



# Standard Test Method for Oxides of Nitrogen in Gaseous Combustion Products (Phenol-Disulfonic Acid Procedures)<sup>1</sup>

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 reapproval. A superscript epsilon ( $\epsilon$ ) indicates an editorial change since the last revision or reapproval.

## 1. Scope

1.1 This test method describes the phenol-disulfonic acid colorimetric procedure (1)<sup>2</sup> for the determination of total oxides of nitrogen [nitrous oxide ( $\text{N}_2\text{O}$ ) 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 ( $\text{NO}_2$ ) 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.)

<sup>1</sup> 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.

Current edition approved March 1, 2016. Published March 2016. Originally approved in 1958. Last previous edition approved in 2009 as D1608 – 98 (2009). DOI: 10.1520/D1608-16.

## 2. Referenced Documents

### 2.1 ASTM Standards:<sup>2</sup>

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)<sup>3</sup>

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.

## 5. Significance and Use

5.1 This test method provides a means to measure the total nitrogen oxides ( $\text{NO}_x$ ) content of gaseous emissions for purposes such as determining compliance with regulations, studying the effect of various abatement procedures on  $\text{NO}_x$  emissions, and checking the validity of instrumental measurements.

<sup>2</sup> 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.

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

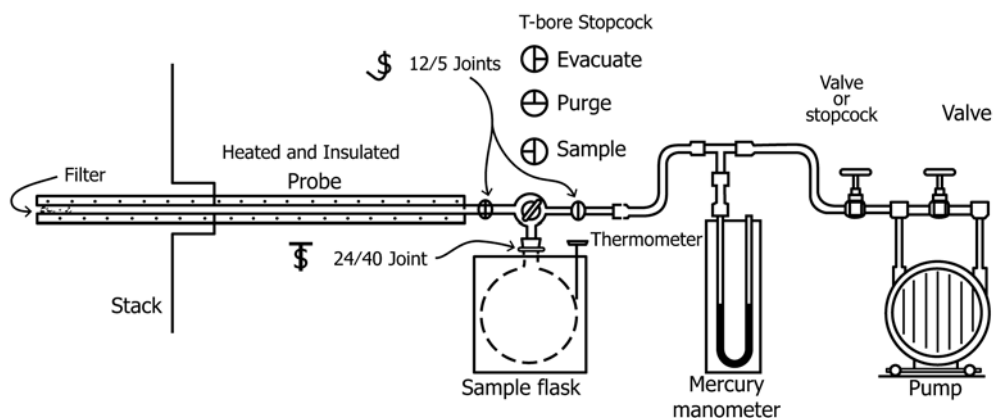


FIG. 1 Diagram of Typical Sampling Apparatus used for Determination of Oxides of Nitrogen by Test Method D1608

## 6. Interferences (1, 2)<sup>4</sup>

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<sub>2</sub>), 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  $\pm 250$  Pa [ $\pm 2$  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.

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.

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

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.<sup>5</sup> 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 (H<sub>2</sub>O<sub>2</sub>, 3 %) to 100 mL with sulfuric acid solution (H<sub>2</sub>SO<sub>4</sub>, 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 (NH<sub>4</sub>OH). A fresh solution shall be used.

8.5 *Fuming Sulfuric Acid (H<sub>2</sub>SO<sub>4</sub> · XSO<sub>3</sub>)*, 15 to 18 weight % free sulfur trioxide. (**Warning**—Handle with care)

8.6 *Hydrogen Peroxide (3 %)*—Dilute 10 mL of concentrated H<sub>2</sub>O<sub>2</sub> (30 %) to 100 mL. A fresh solution shall be prepared each time new absorbing solution is prepared.

NOTE 3—If the strength of the H<sub>2</sub>O<sub>2</sub> (30 %) is in doubt, test as follows: Weigh accurately about 5 mL of the H<sub>2</sub>O<sub>2</sub> solution and dilute to exactly 500 mL. To 20 mL of the dilute solution add 20 mL of H<sub>2</sub>SO<sub>4</sub> (1+9) and titrate with 0.1 N potassium permanganate (KMnO<sub>4</sub>) solution to a permanent pink color. One millilitre of 0.1 N KMnO<sub>4</sub> solution = 0.001701 g of H<sub>2</sub>O<sub>2</sub>.

8.7 *Phenol (C<sub>6</sub>H<sub>5</sub> OH)*, pure white solid.

8.8 *Phenol Disulfonic Acid Solution*—Dissolve 25 g of phenol in 150 mL of concentrated H<sub>2</sub>SO<sub>4</sub> (sp gr 1.84) by heating on a steam bath. Cool, add 75 mL of fuming H<sub>2</sub>SO<sub>4</sub> (15 to 18 % SO<sub>3</sub>) 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.

8.9 *Potassium Nitrate (KNO<sub>3</sub>)*—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 NO<sub>2</sub>)*—Dissolve exactly 2.1980 g of dried KNO<sub>3</sub> in water and dilute to 1 L in a volumetric flask.

8.11 *Potassium Nitrate, Working Standard Solution (1 mL = 100 µg NO<sub>2</sub>)*—Dilute 10 mL of the stock standard potassium nitrate solution (1 mL = 1 mg NO<sub>2</sub>) 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 H<sub>2</sub>SO<sub>4</sub>, minimum assay 95 %.

8.14 *Sulfuric Acid (3+997)*—Carefully add 3 mL of concentrated H<sub>2</sub>SO<sub>4</sub> (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 pump valve and then the pump. Check for leakage by observing the manometer for any pressure increase. Any increase greater than 1.33 kPa [10 torr or 0.4 in. Hg] over a 1-min period is not acceptable; do not take a sample until the leakage problem is corrected. Turn the flask stopcock to the purge position. Using a pump or a valved rubber squeeze bulb,

<sup>5</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 *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.



thoroughly purge the sampling probe and the flask stopcock with the sample gas until the probe and stopcock are warmed to the gas temperature and free of condensate. If condensation remains, heat the probe and purge until the condensation disappears. With the pump valve and pump shut off, turn the flask stopcock to the evacuate position and record the flask temperature, the difference in mercury levels in the manometer, and the barometric pressure. The absolute pressure in the flask is equal to the barometric pressure minus the manometer reading. Immediately, turn the stopcock to the sample position so that the gas enters the flask and the pressures in the flask and the sample line are equalized (usually about 15 s are sufficient). Turn the stopcock to the purge position to seal the flask and allow the gas to remain in contact with the absorbing solution overnight (see **Note 5**) at room temperature. For further information on sampling, refer to Practices **D1357** and **D1605**.

**NOTE 4**—The end 6 mm [ $\frac{1}{4}$  in.] of the male 24/40 standard-taper joint is not lubricated to minimize contact of the gas sample with stopcock grease during absorption.

**NOTE 5**—If an overnight absorption period is not feasible, the sample can be shaken initially and every 20 min for a 2-h period. The result will not be significantly different than for a static overnight absorption period, provided that the oxygen concentration in the flask is greater than 1 %.

## 11. Calibration

**11.1 Sample Collection Flask Volume**—Fill the sample flask and stopcock assembly with water up to the stopcock plug. Determine the volume to  $\pm 10$  mL by measuring either the volume or weight of the water contained in the assembly. Number and record the volume on the flask.

**11.2 Spectrophotometer Calibration**—Prepare a calibration curve to cover a range from about 0 to 125 ppm  $\text{NO}_2$ , based on 2000-mL samples of dry gas at 21°C [70°F] and 101.33 kPa [760 torr 29.92 in. Hg]. Using a microburet or pipets, transfer 0.0, 1.0, 2.0, 3.0, 4.0, and 5.0 mL of the working standard  $\text{KNO}_3$  solution (1 mL = 100  $\mu\text{g}$   $\text{NO}_2$ ) into the 200-mL evaporating dishes and add 25.0 mL of absorbing solution to each. Proceed in accordance with **12.3** to **12.5**. Construct a calibration curve by plotting the absorbencies of the solutions at 405 nm against the micrograms of  $\text{NO}_2$ .

**NOTE 6**—Higher sample concentrations may be analyzed using this curve by taking smaller aliquots of the absorbing solution or by dilution, or both, of the color-developed solution before reading in the spectrophotometer.

## 12. Procedure

**12.1** After the absorption period is completed, record the barometric pressure and the room temperature where the sample has stood. Connect one arm of the sample flask stopcock to the open-end manometer, turn the stopcock to open the flask to the manometer, and read the difference between the mercury levels in the manometer. The absolute internal pressure in the flask is then the barometric pressure less this difference. Correct the gas volume in the flask as directed in **13.1**.

**12.2** Transfer the absorbing solution quantitatively from the flask into a 200-mL evaporating dish (see **Note 7**). Pipet 25.0 mL of unused absorbing solution into another evaporating dish for a blank and add the same amount of water to this dish as

was used in transferring the sample. Proceed with the blank in the same manner as directed for the sample.

**NOTE 7**—If the sample is expected to have a high concentration of oxides of nitrogen, transfer it to a 50-mL volumetric flask instead of the evaporating dish, and dilute to the mark with water. Select a suitable aliquot and pipet it into a 200-mL evaporating dish. Likewise dilute 25.0 mL of unused absorbing solution to 50 mL and pipet an aliquot equal to that of the sample into a 200-mL evaporating dish for a blank.

**NOTE 8**—To save time, a 15-mL aliquot of the used absorbing solution may be pipetted into the evaporating dish, rather than quantitatively transferring the whole solution. This is permissible if the concentration of nitrogen dioxide ( $\text{NO}_2$ ) is greater than 10 ppm, and if the evacuation of the flask prior to admitting the sample was to the incipient or flash boiling point of the unused absorbing solution. Evacuation up to 1 min after flash boiling appears to result in about 1 % decrease in the volume of the solution.

**NOTE 9**—If necessary, to immediately reuse the sampling flask or to ship the used absorbing solution back to a laboratory for analysis, the entire used absorbing solution or a 15-mL aliquot may be quantitatively transferred to a leak-free glass or polyethylene bottle until ready for analysis.

**12.3** Add NaOH solution to the sample solution to the evaporating dish and to the blank until each is just basic to litmus or pH paper. Do not add any excess NaOH (**3**). Evaporate each to dryness on the water bath and allow to cool. Very carefully add 2 mL of phenol disulfonic acid solution to each residue and triturate thoroughly with a polyethylene rod to ensure complete contact of the residue with the solution. Add 1 mL of water and 4 drops of  $\text{H}_2\text{SO}_4$  (sp gr 1.84) to each and heat on the water bath for 3 min with occasional stirring. Allow the mixture to cool, add 10 mL of water to each, and mix well by stirring. Add 15 mL of fresh, cool  $\text{NH}_4\text{OH}$  dropwise to each, with constant stirring. Test with litmus paper to make sure an excess of the  $\text{NH}_4\text{OH}$  is present.

**12.4** Filter the solutions through 7-cm, rapid, medium-texture filter papers (see **Note 10**) into 50-mL volumetric flasks. Wash the evaporating dishes three times with 4 to 5 mL of water and pass the washing through the filters. Make up the volumes of the solutions to 50 mL with water and mix thoroughly.

**NOTE 10**—Reference (**3**) recommends discarding any sample for which a significant precipitate is present or the evaporating dish is visually etched. However, the need for this has not been demonstrated. The same grade filter paper should, however, be used both in preparing the calibration curves and in running the samples. It has been found that some yellow color is retained on the paper when filtering more concentrated samples and this factor must be taken into account by use of the sample type of filter paper throughout, or by continued washing until no color is retained in any case. Alternatively, the ammoniacal solutions may be centrifuged, instead of filtered, after dilution to 50 mL.

**12.5** Read the absorbance of the sample solution against the blank in suitable equipment for measurement at 405 nm. If the absorbance falls beyond the range of calibration, thinner cells may be used or a suitable aliquot selected. Dilute the aliquot and the blank to the same volume and read the absorbance of the sample aliquot against that of the blank aliquot.

**12.6** Convert the photometric readings to micrograms of  $\text{NO}_2$  by means of the calibration curves.

**NOTE 11**—The calibration curves must not be assumed to be usable over any protracted length of time. One or more standards should be run along with the samples each time a set is run, or at least every few days if

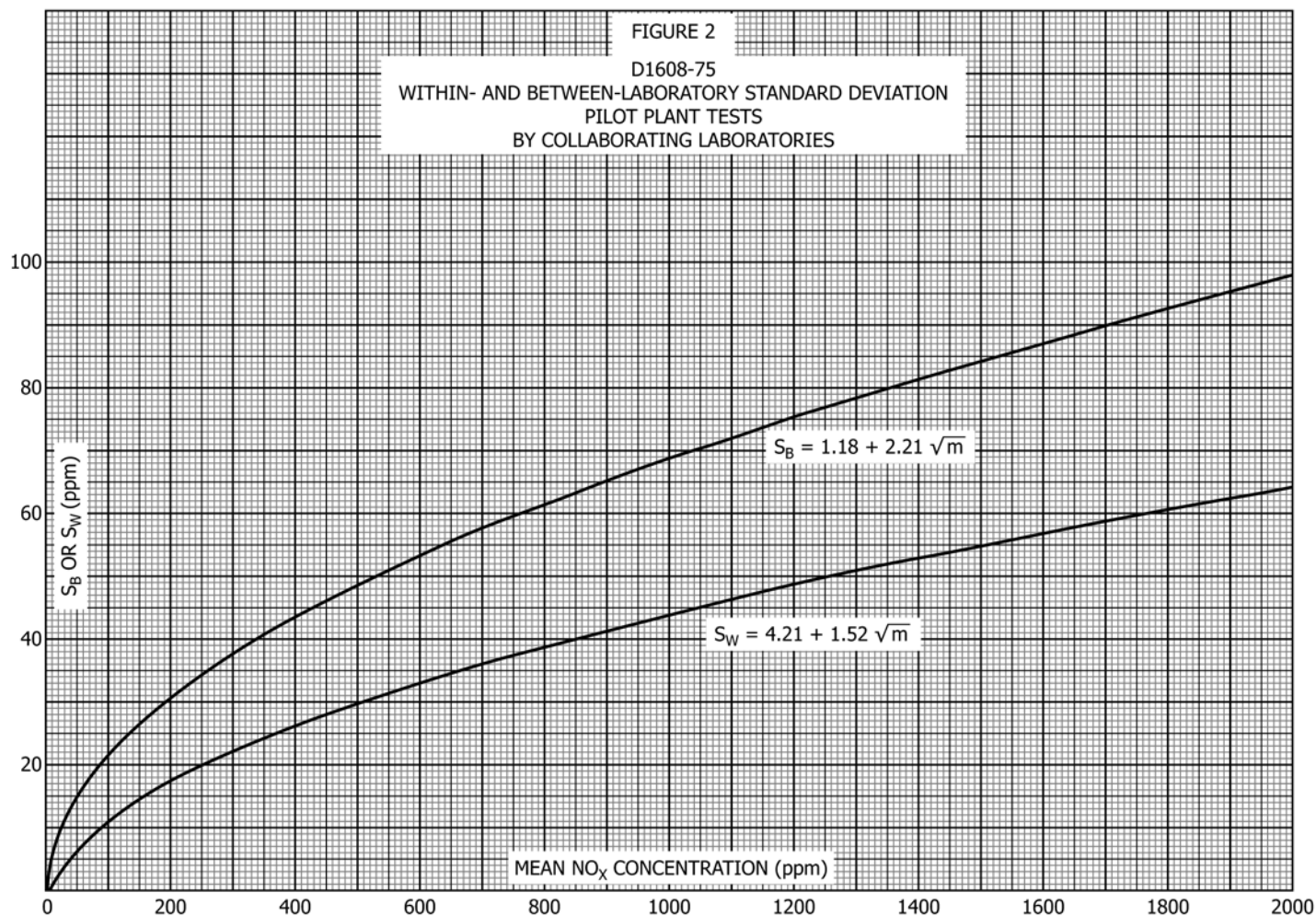


FIG. 2 Within- and Between-Laboratory Standard Deviation Pilot Plant Tests by Collaborating Laboratories

samples are being run daily.

### 13. Calculations

13.1 *Gas Sample Volume Correction*—Correct the volume of the dry gas sample (after removal of absorbed constituents) to 21°C [70°F] and 101.33 kPa [760 torr or 29.92 in. Hg].

13.1.1 Calculate the volume of gas sample as follows:

$$V_c = (V_r - V_a)(P_f/T_f - P_i/T_i)(21 + 273.2)/101.33$$

where:

- $V_c$  = corrected volume of sample gas, mL,
- $V_f$  = volume of sample collection flask, mL,
- $V_a$  = volume of absorbing solution used, 25 mL,
- $P_i$  = initial absolute pressure in flask prior to sampling, kPa,
- $P_f$  = final absolute pressure in flask after absorption period, kPa,
- $T_i$  = initial absolute temperature of flask prior to sampling, K ( $^{\circ}\text{C} + 273.2$ ), and,
- $T_f$  = final absolute temperature of flask after absorption period, K ( $^{\circ}\text{C} + 273.2$ ).

13.2 Calculate the concentration of  $\text{NO}_2$  in parts per million by volume (ppm), dry basis, as follows:

$$\text{NO}_2, \text{ ppm} = (24.1 W \times 10^3)/46V_c$$

where:

- $V_c$  = corrected volume of sample gas, mL,
- $W$  = weight of  $\text{NO}_2$  found in gas sample,  $\mu\text{g}$ ,
- $24.1 \times 10^3$  = standard molar gas volume at 21°C [70°F] and 101.33 kPa [760 torr or 29.92 in. Hg], mL, and
- 46 = formula weight of  $\text{NO}_2$ .

NOTE 12—Parts per million by volume of  $\text{NO}_2$  may be converted to milligrams per cubic metre ( $\text{mg}/\text{m}^3$ ) or to pounds per cubic foot ( $\text{lb}/\text{ft}^3$ ) by multiplying by 1.91 and by  $1.19 \times 10^{-7}$ , respectively.

### 14. Precision and Bias (4, 6, 7)

14.1 In an ASTM-sponsored collaborative effort, laboratories, which had not worked under such conditions before, performed a series of pilot-plant tests indicating a correlation between the precision and the square root of the mean concentration of the  $\text{NO}_x$  over the range from 20 to 2000 ppm. The measures of precision used presented standard deviations for the components of variance between-laboratories ( $S_R$ ) and within-laboratories ( $S_W$ ) obtained from the analysis of variance technique. These correlations are shown in Fig. 2 (7).

14.2 These same laboratories, working in the field at an oil-fired power plant and cement kiln, showed a mean between-laboratory standard error of 14.5 ppm over NO<sub>x</sub> concentrations in the range from 90 to 260 ppm. The mean between-laboratory standard error obtained from the field data is significantly lower than the comparable standard error measure calculated from the pilot plant work. Presumably, the increased experience of the operators contributed to the improved precision.

14.3 To use these data to determine the 95 % confidence limits (95 % CL) of the mean of  $n$  replicate analyses by a single laboratory, the mean level,  $m$ , is calculated and the appropriate value of  $S_w$  is found from Fig. 2. The 95 % CL of the mean is  $m \pm (1.95/\sqrt{n}) \times S_w$ .

14.4 The 95 % CL of the estimate that the mean of  $n$  replicate analysis by one laboratory represents the mean of a similar number of analyses by a large number of laboratories is calculated from the standard error,  $S_T$ , which in turn, can be calculated from the data in Fig. 2 using the equation:

$$S_T = \sqrt{((S_B^2 + S_w^2) / n)}$$

If the experience of the laboratories with the method is appropriate and the NO<sub>2</sub> levels is similar to the field tests, the relation can be used:

$$S_T = 14.5 \text{ ppm NO}_2$$

Finally, the 95 % CL of a single laboratory's data with respect to a mean value determined by many laboratories is  $\pm 1.96 \times S_T$ .

14.5 In the same collaborative study, it was shown that the test method had no significant bias over the range studied. Thus, it can be stated that the accuracy of a single laboratory's analysis is  $\pm 1.96 \times S_T$  from 20 to 2000 ppm of NO<sub>2</sub>.

14.6 Analysis of standard nitrate solutions following each test indicated that variations introduced by the color formation and measurement portion of the test method accounts for roughly 2/3 of the total observed variability. In addition, predominantly negative biases were associated with analysis of these standards ranging from -3.6 to -7.7 % of the true value. Although not statistically significant, the pilot plant spiking tests also produced a negative bias of -3.25 %, suggesting that there was an influence of a negative bias in the chemical portion of the method on the overall results.

14.7 Additional collaborative data concerning precision and accuracy of the phenoldisulfonic acid test method, as applied in analysis of effluents by the EPA Method 7, are given in Refs (4) and (6). Generally, these studies showed significantly better precision than indicated by Fig. 2 at NO<sub>x</sub> concentrations lower than 400 ppm. The difference in findings may well represent differences in experience of the collaborating laboratories since the field data of the ASTM teams, which were obtained after the initial pilot plant work, was within the range of significance of the EPA correlations.

## 15. Keywords

15.1 combustion sources; emissions; EPA Method 7; Method 7; oxides of nitrogen; phenol-disulfonic acid procedure; stack emissions; total oxides of nitrogen

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