



## Standard Test Method for Nitrogen Oxides (Combined) Content in the Atmosphere by the Griess-Saltzman Reaction<sup>1</sup>

This standard is issued under the fixed designation D 3608; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon ( $\epsilon$ ) indicates an editorial change since the last revision or reapproval.

<sup>e1</sup> NOTE—Footnote was removed from 7.2 in September 2000

### 1. Scope

1.1 This test method covers the manual determination of the combined nitrogen dioxide (NO<sub>2</sub>) and nitric oxide (NO) content, total NO<sub>x</sub>; in the atmosphere in the range from 4 to 10 000 µg/m<sup>3</sup> (0.002 to 5 ppm (v)).

1.2 The maximum sampling period is 60 min at a flow rate of 0.4 L/min.

1.3 The values stated in SI units are to be regarded as the standard. The values given in parentheses are for information only.

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.*

### 2. Referenced Documents

#### 2.1 ASTM Standards:

- D 1071 Test Methods for Volumetric Measurement of Gaseous Fuel Samples<sup>2</sup>
- D 1193 Specification for Reagent Water<sup>3</sup>
- D 1356 Terminology Relating to Sampling and Analysis of Atmospheres<sup>4</sup>
- D 1357 Practice for Planning the Sampling of the Ambient Atmosphere<sup>4</sup>
- D 3195 Practice for Rotameter Calibration<sup>4</sup>
- D 3609 Practice for Calibration Techniques Using Permeation Tubes<sup>4</sup>
- D 3631 Test Methods for Measuring Surface Atmospheric Pressure<sup>4</sup>
- E 1 Specification for ASTM Thermometers<sup>5</sup>

<sup>1</sup> This test method is under the jurisdiction of ASTM Committee D22 on Sampling and Analysis of Atmospheres and is the direct responsibility of Subcommittee D22.03 on Ambient Atmospheres and Source Emissions.

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<sup>2</sup> *Annual Book of ASTM Standards*, Vol 05.05.

<sup>3</sup> *Annual Book of ASTM Standards*, Vol 11.01.

<sup>4</sup> *Annual Book of ASTM Standards*, Vol 11.03.

<sup>5</sup> *Annual Book of ASTM Standards*, Vol 14.03.

E 128 Test Method for Maximum Pore Diameter and Permeability of Rigid Porous Filters for Laboratory Use<sup>6</sup>

### 3. Terminology

3.1 *Definitions*—For definitions of terms used in this test method, refer to Terminology D 1356.

### 4. Summary of Test Method

4.1 The NO is quantitatively (1)<sup>7</sup> converted to NO<sub>2</sub> by a chromic acid oxidizer. The resulting NO<sub>2</sub>, plus the NO<sub>2</sub> already present, are absorbed in an azo-dye-forming reagent (2). A red-violet color is produced within 15 min, the intensity of which is measured spectrophotometrically at 550 nm.

### 5. Significance and Use

5.1 Both NO<sub>2</sub> and NO play an important role in photochemical-smog-forming reactions. In sufficient concentrations NO<sub>2</sub> is deleterious to health, agriculture, materials, and visibility.

5.2 In combustion processes, significant amounts of NO may be produced by combination of atmospheric nitrogen and oxygen; at ambient temperatures, NO can be converted to NO<sub>2</sub> by oxygen and other atmospheric oxidants. Nitrogen dioxide also may be generated from processes involving nitric acid, nitrates, the use of explosives, and welding.

### 6. Interferences

6.1 Any significant interferences due to sulfur dioxide (SO<sub>2</sub>) should be negated by the oxidation step. The addition of acetone to the reagent retards color-fading by forming a temporary addition product with SO<sub>2</sub>. This will protect the reagent from incidental exposure to SO<sub>2</sub> and will permit reading the color intensity within 4 to 5 h (instead of the 45 min required without acetone) without appreciable losses.

<sup>6</sup> *Annual Book of ASTM Standards*, Vol 14.02.

<sup>7</sup> The boldface numbers in parentheses refer to the list of references appended to this test method.

6.2 A five-fold ratio of ozone to NO<sub>2</sub> will cause a small interference, the maximal effect occurring in 3 h. The reagent assumes a slightly orange tint.

6.3 The interferences from nitrous oxide and nitrogen pentoxide, and other gases that might be found in polluted air are considered to be negligible.

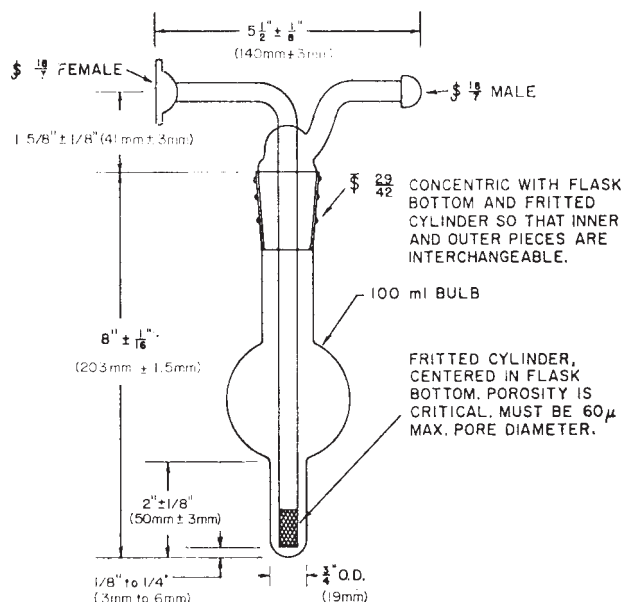


FIG. 1 Fritted Bubbler for Sampling Combined Nitrogen Oxides

## 7. Apparatus

7.1 *Sampling Probe*—A glass or TFE-fluorocarbon (preferred) tube, 6 to 10 mm in diameter, provided with a downward-facing intake (funnel or tip). The dead volume of the system should be kept minimal, to avoid loss of NO<sub>x</sub> on the surfaces of the apparatus.

7.2 *Oxidizer Tube*—Soak 14 to 16-mesh firebrick or 1/16-in. (1.5 mm) molecular sieve pellets in a 17 % aqueous solution of chromium trioxide (CrO<sub>3</sub>) for 10 to 30 min. After draining the excess solution and drying in an oven at 105°C for 30 min, the solid oxidizer has a dull pink color. This color changes to rich yellow (active color) after 24-h equilibration with ambient air at 40 to 70 % relative humidity, or after drawing ambient air through at a flow rate of 0.5 L/min for 1 h. A change in color to a greenish brown indicates the exhaustion of oxidizing ability, and progresses with a sharp boundary. Place about 3 g of the oxidizer in a 30-mL midget impinger, or fill a 5-mm tube to a height of 80 mm and plug each end with glass wool.

7.3 *Absorber*—An all-glass bubbler with a 60-μm maximum pore diameter frit, commonly labeled “coarse,” similar to that illustrated in Fig. 1.

7.3.1 The porosity of the fritted bubbler, as well as the sampling flow rate, affect absorption efficiency. An efficiency of over 95 % may be expected with a flow rate of 0.4 L/min or less and a maximum pore diameter of 60 μm. Frits having a maximum pore diameter less than 60 μm will have a higher efficiency but will require an inconvenient pressure drop for sampling.

7.3.2 Measure the porosity of an absorber in accordance with Test Method E 128. If the frit is clogged or visibly discolored, carefully clean with concentrated chromic-sulfuric acid mixture, rinse well with water, and redetermine the maximum pore diameter.

7.3.3 Rinse the bubbler thoroughly with water and allow to dry before using.

7.4 *Mist Eliminator or Gas Drying Tube* filled with activated charcoal or soda lime is used to prevent damage to the flowmeter and pump.

7.5 *Air-Metering Device*—A calibrated glass variable-area flowmeter, or dry gas meter coupled with a flow indicator capable of accurately measuring a flow of 0.4 L/min is suitable.

7.6 *Thermometer*—ASTM Thermometer 33C, meeting the requirements of Specification E 1, will be suitable for most applications of the method.

7.7 *Manometer*, accurate to 670 Pa (0.20 in Hg).

7.8 *Air Pump*—A suction pump capable of drawing the required sample flow for intervals of up to 60 min.

7.9 *Spectrophotometer or Colorimeter*—A laboratory instrument suitable for measuring the intensity of the red-violet color at 550 nm, with stoppered tubes or cuvettes. The wavelength band-width is not critical for this determination.

7.10 *Stopwatch or Timer*.

## 8. Reagents and Materials

8.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. All reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.<sup>8</sup> Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

8.2 *Purity of Water*—Water shall be deionized water in accordance with Specification D 1193 for Type I and II reagent water. Water must be nitrite-free.

8.3 *Absorbing Reagent*—Dissolve 5 g of anhydrous sulfanilic acid (or 5.5 g of the monohydrate) in almost a litre of water containing 140 mL of glacial acetic acid. Gentle heating is permissible to speed up the process. To the cooled mixture, add 20 mL of the 0.1 % stock solution of *N*-(1-naphthyl)-ethylenediamine dihydrochloride and 10-mL acetone. Dilute to 1 L. The solution will be stable for several months if kept well-stoppered in a brown bottle in the refrigerator. The absorbing reagent must be at room temperature before use. Avoid lengthy contact with air during both preparation and use, since absorption of nitrogen dioxide will discolor the reagent.

8.4 *Chromic Acid Oxidant*—Dissolve 17 g of chromium trioxide (CrO<sub>3</sub>) in 100 mL of water.

8.5 *N-(1-Naphthyl)-Ethylenediamine Dihydrochloride, Stock Solution (0.1 %)*—Dissolve 0.1 g of the reagent in 100 mL of water. The solution will be stable for several months if

<sup>8</sup> *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Anal. Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

kept well-stoppered in a brown bottle in the refrigerator. (Alternatively, weighed small amounts of the solid reagent may be stored.)

8.6 *Sodium Nitrite (NaNO<sub>2</sub>), Standard Solution (0.0246 g/L)*—One mL of this working solution of NaNO<sub>2</sub> produces a color equivalent to that of 20 µg of NO<sub>2</sub> in 1 L of air at 101 kPa (29.92 in Hg) and 25°C (see 10.2.2). Prepare fresh just before use by diluting from a stock solution containing 2.460 g/L of NaNO<sub>2</sub> (calculated as 100 %). It is desirable to assay the solid reagent (3). The stock solution is stable for 90 days at room temperatures, and for a year in a brown bottle under refrigeration.

8.7 *NO<sub>2</sub> Permeation Device*—See Practice D 3609.

## 9. Sampling

9.1 Sampling procedures are described in Section 11. Different combinations of sampling rates and time may be chosen to meet special needs, but sample volumes and air flow rates must be adjusted so that linearity is maintained between absorbance and concentration over the dynamic range.

9.2 See Practices D 1357 for sampling guidelines.

## 10. Calibration and Standardization

10.1 *Sampling Equipment*—If a flowmeter is used to measure sample air, calibrate it prior to use using Practice D 3195. If a gas meter is used, calibrate it prior to use according to Method D 1071.

10.2 *Analysis:*

10.2.1 *Recommended Procedure:*

10.2.1.1 Calibrated permeation tubes that contain liquefied NO<sub>2</sub> can be used to prepare standard concentrations of NO<sub>2</sub> in air (4). See Practice D 3609 for details. Analyses of these known concentrations give calibration curves that simulate all the operational conditions performed during the sampling and chemical procedures. This calibration curve includes the important correction for collection efficiency at various concentrations of NO<sub>2</sub>.

10.2.1.2 Prepare or obtain a TFE-fluorocarbon permeation tube that emits NO<sub>2</sub> at a rate of 0.1 to 0.2 µg/min (0.05 to 0.1 µL/min at standard conditions of 25°C and 101.3 kPa (29.92 in Hg)). Calibrate permeation tubes under a stream of dry nitrogen, using Practice D 3609.

10.2.1.3 To prepare standard concentrations of NO<sub>2</sub> assemble the apparatus, as shown in Practice D 3609, consisting of a water-cooled condenser; constant-temperature water bath maintained at 20°C; cylinders containing pure dry nitrogen and pure dry air, with appropriate pressure regulators; needle valves and flowmeters for the nitrogen and dry air diluent gas streams. Bring the diluent gases to temperature by passage through a 2-m long copper coil immersed in the water bath. Insert a calibrated permeation tube into the central tube of the condenser maintained at 20°C by circulating water from the constant-temperature bath and pass a stream of nitrogen over the tube at a fixed rate of approximately 50 mL/min. Dilute this gas stream to the desired concentration by varying the flow rate of the “clean dry air.” This flow rate can normally be varied from 0.2 to 15 L/min. The flow rate of the sampling system determines the lower limit for the flow rate of diluent gases. The flow rates of the nitrogen and the diluent air must be

measured to an accuracy of 1 to 2 %. With a tube permeating NO<sub>2</sub> at a rate of 0.1 µL/min (0.19 µg/min), the range of concentration of NO<sub>2</sub> will be between 20 to 1000 µg/m<sup>3</sup> (0.01 to 0.50 ppm (v)), a generally satisfactory range for ambient air conditions. When higher concentrations are desired, calibrate using longer permeation tubes.

10.2.1.4 *Procedure for Preparing Simulated Calibration Curves*—A multitude of curves may be prepared by selecting different combinations of sampling rate and sampling time. The following description represents a typical procedure for ambient air sampling of short duration. The system is designed to provide an accurate measure of NO<sub>2</sub> in the 40 to 10 000 µg/m<sup>3</sup> (0.02 to 5 ppm (v)) range. It can be modified to meet special needs.

10.2.1.5 The dynamic range of the colorimetric procedure fixes the total volume of the sample at 24 L, then to obtain linearity between the absorbance of the solution and the concentration of NO<sub>2</sub> in parts per million by volume, select a constant sampling time. This fixing of sampling time is also desirable from a practical standpoint. In this case, select a sampling time of 60 min. Then, to obtain a 24-L sample requires a flow rate of 0.4 L/min. Calculate the concentration of standard NO<sub>2</sub> in air as follows:

$$C = \frac{P(1000)}{R + r} \quad (1)$$

where:

- $C$  = concentration of NO<sub>2</sub> µg/m<sup>3</sup>,
- $P$  = permeation rate, µg/min,
- $R$  = flow rate of diluent air, L/min,
- $r$  = flow rate of diluent nitrogen, L/min, and
- 1000 = conversion factor to convert L to m<sup>3</sup>.

10.2.1.6 A plot of the concentration of NO<sub>2</sub> in µg/m<sup>3</sup> (x-axis) against absorbance of the final solution (y-axis) will yield a straight line, the inverse or the slope of which is the factor for conversion of absorbance to µg/m<sup>3</sup>. This factor includes the correction for collection efficiency. Any deviation from linearity at the lower concentration range indicates a change in collection efficiency of the sampling system. Actually, the standard concentration of 20 µg/m<sup>3</sup> is slightly below the dynamic range of the method. If this is the range of interest, the total volume of air collected should be increased to obtain sufficient color within the dynamic range of the colorimetric procedure. Also, once the calibration factor has been established under simulated conditions, the conditions can be modified so that the concentration of NO<sub>2</sub> is a simple multiple of the absorbance of the colored solution.

10.2.2 *Alternate Procedure:*

10.2.2.1 Standardization is based upon the empirical observation (5) that 0.82 mol of NaNO<sub>2</sub> produces the same color as 1 mol of NO<sub>2</sub>. One mL of the working standard contains 24.6 µg of NaNO<sub>2</sub>. Since the molecular weight of NaNO<sub>2</sub> is 69.1, this is equivalent to:  $(24.6/69.1) \times (46.0/0.82) = 20$  µg of NO<sub>2</sub>.

10.2.2.2 For convenience, standard conditions are taken as 101 kPa (29.92 in. Hg) and 25°C, at which the molar gas volume is 24.47 L. This is very close to the standard conditions used for air-handling equipment, 101 kPa (29.92 in. Hg), 21.1°C (70°F), and 50 % relative humidity, at which the molar gas volume is 24.76 L, or 1.2 % greater. Ordinarily, the

correction of the sample volume to these standard conditions is slight and may be omitted, however, for greatest accuracy, it may be made by means of the perfect gas equation.

10.2.2.3 Add graduated amounts of NaNO<sub>2</sub> solution up to 1 mL (measured accurately in a graduated pipet or small buret) to a series of 25-mL volumetric flasks, and dilute to the marks with absorbing reagent. Mix, allow 15 min for complete color development, and read the absorbance (see 8.2).

10.2.2.4 Good results can be obtained with these small volumes of standard solution if they are carefully measured. Making the calibration solutions up to 25 mL total volume, rather than the 10-mL volume used for samples, increases accuracy.

10.3 Plot the absorbances of the standards against micrograms of NO<sub>2</sub> per millilitre of absorbing reagent. The plot follows Beer's law. Draw the line of best fit using regression analysis by the method of least squares. Determine the reciprocal of the slope of the line and denote it as the standardization factor, *K*, the number of micrograms of NO<sub>2</sub> intercepted at an absorbance of exactly 1.0.

### 11. Procedure

11.1 *Operation*—Assemble in order as shown in Fig. 2, sampling probe (optional), oxidizer, impinger or fritted-tube absorber, mist eliminator or trap, flowmeter, and pump. Measure temperature and pressure drop across the flowmeter so that corrections for gas volume may be applied. The flowmeter must be kept free from spray or dust. Use ground-glass

connections upstream from the absorber. Butt-to-butt glass connections with vinyl tubing also may be used for connections without losses if lengths are kept minimal.

11.2 Pipet 10.0 mL of absorbing reagent into a dry fritted bubbler, and draw an air sample through it at the rate of 0.4 L/min long enough to develop sufficient final color (about 10 to 60 min). Note the total air volume sampled. Measure and record the air temperature and pressure. After using the bubbler, rinse well with distilled water and dry. If the fritted tip is visibly discolored, clean according to the procedure in 7.3.2.

11.3 After sampling, development of the red-violet color is complete within 15 min at room temperatures. Transfer to a stoppered cuvette and read in a spectrophotometer at 550 nm, using distilled water as a reference. The absorbance of the reagent blank must be deducted from that of the sample.

11.4 Colors too dark to read may be quantitatively diluted with unexposed absorbing reagent. The measured absorbance is then multiplied by the dilution factor.

### 12. Calculation

12.1 Sample air volume—Convert the measured volume of air sampled to standard conditions of 25°C and 101.3 kPa (29.92 in. Hg) as follows:

$$V_r = V \times \frac{P}{101.3} \times \frac{298.15}{T} \quad (2)$$

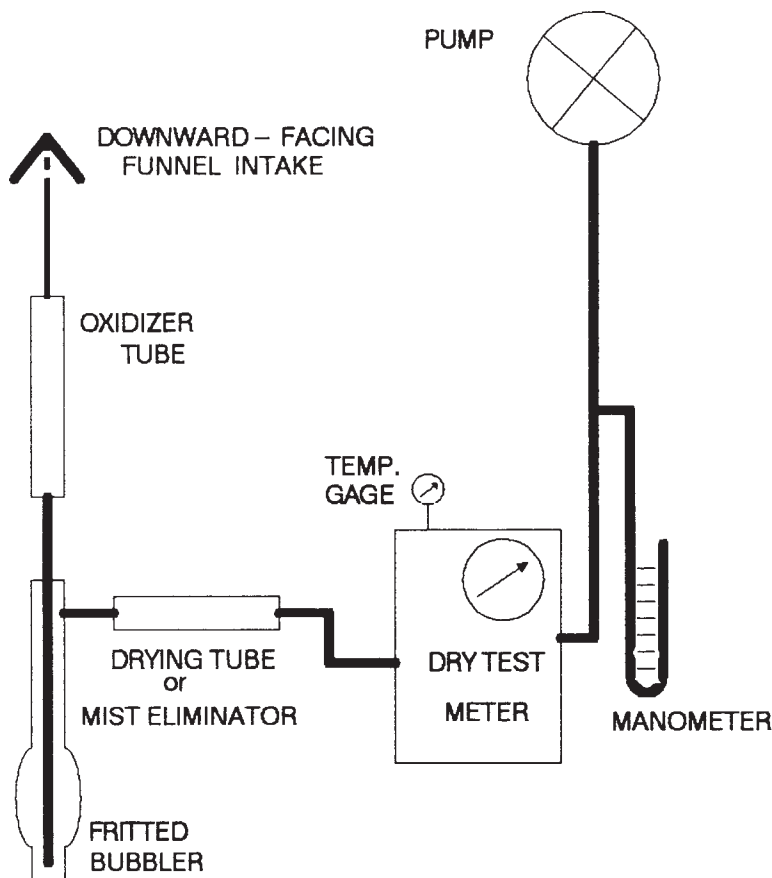


FIG. 2 Sampling Train

where:

$V_r$  = volume of air at standard conditions, L,  
 $V$  = measured volume of air, L,  
 $P$  = average atmospheric pressure, kPa,  
 $T$  = average temperature of air sample, K,  
 101.3 = pressure of standard atmosphere, kPa, and  
 298.15 = temperature of standard atmosphere, K.

### 12.2 NO<sub>x</sub> Concentration in the Air

#### 12.2.1 Recommended Procedure:

12.2.1.1 Calculate the concentration of NO<sub>x</sub> in the sample as follows:

$$C = \frac{(A - A')10^3 K}{V} \quad (3)$$

where:

$C$  = concentration of NO<sub>x</sub> µg/m<sup>3</sup>,  
 $A$  = sample absorbance,  
 $A'$  = reagent blank absorbance,  
 $K$  = calibration factor, µg/absorbance unit,  
 $V$  = sample volume, L, corrected to 25°C and 101.3 kPa,  
 and  
 $10^3$  = factor to correct L to m<sup>3</sup>.

#### 12.2.2 Alternate Procedure:

12.2.2.1 Compute the concentration of total NO plus NO<sub>2</sub> in the sample as follows:

$$\text{Total NO plus NO}_2, \mu\text{g/m}^3 = \frac{\text{absorbance} \times K \times 10^3 \times v}{V} \quad (4)$$

where:

$K$  = standardization factor (micrograms of total NO plus NO<sub>2</sub> per mL of absorbing solution/absorbance),<sub>3</sub>  
 $V$  = volume of air sample, L (see section 12.1.1),  $10^3 = \text{L}/\text{m}^3$ , and  
 $v$  = volume of absorbing solution, mL.

For NO<sub>x</sub> in ppm (v), the calculation equation is:

$$\frac{\text{absorbance} \times K \times v \times 0.532}{V} \quad (5)$$

### 13. Precision and Bias

13.1 A precision of 7 percent of the mean has been reported for the measurement of NO (6); a precision of 0.524 (mean)<sup>1/2</sup> has been reported for the measurement of NO<sub>2</sub>(7). At present, accuracy and precision data for the measurement of total NO<sub>x</sub> are not available.

### 14. Keywords

14.1 ambient atmospheres; analysis; colorimetric analysis; Greiss-Saltzman reaction; nitric oxide; nitrogen dioxide; nitrogen oxides; sampling

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