



Designation: D1608 – 16

Standard Test Method for Oxides of Nitrogen in Gaseous Combustion Products (Phenol-Disulfonic Acid Procedures)¹

This standard is issued under the fixed designation D1608; 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 reappraisal. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reappraisal.

1. Scope

1.1 This test method describes the phenol-disulfonic acid colorimetric procedure (1)² for the determination of total oxides of nitrogen [nitrous oxide (N₂O) excepted] in gaseous effluents from combustion and other nitrogen oxidation processes.

1.2 It is applicable to a concentration range of oxides of nitrogen as nitrogen dioxide (NO₂) of 5 ppm to several thousand parts per million by volume (four to several thousand milligrams per dry standard cubic metre).

1.3 Since the grab sampling technique used takes a relatively small sample over a very short period of time, the result obtained will be an instantaneous measure of the nitrogen oxides and, therefore, will be representative of the emissions only if the gas stream is well mixed and the concentration constant with time. Multiple samples are recommended.

1.4 The values stated in SI units are to be regarded as standard. The values given in parentheses are mathematical conversions to inch-pound units that are provided for information only and are not considered standard.

1.5 *Warning—Mercury has been designated by many regulatory agencies as a hazardous material that can cause serious medical issues. Mercury, or its vapor, has been demonstrated to be hazardous to health and corrosive to materials. Caution should be taken when handling mercury and mercury containing products. See the applicable product Safety Data Sheet (SDS) for additional information. Users should be aware that selling mercury and/or mercury containing products into your state or country may be prohibited by law.*

1.6 *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 more specific safety precautionary information see 8.5 and Section 3.)

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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1.7 *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

D1193 Specification for Reagent Water

D1356 Terminology Relating to Sampling and Analysis of Atmospheres

D1357 Practice for Planning the Sampling of the Ambient Atmosphere

D1605 Practices for Sampling Atmospheres for Analysis of Gases and Vapors (Withdrawn 1992)³

E1 Specification for ASTM Liquid-in-Glass Thermometers

E2251 Specification for Liquid-in-Glass ASTM Thermometers with Low-Hazard Precision Liquids

3. Terminology

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

4. Summary of Test Method

4.1 The gas sample is admitted into an evacuated flask containing an oxidizing absorbing solution consisting of hydrogen peroxide in dilute sulfuric acid. The oxides of nitrogen are converted to nitric acid by gas phase oxidation due to oxygen in the sample and by the absorbent solution. The resulting nitrate ion is reacted with phenol disulfonic acid to produce a yellow compound (the tri-ammonium salt of 6-nitro-1-phenol-2,4-disulfonic acid), which is measured colorimetrically. Calibration curves, prepared from samples of known nitrate content, are used to determine the amount of nitrate in the sample with results expressed as nitrogen dioxide.

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.

³ The last approved version of this historical standard is referenced on www.astm.org.

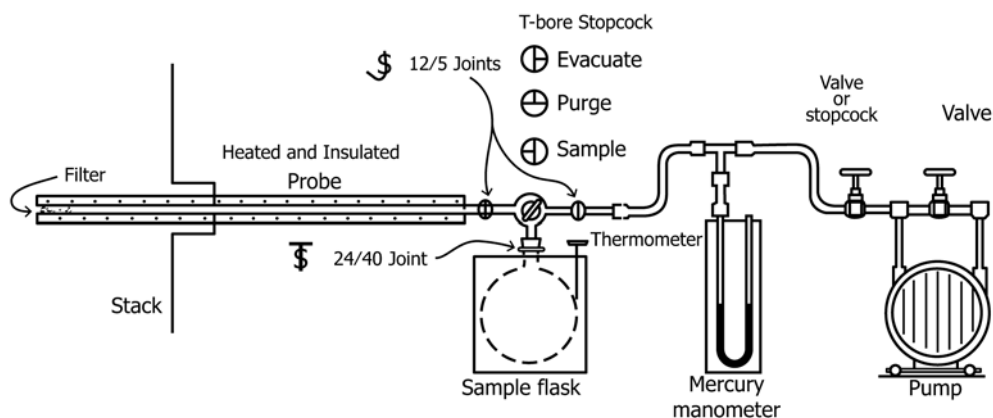


FIG. 1 Diagram of Typical Sampling Apparatus used for Determination of Oxides of Nitrogen by Test Method D1608

5. Significance and Use

5.1 This test method provides a means to measure the total nitrogen oxides (NO_x) content of gaseous emissions for purposes such as determining compliance with regulations, studying the effect of various abatement procedures on NO_x emissions, and checking the validity of instrumental measurements.

6. Interferences (1, 2)⁴

6.1 Inorganic nitrates, nitrites, or organic nitrogen compounds that are easily oxidized to nitrates interfere with the test method and give erroneously high results. The presence of certain reducing agents, for example, sulfur dioxide (SO_2), may interfere by consuming part of the hydrogen peroxide in the absorbing solution to leave an inadequate amount for reaction with the oxides of nitrogen. Halides lower the results, but interference from halide ion (and lead) are negligible in the concentration usually encountered in combustion sources.

6.2 The role of some of the constituents of combustion effluents as possible interfering substances has not been thoroughly investigated.

7. Apparatus

7.1 The assembled sampling apparatus is shown in Fig. 1.

7.2 *Barometer*, capable of measuring atmospheric pressure to ± 250 Pa [± 2 mm Hg].

7.3 *Bottles*, 120-mL or 4-oz, glass or polyethylene, with leak-free noncontaminating caps.

7.4 *Evaporating Dishes*, new condition, unetched borosilicate glass or porcelain, about 200-mL capacity. Do not use platinum ware (3).

7.5 *Mercury Manometer*, open-end U-tube, 1 mm [or 36 in.] with 1-mm [or 0.1-in.] divisions.

NOTE 1—An unbreakable, roll-up type is convenient for this application.

7.6 *Microburet*, 10-mL capacity, with 0.01-mL divisions.

7.7 *pH Paper*, or litmus paper, covering the range from 7 to 14 pH.

7.8 *Sample Collection Flask, Calibrated*—Two-litre round-bottom glass flask with a short neck 24/40 standard-taper joint, protected against implosion or breakage with tape or foamed plastic, with known volume.

7.9 *Sampling Probe*, borosilicate glass, approximately 6-mm inside diameter, fitted with a 12/5 spherical joint for attachment to the three-way stopcock on the sample collection flask, provided with a filter on the inlet end for removal of particulate matter, long enough to extend from approximately one-third to halfway into the stack or duct (or at least 1 m beyond inside wall of stacks greater than 2 m in diameter), and heated or insulated, or both, sufficiently well to prevent condensation of moisture while purging and sampling.

7.10 *Spectrophotometer*, or filter photometer, capable of measuring absorbance at 405 nm.

NOTE 2—A wavelength of 400 nm was actually used in the Project Threshold tests, but recent work (4, 5, 3) has shown that the absorbance peak maximum is actually at 405 nm, which is therefore a better choice. This change should tend to improve the precision and bias of the test method.

7.11 *Squeeze-Bulb*, rubber, valved for one-way flow to purge sampling probe.

7.12 *Stirring Rod*, polyethylene, to avoid scratching the evaporating dishes.

7.13 *Stopcock, Three-Way, T-Tore*, with a 24/40 joint for attachment to the sample collection flask, and a 12/5 spherical joint for attachment to the sampling probe.

7.14 *Stopcock Grease*, high vacuum, high temperature, inert.

7.15 *Thermometer*, dial-type or glass, with 1°C [2°F] divisions and an approximate range from -5 to 50°C [25 to 125°F]. ASTM Thermometer 33C, meeting the requirements of Specification E1 will meet the requirements of most applications in this method. A comparable precision low-hazard liquid thermometer, ASTM Thermometer S33C, meeting the requirements of Specification E2251, may also be used.

⁴ The boldface numbers in parentheses refer to a list of references at the end of this standard.

7.16 *Vacuum Pump*, portable, capable of evacuating the sample collection flask to a pressure of about 2.5 kPa [25 mm Hg] or less.

7.17 *Volumetric Flasks*, 50, 100, 1000-mL capacity.

7.18 *Volumetric Pipets*, 1, 2, 3, 4, and 5-mL capacity.

7.19 *Water Bath or Steam Bath*, operating at approximately 100°C [212°F] (an electric hot plate is not suitable because it tends to cause spattering and possible loss of sample).

8. Reagents

8.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that 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 reagents may be used provided it can be demonstrated that they are of sufficiently high purity to permit their use without decreasing the accuracy of the determination.

8.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water conforming to Type III or better of Specification D1193. Additionally, this test method requires water that is nitrate-free as demonstrated by a low-blank absorbance reading (less than 0.002 nm) in Section 5.

8.3 *Absorbing Solution*—Dilute 3.0 mL of hydrogen peroxide (H₂O₂, 3 %) to 100 mL with sulfuric acid solution (H₂SO₄, 3+997). A fresh solution shall be prepared weekly. Do not expose to excessive heat or direct sunlight for prolonged time.

8.4 *Ammonium Hydroxide (sp gr 0.90)*—Concentrated ammonium hydroxide (NH₄OH). A fresh solution shall be used.

8.5 *Fuming Sulfuric Acid (H₂SO₄ · XSO₃)*, 15 to 18 weight % free sulfur trioxide. (**Warning**—Handle with care)

8.6 *Hydrogen Peroxide (3 %)*—Dilute 10 mL of concentrated H₂O₂ (30 %) to 100 mL. A fresh solution shall be prepared each time new absorbing solution is prepared.

NOTE 3—If the strength of the H₂O₂ (30 %) is in doubt, test as follows: Weigh accurately about 5 mL of the H₂O₂ solution and dilute to exactly 500 mL. To 20 mL of the dilute solution add 20 mL of H₂SO₄ (1+9) and titrate with 0.1 N potassium permanganate (KMnO₄) solution to a permanent pink color. One millilitre of 0.1 N KMnO₄ solution = 0.001701 g of H₂O₂.

8.7 *Phenol (C₆H₅ OH)*, pure white solid.

8.8 *Phenol Disulfonic Acid Solution*—Dissolve 25 g of phenol in 150 mL of concentrated H₂SO₄ (sp gr 1.84) by heating on a steam bath. Cool, add 75 mL of fuming H₂SO₄ (15 to 18 % SO₃) and heat on the steam bath at 100°C [212°F] for 2 h. Cool and store in a dark glass-stoppered bottle. The solution should be colorless; it deteriorates on long standing. Discard if a yellow color develops.

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.

8.9 *Potassium Nitrate (KNO₃)*—Dry in an oven at 105 to 110°C for 2 h just before preparation of the standard solution.

8.10 *Potassium Nitrate, Stock Standard Solution (1 mL = 1 mg NO₂)*—Dissolve exactly 2.1980 g of dried KNO₃ in water and dilute to 1 L in a volumetric flask.

8.11 *Potassium Nitrate, Working Standard Solution (1 mL = 100 µg NO₂)*—Dilute 10 mL of the stock standard potassium nitrate solution (1 mL = 1 mg NO₂) to 100 mL with water in a volumetric flask.

8.12 *Sodium Hydroxide Solution (~1 N)*—Slowly add 40 g of sodium hydroxide (NaOH) pellets to 800 to 900 mL of water in a 2-L beaker with stirring until all pellets are dissolved. Dilute to 1 L with water and mix well. Store in an airtight polyethylene or polypropylene bottle.

8.13 *Sulfuric Acid (sp gr 1.84)*—Concentrated H₂SO₄, minimum assay 95 %.

8.14 *Sulfuric Acid (3+997)*—Carefully add 3 mL of concentrated H₂SO₄ (sp gr 1.84) to water and dilute to 1 L.

9. Safety Precautions

9.1 **Warning**—Reagents used in this method are potentially hazardous and many are extremely reactive. Concentrated acids and bases are used throughout the laboratory procedure. Use care when adding them to other solutions to avoid overheating and skin contact. Refer to material safety datasheets for reagents.

9.2 **Warning**—Avoid exposure to chemicals and solvents used in this method. Sample and standard preparations should be done in an efficient operating hood.

9.3 **Warning**—Wear safety glasses at all times and other laboratory protective equipment as appropriate.

9.4 **Warning**—Cover the glass sample collection flask, which is evacuated during the sampling procedure, with tape or foamed plastic to avoid injury in case of implosion or breakage.

9.5 **Warning**—The fuming sulfuric acid used in preparing the phenol disulfonic acid reagent is highly corrosive and fumes in moist air. Wear protective gloves, apron, and face shield, and carry out the reagent preparation in a hood.

10. Sampling

10.1 Pipet 25.0 mL of absorbing solution into a calibrated sampling flask and attach the three-way stopcock to the flask (see Note 4) with the T-bore in the purge position. Insert the sampling probe tip from approximately one-third to halfway into the stack or duct, or at least 1 m into stacks greater than 2 m in diameter, in such a way as to prevent leakage of air into the stack around the probe. Assemble as shown in Fig. 1, making sure that all ground-glass joints have been properly greased, and that all joints and fittings are tight and leak-free. Turn the flask stopcock to the evacuate position and evacuate the flask to the incipient boiling of the solution. If the incipient boiling of the solution cannot be seen, this will be indicated on the manometer by a low and constant reading (usually around 2.5 to 4.0 kPa [20 to 30 torr or 0.8 to 1.2 in. Hg]). Shut off the