Designation: D1607 − 91 (Reapproved 2011)

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 U.S. Department of Defense.

1. Scope

1.1 This test method[2] covers the manual determination of nitrogen dioxide (NO_2) in the atmosphere in the range from 4 to 10 000 µg/m^3 (0.002 to 5 ppm(v)) when sampling is conducted in fritted-tip bubblers.

1.2 For concentrations of NO_2 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 parentheses 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
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 NO_2 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 NO_2 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 (SO_2) to NO_2 produces no effect. A thirty-fold ratio slowly bleaches the color to a

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[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.

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

slight extent. The addition of acetone to the reagent retards the fading by forming a temporary addition product with SO_2. 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 NO_2 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 NO_2.

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 NO_2 on the surfaces of the apparatus.

7.2 *Absorber*—An all-glass bubbler with a 60-µm 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 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. 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.

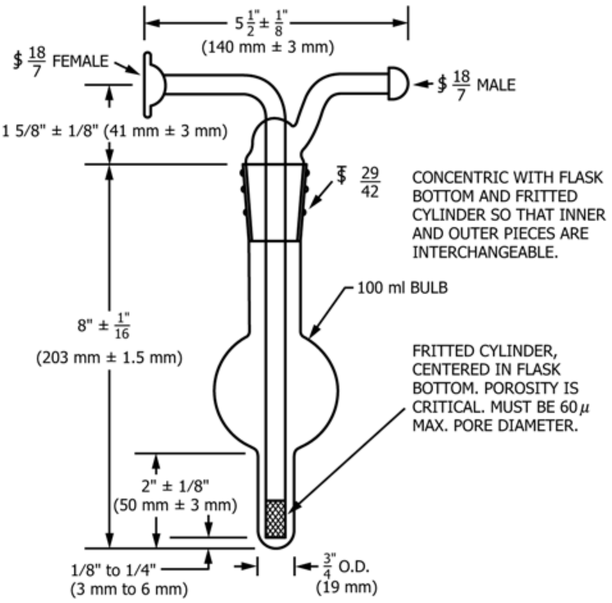

FIG. 1 Fritted Bubbler for Sampling Nitrogen Dioxide

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

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 NO_2.

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[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.

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 ($NaNO_2$) produces a color equivalent to that of 20 µg of NO_2 in 1 L of air at 101 kPa (29.92 in. Hg) and 25°C (see 10.1). Prepare fresh just before use by dilution from a stock solution containing 2.46 g of the reagent grade granular solid per litre. Assay the solid reagent. The stock solution is stable for 90 days at room temperature, and for 1 year in a brown bottle under refrigeration.

8.6 *NO_2 Permeation Device*—With a permeation rate of 0.1 to 0.2 µg/min.

9. Sampling

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

9.2 See Practice D1357 for sampling guidelines.

10. Calibration and Standardization

10.1 *Sampling Equipment:*

10.1.1 *Flowmeter*—Calibrate flowmeter prior to use, using Practice D3195.

10.1.2 *Gas Meter*—Calibrate gas meter prior to use, using Test Method D1071.

10.2 *Analysis:*

10.2.1 *Recommended Procedure:*

10.2.1.1 The recommended procedure for preparation of calibration standards is by the use of permeation devices (**2**). Analysis of known concentrations gives calibration curves that simulate all of the operational conditions performed during sampling and analytical procedures.

10.2.1.2 Using the apparatus described in Practice D3609, generate a gas stream of known concentration. Sample it as described in 11.1, five times, adjusting the sample times so that the amount of NO_2 in each collected sample solution covers the dynamic range of the method. Analyze each as described in 11.2, and prepare a calibration curve using regression analysis by the method of least squares. Determine the reciprocal of the slope of the line, and denote it as K, the volume of NO_2, in µL, intercepted at an absorbance of 1.0.

10.2.2 *Alternate Procedure:*

10.2.2.1 Standardization is based upon the empirical observation (**1, 3, 4**) that 0.82 mol of $NaNO_2$ produces the same color as 1 mol of NO_2. One mL of the working standard solution contains 24.6 µg of $NaNO_2$. Since the molecular weight of $NaNO_2$ is 69.1, this is equivalent to $(24.6/69.1) \times (46.0/0.82) = 20$ µg NO_2.

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), 70°F (21.1°C), 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 bias, it may be made by means of the perfect gas equation.

10.2.2.3 Add graduated amounts of $NaNO_2$ 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 11.2).

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.

10.2.2.5 Plot absorbances of the standards against micrograms of NO_2 per mL of absorbing reagent. The plot follows Beer's law. Find the standardization factor, *K*, as described in 10.2.1.1.

11. Procedure

11.1 Assemble in order as shown in Fig. 2, a sampling probe (optional), fritted-tip absorber, mist eliminator or trap, flowmeter, and pump. Measure temperature and pressure difference from atmospheric so that corrections for gas volume may be applied. Keep the flowmeter free from spray or dust. Use ground-glass connections. 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. 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 air temperature and pressure. After using the bubbler, rinse well with water and dry. If fritted tip is visibly discolored, clean in accordance with the procedure in 7.2.2.

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. Deduct the absorbance of the reagent blank from that of the sample.

11.4 Colors too dark to read may be quantitatively diluted with unexposed absorbing reagent. Then multiply the measured absorbance by the dilution factor.

12. Calculation

12.1 *Air Volume*—Convert the volume of air sampled to the volume at standard conditions of 25° C and 101.3 kPA (1 atm), as follows:

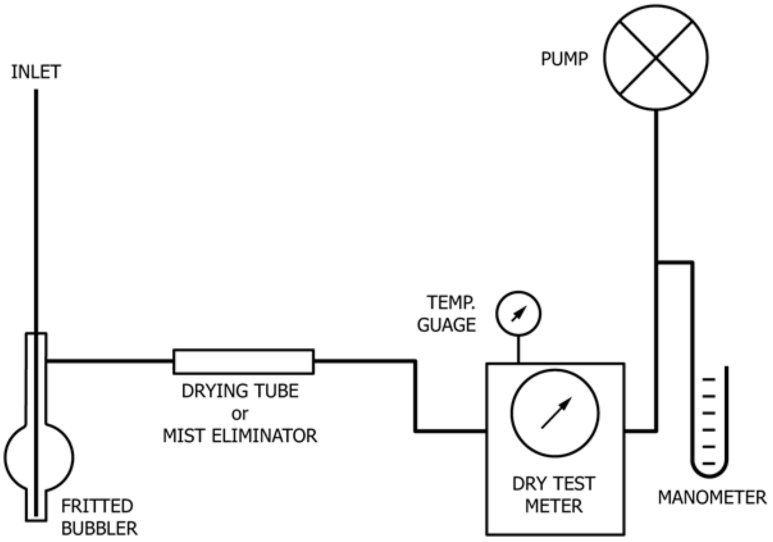

FIG. 2 Sampling Train

$$V_R = [V \times P/101.3] \times [298.15/T] \quad (1)$$

where:

V_R = volume of air sampled at standard conditions, L
V = volume of air sampled at ambient conditions, L
P = average ambient atmospheric pressure, kPa
T = average ambient atmospheric temperature, K
101.3 = pressure of standard atmosphere, kPa, and
290.15 = temperature of standard atmosphere, K.

12.2 Compute the concentrations of NO_2 in the sample as follows:

$$NO_2,\ \mu g/m^3 = (\text{absorbance} \times K \times 10^3 \times v)/V \quad (2)$$

where:

K = standardization factor (micrograms of NO_2 per mL of absorbing solution/absorbance),
V_r = volume of air sample, L (see 12.1),
10^3 = L/m³, and
v = volume of absorbing reagent, mL.

13. Precision and Bias

13.1 The information in this section is derived from the data collected and analyzed as part of ASTM "Project Threshold" (**5**).

13.2 *Repeatability (Single-Analyst)*—The standard deviation of results obtained by a single analyst on separate samples from the same flowing air stream is also shown in Fig. 3 as a function of the mean value of NO_2 determined. The range of data used is 10 to 400 µg/m³. Duplicate analyses should be considered suspect (95 % confidence level) if they differ by more than 2.89 times the standard deviation of repeatability.

13.3 *Reproducibility (Multilaboratory)*—The standard deviation of single analyses, obtained by analysts from different laboratories taking separate samples from the flowing air stream, is plotted in Fig. 3 against the mean value of NO_2 determined. The range of data used is 16 to 400 µg/m³.

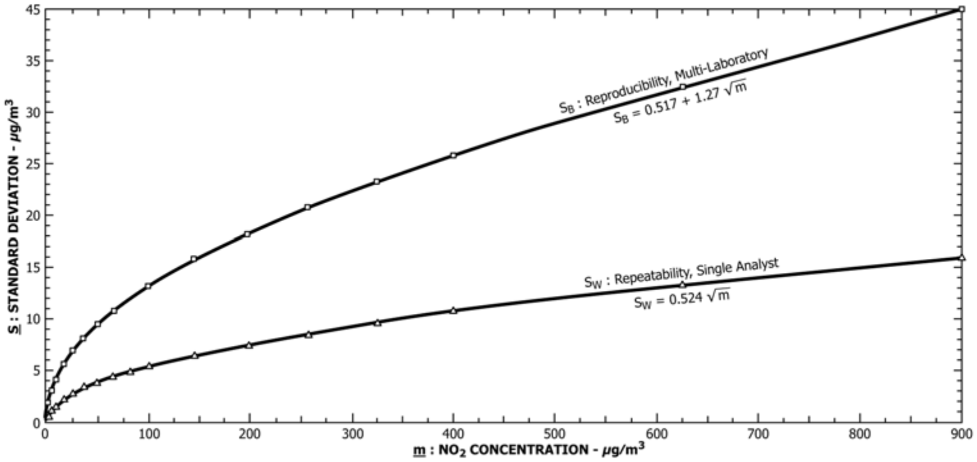

FIG. 3 Repeatability and Reproducibility (6)

Duplicate values should be considered suspect (95 % confidence level) if they differ by more than 2.81 times the standard deviation of reproducibility.

13.4 *Bias*—Although the measurement of bias was designed to produce data that described the bias of this method, no generally applicable statements regarding bias can be made. Table 1 gives the average bias found at each of the three locations used during the interlaboratory test program. The method of evaluating bias consisted of adding a known amount of NO_2 gas to a sample stream and determining the percent recovery on the basis of simultaneous analyses of spiked and "unspiked" samples. Bias is the difference between the determined recovery and 100 %.

TABLE 1 Bias Found in NO_2 Measurement Found During Project Threshold (6)

Location	Mean Bias	Degrees of Freedom	Mean NO_2 Measured	Uncertainty of mean (95 % Confidence)
Los Angeles, CA	+11 %	86	150 μg/m^3	±10 %
Bloomington, IN	–11 %	82	50 μg/m^3	±10 %
New York, NY	+35 %	70	210 μg/m^3	±10 %

13.5 The method for determining the bias detects only those errors that are proportional to the NO_2 level; fixed errors are cancelled in the subtraction process. Fixed errors shall refer to interferences. For this reason, bias is expressed in percentage terms rather than in absolute units.

13.6 Based on the data in Table 1, it is clear that the bias found in Manhattan, NY, is significantly higher than that found in Los Angeles, CA, or Bloomington, IL. This difference in bias is not due to the fact that the average NO_2 levels found in Manhattan were higher than those found at the other two sites (**5**). The difference in bias may be caused by other interfering substances, such as NO or other nitrogen oxides, but these data alone are not conclusive.

14. Keywords

14.1 ambient atmospheres; analysis; colorimetric analysis; Griess-Saltzman Reaction; nitrogen dioxide; sampling

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(5) Foster, J. F., and Beatty, G. H., "Final Report on Interlaboratory Cooperation, Study of the Precision and Accuracy of the Measurement of Nitrogen Dioxide Content in the Atmosphere Using ASTM Method D1607," Battelle, Columbus Laboratories, Columbus, Ohio, 1973.