



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

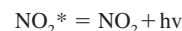
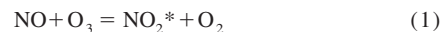
3. Terminology

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 (**I**).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.

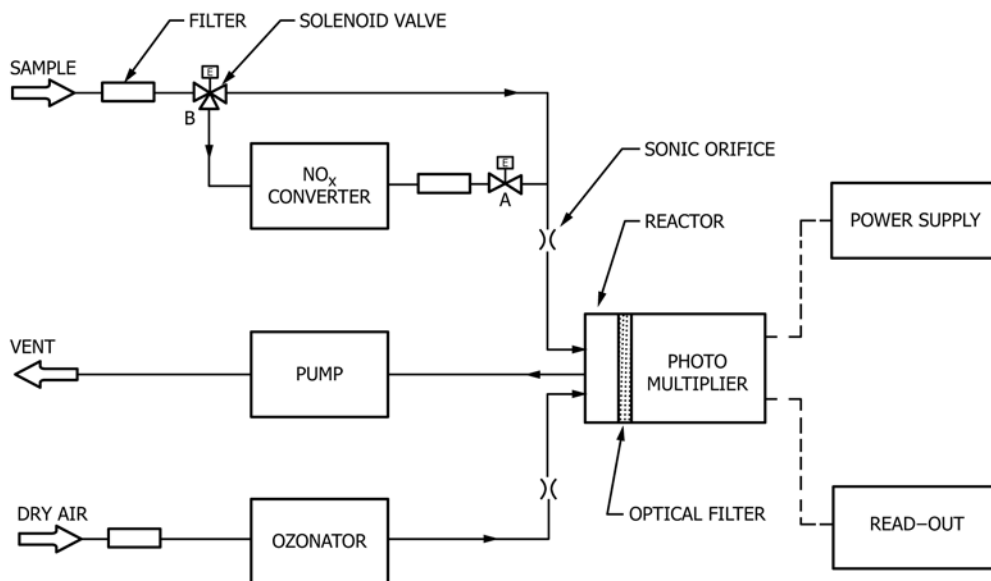


FIG. 1 Schematic of NO-NO_x Chemiluminescence Monitor

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 ±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.

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 ±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 ±2 %.

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

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. Alternatively, an ozone generation using a 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 µg/m³ of NO (0.002 ppm), 4 µg/m³ of NO₂ (0.002 ppm), and 4 µg/m³ of O₃ (0.002 ppm).

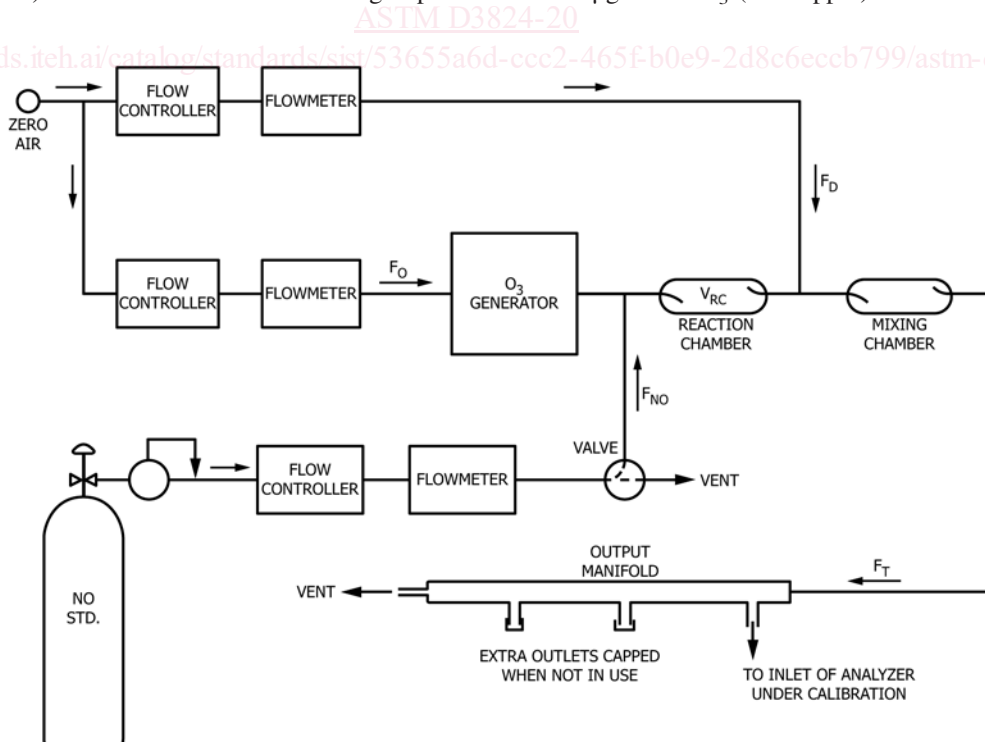


FIG. 2 Schematic Diagram of a Typical GPT Calibration System

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/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*, ultra high purity nitrogen, oxygen-free, containing less than $10 \text{ }\mu\text{g/m}^3$ of NO or $20 \text{ }\mu\text{g/m}^3$ of NO_2 (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 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 [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 NO_2 directly from the calibration curves in desired units of parts per million.

12.3 Check the NO_2 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](#).

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 at least every three months.

12.8 Replace the aerosol filter in the sampling line at least weekly.

13. Calculations

13.1 The signal output of the analyzer is frequently displayed on a computer screen or potentiometric recorder and is recorded in an electronic data file.

13.2 To convert ppm to $\mu\text{g}/\text{m}^3$ or mg/m^3 , refer to Practice D1914.

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 $\mu\text{g}/\text{m}^3$ (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 4—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

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ANNEXES

(Mandatory Information)

A1. MINIMUM PERFORMANCE SPECIFICATIONS FOR AMBIENT AND WORKPLACE ATMOSPHERES

ASTM D3824-20

Specification	Ambient (see for example 40 CFR, Part 50)	Workplace (see for example 29 CFR, Part 1910)
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, NO₂, 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 (NO₂), and total oxides of nitrogen (NO_x) analyzers. The technique is based upon application of the rapid homogeneous gas-phase reaction between NO and O₃ to produce a stoichiometric quantity of NO₂ (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 NO₂ is determined. The NO and NO_x channels of the NO/NO_x/NO₂ 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 O₃, the decrease in NO concentration observed on the calibrated NO analyzer is equivalent to the concentration of NO₂ produced. The amount of NO₂ generated is varied by changing the concentration of O₃ added.

A2.2 Total Air Flow Requirements

A2.2.1 Determine the minimum total flow required at the sample manifold. This flow rate 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 O₃ 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 O₃ concentration versus the reciprocal air flow should be linear. The air flow that gives the desired maximum O₃ concentration, as determined by the maximum concentration of NO₂ 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 O₃ 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 O₃ in gas phase titration is providing a reaction chamber of sufficient volume to allow the reactants to remain in proximity for a minimum time such that the reaction goes to completion (less than 1 % residual O₃). 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:

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

where:

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

$$t_R = \frac{V_{\text{RC}}}{F_{\text{O}} + F_{\text{ND}}} < 2 \text{ min} \quad (\text{A2.3})$$

- 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 O₃ 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 primary standard traceable to a standard reference material (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:

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

A2.3.2.6 Calculate the flow required through the O₃ 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:

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

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:

$$F_D = F_T - F_O - F_{NO} \quad (A2.6)$$

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:

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

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

- (1) Decrease in F_O → increase in P_R.
- (2) Increase in V_{RC} → increase in P_R.
- (3) Increase in F_{NO} → increase in P_R.

A2.4 Example

A2.4.1 Calibrate two NO₂ analyzers, each requiring a sample flow of 250 mL/min. The calibration range for each is 0 to 0.5 ppm NO₂. Set up a GPT dynamic calibration system using an available ozone generator that will produce about 0.5 ppm O₃ 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 N₂ 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:

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

$$= \left[\frac{(52 \text{ ppm})(26 \text{ mL/min})(300 \text{ mL})}{2.75 \text{ ppm} \cdot \text{min}} \right]^{\frac{1}{2}} - 26 \text{ mL/min}$$

$$= 384 \text{ mL/min} - 26 \text{ mL/min}$$

$$= 358 \text{ mL/min}$$

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

$$t_R = \frac{V_{RC}}{F_O + F_{NO}}$$

$$= \frac{300 \text{ mL}}{(358 + 26) \text{ mL/min}}$$

$$= 0.781 \text{ min}$$

A2.4.10

$$P_R = [NO]_{RC} \times t_R$$

$$= (3.52 \text{ ppm})(0.781 \text{ min})$$

$$= 2.75 \text{ ppm} \cdot \text{min}$$

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

$$F_T = 3000 \text{ mL/min,}$$

$$V_{RC} = 300 \text{ mL,}$$

$$F_{NO} = 26.0 \text{ mL/min,}$$

$$F_O = 358 \text{ mL/min, and}$$

$$F_D = 2616 \text{ mL/min.}$$

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

A2.5 *Completeness of NO-O₃ Reaction*—After the gas phase titration apparatus has been assembled, verify the calibrations. The O₃ 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 O₃ to produce an NO₂ concentration of approximately 80 % of the upper range limit of the NO₂ range. For an NO₂ range of 0 to 0.5 ppm, the required O₃ and NO₂ concentrations would be about 0.4 ppm. This is the most critical point in the gas phase