



Designation: D1607 – 91 (Reapproved 2005)

Standard Test Method for Nitrogen Dioxide Content of the Atmosphere (Griess-Saltzman Reaction)¹

This standard is issued under the fixed designation D1607; 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.

This standard has been approved for use by agencies of the Department of Defense.

1. Scope

1.1 This test method² covers the manual determination of nitrogen dioxide (NO₂) in the atmosphere in the range from 4 to 10 000 $\mu\text{g}/\text{m}^3$ (0.002 to 5 ppm(v)) when sampling is conducted in fritted-tip bubblers.

1.2 For concentrations of NO₂ in excess of 10 mg/m^3 (5 ppm(v)), as occur in industrial atmospheres, gas burner stacks, or automotive exhaust, or for samples relatively high in sulfur dioxide content, other methods should be applied. See for example Test Method D1608.

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

1.4 The values stated in SI units are to be regarded as standard. The values given in brackets are for information only.

1.5 *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.* See also 7.2.2 for other precautions.

2. Referenced Documents

2.1 *ASTM Standards:*³

D1071 Test Methods for Volumetric Measurement of Gaseous Fuel Samples

D1193 Specification for Reagent Water

D1356 Terminology Relating to Sampling and Analysis of Atmospheres

¹ This test method is under the jurisdiction of ASTM Committee D22 on Air Quality and is the direct responsibility of Subcommittee D22.03 on Ambient Atmospheres and Source Emissions.

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² Adapted from "Selected Methods for the Measurement of Air Pollutants," PHS Publication No 999-AP-11, May 1965. A similar version has been submitted to the Intersociety Committee.

³ 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.

D1357 Practice for Planning the Sampling of the Ambient Atmosphere

D1608 Test Method for Oxides of Nitrogen in Gaseous Combustion Products (Phenol-Disulfonic Acid Procedures)

D3195 Practice for Rotameter Calibration

D3609 Practice for Calibration Techniques Using Permeation Tubes

D3631 Test Methods for Measuring Surface Atmospheric Pressure

E1 Specification for ASTM Liquid-in-Glass Thermometers

E128 Test Method for Maximum Pore Diameter and Permeability of Rigid Porous Filters for Laboratory Use

3. Terminology

3.1 For definitions of terms used in this test method, refer to Terminology D1356.

4. Summary of Test Method

4.1 The NO₂ is absorbed in an azo-dye-forming reagent (1).⁴ 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 Nitrogen dioxide plays an important role in photochemical smog-forming reactions and, in sufficient concentrations, is deleterious to health, agriculture, materials, and visibility.

5.2 In combustion processes, significant amounts of nitric oxide (NO) may be produced by combination of atmospheric nitrogen and oxygen; at ambient temperatures NO can be converted to NO₂ by oxygen and other atmospheric oxidants. Nitrogen dioxide may also be generated from processes involving nitric acid, nitrates, the use of explosives, and welding.

6. Interferences

6.1 A ten-fold ratio of sulfur dioxide (SO₂) to NO₂ produces no effect. A thirty-fold ratio slowly bleaches the color to a slight extent. The addition of acetone to the reagent retards the

⁴ The boldface numbers in parentheses refer to the list of references appended to this method.

fading by forming a temporary addition product with SO₂. This permits reading the color intensity within 4 to 5 h (instead of the 45 min required without the acetone) without appreciable losses.

6.2 A five-fold ratio of ozone to NO₂ will cause a small interference, the maximal effect occurring in 3 h. The reagent assumes a slightly orange tint.

6.3 Peroxyacetyl nitrate (PAN) can produce a color change in the absorbing reagent. However, in ordinary ambient air, the concentration of PAN is too low to cause any significant error in the measurement of NO₂.

6.4 Interferences may exist from other nitrogen oxides and other gases that might be found in polluted air.

7. Apparatus

7.1 *Sampling Probe*—A glass or TFE-fluorocarbon (preferred) tube, 6 to 10 mm in diameter provided with a downwind facing intake (funnel or tip). The dead volume of the system should be kept minimal to avoid losses of NO₂ on the surfaces of the apparatus.

7.2 *Absorber*—An all-glass bubbler with a 60- μ m maximum pore diameter frit, similar to that illustrated in Fig. 1.

7.2.1 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 μ m. Frits having a maximum pore diameter less than 60 μ m will have a higher efficiency but will require an inconvenient pressure drop for sampling. Considerably lower efficiencies are obtained with coarser frits.

7.2.2 Measure the porosity of an absorber in accordance with Test Method E128. If the frit is clogged or visibly discolored, carefully clean with concentrated chromic-sulfuric acid mixture, and rinse well with water and redetermine the maximum pore diameter.

NOTE 1—**Caution:** Do not dispose of this reagent in the drain system.

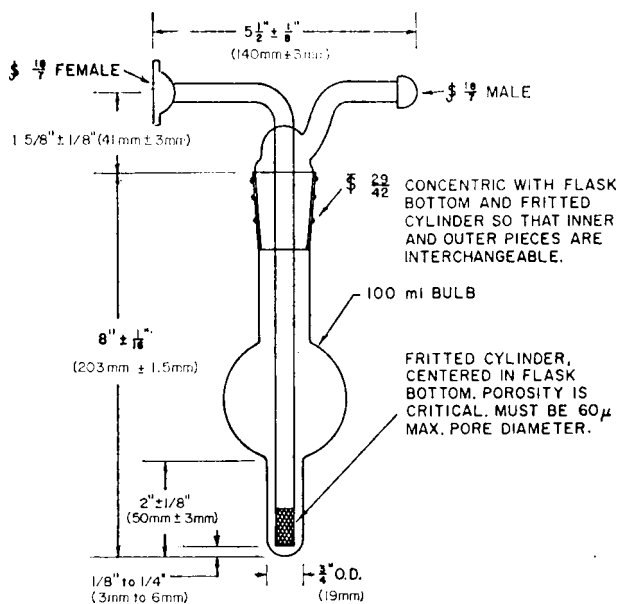


FIG. 1 Fritted Bubbler for Sampling Nitrogen Dioxide

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

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

7.4 *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.

7.5 *Thermometer*—ASTM Thermometer 33C, meeting the requirements of Specification E1, will be suitable for most applications of this test method.

7.6 *Manometer*, accurate to 670 Pa (0.20 in. Hg). See Test Methods D3631.

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

7.8 *Spectrophotometer or Colorimeter*—An instrument suitable for measuring the intensity of absorption at 550 nm, with stoppered tubes or cuvettes. The wavelength band-width is not critical for this determination.

7.9 *Stopwatch or Timer*.

8. Reagents and Materials

8.1 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.⁵ 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*—Unless otherwise indicated, water shall be deionized water in accordance with Specification D1193 for Type I or II reagent water. Water shall be free of nitrite.

8.3 *Absorbing Reagent*—Dissolve 5 g of anhydrous sulfanilic acid (or 5.5 g of sulfanilic acid monohydrate) in almost a L 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 of 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 shall be at room temperature before use. Avoid lengthy contact with air during preparation and use since discoloration of reagent will result because of absorption of NO₂.

8.4 *N*-(1-Naphthyl)-Ethylenediamine Dihydrochloride, Stock Solution (0.1 %)—Dissolve 0.1 g of the reagent in 100 mL of water. Solution will be stable for several months if kept well-stoppered in a brown bottle in the refrigerator. (Alternatively, preweighed amounts of the solid reagent may be stored.)

8.5 *Sodium Nitrite, Standard Solution (0.0246 g/L)*—One mL of this working solution of sodium nitrite (NaNO₂)

⁵ *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 *Analar 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.