



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

This standard is issued under the fixed designation D 1608; 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 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 SI equivalents are in parentheses and may be approximate.

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

2. Referenced Documents

2.1 ASTM Standards:²

D 1193 Specification for Reagent Water

D 1356 Terminology Relating to Sampling and Analysis of Atmospheres

D 1357 Practice for Planning the Sampling of the Ambient Atmosphere

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 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.

D 1605 Practices for Sampling Atmospheres for Analysis of Gases and Vapors³

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 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.

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)

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 (SO₂), 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.

³ Withdrawn

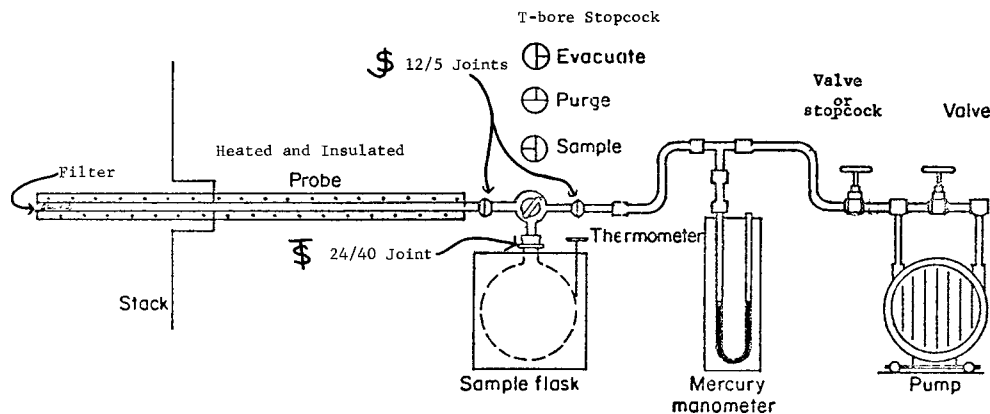


FIG. 1 Diagram of Typical Sampling Apparatus used for Determination of Oxides of Nitrogen by Test Method D 1608

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 (7).

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 (3, 6, 7) 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-bore*, 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].

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.⁴ 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 D 1193. 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.

⁴ *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.