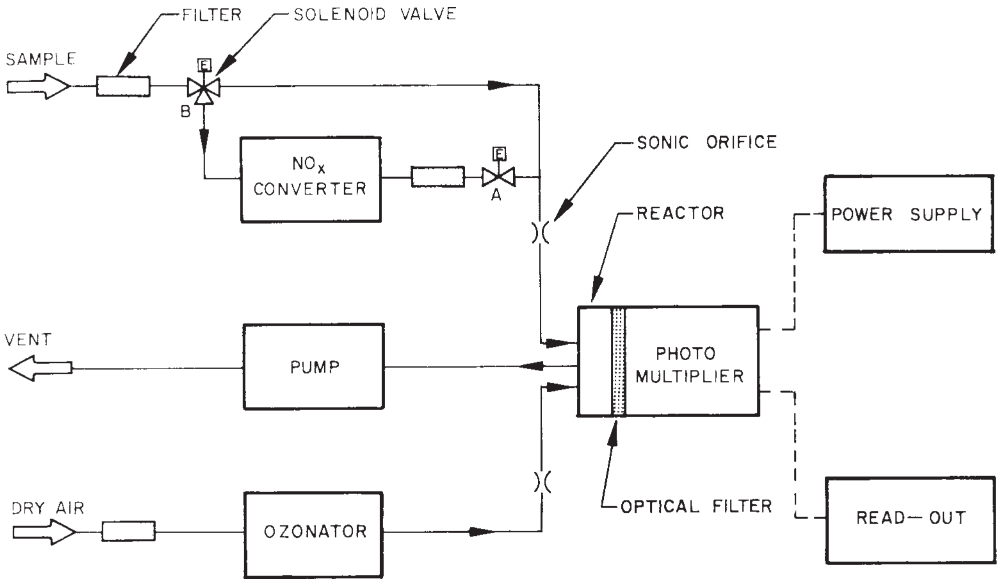

FIG. 1 Schematic of NO-NO_x Chemiluminescence Monitor

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 D 3609), 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*—An ASTM low aniline point thermometer having a range from −38 to +42°C and conforming to the requirements for Thermometer 33C as prescribed in Specification E 1 will meet the requirements of most applications.

7.7 *Barograph or Barometer*, capable of measuring atmospheric pressure to ± 0.5 kPa (see Test Methods D 3631).

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):

8.1.1 *Nitric Oxide Standard Cylinder*, traceable to National Institute of Standards and Technology (NIST) Reference Material SRM-1683 cylinder containing 60 mg/m^3 (50 ppm) of NO in N_2, or SRM-1684a cylinder containing 120 mg/m^3 (100 ppm) of NO in N_2.

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/m^3(50 to 100 ppm) NO in oxygen-free nitrogen and less than 2 mg/m^3(1 ppm) of NO_2.

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

8.4 *Nitrogen*, zero nitrogen, oxygen-free, containing less than 10 $\mu g/m^3$ of NO or 20 $\mu g/m^3$ of NO_2(0.01 ppm).

8.5 *Molecular Sieve*, type 4E, 6 to 14 mesh.

8.6 *Calcium Sulfate*, indicating.

8.7 *Activated Coconut Charcoal*, 6 to 14 mesh.

8.8 *Silica Gel*, indicating, 6 to 14 mesh.

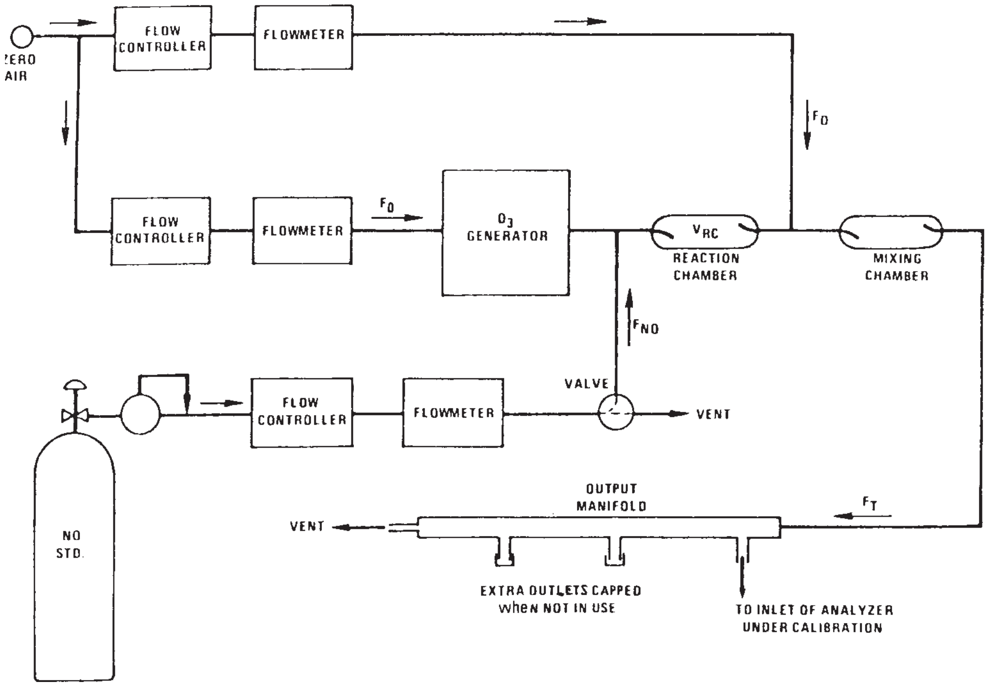

FIG. 2 Schematic Diagram of a Typical GPT Calibration System

9. Precautions

9.1 The handling and storage of compressed gas cylinders and the installation and use of the analyzer shall follow Practice D 3249. 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 NO_2 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 D 1357 and D 3249.

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 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 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 D 3195.

11.2.2 Calibrate any flow orifice with a flowmeter that has been calibrated in accordance with Practice D 3195.

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 every month thereafter.

11.4 *Certification of NO Cylinder*—Procedures for certifying NO working cylinder against an NIST traceable NO cylinder or NIST traceable NO_2 permeation device are given in Annex A7.

12. Procedure

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

12.2 Take the recorder output and determine the concentration of NO, NO_x, or NO_2 directly from the calibration curves in parts per million.

12.3 Check the NO_2 converter efficiency every month in accordance with Annex A5.

12.4 Perform a zero and span check daily in accordance with Annex A6.

12.5 Check the flow rates of all gases in the calibrator daily with the flowmeters and adjust if necessary.

12.6 Check the indicating drying tubes weekly and replace when the color indicates that 75 % of the capacity of the drying material has been reached.

12.7 Replace all nonindicating drying tubes every three months.

12.8 Replace the aerosol filter in the sampling line weekly.

12.9 Check the paper and ink supply in the recorder daily.

13. Calculations

13.1 The signal output of the analyzer is generally displayed on a potentiometric recorder and is read directly in parts per million.

13.2 To convert ppm to $\mu g/m^3$ or mg/m^3, refer to Practice D 1914.

14. Precision and Bias

14.1 *Precision:* **(7)**

14.1.1 The within-laboratory relative standard deviation has been found to be 6 % of the NO_2 concentration over the range 75 to 300 $\mu g\ NO_2/m^3$ (0.04 to 0.16 ppm), based on 1-h averages **(7)**.

14.1.2 The between-laboratories relative standard deviation has been found to be approximately 14 % over the same range, based on 1-h averages **(7)**.

NOTE 3—The stated precision data are for NO_2 modes. There are no precision data available for NO or NO_x modes.

14.2 *Bias*—The bias is determined by the summation of errors that occur during instrument calibration and data collection. The principal uncertainties are introduced during the calibration procedure and are primarily determined by the accuracy and calibration of the flowmeters used and the accuracy of the certification of the NIST traceable reference cylinder or permeation tube.

15. Keywords

15.1 ambient atmospheres; analysis; chemiluminescence reaction; nitric oxide; nitrogen dioxide; oxides of nitrogen; sampling; workplace atmospheres

ANNEXES

(Mandatory Information)

A1. MINIMUM PERFORMANCE SPECIFICATION FOR AMBIENT AND WORKPLACE ATMOSPHERES

Specification	Ambient (See 40 CFR Part 50)	Workplace
Range, ppm	50 to 0.5	0 to 25
Noise, ppm	0.005	0.25
Lower detection limit, ppm	0.01	0.5
Zero drift, 12 and 24 h, ppm	±0.02	± 1.0
Span drift, 24 h,% :		
20 % of upper range limit	± 20	± 10
80 % of upper range limit	± 5	± 2.5
Lag time, min	0.5	0.5
Rise time, min	1.0	1.0
Fall time, min	1.0	1.0
Precision, ppm:		
20 % of upper range limit	0.02	1.0
80 % of upper range limit	0.03	1.5

A2. METHOD OF CALIBRATION OF AMBIENT NO, NO_2, AND NO_x ANALYZERS BY GAS-PHASE TITRATION (8)

A2.1 Principle and Applicability

A2.1.1 The following is a gas-phase technique for the dynamic calibration of ambient air monitors for nitric oxide (NO), nitrogen dioxide (NO_2), and total oxides of nitrogen (NO_x) analyzers. The technique is based upon application of the rapid homogeneous gas-phase reaction between NO and O_3 to produce a stoichiometric quantity of NO_2**(9)**. The quantitative nature of the reaction is used in a manner such that, once the concentration of reacted NO is known, the concentration of NO_2 is determined. The NO and NO_x channels of the NO/NO_x/NO_2 analyzer are first calibrated by flow dilution of a standard NO cylinder. Ozone is then added to excess NO in a dynamic calibration system, and the NO channel is used to measure changes in NO concentration. Upon the addition of O_3, the decrease in NO concentration observed on the calibrated NO analyzer is equivalent to the concentration of NO_2 produced. The amount of NO_2 generated is varied by changing the concentration of O_3 added.

A2.2 Total Air Flow Requirements

A2.2.1 Determine the minimum total flow required at the sample manifold. This flow is controlled by the number and sample flow rate demand of the individual analyzers to be connected to the manifold at the same time. Allow at least 10 to 50 % flow in excess of the required total flow.

A2.2.2 The operational characteristics of the ozone source limit the maximum flow of the calibration system. To determine this flow, adjust the ozone source to near maximum irradiation, then measure the O_3 produced at different levels of air flow through the generator, for example, 1 to 10 L/min, with the ozone monitor. A plot of the O_3 concentration versus the reciprocal air flow should be linear. The air flow that gives the desired maximum O_3 concentration, as determined by the maximum concentration of NO_2 needed for calibration, represents the maximum total flow for a calibration system using the generator. Lower air flows can be used to generate the required O_3 concentrations by reducing the level of irradiation of the ultraviolet lamp. If the air flow characteristics of the ozone generator do not meet the minimum total flow requirements of the analyzer under calibration, then either the generator must be replaced or the number of analyzers to be calibrated simultaneously must be reduced.

A2.3 Dynamic Parameter Specification

A2.3.1 The key to a quantitative reaction between NO and O_3 in gas phase titration is providing a reaction chamber of sufficient volume to allow the reactants to remain in close proximity for a minimum time such that the reaction goes to completion (less than 1 % residual O_3). This will occur if the following criterion is met: The product of the concentration of NO in the reaction chamber, $[NO]_{RC}$, in ppm, times the residence time of the reactants in the chamber, t_R, in minutes, must be at least 2.75 ppm-minutes or greater. This product is called the dynamic parameter specification, P_R. Expressed algebraically, the specified condition is

$$P_R = [NO]_{RC} \times t_R \geq (2.75 \text{ ppm}-\text{min}) \tag{A2.1}$$

where:

$$[NO]_{RC} = [NO]_{STD}\left(\frac{F_{NO}}{F_O + F_{NO}}\right) \tag{A2.2}$$

$$t_R = \frac{V_{RC}}{F_O + F_{ND}} < 2 \text{ min} \tag{A2.3}$$

P_R = dynamic parameter specification, ppm·min,
$[NO]_{RC}$ = NO concentration in reaction chamber, ppm,
t_R = resident time of reactant gases in reaction chamber, min,
$[NO]_{STD}$ = concentration of the undiluted working NO standard, ppm,
V_{RC} = volume of reaction chamber, mL,
F_O = air flow through O_3 generator, mL/min,

F_{NO} = NO flow, mL/min,
F_T = $F_O + F_{NO} + F_D$ = total flow at manifold, mL/min, and
F_D = diluent air flow, mL/min.

A2.3.2 *Application of Dynamic Parameter Specification*:

A2.3.2.1 *General*—A wide range of combinations of reactant NO concentrations and residence times is possible, giving the analyst broad latitude in designing a GPT calibration system to meet individual requirements. For rapid calibration, it is suggested that the residence time be restricted to times shorter than 2 min. Use the dynamic parameter specification to set up a GPT dynamic calibration system as follows:

A2.3.2.2 Select the total flow, F_T, for the calibration system as measured at the sampling manifold. The recommended range for F_T is 1000 to 10 000 mL/min. For a particular system the minimum value for F_T is determined from the sample flow requirements of the analyzer(s) under calibration with provision made for a suitable excess flow. (An excess flow of at least 10 to 50 % is suggested.) The maximum value for F_T is determined by the operation characteristics of the particular ozone source. Considering the restraints on F_T, the analyst should select a suitable value for F_T.

A2.3.2.3 Select a suitable volume, V_{RC}, for the reaction chamber. This volume will be fixed (and can be estimated) if a commercial calibration system is used. The recommended range for V_{RC} is 100 to 500 mL.

A2.3.2.4 Select a working NO standard cylinder to be used for GPT that has a nominal concentration in the range of about 50 to 100 ppm NO. The exact cylinder concentration, $[NO]_{STD}$, is determined by referencing the cylinder against an NIST traceable NO or NO_2 standard (see Annex A7).

A2.3.2.5 Once F_T, V_{RC}, and $[NO]_{STD}$ are determined, calculate the flow of NO, F_{NO}, required to generate an NO concentration at the manifold, $[NO]_{OUT}$, of 90 % of the upper range limit (URL) of the NO channel. For example, if the URL for NO is 0.5 ppm, then the required NO concentration is 0.45 ppm. The resulting expression is

$$F_{NO} = \frac{[NO]_{OUT} \times F_T}{[NO]_{STD}} \tag{A2.4}$$

A2.3.2.6 Calculate the flow required through the O_3 generator, F_O, which results in the product of the reactant NO concentration and the residence time being equal to 2.75; that is, set the left hand side of Eq A2.1 equal to 2.75 and solve for F_O using Eq A2.2 and A2.3. The resulting expression is

$$F_O = \left[\frac{[NO]_{STD} \times F_{NO} \times V_{RC}}{2.75}\right]^{\frac{1}{2}} - F_{NO} \tag{A2.5}$$

NOTE A2.1—The value of F_O determined by Eq A2.5 is the maximum value for F_O. Lower values of F_O may be used.

A2.3.2.7 Calculate the diluent air flow, F_D,

$$F_D = F_T - F_O - F_{NO} \tag{A2.6}$$

A2.3.2.8 Calculate the reactant NO concentration from Eq A2.2.

A2.3.2.9 Calculate the residence time in the reaction chamber from Eq A2.3. For a rapid calibration, the residence time should be less than 2 min.

A2.3.2.10 As a final check, calculate the dynamic parameter, P_R, for the reactant NO concentration and the residence time as determined in A2.3.2.8 and A2.3.2.9:

$$P_R = [NO]_{RC} \times t_R = [NO]_{STD}\left[\frac{F_{NO}}{F_O + F_{NO}}\right]\left[\frac{V_{RC}}{F_O + F_{NO}}\right] \tag{A2.7}$$

Varying any single parameter on the right-hand side of Eq A2.7 affects P_R as follows:

(*1*) Decrease in $F_O \rightarrow$ increase in P_R.
(*2*) Increase in $V_{RC} \rightarrow$ increase in P_R.
(*3*) Increase in $F_{NO} \rightarrow$ increase in P_R.

A2.4 *Example*:

A2.4.1 —Calibrate two NO_2 analyzers, each requiring a sample flow of 250 mL/min. The calibration range for each is 0 to 0.5 ppm NO_2. Set up a GPT dynamic calibration system using an available ozone generator that will produce about 0.5 ppm O_3 at a total air flow of about 5 L/min.

A2.4.2 Select the total flow, F_T,

$$F_T \text{ (min)} = 2\,(250) + 500 \text{ (excess)} = 1000 \text{ mL/min}$$

$$F_T \text{ (max)} = 5000 \text{ mL/min}$$

Let F_T = 3000 mL/min.

A2.4.3 Select a reaction chamber volume, V_{RC}. A Kjeldahl connecting bulb of about 300 mL in volume is available.

A2.4.4 A working NO standard cylinder containing 52.0 ppm NO in N_2 is available.

$$[NO]_{STD} = 52.0 \text{ ppm}$$

A2.4.5 Calculate F_{NO}. The required NO concentration is 0.45 ppm (90 % of URL of 0.5 ppm).

$$F_{NO} = \frac{[NO]_{OUT} \times F_T}{[NO]_{STD}} = \frac{(0.45 \text{ ppm})(3000 \text{ mL/min})}{52.0 \text{ ppm}}$$
$$= 26.0 \text{ mL/min}$$

A2.4.6 Calculate F_O:

$$F_O = \left[\frac{[NO]_{STD} \times F_{NO} \times V_{RC}}{2.75}\right]^{1/2} - F_{NO}$$
$$= \left[\frac{(52 \text{ ppm})(26 \text{ mL/min})(300 \text{ mL})}{2.75 \text{ ppm} \cdot \text{min}}\right]^{1/2} - 26\ mL/min$$
$$= 384 \text{ mL/min} - 26 \text{ mL/min}$$
$$= 358 \text{ mL/min}$$

A2.4.7 Calculate F_D:

$$F_D = F_T - F_O - F_{NO}$$
$$= (3000 - 358 - 26) \text{ mL/min}$$
$$= 2616 \text{ mL/min}$$

A2.4.8

$$[NO]_{RC} = [NO]_{STD}\left[\frac{F_{NO}}{F_O + F_{NO}}\right]$$
$$= 52 \text{ ppm} \times \left[\frac{26 \text{ mL/min}}{(358 + 26) \text{ mL/min}}\right]$$
$$= 3.52 \text{ ppm}$$

A2.4.9

$$\begin{aligned} t_R &= \frac{V_{RC}}{F_O + F_{NO}} \\ &= \frac{300\ \text{mL}}{(358 + 26)\ \text{mL/min}} \\ &= 0.781\ \text{min} \end{aligned}$$

A2.4.10

$$\begin{aligned} P_R &= [NO]_{RC} \times t_R \\ &= (3.52\ \text{ppm})(0.781\ \text{min}) \\ &= 2.75\ \text{ppm} \cdot \text{min} \end{aligned}$$

A2.4.11 A GPT system with the following operating conditions will be suitable to perform the calibration:

F_T = 3000 mL/min,
V_{RC} = 300 mL,
F_{NO} = 26.0 mL/min,
F_O = 358 mL/min, and
F_D = 2616 mL/min.

Changes in the above conditions are possible as long as the dynamic parameter ≥ 2.75 is maintained.

A2.5 *Completeness of NO-O_3 Reaction*—After the gas phase titration apparatus has been assembled, verify the calibrations. The O_3 analyzer is connected to the manifold for this experiment. Generate an NO concentration near 90 % of the upper range limit of the desired NO range; for 0 to 0.5 ppm ranges, the required NO concentration is about 0.45 ppm NO. Next, adjust the ozone source to generate enough O_3 to produce an NO_2 concentration of approximately 80 % of the upper range limit of the NO_2 range. For an NO_2 range of 0 to 0.5 ppm, the required O_3 and NO_2 concentrations would be about 0.4 ppm. This is the most critical point in the gas phase titration since about 90 % of the available NO must be reacted for the reaction to be complete. Note the response of the ozone monitor. There should be no detectable O_3 response measured by the O_3 analyzer if the NO-O_3 reaction goes to completion in the reaction chamber. An O_3 response greater than 1 % of the available O_3 concentration indicates an incomplete NO-O_3 reaction.

A2.6 *Set Up of Analyzer*:

A2.6.1 Select the operating range of the NO/NO_x/NO_2 analyzer to be calibrated. In order to obtain maximum precision and accuracy for NO_2 calibration, all three channels of the analyzer should be set to the same range.

NOTE A2.2—Some analyzer designs may require identical ranges for NO, NO_x, and NO_2 during operation of the analyzer.

A2.6.2 Connect strip chart recorders to the analyzer NO/NO_x/NO_2 output terminals. All adjustments to the analyzer should be performed based on the appropriate strip chart readings. References to analyzer responses in the procedures given below refer to recorder responses.

A2.6.3 Determine the GPT flow conditions required to meet the dynamic parameter specification as indicated in A2.3.

A2.6.4 Adjust the diluent air and O_3 generator air flows to obtain the flows determined in A2.2. The total air flow must exceed the total demand of the analyzer connected to the output manifold to ensure that no ambient air is pulled into the manifold vent. Allow the analyzer to sample zero air until stable NO, NO_x, and NO_2 responses are obtained. After the responses have stabilized, adjust the analyzer zero control.

NOTE A2.3—Some analyzers may have separate zero controls for NO, NO_x, NO_2. Other analyzers may have separate zero controls only for NO and NO_x, while still others may have only one zero control common to all three channels.

A2.6.5 Offsetting the analyzer zero adjustments to + 5 % of full scale is recommended to facilitate observing negative zero drift. Record the stable zero air responses as Z_{NO}, Z_{NO_x}, and Z_{NO_2}.

A2.7 *Preparation of NO and NO_x Calibration Curves*:

A2.7.1 *Adjustment of NO Span Control*:

A2.7.1.1 Adjust the NO flow from the working NO standard cylinder to generate an NO concentration of approximately 80 % of the URL of the NO range. The exact NO concentration is calculated from

$$[NO]_{OUT} = \frac{F_{NO} \times [NO]_{STD}}{F_{NO} + F_O + F_D} \quad \text{(A2.8)}$$

where $[NO]_{OUT}$ = diluted concentration at the output manifold, ppm.

A2.7.1.2 Sample this NO concentration until the NO and NO_x responses have stabilized. Adjust the NO span control to obtain a recorder response as indicated below:

$$\text{Recorder response, \% scale} = \left(\frac{[NO]_{OUT}}{\text{URL}} \times 100\right) + Z_{NO} \quad \text{(A2.9)}$$

where URL = nominal upper range limit of the NO channel, ppm.

NOTE A2.4—Some analyzers may have separate span controls for NO, NO_x, and NO_2. Other analyzers may have separate span controls only for NO and NO_x, while still others may have only one span control common to all three channels. When only one span control is available, the span adjustment is made on the NO channel of the analyzer.

A2.7.1.3 If substantial adjustment of the NO span control is necessary, it may be necessary to recheck the zero and span adjustments by repeating steps A2.6.4 and A2.7.1. Record the NO concentration and the NO response of the analyzer.

A2.7.2 *Adjustment of NO_x Span Control*:

A2.7.2.1 When adjusting the NO_x span control of the analyzer, the presence of any NO_2 impurity in the working NO standard cylinder must be taken into account. Procedures for determining the amount of NO_2 impurity in the working NO standard cylinder are given inAnnex A7. The exact NO_x concentration is calculated from

$$[NO_x]_{OUT} = \frac{F_{NO} \times ([NO]_{STD} + [NO_2]_{IMP})}{F_{NO} + F_O + F_D} \quad \text{(A2.10)}$$

where:
$[NO_x]_{OUT}$ = diluted NO_x concentration at the output manifold, ppm, and

$[NO_2]_{IMP}$ = concentration of NO_2 impurity in the working NO standard cylinder, ppm.

A2.7.2.2 Adjust the NO_x span control to obtain a recorder response as indicated below:

$$\text{Record response, \% scale} = \left(\frac{[NO_x]_{OUT}}{URL} \times 100\right) + Z_{NO_x} \tag{A2.11}$$

NOTE A2.5—If the analyzer has only one span control, the span adjustment is made on the NO channel; no further adjustment is made here for NO_x.

A2.7.2.3 If substantial adjustment of the NO_x span control is necessary, it may be necessary to recheck the zero and span adjustments by repeating steps A2.6.4 and A2.7.2. Record the NO_x concentration and the NO_x response of the analyzer.

A2.7.3 Generate several additional concentrations (at least five evenly spaced points across the remaining scale are suggested to verify linearity) by decreasing F_{NO} or increasing F_D. For each concentration generated, calculate the exact NO and NO_x concentrations using Eq A2.8 and Eq A2.10, respectively. Record the NO and NO_x responses of the analyzer for each concentration. Plot the analyzer responses versus the respective calculated NO and NO_x concentrations and draw or calculate the NO and NO_x calibration curves.

A2.8 *Preparation of NO_2 Calibration Curve*:

A2.8.1 Assuming the NO_2 zero has been properly adjusted while sampling zero air in A2.6.4, adjust F_O and F_D as determined in A2.3.2. Adjust F_{NO} to generate an NO concentration near 90 % of the URL of the NO range. Sample this NO concentration until the NO and NO_x responses have stabilized. Using the NO calibration curve obtained in A2.7, measure and record the NO concentration as $[NO]_{orig}$. Using the NO_x calibration curve obtained in A2.7, measure and record the NO_x concentration as $[NO_x]_{orig}$.

A2.8.2 Adjust the O_3 generator to generate sufficient O_3 to produce a decrease in the NO concentration equivalent to approximately 80 % of the URL of the NO_2 range. The decrease must not exceed 90 % of the NO concentration determined in A2.8.1. After the analyzer responses have been stabilized, record the resultant NO and NO_x concentrations as $[NO]_{rem}$ and $[NO_x]_{rem}$.

A2.8.3 Calculate the resulting NO_2 concentration from

$$[NO_2]_{OUT} = [NO]_{orig} - [NO]_{rem} = \frac{F_{NO} \times [NO_2]_{IMP}}{F_{NO} + F_O + F_D} \tag{A2.12}$$

where:

$[NO_2]_{OUT}$ = diluted NO_2 concentration at the output manifold, ppm,

$[NO]_{orig}$ = original NO concentration, prior to addition of O_3 ppm, and

$[NO]_{rem}$ = NO concentration remaining after addition of O_3, ppm.

Adjust the NO_2 span control to obtain a recorder response as indicated below:

$$\text{Record response, \% scale} = \left(\frac{[NO_2]_{OUT}}{URL} \times 100\right) + Z_{NO_2} \tag{A2.13}$$

NOTE A2.6—If the analyzer has only one or two span controls, the span adjustments are made on the NO channel or NO and NO_x channels and no further adjustment is made here for NO_2.

A2.8.4 If substantial adjustment of the NO_2 span control is necessary, it may be necessary to recheck the zero and span adjustments by repeating steps A2.6.4 and A2.8.3. Record the NO_2 concentration and the corresponding analyzer NO_2 and NO_x responses.

A2.8.5 Maintaining the same F_{NO}, F_O, and F_D as A2.8.1, adjust the ozone generator to obtain several other concentrations of NO_2 over the NO_2 range (at least five evenly spaced points across the remaining scale are suggested). Calculate each NO_2 concentration using Eq A2.12 and record the corresponding analyzer NO_2 and NO_x responses. Plot the NO_2 responses of the analyzer versus the corresponding calculated NO_2 concentrations and draw or calculate the NO_2 calibration curve.

A3. METHOD OF CALIBRATION OF WORKPLACE ATMOSPHERE NO/NO_x/NO_2 ANALYZER

A3.1 The workplace analyzer can be calibrated by methods similar to those in Annex A2 with appropriate modifications of the flows of F_O, F_D, F_{NO}, and appropriate choice of V_{RC}.

A4. CALIBRATION OF NO_2 PERMEATION DEVICE[8]

A4.1 After the analyzer has been calibrated in accordance with Annex A2 or Annex A3, adjust the flow rate of the NO_2 permeation device calibrator so the analyzer reads 80 % of full scale. Record the flow in litres per minute and analyzer reading in parts per million.

A4.2 Repeat A4.1 for 20 %, 40 %, and 60 % of full scale, in duplicate, in random order.

A4.3 Prepare a curve of best fit of the analyzer reading versus the reciprocal of the flow rate and determine the slope of the line. Calculate the NO_2 permeation rate as follows:

$$R = \frac{S}{K}$$

where:

R = permeation rate in µg NO_2/min,

S = slope of curve in ppm × (L/min), and
K = 0.532 µL NO_2/µg NO_2 (at 25° and 101.3 kPa).

A4.4 Replace the permeation device when the permeation rate decreases suddenly.

A5. DETERMINATION OF CONVERTER EFFICIENCY[8]

A5.1 The total NO_2 concentration generated at manifold $[NO_2]$ out during the gas-phase titration is given by the sum of the NO_2 concentration from the GPT plus any NO_2 impurity from the NO cylinder:

$$[NO_2]_{OUT} = ([NO]_{orig} - [NO]_{rem}) + [NO_2]_{imp}$$

A5.2 The total NO_2 concentration converted to NO in the analyzer, $[NO_2]_{CONV}$ is given by

$$[NO_2]_{CONV} = [NO_2]_{OUT} - ([NO_x]_{orig} - [NO_x]_{rem})$$

where:

$[NO_2]_{CONV}$ = concentration of NO_2 converted, ppm
$[NO_x]_{orig}$ = original NO_x concentration prior to addition of O_3, ppm, and
$[NO_x]_{rem}$ = NO_x concentration remaining after addition of O_3 ppm.

A5.3 Plot $[NO_2]_{CONV}$(y-axis) versus $[NO_2]_{OUT}$(x-axis) and draw or calculate the converter efficiency curve. The slope of the curve is the average converter efficiency, E_C. The average converter efficiency shall be equal to or greater than 96 %; if it is less than 96 % replace or service the converter.

A6. ZERO AND SPAN CHECK

A6.1 Adjust the flow rates of the zero and span calibrator so the NO_2 concentration is about 80 % full scale of analyzer.

A6.2 Allow the analyzer to sample NO_2 span gas for 5 min or until the reading is steady, whichever is greater.

A6.3 Mark the recorder trace as "Unadjusted Span."

A6.4 Allow the analyzer to sample zero gas for 5 min or until the reading is steady, whichever is greater.

A6.5 Mark the recorder trace as "Unadjusted Zero."

A6.6 If the zero trace recording is greater than ± 0.005 ppm, adjust the zero knob so the recorder reads zero.

A6.7 Mark the reading as "Adjusted Zero."

A6.8 Repeat A6.2

A6.9 If the recorder trace is greater than ± 0.005 ppm from the known value of the span gas, readjust the span knob so the recorder reads the standard value.

A6.10 Mark the readings as "Adjusted Span."

A6.11 Repeat A6.1-A6.10 with the analyzer in the NO and NO_x modes.

A6.12 Return the analyzer to the sampling mode.

A7. CERTIFICATION OF NO IN N_2 WORKING STANDARD AGAINST NIST TRACEABLE STANDARDS (8)

A7.1 The NO content of the NO working standard shall be periodically assayed against NIST traceable NO or NO_2 standards. Any NO_2 impurity in the working NO standard cylinder shall also be assayed. Certification of the NO working standard shall be made on a quarterly basis or more frequently as required. Procedures are outlined below for certification against either an NO or NO_2 NBS traceable standard.

NOTE A7.1—If the assayed NO_2 impurity concentration, $[NO_2]_{IMP}$, is greater than the 1 ppm value allowed in the calibration procedure, make certain that the NO delivery system is not the source of contamination before discarding the NO standard.

A7.2 *Certification of NO Working Standard Against an NIST Traceable NO Standard*:

A7.2.1 In this procedure it is possible to assay the NO content of the working standard without first calibrating the NO and NO_x responses of the analyzer. This is done by comparing relative NO responses of the working NO standard to the NIST traceable NO standard. The NO_2 impurity can be determined from the analyzer NO_x responses provided the converter efficiency is known.

A7.2.2 Use the NIST traceable NO standard and the GPT calibration procedure to calibrate the NO, NO_x, and NO_2 responses of a chemiluminescence analyzer. Also determine the converter efficiency of the analyzer. Refer to Annex A2 and Annex A5 for exact details; ignore the recommended zero offset adjustments.

A7.2.3 Generate several NO concentrations by dilution of the NO working standard. Use the nominal concentration, $[NO]_{NOM}$, to calculate the diluted concentrations. Plot the analyzer NO response (in ppm) versus the nominal diluted NO concentration and determine the slope, S_{NOM}. Calculate the NO concentration of the working standard, $[NO]_{STD}$, from

$$[NO]_{STD} = [NO]_{NOM} \times S_{NOM} \quad (A7.1)$$

A7.2.4 If the nominal NO concentration of the working standard is unknown, generate several NO concentrations to give on-scale NO responses. Measure and record F_{NO} and F_T

for each NO concentration generated. Plot the analyzer NO response versus F_{NO}/F_T and determine the slope that gives $[NO]_{STD}$ directly.

A7.2.5 The analyzer NO_x responses to the generated NO concentrations reflect any NO_2 impurity in the NO working standard. Plot the difference between the analyzer NO_x and NO responses versus F_{NO}/F_T. The slope of this plot is $[NO_2]_{IMP}$.

A7.3 *Certification of NO Working Standard Against an NBS Traceable NO_2 Standard*:

A7.3.1 Use the NO working standard and the GPT calibration procedure to "calibrate" the NO, NO_x, and NO_2 responses of the chemiluminescence analyzer. Refer to Annex A2 for exact details; ignore the recommended zero offset adjustments. For this pseudo-calibration use the nominal NO cylinder value and assume no NO_2 impurity is in the cylinder. For an analyzer with dual detectors, the NO_x span adjustment must be made by diverting the sample flow around the converter and routing it directly to the NO_x detector. This operation electronically balances the two detectors.

A7.3.2 From the GPT data, plot the analyzer NO_2 response versus the NO_2 concentration generated by GPT. Determine the slope, S_{NOM}, and the x-intercept of the curve. Generate several NO_2 concentrations by dilution of the NIST traceable NO_2 standard. Plot the analyzer NO_2 response versus NO_2 concentration. Determine the slope, S_{NIST}. Calculate the NO concentration of the working standard, $[NO]_{STD}$, from

$$[NO]_{STD} = [NO]_{NOM} \times \frac{S_{NOM}}{S_{NIST}} \tag{A7.2}$$

A7.3.3 Calculate the NO_2 impurity from

$$[NO_2]_{IMP} = \frac{(x-\text{intercept})}{F_{NO}} \times \frac{S_{NOM}}{S_{NIST}} \tag{A7.3}$$

A8. REPORTED INTERFERENT SPECIES IN CHEMILUMINESCENT NO $_x$ METHODS

Compound	Response,% of Concentration		References
	NO mode	NO_2 mode	
	Nitrogen Species		
Nitric acid	0	100	**(3)**
Nitrous acid	0	100	**(3,6)**
Nitrogen pentoxide	0	100	**(3)**
Nitrogen trioxide	0	100	**(3)**
Ammonium nitrate	...	...	**(6)**
PAN	0	20–100	**(3,6)**
Methyl nitrate	0	100	**(3)**
Ethyl nitrate	0	103	**(10)**
n-Propyl nitrate	0	100	**(3)**
n-Butyl nitrate	0	100	**(3)**
Nitroethane	0	7	**(10)**
Nitrocresol	0	3–11	**(3)**
Ethyl nitrite	0	92	**(10)**
Alkanol amines		+	**(11)**
Alkyl amines		+	**(6)**
	Sulfur Species^A		
Hydrogen sulfide	0.2	−0.2	**(12)**
Carbonyl sulfide	0.4	0.05	**(12)**
Carbon disulfide	0	0.05	**(12)**
Methane thiol	0.3–0.9	−(0.1–0.9)	**(3,12)**
Ethane thiol	1	−1.1	**(12)**
Methyl sulfide	0.3–0.7	−(0.1–0.3)	**(3,12)**
Ethyl sulfide	0.6–3	−(0.3–2)	**(12)**
Methylethyl sulfide	1	−0.5	**(12)**
Methyl disulfide	0.7	−0.5	**(12)**
Ethyl disulfide	2	−1.4	**(12)**
Thiophene	0.4	−0.2	**(12)**
2-methyl	0.8	0	**(12)**
3-methyl	9	−8	**(12)**
2,5-dimethyl	2	−1	**(12)**
	Chlorine Species^B		
HCl	0	+	**(5)**
Cl_2	+,0	+	**(3,5)**
$ClNO_x$	+	+	**(3)**
$COCl_2$	0	+	**(5)**
$CHCl_3$	0	+	**(5)**
Cl_3CCOCl	0	+	**(5)**

[A] Interferent response may be enhanced in the presence of olefines **(13)**.

[B] Variable Response.

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