

Pt. 60, App. A-4

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APPENDIX A-4 TO PART 60—TEST  
METHODS 6 THROUGH 10B

- Method 6—Determination of sulfur dioxide emissions from stationary sources
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The test methods in this appendix are referred to in §60.8 (Performance Tests) and §60.11 (Compliance With Standards and Maintenance Requirements) of 40 CFR part 60, subpart A (General Provisions). Specific uses of these test methods are described in the standards of performance contained in the subparts, beginning with Subpart D.

Within each standard of performance, a section title "Test Methods and Procedures" is provided to: (1) Identify the test methods to be used as reference methods to the facility subject to the respective standard and (2) identify any special instructions or conditions to be followed when applying a method to the respective facility. Such instructions (for example, establish sampling rates, volumes, or temperatures) are to be used either

in addition to, or as a substitute for procedures in a test method. Similarly, for sources subject to emission monitoring requirements, specific instructions pertaining to any use of a test method as a reference method are provided in the subpart or in Appendix B.

Inclusion of methods in this appendix is not intended as an endorsement or denial of their applicability to sources that are not subject to standards of performance. The methods are potentially applicable to other sources; however, applicability should be confirmed by careful and appropriate evaluation of the conditions prevalent at such sources.

The approach followed in the formulation of the test methods involves specifications for equipment, procedures, and performance. In concept, a performance specification approach would be preferable in all methods because this allows the greatest flexibility to the user. In practice, however, this approach is impractical in most cases because performance specifications cannot be established. Most of the methods described herein, therefore, involve specific equipment specifications and procedures, and only a few methods in this appendix rely on performance criteria.

Minor changes in the test methods should not necessarily affect the validity of the results and it is recognized that alternative and equivalent methods exist. Section 60.8 provides authority for the Administrator to specify or approve (1) equivalent methods, (2) alternative methods, and (3) minor changes in the methodology of the test methods. It should be clearly understood that unless otherwise identified all such methods and changes must have prior approval of the Administrator. An owner employing such methods or deviations from the test methods without obtaining prior approval does so at the risk of subsequent disapproval and retesting with approved methods.

Within the test methods, certain specific equipment or procedures are recognized as being acceptable or potentially acceptable and are specifically identified in the methods. The items identified as acceptable options may be used without approval but must be identified in the test report. The potentially approvable options are cited as "subject to the approval of the Administrator" or as "or equivalent." Such potentially approvable techniques or alternatives may be used at the discretion of the owner without prior approval. However, detailed descriptions for applying these potentially approvable techniques or alternatives are not provided in the test methods. Also, the potentially approvable options are not necessarily acceptable in all applications. Therefore, an owner electing to use such potentially approvable techniques or alternatives is responsible for: (1) assuring that

the techniques or alternatives are in fact applicable and are properly executed; (2) including a written description of the alternative method in the test report (the written method must be clear and must be capable of being performed without additional instruction, and the degree of detail should be similar to the detail contained in the test methods); and (3) providing any rationale or supporting data necessary to show the validity of the alternative in the particular application. Failure to meet these requirements can result in the Administrator's disapproval of the alternative.

#### METHOD 6—DETERMINATION OF SULFUR DIOXIDE EMISSIONS FROM STATIONARY SOURCES

NOTE: This method does not include all of the specifications (*e.g.*, equipment and supplies) and procedures (*e.g.*, sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 1, Method 2, Method 3, Method 5, and Method 8.

##### 1.0 Scope and Application

###### 1.1 Analytes.

Analyte	CAS No.	Sensitivity
SO <sub>2</sub> .....	7449-09-5	3.4 mg SO <sub>2</sub> /m <sup>3</sup> (2.12 × 10 <sup>-7</sup> lb/ft <sup>3</sup> )

1.2 Applicability. This method applies to the measurement of sulfur dioxide (SO<sub>2</sub>) emissions from stationary sources.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

##### 2.0 Summary of Method

2.1 A gas sample is extracted from the sampling point in the stack. The SO<sub>2</sub> and the sulfur trioxide, including those fractions in any sulfur acid mist, are separated. The SO<sub>2</sub> fraction is measured by the barium-thorin titration method.

##### 3.0 Definitions [Reserved]

##### 4.0 Interferences

4.1 Free Ammonia. Free ammonia interferes with this method by reacting with SO<sub>2</sub> to form particulate sulfite and by reacting with the indicator. If free ammonia is present (this can be determined by knowledge of the process and/or noticing white particulate matter in the probe and isopropanol bubbler), alternative methods, subject to the approval of the Administrator, are required. One approved alternative is listed in Reference 13 of section 17.0.

4.2 Water-Soluble Cations and Fluorides. The cations and fluorides are removed by a glass wool filter and an isopropanol bubbler; therefore, they do not affect the SO<sub>2</sub> analysis. When samples are collected from a gas stream with high concentrations of metallic fumes (*i.e.*, very fine cation aerosols) a high-efficiency glass fiber filter must be used in place of the glass wool plug (*i.e.*, the one in the probe) to remove the cation interferent.

##### 5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user to establish appropriate safety and health practices and determine the applicability of regulatory limitations before performing this test method.

5.2 Corrosive reagents. The following reagents are hazardous. Personal protective equipment and safe procedures are useful in preventing chemical splashes. If contact occurs, immediately flush with copious amounts of water for at least 15 minutes. Remove clothing under shower and decontaminate. Treat residual chemical burns as thermal burns.

5.2.1 Hydrogen Peroxide (H<sub>2</sub>O<sub>2</sub>). Irritating to eyes, skin, nose, and lungs. 30% H<sub>2</sub>O<sub>2</sub> is a strong oxidizing agent. Avoid contact with skin, eyes, and combustible material. Wear gloves when handling.

5.2.2 Sodium Hydroxide (NaOH). Causes severe damage to eyes and skin. Inhalation causes irritation to nose, throat, and lungs. Reacts exothermically with limited amounts of water.

5.2.3 Sulfuric Acid (H<sub>2</sub>SO<sub>4</sub>). Rapidly destructive to body tissue. Will cause third degree burns. Eye damage may result in blindness. Inhalation may be fatal from spasm of the larynx, usually within 30 minutes. May cause lung tissue damage with edema. 1 mg/m<sup>3</sup> for 8 hours will cause lung damage or, in higher concentrations, death. Provide ventilation to limit inhalation. Reacts violently with metals and organics.

##### 6.0 Equipment and Supplies

6.1 Sample Collection. The following items are required for sample collection:

6.1.1 Sampling Train. A schematic of the sampling train is shown in Figure 6-1. The sampling equipment described in Method 8 may be substituted in place of the midjet impinger equipment of Method 6. However, the Method 8 train must be modified to include a heated filter between the probe and isopropanol impinger, and the operation of the sampling train and sample analysis must be at the flow rates and solution volumes defined in Method 8. Alternatively, SO<sub>2</sub> may be determined simultaneously with particulate

matter and moisture determinations by either (1) replacing the water in a Method 5 impinger system with a 3 percent  $\text{H}_2\text{O}_2$  solution, or (2) replacing the Method 5 water impinger system with a Method 8 isopropanol-filter- $\text{H}_2\text{O}_2$  system. The analysis for  $\text{SO}_2$  must be consistent with the procedure of Method 8. The Method 6 sampling train consists of the following components:

6.1.1.1 Probe. Borosilicate glass or stainless steel (other materials of construction may be used, subject to the approval of the Administrator), approximately 6 mm (0.25 in.) inside diameter, with a heating system to prevent water condensation and a filter (either in-stack or heated out-of-stack) to remove particulate matter, including sulfuric acid mist. A plug of glass wool is a satisfactory filter.

6.1.1.2 Bubbler and Impingers. One midget bubbler with medium-coarse glass frit and borosilicate or quartz glass wool packed in top (see Figure 6-1) to prevent sulfuric acid mist carryover, and three 30-ml midget impingers. The midget bubbler and midget impingers must be connected in series with leak-free glass connectors. Silicone grease may be used, if necessary, to prevent leakage. A midget impinger may be used in place of the midget bubbler.

NOTE: Other collection absorbers and flow rates may be used, subject to the approval of the Administrator, but the collection efficiency must be shown to be at least 99 percent for each test run and must be documented in the report. If the efficiency is found to be acceptable after a series of three tests, further documentation is not required. To conduct the efficiency test, an extra absorber must be added and analyzed separately. This extra absorber must not contain more than 1 percent of the total  $\text{SO}_2$ .

6.1.1.3 Glass Wool. Borosilicate or quartz.

6.1.1.4 Stopcock Grease. Acetone-insoluble, heat-stable silicone grease may be used, if necessary.

6.1.1.5 Temperature Sensor. Dial thermometer, or equivalent, to measure temperature of gas leaving impinger train to within 1 °C (2 °F).

6.1.1.6 Drying Tube. Tube packed with 6- to 16- mesh indicating-type silica gel, or equivalent, to dry the gas sample and to protect the meter and pump. If silica gel is previously used, dry at 177 °C (350 °F) for 2 hours. New silica gel may be used as received. Alternatively, other types of desiccants (equivalent or better) may be used, subject to the approval of the Administrator.

6.1.1.7 Valve. Needle valve, to regulate sample gas flow rate.

6.1.1.8 Pump. Leak-free diaphragm pump, or equivalent, to pull gas through the train. Install a small surge tank between the pump

and rate meter to negate the pulsation effect of the diaphragm pump on the rate meter.

6.1.1.9 Rate Meter. Rotameter, or equivalent, capable of measuring flow rate to within 2 percent of the selected flow rate of about 1 liter/min (0.035 cfm).

6.1.1.10 Volume Meter. Dry gas meter (DGM), sufficiently accurate to measure the sample volume to within 2 percent, calibrated at the selected flow rate and conditions actually encountered during sampling, and equipped with a temperature sensor (dial thermometer, or equivalent) capable of measuring temperature accurately to within 3 °C (5.4 °F). A critical orifice may be used in place of the DGM specified in this section provided that it is selected, calibrated, and used as specified in section 16.0.

6.1.2 Barometer. Mercury, aneroid, or other barometer capable of measuring atmospheric pressure to within 2.5 mm Hg (0.1 in. Hg). See the note in Method 5, section 6.1.2.

6.1.3 Vacuum Gauge and Rotameter. At least 760-mm Hg (30-in. Hg) gauge and 0- to 40-ml/min rotameter, to be used for leak-check of the sampling train.

6.2 Sample Recovery. The following items are needed for sample recovery:

6.2.1 Wash Bottles. Two polyethylene or glass bottles, 500-ml.

6.2.2 Storage Bottles. Polyethylene bottles, 100-ml, to store impinger samples (one per sample).

6.3 Sample Analysis. The following equipment is needed for sample analysis:

6.3.1 Pipettes. Volumetric type, 5-ml, 20-ml (one needed per sample), and 25-ml sizes.

6.3.2 Volumetric Flasks. 100-ml size (one per sample) and 1000-ml size.

6.3.3 Burettes. 5- and 50-ml sizes.

6.3.4 Erlenmeyer Flasks. 250-ml size (one for each sample, blank, and standard).

6.3.5 Dropping Bottle. 125-ml size, to add indicator.

6.3.6 Graduated Cylinder. 100-ml size.

6.3.7 Spectrophotometer. To measure absorbance at 352 nm.

#### 7.0 Reagents and Standards

NOTE: Unless otherwise indicated, all reagents must conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society. Where such specifications are not available, use the best available grade.

7.1 Sample Collection. The following reagents are required for sample collection:

7.1.1 Water. Deionized distilled to conform to ASTM Specification D 1193-77 or 91 Type 3 (incorporated by reference—see § 60.17). The  $\text{KMnO}_4$  test for oxidizable organic matter may be omitted when high concentrations of organic matter are not expected to be present.

7.1.2 Isopropanol, 80 Percent by Volume. Mix 80 ml of isopropanol with 20 ml of water.

7.1.2.1 Check each lot of isopropanol for peroxide impurities as follows: Shake 10 ml of isopropanol with 10 ml of freshly prepared 10 percent potassium iodide solution. Prepare a blank by similarly treating 10 ml of water. After 1 minute, read the absorbance at 352 nm on a spectrophotometer using a 1-cm path length. If absorbance exceeds 0.1, reject alcohol for use.

7.1.2.2 Peroxides may be removed from isopropanol by redistilling or by passage through a column of activated alumina; however, reagent grade isopropanol with suitably low peroxide levels may be obtained from commercial sources. Rejection of contaminated lots may, therefore, be a more efficient procedure.

7.1.3 Hydrogen Peroxide (H<sub>2</sub>O<sub>2</sub>), 3 Percent by Volume. Add 10 ml of 30 percent H<sub>2</sub>O<sub>2</sub> to 90 ml of water. Prepare fresh daily.

7.1.4 Potassium Iodide Solution, 10 Percent Weight by Volume (w/v). Dissolve 10.0 g of KI in water, and dilute to 100 ml. Prepare when needed.

7.2 Sample Recovery. The following reagents are required for sample recovery:

7.2.1 Water. Same as in section 7.1.1.

7.2.2 Isopropanol, 80 Percent by Volume. Same as in section 7.1.2.

7.3 Sample Analysis. The following reagents and standards are required for sample analysis:

7.3.1 Water. Same as in section 7.1.1.

7.3.2 Isopropanol, 100 Percent.

7.3.3 Thorin Indicator. 1-(o-arsenophenylazo)-2-naphthol-3,6-disulfonic acid, disodium salt, or equivalent. Dissolve 0.20 g in 100 ml of water.

7.3.4 Barium Standard Solution, 0.0100 N. Dissolve 1.95 g of barium perchlorate trihydrate [Ba(ClO<sub>4</sub>)<sub>2</sub>·3H<sub>2</sub>O] in 200 ml water, and dilute to 1 liter with isopropanol. Alternatively, 1.22 g of barium chloride dihydrate [BaCl<sub>2</sub>·2H<sub>2</sub>O] may be used instead of the barium perchlorate trihydrate. Standardize as in section 10.5.

7.3.5 Sulfuric Acid Standard, 0.0100 N. Purchase or standardize to ±0.0002 N against 0.0100 N NaOH which has previously been standardized against potassium acid phthalate (primary standard grade).

#### 8.0 Sample Collection, Preservation, Storage and Transport

8.1 Preparation of Sampling Train. Measure 15 ml of 80 percent isopropanol into the midjet bubbler and 15 ml of 3 percent H<sub>2</sub>O<sub>2</sub> into each of the first two midjet impingers. Leave the final midjet impinger dry. Assemble the train as shown in Figure 6-1. Adjust the probe heater to a temperature sufficient to prevent water condensation. Place crushed ice and water around the impingers.

8.2 Sampling Train Leak-Check Procedure. A leak-check prior to the sampling run is recommended, but not required. A leak-

check after the sampling run is mandatory. The leak-check procedure is as follows:

8.2.1 Temporarily attach a suitable (*e.g.*, 0- to 40- ml/min) rotameter to the outlet of the DGM, and place a vacuum gauge at or near the probe inlet. Plug the probe inlet, pull a vacuum of at least 250 mm Hg (10 in. Hg), and note the flow rate as indicated by the rotameter. A leakage rate in excess of 2 percent of the average sampling rate is not acceptable.

NOTE: Carefully (*i.e.*, slowly) release the probe inlet plug before turning off the pump.

8.2.2 It is suggested (not mandatory) that the pump be leak-checked separately, either prior to or after the sampling run. To leak-check the pump, proceed as follows: Disconnect the drying tube from the probe-impinger assembly. Place a vacuum gauge at the inlet to either the drying tube or the pump, pull a vacuum of 250 mm Hg (10 in. Hg), plug or pinch off the outlet of the flow meter, and then turn off the pump. The vacuum should remain stable for at least 30 seconds.

If performed prior to the sampling run, the pump leak-check shall precede the leak-check of the sampling train described immediately above; if performed after the sampling run, the pump leak-check shall follow the sampling train leak-check.

8.2.3 Other leak-check procedures may be used, subject to the approval of the Administrator.

#### 8.3 Sample Collection.

8.3.1 Record the initial DGM reading and barometric pressure. To begin sampling, position the tip of the probe at the sampling point, connect the probe to the bubbler, and start the pump. Adjust the sample flow to a constant rate of approximately 1.0 liter/min as indicated by the rate meter. Maintain this constant rate (±10 percent) during the entire sampling run.

8.3.2 Take readings (DGM volume, temperatures at DGM and at impinger outlet, and rate meter flow rate) at least every 5 minutes. Add more ice during the run to keep the temperature of the gases leaving the last impinger at 20 °C (68 °F) or less.

8.3.3 At the conclusion of each run, turn off the pump, remove the probe from the stack, and record the final readings. Conduct a leak-check as described in section 8.2. (This leak-check is mandatory.) If a leak is detected, void the test run or use procedures acceptable to the Administrator to adjust the sample volume for the leakage.

8.3.4 Drain the ice bath, and purge the remaining part of the train by drawing clean ambient air through the system for 15 minutes at the sampling rate. Clean ambient air can be provided by passing air through a charcoal filter or through an extra midjet impinger containing 15 ml of 3 percent H<sub>2</sub>O<sub>2</sub>. Alternatively, ambient air without purification may be used.

8.4 Sample Recovery. Disconnect the impingers after purging. Discard the contents of the midget bubbler. Pour the contents of the midget impingers into a leak-free polyethylene bottle for shipment. Rinse the three midget impingers and the con-

necting tubes with water, and add the rinse to the same storage container. Mark the fluid level. Seal and identify the sample container.

9.0 Quality Control

Section	Quality control measure	Effect
7.1.2	Isopropanol check	Ensure acceptable level of peroxide impurities in isopropanol.
8.2, 10.1-10.4	Sampling equipment leak-check and calibration.	Ensure accurate measurement of stack gas flow rate, sample volume.
10.5	Barium standard solution standardization	Ensure precision of normality determination
11.2.3	Replicate titrations	Ensure precision of titration determinations.

10.0 Calibration and Standardization

10.1 Volume Metering System.

10.1.1 Initial Calibration.

10.1.1.1 Before its initial use in the field, leak-check the metering system (drying tube, needle valve, pump, rate meter, and DGM) as follows: Place a vacuum gauge at the inlet to the drying tube and pull a vacuum of 250 mm Hg (10 in. Hg). Plug or pinch off the outlet of the flow meter, and then turn off the pump. The vacuum must remain stable for at least 30 seconds. Carefully release the vacuum gauge before releasing the flow meter end.

10.1.1.2 Remove the drying tube, and calibrate the metering system (at the sampling flow rate specified by the method) as follows: Connect an appropriately sized wet-test meter (e.g., 1 liter per revolution) to the inlet of the needle valve. Make three independent calibration runs, using at least five revolutions of the DGM per run. Calculate the calibration factor Y (wet-test meter calibration volume divided by the DGM volume, both volumes adjusted to the same reference temperature and pressure) for each run, and average the results (Y<sub>i</sub>). If any Y-value deviates by more than 2 percent from (Y<sub>i</sub>), the metering system is unacceptable for use. If the metering system is acceptable, use (Y<sub>i</sub>) as the calibration factor for subsequent test runs.

10.1.2 Post-Test Calibration Check. After each field test series, conduct a calibration check using the procedures outlined in section 10.1.1.2, except that three or more revolutions of the DGM may be used, and only two independent runs need be made. If the average of the two post-test calibration factors does not deviate by more than 5 percent from Y<sub>i</sub>, then Y<sub>i</sub> is accepted as the DGM calibration factor (Y), which is used in Equation 6-1 to calculate collected sample volume (see section 12.2). If the deviation is more than 5 percent, recalibrate the metering system as in section 10.1.1, and determine a post-test calibration factor (Y<sub>i</sub>). Compare Y<sub>i</sub> and Y<sub>i</sub>; the smaller of the two factors is accepted as the DGM calibration factor. If recalibration indicates that the metering system is un-

acceptable for use, either void the test run or use methods, subject to the approval of the Administrator, to determine an acceptable value for the collected sample volume.

10.1.3 DGM as a Calibration Standard. A DGM may be used as a calibration standard for volume measurements in place of the wet-test meter specified in section 10.1.1.2, provided that it is calibrated initially and recalibrated periodically according to the same procedures outlined in Method 5, section 10.3 with the following exceptions: (a) the DGM is calibrated against a wet-test meter having a capacity of 1 liter/rev (0.035 ft<sup>3</sup>/rev) or 3 liters/rev (0.1 ft<sup>3</sup>/rev) and having the capability of measuring volume to within 1 percent; (b) the DGM is calibrated at 1 liter/min (0.035 cfm); and (c) the meter box of the Method 6 sampling train is calibrated at the same flow rate.

10.2 Temperature Sensors. Calibrate against mercury-in-glass thermometers. An alternative mercury-free thermometer may be used if the thermometer is, at a minimum, equivalent in terms of performance or suitably effective for the specific temperature measurement application.

10.3 Rate Meter. The rate meter need not be calibrated, but should be cleaned and maintained according to the manufacturer's instructions.

10.4 Barometer. Calibrate against a mercury barometer or NIST-traceable barometer prior to the field test.

10.5 Barium Standard Solution. Standardize the barium perchlorate or chloride solution against 25 ml of standard sulfuric acid to which 100 ml of 100 percent isopropanol has been added. Run duplicate analyses. Calculate the normality using the average of duplicate analyses where the titrations agree within 1 percent or 0.2 ml, whichever is larger.

11.0 Analytical Procedure

11.1 Sample Loss Check. Note level of liquid in container and confirm whether any sample was lost during shipment; note this

finding on the analytical data sheet. If a noticeable amount of leakage has occurred, either void the sample or use methods, subject to the approval of the Administrator, to correct the final results.

11.2 Sample Analysis.

11.2.1 Transfer the contents of the storage container to a 100-ml volumetric flask, dilute to exactly 100 ml with water, and mix the diluted sample.

11.2.2 Pipette a 20-ml aliquot of the diluted sample into a 250-ml Erlenmeyer flask and add 80 ml of 100 percent isopropanol plus two to four drops of thiorin indicator. While stirring the solution, titrate to a pink endpoint using 0.0100 N barium standard solution.

11.2.3 Repeat the procedures in section 11.2.2, and average the titration volumes. Run a blank with each series of samples. Replicate titrations must agree within 1 percent or 0.2 ml, whichever is larger.

NOTE: Protect the 0.0100 N barium standard solution from evaporation at all times.

12.0 Data Analysis and Calculations

Carry out calculations, retaining at least one extra significant figure beyond that of the acquired data. Round off figures after final calculation.

12.1 NOMENCLATURE

C<sub>SO2</sub> = Concentration of SO<sub>2</sub>, dry basis, corrected to standard conditions, mg/dscm (lb/dscf).  
 N = Normality of barium standard titrant, meq/ml.

P<sub>bar</sub> = Barometric pressure, mm Hg (in. Hg).  
 P<sub>std</sub> = Standard absolute pressure, 760 mm Hg (29.92 in. Hg).

T<sub>m</sub> = Average DGM absolute temperature, °K (°R).

T<sub>std</sub> = Standard absolute temperature, 293 °K (528 °R).

V<sub>a</sub> = Volume of sample aliquot titrated, ml.

V<sub>m</sub> = Dry gas volume as measured by the DGM, dcm (dcf).

V<sub>m(std)</sub> = Dry gas volume measured by the DGM, corrected to standard conditions, dscm (dscf).

V<sub>soln</sub> = Total volume of solution in which the SO<sub>2</sub> sample is contained, 100 ml.

V<sub>t</sub> = Volume of barium standard titrant used for the sample (average of replicate titration), ml.

V<sub>tb</sub> = Volume of barium standard titrant used for the blank, ml.

Y = DGM calibration factor.

12.2 Dry Sample Gas Volume, Corrected to Standard Conditions.

$$V_{m(std)} = \frac{(V_m Y T_{std} P_{bar})}{(T_m P_{std})} \quad \text{Eq. 6-1}$$

$$= \frac{K_1 Y V_m P_{bar}}{T_m}$$

Where:

K<sub>1</sub> = 0.3855 °K/mm Hg for metric units,

K<sub>1</sub> = 17.65 °R/in. Hg for English units.

12.3 SO<sub>2</sub> Concentration.

$$C_{SO_2} = \frac{K_2 N (V_t - V_{tb})(V_{soln}/V_a)}{V_{m(std)}} \quad \text{Eq. 6-2}$$

Where:

K<sub>2</sub> = 32.03 mg SO<sub>2</sub>/meq for metric units,

K<sub>2</sub> = 7.061 × 10<sup>-5</sup> lb SO<sub>2</sub>/meq for English units.

13.0 Method Performance

13.1 Range. The minimum detectable limit of the method has been determined to be 3.4 mg SO<sub>2</sub>/m<sup>3</sup> (2.12 × 10<sup>-7</sup> lb/ft<sup>3</sup>). Although no upper limit has been established, tests have shown that concentrations as high as 80,000 mg/m<sup>3</sup> (0.005 lb/ft<sup>3</sup>) of SO<sub>2</sub> can be collected efficiently at a rate of 1.0 liter/min (0.035 cfm) for 20 minutes in two midjet impingers, each containing 15 ml of 3 percent H<sub>2</sub>O<sub>2</sub>. Based on theoretical calculations, the upper concentration limit in a 20 liter (0.7 ft<sup>3</sup>) sample is about 93,300 mg/m<sup>3</sup> (0.00583 lb/ft<sup>3</sup>).

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 Alternative Procedures

16.1 Nomenclature. Same as section 12.1, with the following additions:

B<sub>wa</sub> = Water vapor in ambient air, proportion by volume.

M<sub>a</sub> = Molecular weight of the ambient air saturated at impinger temperature, g/g-mole (lb/lb-mole).

M<sub>s</sub> = Molecular weight of the sample gas saturated at impinger temperature, g/g-mole (lb/lb-mole).

P<sub>i</sub> = Inlet vacuum reading obtained during the calibration run, mm Hg (in. Hg).

P<sub>s</sub> = Inlet vacuum reading obtained during the sampling run, mm Hg (in. Hg).

$\bar{Q}_{std}$  = Volumetric flow rate through critical orifice, scm/min (scf/min).

$Q_{std}$  = Average flow rate of pre-test and post-test calibration runs, scm/min (scf/min).

$T_{amb}$  = Ambient absolute temperature of air, °K (°R).

$V_{sb}$  = Volume of gas as measured by the soap bubble meter, m<sup>3</sup> (ft<sup>3</sup>).

$V_{sb(std)}$  = Volume of gas as measured by the soap bubble meter, corrected to standard conditions, scm (scf).

$\theta$  = Soap bubble travel time, min.

$\theta_s$  = Time, min.

16.2 Critical Orifices for Volume and Rate Measurements. A critical orifice may be used in place of the DGM specified in section 6.1.1.10, provided that it is selected, calibrated, and used as follows:

16.2.1 Preparation of Sampling Train. Assemble the sampling train as shown in Figure 6-2. The rate meter and surge tank are optional but are recommended in order to detect changes in the flow rate.

NOTE: The critical orifices can be adapted to a Method 6 type sampling train as follows: Insert sleeve type, serum bottle stoppers into two reducing unions. Insert the needle into the stoppers as shown in Figure 6-3.

16.2.2 Selection of Critical Orifices.

16.2.2.1 The procedure that follows describes the use of hypodermic needles and stainless steel needle tubings, which have been found suitable for use as critical orifices. Other materials and critical orifice designs may be used provided the orifices act as true critical orifices, (i.e., a critical vacuum can be obtained) as described in this section. Select a critical orifice that is sized to operate at the desired flow rate. The needle sizes and tubing lengths shown in Table 6-1 give the following approximate flow rates.

16.2.2.2 Determine the suitability and the appropriate operating vacuum of the critical orifice as follows: If applicable, temporarily attach a rate meter and surge tank to the

outlet of the sampling train, if said equipment is not present (see section 16.2.1). Turn on the pump and adjust the valve to give an outlet vacuum reading corresponding to about half of the atmospheric pressure. Observe the rate meter reading. Slowly increase the vacuum until a stable reading is obtained on the rate meter. Record the critical vacuum, which is the outlet vacuum when the rate meter first reaches a stable value. Orifices that do not reach a critical value must not be used.

16.2.3 Field Procedures.

16.2.3.1 Leak-Check Procedure. A leak-check before the sampling run is recommended, but not required. The leak-check procedure is as follows: Temporarily attach a suitable (e.g., 0-40 ml/min) rotameter and surge tank, or a soap bubble meter and surge tank to the outlet of the pump. Plug the probe inlet, pull an outlet vacuum of at least 250 mm Hg (10 in. Hg), and note the flow rate as indicated by the rotameter or bubble meter. A leakage rate in excess of 2 percent of the average sampling rate ( $\bar{Q}_{std}$ ) is not acceptable. Carefully release the probe inlet plug before turning off the pump.

16.2.3.2 Moisture Determination. At the sampling location, prior to testing, determine the percent moisture of the ambient air using the wet and dry bulb temperatures or, if appropriate, a relative humidity meter.

16.2.3.3 Critical Orifice Calibration. At the sampling location, prior to testing, calibrate the entire sampling train (i.e., determine the flow rate of the sampling train when operated at critical conditions). Attach a 500-ml soap bubble meter to the inlet of the probe, and operate the sampling train at an outlet vacuum of 25 to 50 mm Hg (1 to 2 in. Hg) above the critical vacuum. Record the information listed in Figure 6-4. Calculate the standard volume of air measured by the soap bubble meter and the volumetric flow rate using the equations below:

$$V_{sb(std)} = V_{sb} (T_{std}/T_{amb}) (P_{bar}/P_{std}) \quad \text{Eq. 6-4}$$

$$Q_{std} = \frac{V_{sb(std)}}{\theta} \quad \text{Eq. 6-5}$$

16.2.3.4 Sampling.

16.2.3.4.1 Operate the sampling train for sample collection at the same vacuum used during the calibration run. Start the watch and pump simultaneously. Take readings (temperature, rate meter, inlet vacuum, and outlet vacuum) at least every 5 minutes. At the end of the sampling run, stop the watch and pump simultaneously.

16.2.3.4.2 Conduct a post-test calibration run using the calibration procedure outlined in section 16.2.3.3. If the  $Q_{std}$  obtained before and after the test differ by more than 5 percent, void the test run; if not, calculate the volume of the gas measured with the critical orifice using Equation 6-6 as follows:

$$V_{m(\text{std})} = \frac{\bar{Q}_{\text{std}} \theta_s (1 - B_{\text{wa}})(P_{\text{bar}} + P_{\text{sr}})}{(P_{\text{bar}} + P_c)} \quad \text{Eq. 6-6}$$

16.2.3.4.3 If the percent difference between the molecular weight of the ambient air at saturated conditions and the sample gas is more than  $\pm 3$  percent, then the molecular

weight of the gas sample must be considered in the calculations using the following equation:

$$V_{m(\text{std})} = \frac{\bar{Q}_{\text{std}} \theta_s (1 - B_{\text{wa}})(P_{\text{bar}} + P_{\text{sr}})(M_a/M_s)^{1/2}}{(P_{\text{bar}} + P_c)} \quad \text{Eq. 6-7}$$

NOTE: A post-test leak-check is not necessary because the post-test calibration run results will indicate whether there is any leakage.

16.2.3.4.4 Drain the ice bath, and purge the sampling train using the procedure described in section 8.3.4.

16.3 Elimination of Ammonia Interference. The following alternative procedures must be used in addition to those specified in the method when sampling at sources having ammonia emissions.

16.3.1 Sampling. The probe shall be maintained at 275 °C (527 °F) and equipped with a high-efficiency in-stack filter (glass fiber) to remove particulate matter. The filter material shall be unreactive to SO<sub>2</sub>. Whatman 934AH (formerly Reeve Angel 934AH) filters treated as described in Reference 10 in section 17.0 of Method 5 is an example of a filter that has been shown to work. Where alkaline particulate matter and condensed moisture are present in the gas stream, the filter shall be heated above the moisture dew point but below 225 °C (437 °F).

16.3.2 Sample Recovery. Recover the sample according to section 8.4 except for discarding the contents of the midget bubbler. Add the bubbler contents, including the rinsings of the bubbler with water, to a separate polyethylene bottle from the rest of the sample. Under normal testing conditions where sulfur trioxide will not be present significantly, the tester may opt to delete the midget bubbler from the sampling train. If an approximation of the sulfur trioxide concentration is desired, transfer the contents of the midget bubbler to a separate polyethylene bottle.

16.3.3 Sample Analysis. Follow the procedures in sections 11.1 and 11.2, except add 0.5 ml of 0.1 N HCl to the Erlenmeyer flask and mix before adding the indicator. The following analysis procedure may be used for an approximation of the sulfur trioxide concentration. The accuracy of the calculated

concentration will depend upon the ammonia to SO<sub>2</sub> ratio and the level of oxygen present in the gas stream. A fraction of the SO<sub>2</sub> will be counted as sulfur trioxide as the ammonia to SO<sub>2</sub> ratio and the sample oxygen content increases. Generally, when this ratio is 1 or less and the oxygen content is in the range of 5 percent, less than 10 percent of the SO<sub>2</sub> will be counted as sulfur trioxide. Analyze the peroxide and isopropanol sample portions separately. Analyze the peroxide portion as described above. Sulfur trioxide is determined by difference using sequential titration of the isopropanol portion of the sample. Transfer the contents of the isopropanol storage container to a 100-ml volumetric flask, and dilute to exactly 100 ml with water. Pipette a 20-ml aliquot of this solution into a 250-ml Erlenmeyer flask, add 0.5 ml of 0.1 N HCl, 80 ml of 100 percent isopropanol, and two to four drops of thiorin indicator. Titrate to a pink endpoint using 0.0100 N barium perchlorate. Repeat and average the titration volumes that agree within 1 percent or 0.2 ml, whichever is larger. Use this volume in Equation 6-2 to determine the sulfur trioxide concentration. From the flask containing the remainder of the isopropanol sample, determine the fraction of SO<sub>2</sub> collected in the bubbler by pipetting 20-ml aliquots into 250-ml Erlenmeyer flasks. Add 5 ml of 3 percent H<sub>2</sub>O<sub>2</sub>, 100 ml of 100 percent isopropanol, and two to four drips of thiorin indicator, and titrate as before. From this titration volume, subtract the titrant volume determined for sulfur trioxide, and add the titrant volume determined for the peroxide portion. This final volume constitutes V<sub>1</sub>, the volume of barium perchlorate used for the SO<sub>2</sub> sample.

#### 17.0 References

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18.0 Tables, Diagrams, Flowcharts and Validation Data

TABLE 6-1—APPROXIMATE FLOW RATES FOR VARIOUS NEEDLE SIZES

Needle size (gauge)	Needle length (cm)	Flow rate (ml/min)
21 .....	7.6	1,100
22 .....	2.9	1,000
22 .....	3.8	900
23 .....	3.8	500
23 .....	5.1	450
24 .....	3.2	400

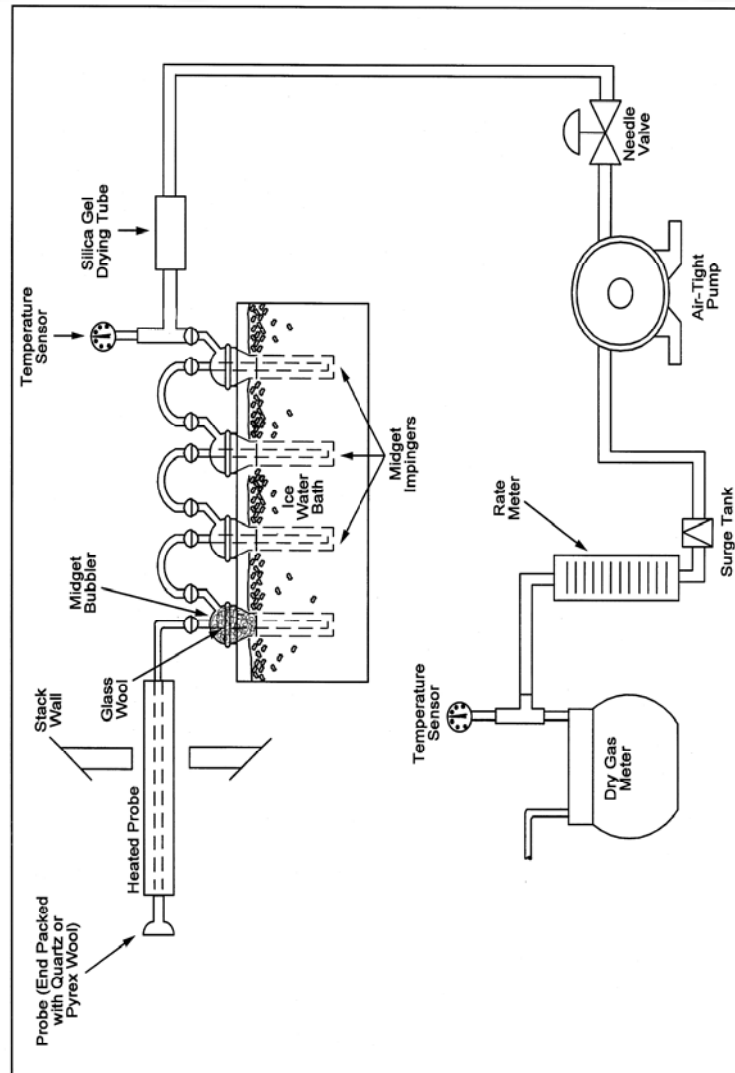


Figure 6-1. Sulfur Dioxide Sampling Train.

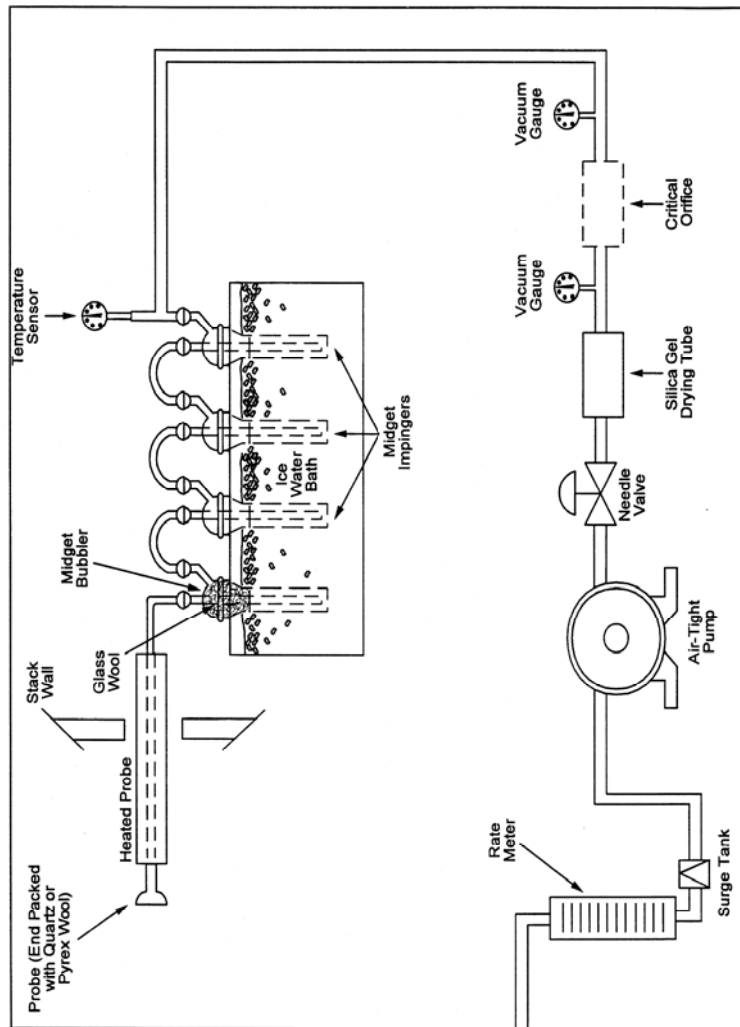


Figure 6-2. Sulfur Dioxide Sampling Train Using a Critical Orifice.

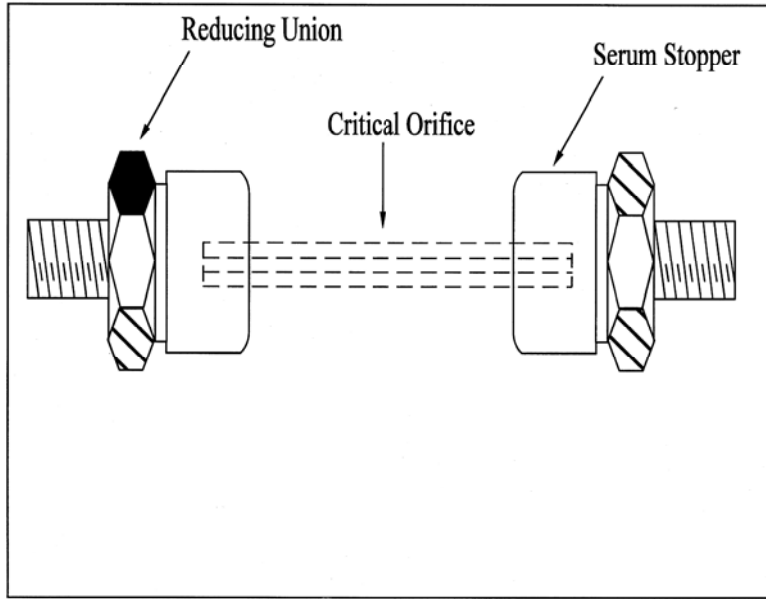


Figure 6-3. Critical Orifice Adaptation for the Method 6 Sampling Train.

Date _____	Train ID _____		
Critical orifice size _____	Critical vacuum _____		
		<u>Pretest</u>	<u>Post-test</u>
Soap bubble meter volume, cc		_____	_____
$V_{sb}$			
	m <sup>3</sup> (ft <sup>3</sup> )	_____	_____
Time, $\theta$	sec	_____	_____
	min	_____	_____
Barometric pressure, $P_{bar}$	mm Hg (in. Hg)	_____	_____
Ambient temperature, $t_{amb}$	°C (°F)	_____	_____
Inlet vacuum, $P_c$	mm Hg (in. Hg)	_____	_____
Outlet vacuum	mm Hg (in. Hg)	_____	_____
$V_{sb(Std)}$	m <sup>3</sup> (ft <sup>3</sup> )	_____	_____
Flow rate, $Q_{Std}$	$\frac{m^3}{min} \left( \frac{ft^3}{min} \right)$	_____	_____

Figure 6-4. Critical Orifice Calibration Data Sheet.

**METHOD 6A—DETERMINATION OF SULFUR DIOXIDE, MOISTURE, AND CARBON DIOXIDE FROM FOSSIL FUEL COMBUSTION SOURCES**

NOTE: This method does not include all of the specifications (e.g., equipment and supplies) and procedures (e.g., sampling and analytical) essential to its performance. Some material is incorporated by reference from

other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 1, Method 2, Method 3, Method 5, Method 6, and Method 19.

*1.0 Scope and Application*

1.1 Analytes.

Analyte	CAS No.	Sensitivity
SO <sub>2</sub> .....	7449-09-05	3.4 mg SO <sub>2</sub> /m <sup>3</sup> (2.12 × 10 <sup>-7</sup> lb/ft <sup>3</sup> )
CO <sub>2</sub> .....	124-38-9	N/A
H <sub>2</sub> O .....	7732-18-5	N/A

1.2 **Applicability.** This method is applicable for the determination of sulfur dioxide (SO<sub>2</sub>) emissions from fossil fuel combustion sources in terms of concentration (mg/dscm or lb/dscf) and in terms of emission rate (ng/J or lb/10<sup>9</sup> Btu) and for the determination of carbon dioxide (CO<sub>2</sub>) concentration (percent), Moisture content (percent), if desired, may also be determined by this method.

1.3 **Data Quality Objectives.** Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

#### 2.0 Summary of Method

2.1 A gas sample is extracted from a sampling point in the stack. The SO<sub>2</sub> and the sulfur trioxide, including those fractions in any sulfur acid mist, are separated. The SO<sub>2</sub> fraction is measured by the barium-thorin titration method. Moisture and CO<sub>2</sub> fractions are collected in the same sampling train, and are determined gravimetrically.

#### 3.0 Definitions [Reserved]

#### 4.0 Interferences

Same as Method 6, section 4.0.

#### 5.0 Safety

5.1 **Disclaimer.** This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to performing this test method.

5.2 **Corrosive reagents.** Same as Method 6, section 5.2.

#### 6.0 Equipment and Supplies

6.1 **Sample Collection.** Same as Method 6, section 6.1, with the exception of the following:

6.1.1 **Sampling Train.** A schematic of the sampling train used in this method is shown in Figure 6A-1.

6.1.1.1 **Impingers and Bubblers.** Two 30 = ml midget impingers with a 1 = mm restricted tip and two 30 = ml midget bubblers with unrestricted tips. Other types of impingers and bubblers (e.g., Mae West for SO<sub>2</sub> collection and rigid cylinders containing Drierite for moisture absorbers), may be used with proper attention to reagent volumes and levels, subject to the approval of the Administrator.

6.1.1.2 **CO<sub>2</sub> Absorber.** A sealable rigid cylinder or bottle with an inside diameter between 30 and 90 mm, a length between 125 and 250 mm, and appropriate connections at both ends. The filter may be a separate heated unit or may be within the heated portion of the probe. If the filter is within the sampling probe, the filter should not be within 15 cm of the probe inlet or any unheated section of the probe, such as the connection to the first bubbler. The probe and filter should be heated to at least 20 °C (68 °F) above the source temperature, but not greater than 120 °C (248 °F). The filter temperature (i.e., the sample gas temperature) should be monitored to assure the desired temperature is maintained. A heated Teflon connector may be used to connect the filter holder or probe to the first impinger.

**NOTE:** For applications downstream of wet scrubbers, a heated out-of-stack filter (either borosilicate glass wool or glass fiber mat) is necessary.

6.2 **Sample Recovery.** Same as Method 6, section 6.2.

6.3 **Sample Analysis.** Same as Method 6, section 6.3, with the addition of a balance to measure within 0.05 g.

#### 7.0 Reagents and Standards

**NOTE:** Unless otherwise indicated, all reagents must conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society. Where such specifications are not available, use the best available grade.

7.1 **Sample Collection.** Same as Method 6, section 7.1, with the addition of the following:

7.1.1 **Drierite.** Anhydrous calcium sulfate (CaSO<sub>4</sub>) desiccant, 8 mesh, indicating type is recommended.

**NOTE:** Do not use silica gel or similar desiccant in this application.

7.1.2 **CO<sub>2</sub> Absorbing Material.** Ascarite II. Sodium hydroxide-coated silica, 8- to 20-mesh.

7.2 **Sample Recovery and Analysis.** Same as Method 6, sections 7.2 and 7.3, respectively.

#### 8.0 Sample Collection, Preservation, Transport, and Storage

##### 8.1 Preparation of Sampling Train.

8.1.1 Measure 15 ml of 80 percent isopropanol into the first midget bubbler and 15 ml of 3 percent hydrogen peroxide into each of the two midget impingers (the second

and third vessels in the train) as described in Method 6, section 8.1. Insert the glass wool into the top of the isopropanol bubbler as shown in Figure 6A-1. Place about 25 g of Drierite into the second midget bubbler (the fourth vessel in the train). Clean the outside of the bubblers and impingers and allow the vessels to reach room temperature. Weigh the four vessels simultaneously to the nearest 0.1 g, and record this initial weight ( $m_{wi}$ ).

8.1.2 With one end of the CO<sub>2</sub> absorber sealed, place glass wool into the cylinder to a depth of about 1 cm (0.5 in.). Place about 150 g of CO<sub>2</sub> absorbing material in the cylinder on top of the glass wool, and fill the remaining space in the cylinder with glass wool. Assemble the cylinder as shown in figure 6A-2. With the cylinder in a horizontal position, rotate it around the horizontal axis. The CO<sub>2</sub> absorbing material should remain in position during the rotation, and no open spaces or channels should be formed. If necessary, pack more glass wool into the cylinder to make the CO<sub>2</sub> absorbing material stable. Clean the outside of the cylinder of loose dirt and moisture and allow the cylinder to reach room temperature. Weigh the cylinder to the nearest 0.1 g, and record this initial weight ( $m_{ai}$ ).

8.1.3 Assemble the train as shown in figure 6A-1. Adjust the probe heater to a temperature sufficient to prevent condensation (see note in section 6.1). Place crushed ice and water around the impingers and bubblers. Mount the CO<sub>2</sub> absorber outside the water bath in a vertical flow position with the sample gas inlet at the bottom. Flexible tubing (e.g., Tygon) may be used to connect the last SO<sub>2</sub> absorbing impinger to the moisture absorber and to connect the moisture absorber to the CO<sub>2</sub> absorber. A second, smaller CO<sub>2</sub> absorber containing Ascarite II may be added in-line downstream of the primary CO<sub>2</sub> absorber as a breakthrough indicator. Ascarite II turns white when CO<sub>2</sub> is absorbed.

8.2 Sampling Train Leak-Check Procedure and Sample Collection. Same as Method 6, sections 8.2 and 8.3, respectively.

8.3 Sample Recovery.

8.3.1 Moisture Measurement. Disconnect the isopropanol bubbler, the SO<sub>2</sub> impingers, and the moisture absorber from the sample train. Allow about 10 minutes for them to reach room temperature, clean the outside of loose dirt and moisture, and weigh them simultaneously in the same manner as in section 8.1. Record this final weight ( $m_{wf}$ ).

8.3.2 Peroxide Solution. Discard the contents of the isopropanol bubbler and pour the contents of the midget impingers into a leak-free polyethylene bottle for shipping. Rinse the two midget impingers and connecting tubes with water, and add the washing to the same storage container.

8.3.3 CO<sub>2</sub> Absorber. Allow the CO<sub>2</sub> absorber to warm to room temperature (about 10 minutes), clean the outside of loose dirt and moisture, and weigh to the nearest 0.1 g in the same manner as in section 8.1. Record this final weight ( $m_{af}$ ). Discard used Ascarite II material.

9.0 Quality Control

Same as Method 6, section 9.0.

10.0 Calibration and Standardization

Same as Method 6, section 10.0.

11.0 Analytical Procedure

11.1 Sample Analysis. The sample analysis procedure for SO<sub>2</sub> is the same as that specified in Method 6, section 11.0.

12.0 Data Analysis and Calculations

Same as Method 6, section 12.0, with the addition of the following:

12.1 Nomenclature.

- $C_w$  = Concentration of moisture, percent.
- $C_{CO_2}$  = Concentration of CO<sub>2</sub>, dry basis, percent.
- $E_{SO_2}$  = Emission rate of SO<sub>2</sub>, ng/J (lb/10<sup>6</sup> Btu).
- $F_c$  = Carbon F-factor from Method 19 for the fuel burned, dscm/J (dscf/10<sup>6</sup> Btu).
- $m_{wi}$  = Initial weight of impingers, bubblers, and moisture absorber, g.
- $m_{wf}$  = Final weight of impingers, bubblers, and moisture absorber, g.
- $m_{ai}$  = Initial weight of CO<sub>2</sub> absorber, g.
- $m_{af}$  = Final weight of CO<sub>2</sub> absorber, g.
- $m_{SO_2}$  = Mass of SO<sub>2</sub> collected, mg.
- $V_{CO_2(std)}$  = Equivalent volume of CO<sub>2</sub> collected at standard conditions, dscm (dscf).
- $V_{w(std)}$  = Equivalent volume of moisture collected at standard conditions, scm (scf).

12.2 CO<sub>2</sub> Volume Collected, Corrected to Standard Conditions.

$$V_{CO_2(std)} = K_3 (m_{af} - m_{ai}) \quad \text{Eq. 6A-1}$$

Where:

$K_3$  = Equivalent volume of gaseous CO<sub>2</sub> at standard conditions,  $5.467 \times 10^{-4}$  dscm/g ( $1.930 \times 10^{-2}$  dscf/g).

12.3 Moisture Volume Collected, Corrected to Standard Conditions.

$$V_{w(std)} = K_4 (m_{wf} - m_{wi}) \quad \text{Eq. 6A-2}$$

Where:

$K_4$  = Equivalent volume of water vapor at standard conditions,  $1.336 \times 10^{-3}$  scm/g ( $4.717 \times 10^{-2}$  scf/g).

12.4 SO<sub>2</sub> Concentration.

$$C_{\text{SO}_2} = \frac{K_2 N (V_t - V_{\text{tb}}) (V_{\text{soln}} / V_a)}{V_{\text{m(std)}} + V_{\text{CO}_2(\text{std})}} \quad \text{Eq. 6A-3}$$

Where:

$K_2 = 32.03 \text{ mg SO}_2/\text{meq. SO}_2$  ( $7.061 \times 10^{-5} \text{ lb SO}_2/\text{meq. SO}_2$ )

12.5 CO<sub>2</sub> Concentration.

$$C_{\text{CO}_2} = \frac{V_{\text{CO}_2(\text{std})}}{V_{\text{m(std)}} + V_{\text{CO}_2(\text{std})}} \quad \text{Eq. 6A-4}$$

12.6 Moisture Concentration.

$$C_w = \frac{V_{\text{w(std)}}}{V_{\text{m(std)}} + V_{\text{w(std)}} + V_{\text{CO}_2(\text{std})}} \quad \text{Eq. 6A-5}$$

### 13.0 Method Performance

13.1 Range and Precision. The minimum detectable limit and the upper limit for the measurement of SO<sub>2</sub> are the same as for Method 6. For a 20-liter sample, this method has a precision of ±0.5 percent CO<sub>2</sub> for concentrations between 2.5 and 25 percent CO<sub>2</sub> and ±1.0 percent moisture for moisture concentrations greater than 5 percent.

### 14.0 Pollution Prevention [Reserved]

### 15.0 Waste Management [Reserved]

### 16.0 Alternative Methods

If the only emission measurement desired is in terms of emission rate of SO<sub>2</sub> (ng/J or lb/10<sup>6</sup> Btu), an abbreviated procedure may be used. The differences between the above procedure and the abbreviated procedure are described below.

16.1 Sampling Train. The sampling train is the same as that shown in Figure 6A-1 and as

described in section 6.1, except that the dry gas meter is not needed.

16.2 Preparation of the Sampling Train. Follow the same procedure as in section 8.1, except do not weigh the isopropanol bubbler, the SO<sub>2</sub> absorbing impingers, or the moisture absorber.

16.3 Sampling Train Leak-Check Procedure and Sample Collection. Leak-check and operate the sampling train as described in section 8.2, except that dry gas meter readings, barometric pressure, and dry gas meter temperatures need not be recorded during sampling.

16.4 Sample Recovery. Follow the procedure in section 8.3, except do not weigh the isopropanol bubbler, the SO<sub>2</sub> absorbing impingers, or the moisture absorber.

16.5 Sample Analysis. Analysis of the peroxide solution is the same as that described in section 11.1.

16.6 Calculations.

16.6.1 SO<sub>2</sub> Collected.

$$m_{\text{SO}_2} = K_2 N (V_t - V_{\text{tb}}) (V_{\text{soln}} / V_a) \quad \text{Eq. 6A-6}$$

Where:

$K_2 = 32.03 \text{ mg SO}_2/\text{meq. SO}_2$

$K_2 = 7.061 \times 10^{-5} \text{ lb SO}_2/\text{meq. SO}_2$

16.6.2 Sulfur Dioxide Emission Rate.



$$E_{\text{SO}_2} = K_5 F_c m_{\text{SO}_2} / (m_{\text{af}} - m_{\text{ai}}) \quad \text{Eq. 6A-7}$$

Where:

$K_5 = 1.829 \times 10^9 \text{ mg/dscm}$

$K_2 = 0.1142 \text{ lb/dscf}$

#### 17.0 References

Same as Method 6, section 17.0, References 1 through 8, with the addition of the following:

1. Stanley, Jon and P.R. Westlin. An Alternate Method for Stack Gas Moisture Determination. Source Evaluation Society Newsletter. 3(4), November 1978.

2. Whittle, Richard N. and P.R. Westlin. Air Pollution Test Report: Development and Evaluation of an Intermittent Integrated SO<sub>2</sub>/CO<sub>2</sub> Emission Sampling Procedure. Environmental Protection Agency, Emission Standard and Engineering Division, Emission Measurement Branch. Research Triangle Park, NC. December 1979. 14 pp.

#### 18.0 Tables, Diagrams, Flowcharts, and Validation Data

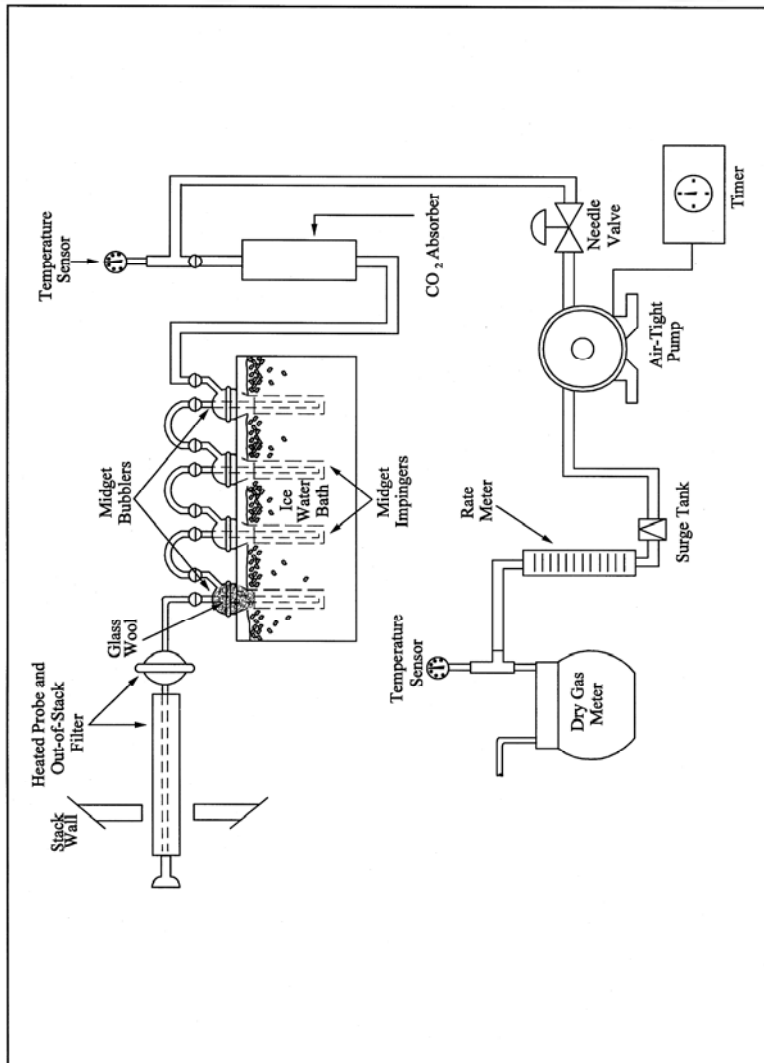
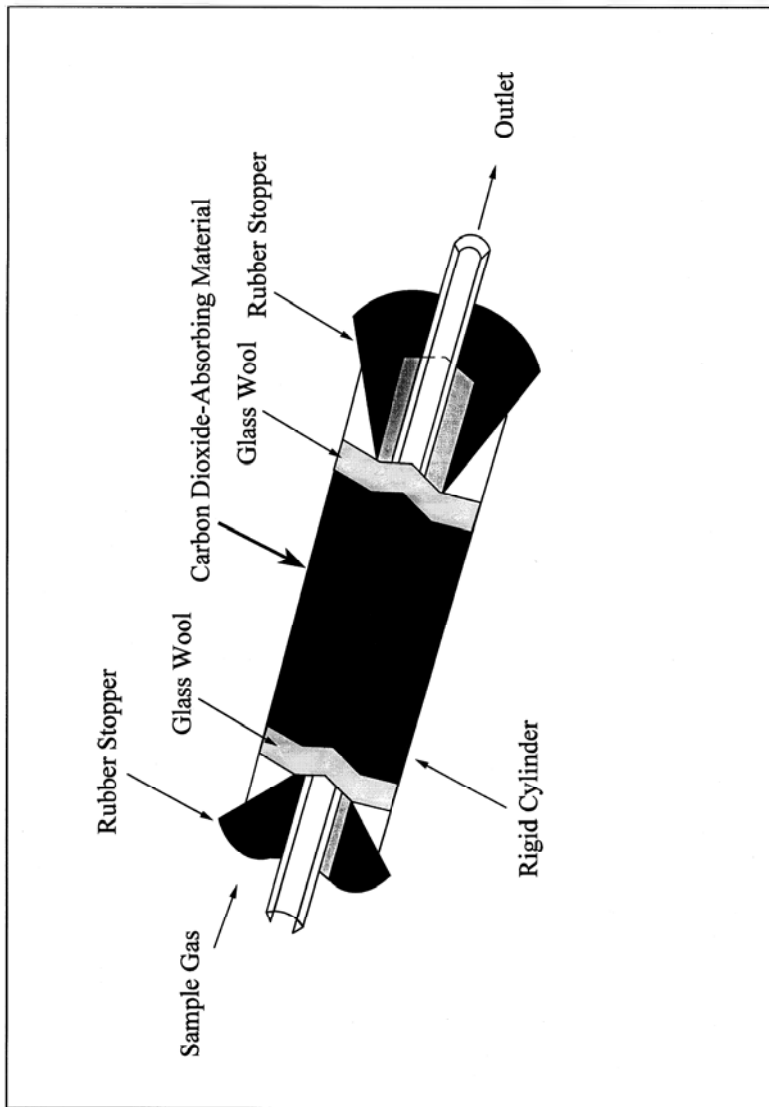


Figure 6A-1. Sampling train.

Figure 6A-2. CO<sub>2</sub> Absorber

**METHOD 6B—DETERMINATION OF SULFUR DIOXIDE AND CARBON DIOXIDE DAILY AVERAGE EMISSIONS FROM FOSSIL FUEL COMBUSTION SOURCES**

NOTE: This method does not include all of the specifications (*e.g.*, equipment and supplies) and procedures (*e.g.*, sampling and analytical) essential to its performance. Some material is incorporated by reference from

other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 1, Method 2, Method 3, Method 5, Method 6, and Method 6A.

*1.0 Scope and Application*

1.1 Analytes.

## Environmental Protection Agency

## Pt. 60, App. A-4, Meth. 6B

Analyte	CAS No.	Sensitivity
Sulfur dioxide (SO <sub>2</sub> )	7449-09-05	3.4 mg SO <sub>2</sub> /m <sup>3</sup> (2.12 × 10 <sup>-7</sup> lb/ft <sup>3</sup> )
Carbon dioxide (CO <sub>2</sub> )	124-38-9	N/A

1.2 **Applicability.** This method is applicable for the determination of SO<sub>2</sub> emissions from combustion sources in terms of concentration (ng/dscm or lb/dscf) and emission rate (ng/J or lb/10<sup>6</sup> Btu), and for the determination of CO<sub>2</sub> concentration (percent) on a daily (24 hours) basis.

1.3 **Data Quality Objectives.** Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

### 2.0 Summary of Method

2.1 A gas sample is extracted from the sampling point in the stack intermittently over a 24-hour or other specified time period. The SO<sub>2</sub> fraction is measured by the bariumthorin titration method. Moisture and CO<sub>2</sub> fractions are collected in the same sampling train, and are determined gravimetrically.

### 3.0 Definitions [Reserved]

### 4.0 Interferences

Same as Method 6, section 4.0.

### 5.0 Safety

5.1 **Disclaimer.** This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to performing this test method.

5.2 **Corrosive Reagents.** Same as Method 6, section 5.2.

### 6.0 Equipment and Supplies

Same as Method 6A, section 6.0, with the following exceptions and additions:

6.1 The isopropanol bubbler is not used. An empty bubbler for the collection of liquid droplets, that does not allow direct contact between the collected liquid and the gas sample, may be included in the sampling train.

6.2 For intermittent operation, include an industrial timer-switch designed to operate in the "on" position at least 2 minutes continuously and "off" the remaining period over a repeating cycle. The cycle of operation is designated in the applicable regulation. At a minimum, the sampling operation should include at least 12, equal, evenly-spaced periods per 24 hours.

6.3 Stainless steel sampling probes, type 316, are not recommended for use with Method 6B because of potential sample contami-

nation due to corrosion. Glass probes or other types of stainless steel, *e.g.*, Hasteloy or Carpenter 20, are recommended for long-term use.

**NOTE:** For applications downstream of wet scrubbers, a heated out-of-stack filter (either borosilicate glass wool or glass fiber mat) is necessary. Probe and filter heating systems capable of maintaining a sample gas temperature of between 20 and 120 °C (68 and 248 °F) at the filter are also required in these cases. The electric supply for these heating systems should be continuous and separate from the timed operation of the sample pump.

### 7.0 Reagents and Standards

Same as Method 6A, section 7.0, with the following exceptions:

7.1 Isopropanol is not used for sampling.

7.2 The hydrogen peroxide absorbing solution shall be diluted to no less than 6 percent by volume, instead of 3 percent as specified in Methods 6 and 6A.

7.3 If the Method 6B sampling train is to be operated in a low sample flow condition (less than 100 ml/min or 0.21 ft<sup>3</sup>/hr), molecular sieve material may be substituted for Ascarite II as the CO<sub>2</sub> absorbing material. The recommended molecular sieve material is Union Carbide 1/16 inch pellets, 5 A°, or equivalent. Molecular sieve material need not be discarded following the sampling run, provided that it is regenerated as per the manufacturer's instruction. Use of molecular sieve material at flow rates higher than 100 ml/min (0.21 ft<sup>3</sup>/hr) may cause erroneous CO<sub>2</sub> results.

### 8.0 Sample Collection, Preservation, Transport, and Storage

8.1 **Preparation of Sampling Train.** Same as Method 6A, section 8.1, with the addition of the following:

8.1.1 The sampling train is assembled as shown in Figure 6A-1 of Method 6A, except that the isopropanol bubbler is not included.

8.1.2 Adjust the timer-switch to operate in the "on" position from 2 to 4 minutes on a 2-hour repeating cycle or other cycle specified in the applicable regulation. Other timer sequences may be used with the restriction that the total sample volume collected is between 25 and 60 liters (0.9 and 2.1 ft<sup>3</sup>) for the amounts of sampling reagents prescribed in this method.

8.1.3 Add cold water to the tank until the impingers and bubblers are covered at least two-thirds of their length. The impingers and bubbler tank must be covered and protected from intense heat and direct sunlight. If freezing conditions exist, the impinger solution and the water bath must be protected.

**NOTE:** Sampling may be conducted continuously if a low flow-rate sample pump [20

to 40 ml/min (0.04 to 0.08 ft<sup>3</sup>/hr) for the reagent volumes described in this method] is used. If sampling is continuous, the timer-switch is not necessary. In addition, if the sample pump is designed for constant rate sampling, the rate meter may be deleted. The total gas volume collected should be between 25 and 60 liters (0.9 and 2.1 ft<sup>3</sup>) for the amounts of sampling reagents prescribed in this method.

8.2 Sampling Train Leak-Check Procedure. Same as Method 6, section 8.2.

### 8.3 Sample Collection.

8.3.1 The probe and filter (either in-stack, out-of-stack, or both) must be heated to a temperature sufficient to prevent water condensation.

8.3.2 Record the initial dry gas meter reading. To begin sampling, position the tip of the probe at the sampling point, connect the probe to the first impinger (or filter), and start the timer and the sample pump. Adjust the sample flow to a constant rate of approximately 1.0 liter/min (0.035 cfm) as indicated by the rotameter. Observe the operation of the timer, and determine that it is operating as intended (*i.e.*, the timer is in the "on" position for the desired period, and the cycle repeats as required).

8.3.3 One time between 9 a.m. and 11 a.m. during the 24-hour sampling period, record the dry gas meter temperature ( $T_m$ ) and the barometric pressure ( $P_{bar}$ ).

8.3.4 At the conclusion of the run, turn off the timer and the sample pump, remove the probe from the stack, and record the final gas meter volume reading. Conduct a leak-check as described in section 8.2. If a leak is found, void the test run or use procedures acceptable to the Administrator to adjust the sample volume for leakage. Repeat the steps in sections 8.3.1 to 8.3.4 for successive runs.

8.4 Sample Recovery. The procedures for sample recovery (moisture measurement, peroxide solution, and CO<sub>2</sub> absorber) are the same as those in Method 6A, section 8.3.

### 9.0 Quality Control

Same as Method 6, section 9.0., with the exception of the isopropanol-check.

### 10.0 Calibration and Standardization

Same as Method 6, section 10.0, with the addition of the following:

10.1 Periodic Calibration Check. After 30 days of operation of the test train, conduct a calibration check according to the same procedures as the post-test calibration check (Method 6, section 10.1.2). If the deviation between initial and periodic calibration factors exceeds 5 percent, use the smaller of the two factors in calculations for the preceding 30 days of data, but use the most recent calibration factor for succeeding test runs.

### 11.0 Analytical Procedures

11.1 Sample Loss Check and Analysis. Same as Method 6, sections 11.1 and 11.2, respectively.

### 12.0 Data Analysis and Calculations

Same as Method 6A, section 12.0, except that  $P_{bar}$  and  $T_m$  correspond to the values recorded in section 8.3.3 of this method. The values are as follows:

$P_{bar}$  = Initial barometric pressure for the test period, mm Hg.

$T_m$  = Absolute meter temperature for the test period, °K.

### 13.0 Method Performance

#### 13.1 Range.

13.1.1 Sulfur Dioxide. Same as Method 6.

13.1.2 Carbon Dioxide. Not determined.

13.2 Repeatability and Reproducibility. EPA-sponsored collaborative studies were undertaken to determine the magnitude of repeatability and reproducibility achievable by qualified testers following the procedures in this method. The results of the studies evolve from 145 field tests including comparisons with Methods 3 and 6. For measurements of emission rates from wet, flue gas desulfurization units in (ng/J), the repeatability (intra-laboratory precision) is 8.0 percent and the reproducibility (inter-laboratory precision) is 11.1 percent.

### 14.0 Pollution Prevention [Reserved]

### 15.0 Waste Management [Reserved]

### 16.0 Alternative Methods

Same as Method 6A, section 16.0, except that the timer is needed and is operated as outlined in this method.

### 17.0 References

Same as Method 6A, section 17.0, with the addition of the following:

- Butler, Frank E., et. al. The Collaborative Test of Method 6B: Twenty-Four-Hour Analysis of SO<sub>2</sub> and CO<sub>2</sub>. JAPCA. Vol. 33, No. 10, October 1983.

### 18.0 Tables, Diagrams, Flowcharts, and Validation Data [Reserved]

METHOD 6C—DETERMINATION OF SULFUR DIOXIDE EMISSIONS FROM STATIONARY SOURCES (INSTRUMENTAL ANALYZER PROCEDURE)

### 1.0 Scope and Application

#### What is Method 6C?

Method 6C is a procedure for measuring sulfur dioxide (SO<sub>2</sub>) in stationary source emissions using a continuous instrumental analyzer. Quality assurance and quality control requirements are included to assure that

you, the tester, collect data of known quality. You must document your adherence to these specific requirements for equipment, supplies, sample collection and analysis, calculations, and data analysis.

This method does not completely describe all equipment, supplies, and sampling and analytical procedures you will need but refers to other methods for some of the details. Therefore, to obtain reliable results, you should also have a thorough knowledge of these additional test methods which are found in appendix A to this part:

- (a) Method 1—Sample and Velocity Traverses for Stationary Sources.
- (b) Method 4—Determination of Moisture Content in Stack Gases.
- (c) Method 6—Determination of Sulfur Dioxide Emissions from Stationary Sources.
- (d) Method 7E—Determination of Nitrogen Oxides Emissions from Stationary Sources (Instrumental Analyzer Procedure).

*1.1 Analytes. What does this method determine?* This method measures the concentration of sulfur dioxide.

Analyte	CAS No.	Sensitivity
SO <sub>2</sub> .....	7446-09-5	Typically <2% of Calibration Span.

*1.2 Applicability. When is this method required?* The use of Method 6C may be required by specific New Source Performance Standards, Clean Air Marketing rules, State Implementation Plans, and permits where SO<sub>2</sub> concentrations in stationary source emissions must be measured, either to determine compliance with an applicable emission standard or to conduct performance testing of a continuous emission monitoring system (CEMS). Other regulations may also require the use of Method 6C.

*1.3 Data Quality Objectives. How good must my collected data be?* Refer to section 1.3 of Method 7E.

**2.0 Summary of Method**

In this method, you continuously sample the effluent gas and convey the sample to an analyzer that measures the concentration of SO<sub>2</sub>. You must meet the performance requirements of this method to validate your data.

**3.0 Definitions**

Refer to section 3.0 of Method 7E for the applicable definitions.

**4.0 Interferences**

Refer to Section 4.0 of Method 7E.

**5.0 Safety**

Refer to section 5.0 of Method 7E.

**6.0 Equipment and Supplies**

Figure 7E-1 of Method 7E is a schematic diagram of an acceptable measurement system.

*6.1 What do I need for the measurement system?* The essential components of the measurement system are the same as those in sections 6.1 and 6.2 of Method 7E, except that the SO<sub>2</sub> analyzer described in section 6.2 of this method must be used instead of the analyzer described in section 6.2 of Method 7E.

You must follow the noted specifications in section 6.1 of Method 7E.

*6.2 What analyzer must I use?* You may use an instrument that uses an ultraviolet, non-dispersive infrared, fluorescence, or other detection principle to continuously measure SO<sub>2</sub> in the gas stream and meets the performance specifications in section 13.0. The low-range and dual-range analyzer provisions in sections 6.2.8.1 and 6.2.8.2 of Method 7E apply.

**7.0 Reagents and Standards**

*7.1 Calibration Gas. What calibration gases do I need?* Refer to section 7.1 of Method 7E for the calibration gas requirements. Example calibration gas mixtures are listed below.

- (a) SO<sub>2</sub> in nitrogen (N<sub>2</sub>).
- (b) SO<sub>2</sub> in air.
- (c) SO<sub>2</sub> and CO<sub>2</sub> in N<sub>2</sub>.
- (d) SO<sub>2</sub> and O<sub>2</sub> in N<sub>2</sub>.
- (e) SO<sub>2</sub>/CO<sub>2</sub>/O<sub>2</sub> gas mixture in N<sub>2</sub>.
- (f) CO<sub>2</sub>/NO<sub>x</sub> gas mixture in N<sub>2</sub>.
- (g) CO<sub>2</sub>/SO<sub>2</sub>/NO<sub>x</sub> gas mixture in N<sub>2</sub>.

*7.2 Interference Check. What additional reagents do I need for the interference check?* The test gases for the interference check are listed in Table 7E-3 of Method 7E. For the alternative interference check, you must use the reagents described in section 7.0 of Method 6.

**8.0 Sample Collection, Preservation, Storage, and Transport**

*8.1 Sampling Site and Sampling Points.* You must follow the procedures of section 8.1 of Method 7E.

*8.2 Initial Measurement System Performance Tests.* You must follow the procedures in section 8.2 of Method 7E. If a dilution-type measurement system is used, the special considerations in section 8.3 of Method 7E also apply.

*8.3 Interference Check.* You must follow the procedures of section 8.2.7 of Method 7E.

to conduct an interference check, substituting SO<sub>2</sub> for NO<sub>x</sub> as the method pollutant. For dilution-type measurement systems, you must use the alternative interference check procedure in section 16 and a co-located, unmodified Method 6 sampling train.

**8.4 Sample Collection.** You must follow the procedures of section 8.4 of Method 7E.

**8.5 Post-Run System Bias Check and Drift Assessment.** You must follow the procedures of section 8.5 of Method 7E.

#### 9.0 Quality Control

Follow quality control procedures in section 9.0 of Method 7E.

#### 10.0 Calibration and Standardization

Follow the procedures for calibration and standardization in section 10.0 of Method 7E.

#### 11.0 Analytical Procedures

Because sample collection and analysis are performed together (see section 8), additional discussion of the analytical procedure is not necessary.

#### 12.0 Calculations and Data Analysis

You must follow the applicable procedures for calculations and data analysis in section 12.0 of Method 7E as applicable, substituting SO<sub>2</sub> for NO<sub>x</sub> as appropriate.

#### 13.0 Method Performance

13.1 The specifications for the applicable performance checks are the same as in section 13.0 of Method 7E.

13.2 **Alternative Interference Check.** The results are acceptable if the difference between the Method 6C result and the modified Method 6 result is less than 7.0 percent of the Method 6 result for each of the three test runs. For the purposes of comparison, the Method 6 and 6C results must be expressed in the same units of measure.

#### 14.0 Pollution Prevention [Reserved]

#### 15.0 Waste Management [Reserved]

#### 16.0 Alternative Procedures

16.1 **Alternative Interference Check.** You may perform an alternative interference check

consisting of at least three comparison runs between Method 6C and Method 6. This check validates the Method 6C results at each particular source category (type of facility) where the check is performed. When testing under conditions of low concentrations (<15 ppm), this alternative interference check is not allowed.

**NOTE:** The procedure described below applies to non-dilution sampling systems only. If this alternative interference check is used for a dilution sampling system, use a standard Method 6 sampling train and extract the sample directly from the exhaust stream at points collocated with the Method 6C sample probe.

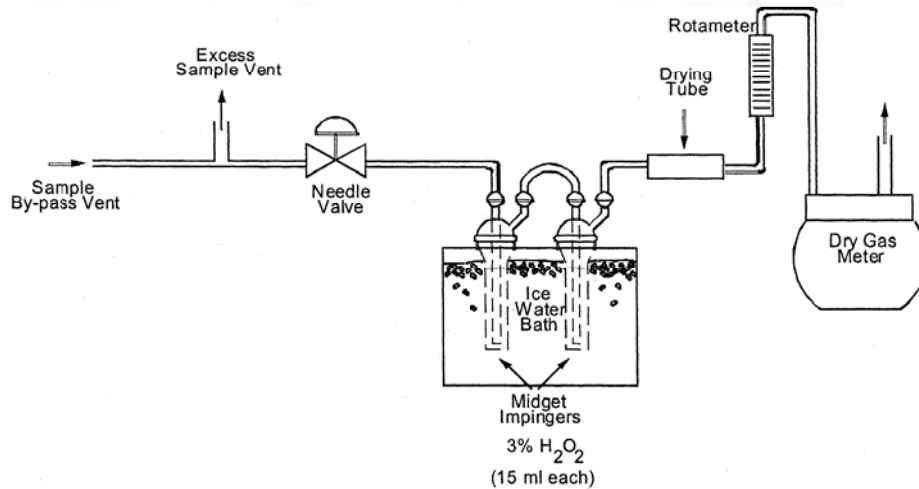
a. Build the modified Method 6 sampling train (flow control valve, two midjet impingers containing 3 percent hydrogen peroxide, and dry gas meter) shown in Figure 6C-1. Connect the sampling train to the sample bypass discharge vent. Record the dry gas meter reading before you begin sampling. Simultaneously collect modified Method 6 and Method 6C samples. Open the flow control valve in the modified Method 6 train as you begin to sample with Method 6C. Adjust the Method 6 sampling rate to 1 liter per minute (.10 percent). The sampling time per run must be the same as for Method 6 plus twice the average measurement system response time. If your modified Method 6 train does not include a pump, you risk biasing the results high if you over-pressurize the midjet impingers and cause a leak. You can reduce this risk by cautiously increasing the flow rate as sampling begins.

b. After completing a run, record the final dry gas meter reading, meter temperature, and barometric pressure. Recover and analyze the contents of the midjet impingers using the procedures in Method 6. Determine the average gas concentration reported by Method 6C for the run.

#### 17.0 References

1. "EPA Traceability Protocol for Assay and Certification of Gaseous Calibration Standards" September 1997 as amended, EPA-600/R-97/121

#### 18.0 Tables, Diagrams, Flowcharts, and Validation Data



**Figure 6C-1. Modified Method 6  
Alternative Interference Check Sampling Train**

**METHOD 7—DETERMINATION OF NITROGEN OXIDE EMISSIONS FROM STATIONARY SOURCES**

NOTE: This method does not include all of the specifications (e.g., equipment and supplies) and procedures (e.g., sampling and analytical) essential to its performance. Some material is incorporated by reference from

other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 1 and Method 5.

*1.0 Scope and Application*

**1.1 Analytes.**

Analyte	CAS No.	Sensitivity
Nitrogen oxides (NO <sub>x</sub> ), as NO <sub>2</sub> , including:		
Nitric oxide (NO) .....	10102-43-9	2-400 mg/dscm
Nitrogen dioxide (NO <sub>2</sub> ) .....	10102-44-0	

**1.2 Applicability.** This method is applicable for the measurement of nitrogen oxides (NO<sub>x</sub>) emitted from stationary sources.

**1.3 Data Quality Objectives.** Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sample methods.

*2.0 Summary of Method*

A grab sample is collected in an evacuated flask containing a dilute sulfuric acid-hydrogen peroxide absorbing solution, and the nitrogen oxides, except nitrous oxide, are measured colorimetrically using the phenoldisulfonic acid (PDS) procedure.

*3.0 Definitions [Reserved]*

*4.0 Interferences*

Biased results have been observed when sampling under conditions of high sulfur dioxide concentrations. At or above 2100 ppm SO<sub>2</sub>, use five times the H<sub>2</sub>O<sub>2</sub> concentration of the Method 7 absorbing solution. Laboratory tests have shown that high concentrations of SO<sub>2</sub> (about 2100 ppm) cause low results in Method 7 and 7A. Increasing the H<sub>2</sub>O<sub>2</sub> concentration to five times the original concentration eliminates this bias. However, when no SO<sub>2</sub> is present, increasing the concentration by five times results in a low bias.



## 5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user to establish appropriate safety and health practices and to determine the applicability of regulatory limitations prior to performing this test method.

5.2 Corrosive Reagents. The following reagents are hazardous. Personal protective equipment and safe procedures are useful in preventing chemical splashes. If contact occurs, immediately flush with copious amounts of water for at least 15 minutes. Remove clothing under shower and decontaminate. Treat residual chemical burns as thermal burns.

5.2.1 Hydrogen Peroxide (H<sub>2</sub>O<sub>2</sub>). Irritating to eyes, skin, nose, and lungs.

5.2.2 Phenoldisulfonic Acid. Irritating to eyes and skin.

5.2.3 Sodium Hydroxide (NaOH). Causes severe damage to eyes and skin. Inhalation causes irritation to nose, throat, and lungs. Reacts exothermically with limited amounts of water.

5.2.4 Sulfuric Acid (H<sub>2</sub>SO<sub>4</sub>). Rapidly destructive to body tissue. Will cause third degree burns. Eye damage may result in blindness. Inhalation may be fatal from spasm of the larynx, usually within 30 minutes. May cause lung tissue damage with edema. 1 mg/m<sup>3</sup> for 8 hours will cause lung damage or, in higher concentrations, death. Provide ventilation to limit inhalation. Reacts violently with metals and organics.

5.2.5 Phenol. Poisonous and caustic. Do not handle with bare hands as it is absorbed through the skin.

## 6.0 Equipment and Supplies

6.1 Sample Collection. A schematic of the sampling train used in performing this method is shown in Figure 7-1. Other grab sampling systems or equipment, capable of measuring sample volume to within 2.0 percent and collecting a sufficient sample volume to allow analytical reproducibility to within 5 percent, will be considered acceptable alternatives, subject to the approval of the Administrator. The following items are required for sample collection:

6.1.1 Probe. Borosilicate glass tubing, sufficiently heated to prevent water condensation and equipped with an in-stack or heated out-of-stack filter to remove particulate matter (a plug of glass wool is satisfactory for this purpose). Stainless steel or Teflon tubing may also be used for the probe. Heating is not necessary if the probe remains dry during the purging period.

6.1.2 Collection Flask. Two-liter borosilicate, round bottom flask, with short

neck and 24/40 standard taper opening, protected against implosion or breakage.

6.1.3 Flask Valve. T-bore stopcock connected to a 24/40 standard taper joint.

6.1.4 Temperature Gauge. Dial-type thermometer, or other temperature gauge, capable of measuring 1 °C (2 °F) intervals from -5 to 50 °C (23 to 122 °F).

6.1.5 Vacuum Line. Tubing capable of withstanding a vacuum of 75 mm (3 in.) Hg absolute pressure, with "T" connection and T-bore stopcock.

6.1.6 Vacuum Gauge. U-tube manometer, 1 meter (39 in.), with 1 mm (0.04 in.) divisions, or other gauge capable of measuring pressure to within 2.5 mm (0.10 in.) Hg.

6.1.7 Pump. Capable of evacuating the collection flask to a pressure equal to or less than 75 mm (3 in.) Hg absolute.

6.1.8 Squeeze Bulb. One-way.

6.1.9 Volumetric Pipette. 25-ml.

6.1.10 Stopcock and Ground Joint Grease. A high-vacuum, high-temperature chlorofluorocarbon grease is required. Halocarbon 25-5S has been found to be effective.

6.1.11 Barometer. Mercury, aneroid, or other barometer capable of measuring atmospheric pressure to within 2.5 mm (0.1 in.) Hg. See note in Method 5, section 6.1.2.

6.2 Sample Recovery. The following items are required for sample recovery:

6.2.1 Graduated Cylinder. 50-ml with 1 ml divisions.

6.2.2 Storage Containers. Leak-free polyethylene bottles.

6.2.3 Wash Bottle. Polyethylene or glass.

6.2.4 Glass Stirring Rod.

6.2.5 Test Paper for Indicating pH. To cover the pH range of 7 to 14.

6.3 Analysis. The following items are required for analysis:

6.3.1 Volumetric Pipettes. Two 1-ml, two 2-ml, one 3-ml, one 4-ml, two 10-ml, and one 25-ml for each sample and standard.

6.3.2 Porcelain Evaporating Dishes. 175- to 250-ml capacity with lip for pouring, one for each sample and each standard. The Coors No. 45006 (shallowform, 195-ml) has been found to be satisfactory. Alternatively, polymethyl pentene beakers (Nalge No. 1203, 150-ml), or glass beakers (150-ml) may be used. When glass beakers are used, etching of the beakers may cause solid matter to be present in the analytical step; the solids should be removed by filtration.

6.3.3 Steam Bath. Low-temperature ovens or thermostatically controlled hot plates kept below 70 °C (160 °F) are acceptable alternatives.

6.3.4 Dropping Pipette or Dropper. Three required.

6.3.5 Polyethylene Policeman. One for each sample and each standard.

6.3.6 Graduated Cylinder. 100-ml with 1-ml divisions.

6.3.7 Volumetric Flasks. 50-ml (one for each sample and each standard), 100-ml (one for each sample and each standard, and one for the working standard  $\text{KNO}_3$  solution), and 1000-ml (one).

6.3.8 Spectrophotometer. To measure at 410 nm.

6.3.9 Graduated Pipette. 10-ml with 0.1-ml divisions.

6.3.10 Test Paper for Indicating pH. To cover the pH range of 7 to 14.

6.3.11 Analytical Balance. To measure to within 0.1 mg.

#### 7.0 Reagents and Standards

Unless otherwise indicated, it is intended that all reagents conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available; otherwise, use the best available grade.

7.1 Sample Collection. The following reagents are required for sampling:

7.1.1 Water. Deionized distilled to conform to ASTM D 1193-77 or 91 Type 3 (incorporated by reference—see §60.17). The  $\text{KMnO}_4$  test for oxidizable organic matter may be omitted when high concentrations of organic matter are not expected to be present.

7.1.2 Absorbing Solution. Cautiously add 2.8 ml concentrated  $\text{H}_2\text{SO}_4$  to a 1-liter flask partially filled with water. Mix well, and add 6 ml of 3 percent hydrogen peroxide, freshly prepared from 30 percent hydrogen peroxide solution. Dilute to 1 liter of water and mix well. The absorbing solution should be used within 1 week of its preparation. Do not expose to extreme heat or direct sunlight.

7.2 Sample Recovery. The following reagents are required for sample recovery:

7.2.1 Water. Same as in 7.1.1.

7.2.2 Sodium Hydroxide, 1 N. Dissolve 40 g NaOH in water, and dilute to 1 liter.

7.3 Analysis. The following reagents and standards are required for analysis:

7.3.1 Water. Same as in 7.1.1.

7.3.2 Fuming Sulfuric Acid, 15 to 18 percent by weight free sulfur trioxide. HANDLE WITH CAUTION.

7.3.3 Phenol. White solid.

7.3.4 Sulfuric Acid. Concentrated, 95 percent minimum assay.

7.3.5 Potassium Nitrate ( $\text{KNO}_3$ ). Dried at 105 to 110 °C (221 to 230 °F) for a minimum of 2 hours just prior to preparation of standard solution.

7.3.6 Standard  $\text{KNO}_3$  Solution. Dissolve exactly 2.198 g of dried  $\text{KNO}_3$  in water, and dilute to 1 liter with water in a 1000-ml volumetric flask.

7.3.7 Working Standard  $\text{KNO}_3$  Solution. Dilute 10 ml of the standard solution to 100 ml with water. One ml of the working standard solution is equivalent to 100 µg nitrogen dioxide ( $\text{NO}_2$ ).

7.3.8 Phenoldisulfonic Acid Solution. Dissolve 25 g of pure white phenol solid in 150 ml

concentrated sulfuric acid on a steam bath. Cool, add 75 ml fuming sulfuric acid (15 to 18 percent by weight free sulfur trioxide—HANDLE WITH CAUTION), and heat at 100 °C (212 °F) for 2 hours. Store in a dark, stoppered bottle.

7.3.9 Concentrated Ammonium Hydroxide.

#### 8.0 Sample Collection, Preservation, Storage and Transport

##### 8.1 Sample Collection.

8.1.1 Flask Volume. The volume of the collection flask and flask valve combination must be known prior to sampling. Assemble the flask and flask valve, and fill with water to the stopcock. Measure the volume of water to  $\pm 10$  ml. Record this volume on the flask.

8.1.2 Pipette 25 ml of absorbing solution into a sample flask, retaining a sufficient quantity for use in preparing the calibration standards. Insert the flask valve stopper into the flask with the valve in the "purge" position. Assemble the sampling train as shown in Figure 7-1, and place the probe at the sampling point. Make sure that all fittings are tight and leak-free, and that all ground glass joints have been greased properly with a high-vacuum, high temperature chlorofluorocarbon-based stopcock grease. Turn the flask valve and the pump valve to their "evacuate" positions. Evacuate the flask to 75 mm (3 in.) Hg absolute pressure, or less. Evacuation to a pressure approaching the vapor pressure of water at the existing temperature is desirable. Turn the pump valve to its "vent" position, and turn off the pump. Check for leakage by observing the manometer for any pressure fluctuation. (Any variation greater than 10 mm (0.4 in.) Hg over a period of 1 minute is not acceptable, and the flask is not to be used until the leakage problem is corrected. Pressure in the flask is not to exceed 75 mm (3 in.) Hg absolute at the time sampling is commenced.) Record the volume of the flask and valve ( $V_1$ ), the flask temperature ( $T_1$ ), and the barometric pressure. Turn the flask valve counterclockwise to its "purge" position, and do the same with the pump valve. Purge the probe and the vacuum tube using the squeeze bulb. If condensation occurs in the probe and the flask valve area, heat the probe, and purge until the condensation disappears. Next, turn the pump valve to its "vent" position. Turn the flask valve clockwise to its "evacuate" position, and record the difference in the mercury levels in the manometer. The absolute internal pressure in the flask ( $P_1$ ) is equal to the barometric pressure less the manometer reading. Immediately turn the flask valve to the "sample" position, and permit the gas to enter the flask until pressures in the flask and sample line (i.e., duct, stack) are equal. This will usually require about 15 seconds; a longer period indicates a plug in the probe, which must be

corrected before sampling is continued. After collecting the sample, turn the flask valve to its "purge" position, and disconnect the flask from the sampling train.

8.1.3 Shake the flask for at least 5 minutes.

8.1.4 If the gas being sampled contains insufficient oxygen for the conversion of NO to NO<sub>2</sub> (e.g., an applicable subpart of the standards may require taking a sample of a calibration gas mixture of NO in N<sub>2</sub>), then introduce oxygen into the flask to permit this conversion. Oxygen may be introduced into the flask by one of three methods: (1) Before evacuating the sampling flask, flush with pure cylinder oxygen, then evacuate flask to 75 mm (3 in.) Hg absolute pressure or less; or (2) inject oxygen into the flask after sampling; or (3) terminate sampling with a minimum of 50 mm (2 in.) Hg vacuum remaining in the flask, record this final pressure, and then vent the flask to the atmosphere until the flask pressure is almost equal to atmospheric pressure.

8.2 Sample Recovery. Let the flask sit for a minimum of 16 hours, and then shake the contents for 2 minutes.

8.2.1 Connect the flask to a mercury filled U-tube manometer. Open the valve from the flask to the manometer, and record the flask temperature (T<sub>f</sub>), the barometric pressure, and the difference between the mercury levels in the manometer. The absolute internal pressure in the flask (P<sub>f</sub>) is the barometric pressure less the manometer reading. Transfer the contents of the flask to a leak-free polyethylene bottle. Rinse the flask twice with 5 ml portions of water, and add the rinse water to the bottle. Adjust the pH to between 9 and 12 by adding 1 N NaOH, dropwise (about 25 to 35 drops). Check the pH by dipping a stirring rod into the solution and then touching the rod to the pH test paper. Remove as little material as possible during this step. Mark the height of the liquid level so that the container can be checked for leakage after transport. Label the container to identify clearly its contents. Seal the container for shipping.

9.0 Quality Control

Section	Quality control measure	Effect
10.1 .....	Spectrophotometer calibration .....	Ensure linearity of spectrophotometer response to standards.

10.0 Calibration and Standardization

10.1 Spectrophotometer.

10.1.1 Optimum Wavelength Determination.

10.1.1.1 Calibrate the wavelength scale of the spectrophotometer every 6 months. The calibration may be accomplished by using an energy source with an intense line emission such as a mercury lamp, or by using a series of glass filters spanning the measuring range of the spectrophotometer. Calibration materials are available commercially and from the National Institute of Standards and Technology. Specific details on the use of such materials should be supplied by the vendor; general information about calibration techniques can be obtained from general reference books on analytical chemistry. The wavelength scale of the spectrophotometer must read correctly within 5 nm at all calibration points; otherwise, repair and recalibrate the spectrophotometer. Once the wavelength scale of the spectrophotometer is in proper calibration, use 410 nm as the optimum wavelength for the measurement of the absorbance of the standards and samples.

10.1.1.2 Alternatively, a scanning procedure may be employed to determine the proper measuring wavelength. If the instrument is a double-beam spectrophotometer, scan the spectrum between 400 and 415 nm using a 200 µg NO<sub>2</sub> standard solution in the sample cell and a blank solution in the reference cell. If a peak does not occur, the spectrophotometer is probably malfunctioning and should

be repaired. When a peak is obtained within the 400 to 415 nm range, the wavelength at which this peak occurs shall be the optimum wavelength for the measurement of absorbance of both the standards and the samples. For a single-beam spectrophotometer, follow the scanning procedure described above, except scan separately the blank and standard solutions. The optimum wavelength shall be the wavelength at which the maximum difference in absorbance between the standard and the blank occurs.

10.1.2 Determination of Spectrophotometer Calibration Factor K<sub>c</sub>. Add 0 ml, 2.0 ml, 4.0 ml, 6.0 ml, and 8.0 ml of the KNO<sub>3</sub> working standard solution (1 ml = 100 µg NO<sub>2</sub>) to a series of five 50-ml volumetric flasks. To each flask, add 25 ml of absorbing solution and 10 ml water. Add 1 N NaOH to each flask until the pH is between 9 and 12 (about 25 to 35 drops). Dilute to the mark with water. Mix thoroughly, and pipette a 25-ml aliquot of each solution into a separate porcelain evaporating dish. Beginning with the evaporation step, follow the analysis procedure of section 11.2 until the solution has been transferred to the 100-ml volumetric flask and diluted to the mark. Measure the absorbance of each solution at the optimum wavelength as determined in section 10.2.1. This calibration procedure must be repeated on each day that samples are analyzed. Calculate the spectrophotometer calibration factor as shown in section 12.2.

10.1.3 Spectrophotometer Calibration Quality Control. Multiply the absorbance value obtained for each standard by the  $K_c$  factor (reciprocal of the least squares slope) to determine the distance each calibration point lies from the theoretical calibration line. The difference between the calculated concentration values and the actual concentrations (*i.e.*, 100, 200, 300, and 400  $\mu\text{g NO}_2$ ) should be less than 7 percent for all standards.

10.2 Barometer. Calibrate against a mercury barometer or NIST-traceable barometer prior to the field test.

10.3 Temperature Gauge. Calibrate dial thermometers against mercury-in-glass thermometers. An alternative mercury-free thermometer may be used if the thermometer is, at a minimum, equivalent in terms of performance or suitably effective for the specific temperature measurement application.

10.4 Vacuum Gauge. Calibrate mechanical gauges, if used, against a mercury manometer such as that specified in section 6.1.6.

10.5 Analytical Balance. Calibrate against standard weights.

#### 11.0 Analytical Procedures

11.1 Sample Loss Check. Note the level of the liquid in the container, and confirm whether any sample was lost during shipment. Note this on the analytical data sheet. If a noticeable amount of leakage has occurred, either void the sample or use methods, subject to the approval of the Administrator, to correct the final results.

11.2 Sample Preparation. Immediately prior to analysis, transfer the contents of the shipping container to a 50 ml volumetric flask, and rinse the container twice with 5 ml portions of water. Add the rinse water to the flask, and dilute to mark with water; mix thoroughly. Pipette a 25-ml aliquot into the porcelain evaporating dish. Return any unused portion of the sample to the polyethylene storage bottle. Evaporate the 25-ml aliquot to dryness on a steam bath, and allow to cool. Add 2 ml phenoldisulfonic acid solution to the dried residue, and triturate thoroughly with a polyethylene policeman. Make sure the solution contacts all the residue. Add 1 ml water and 4 drops of concentrated sulfuric acid. Heat the solution on a steam bath for 3 minutes with occasional stirring. Allow the solution to cool, add 20 ml water, mix well by stirring, and add concentrated ammonium hydroxide, dropwise, with constant stirring, until the pH is 10 (as determined by pH paper). If the sample contains solids, these must be removed by filtration (centrifugation is an acceptable alter-

native, subject to the approval of the Administrator) as follows: Filter through Whatman No. 41 filter paper into a 100-ml volumetric flask. Rinse the evaporating dish with three 5-ml portions of water. Filter these three rinses. Wash the filter with at least three 15-ml portions of water. Add the filter washings to the contents of the volumetric flask, and dilute to the mark with water. If solids are absent, the solution can be transferred directly to the 100-ml volumetric flask and diluted to the mark with water.

11.3 Sample Analysis. Mix the contents of the flask thoroughly, and measure the absorbance at the optimum wavelength used for the standards (Section 10.2.1), using the blank solution as a zero reference. Dilute the sample and the blank with equal volumes of water if the absorbance exceeds  $A_4$ , the absorbance of the 400- $\mu\text{g NO}_2$  standard (see section 10.2.2).

#### 12.0 Data Analysis and Calculations

Carry out the calculations, retaining at least one extra significant figure beyond that of the acquired data. Round off figures after final calculations.

##### 12.1 12.1 Nomenclature

- A = Absorbance of sample.
  - $A_1$  = Absorbance of the 100- $\mu\text{g NO}_2$  standard.
  - $A_2$  = Absorbance of the 200- $\mu\text{g NO}_2$  standard.
  - $A_3$  = Absorbance of the 300- $\mu\text{g NO}_2$  standard.
  - $A_4$  = Absorbance of the 400- $\mu\text{g NO}_2$  standard.
  - C = Concentration of  $\text{NO}_x$  as  $\text{NO}_2$ , dry basis, corrected to standard conditions, mg/dsm<sup>3</sup> (lb/dscf).
  - F = Dilution factor (*i.e.*, 25/5, 25/10, *etc.*, required only if sample dilution was needed to reduce the absorbance into the range of the calibration).
  - $K_c$  = Spectrophotometer calibration factor.
  - M = Mass of  $\text{NO}_x$  as  $\text{NO}_2$  in gas sample,  $\mu\text{g}$ .
  - $P_f$  = Final absolute pressure of flask, mm Hg (in. Hg).
  - $P_i$  = Initial absolute pressure of flask, mm Hg (in. Hg).
  - $P_{\text{std}}$  = Standard absolute pressure, 760 mm Hg (29.92 in. Hg).
  - $T_f$  = Final absolute temperature of flask, °K (°R).
  - $T_i$  = Initial absolute temperature of flask, °K (°R).
  - $T_{\text{std}}$  = Standard absolute temperature, 293 °K (528°R).
  - $V_{\text{sc}}$  = Sample volume at standard conditions (dry basis), ml.
  - $V_f$  = Volume of flask and valve, ml.
  - $V_a$  = Volume of absorbing solution, 25 ml.
- 12.2 Spectrophotometer Calibration Factor.

$$K_c = 100 \frac{A_1 + 2A_2 + 3A_3 + 4A_4}{A_1^2 + A_2^2 + A_3^2 + A_4^2} \quad \text{Eq. 7-1}$$

12.3 Sample Volume, Dry Basis, Corrected to Standard Conditions.

$$V_{sc} = (V_f - V_v) \frac{T_{std}}{P_{std}} \left[ \frac{P_f}{T_f} - \frac{P_i}{T_i} \right] \quad \text{Eq. 7-2}$$

$$= K_1 (V_f - 25) \left[ \frac{P_f}{T_f} - \frac{P_i}{T_i} \right]$$

Where:

$K_1 = 0.3858$  °K/mm Hg for metric units,  
 $K_1 = 17.65$  °R/in. Hg for English units.

12.4 Total  $\mu\text{g}$   $\text{NO}_2$  per sample.

$$m = 2K_c AF \quad \text{Eq. 7-3}$$

Where:

2 = 50/25, the aliquot factor.

NOTE: If other than a 25-ml aliquot is used for analysis, the factor 2 must be replaced by a corresponding factor.

12.5 Sample Concentration, Dry Basis, Corrected to Standard Conditions.

$$C = K_2 (m/V_{sc}) \quad \text{Eq. 7-4}$$

Where:

$K_2 = 10^3$  (mg/m<sup>3</sup>)/( $\mu\text{g}/\text{ml}$ ) for metric units,  
 $K_2 = 6.242 \times 10^{-5}$  (lb/scf)/( $\mu\text{g}/\text{ml}$ ) for English units.

### 13.0 Method Performance

13.1 Range. The analytical range of the method has been determined to be 2 to 400 milligrams  $\text{NO}_x$  (as  $\text{NO}_2$ ) per dry standard cubic meter, without having to dilute the sample.

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

### 16.0 References

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2. Standard Method of Test for Oxides of Nitrogen in Gaseous Combustion Products (Phenoldisulfonic Acid Procedure). In: 1968 Book of ASTM Standards, Part 26. Philadelphia, PA, 1968. ASTM Designation D 1608-60, pp. 725-729.

3. Jacob, M.B. The Chemical Analysis of Air Pollutants. New York, Interscience Publishers, Inc. 1960. Vol. 10, pp. 351-356.

4. Beatty, R.L., L.B. Berger, and H.H. Schrenk. Determination of Oxides of Nitrogen by the Phenoldisulfonic Acid Method. Bureau of Mines, U.S. Dept. of Interior. R.I. 3687. February 1943.

5. Hamil, H.F. and D.E. Camann. Collaborative Study of Method for the Determination of Nitrogen Oxide Emissions from Stationary Sources (Fossil Fuel-Fired Steam Generators). Southwest Research Institute Report for Environmental Protection Agency, Research Triangle Park, NC. October 5, 1973.

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7. Stack Sampling Safety Manual (Draft). U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards, Research Triangle Park, NC. September 1978.

### 17.0 Tables, Diagrams, Flowcharts, and Validation Data

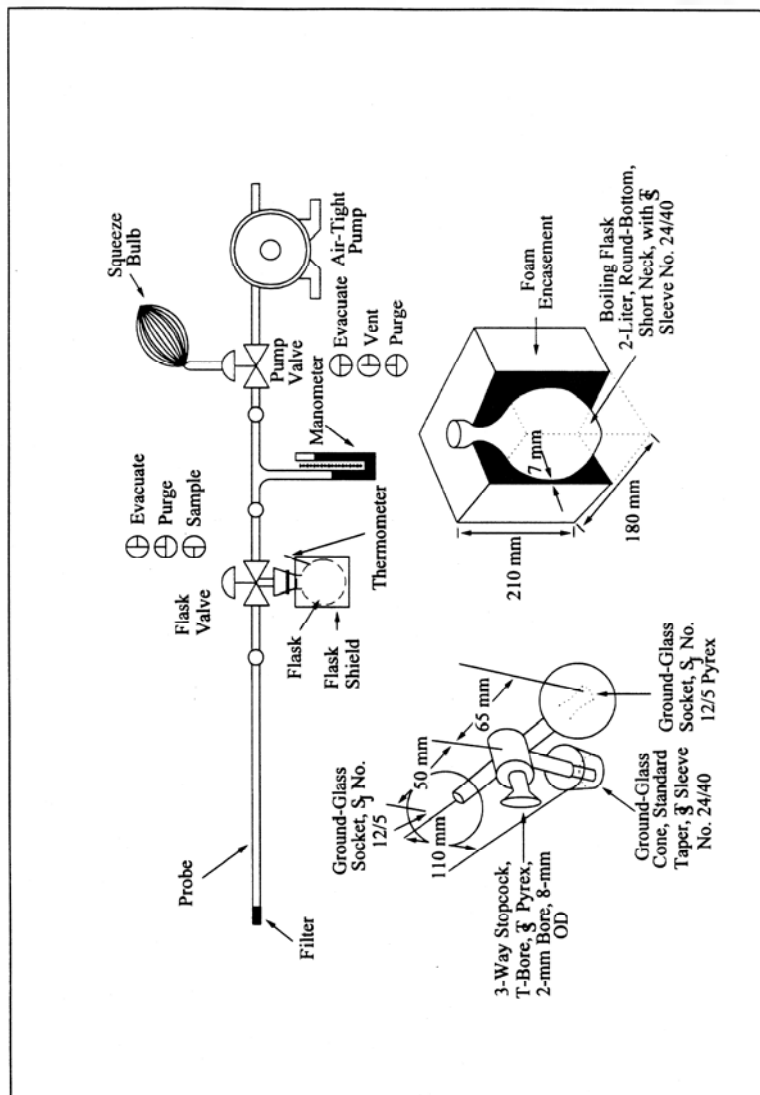


Figure 7-1. Sampling Train, Flask Valve, and Flask.

METHOD 7A—DETERMINATION OF NITROGEN OXIDE EMISSIONS FROM STATIONARY SOURCES (ION CHROMATOGRAPHIC METHOD)

NOTE: This method does not include all of the specifications (e.g., equipment and supplies) and procedures (e.g., sampling and analytical) essential to its performance. Some material is incorporated by reference from

other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 1, Method 3, Method 5, and Method 7.

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS No.	Sensitivity
Nitrogen oxides (NO <sub>x</sub> ), as NO <sub>2</sub> , including:		
Nitric oxide (NO) .....	10102-43-9	
Nitrogen dioxide (NO <sub>2</sub> ) .....	10102-44-0	65-655 ppmv

1.2 Applicability. This method is applicable for the determination of NO<sub>x</sub> emissions from stationary sources.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

#### 2.0 Summary of Method

A grab sample is collected in an evacuated flask containing a dilute sulfuric acid-hydrogen peroxide absorbing solution. The nitrogen oxides, excluding nitrous oxide (N<sub>2</sub>O), are oxidized to nitrate and measured by ion chromatography.

#### 3.0 Definitions [Reserved]

#### 4.0 Interferences

Biased results have been observed when sampling under conditions of high sulfur dioxide concentrations. At or above 2100 ppm SO<sub>2</sub>, use five times the H<sub>2</sub>O<sub>2</sub> concentration of the Method 7 absorbing solution. Laboratory tests have shown that high concentrations of SO<sub>2</sub> (about 2100 ppm) cause low results in Method 7 and 7A. Increasing the H<sub>2</sub>O<sub>2</sub> concentration to five times the original concentration eliminates this bias. However, when no SO<sub>2</sub> is present, increasing the concentration by five times results in a low bias.

#### 5.0 Safety

5.1 This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and to determine the applicability of regulatory limitations prior to performing this test method.

5.2 Corrosive reagents. The following reagents are hazardous. Personal protective equipment and safe procedures are useful in preventing chemical splashes. If contact occurs, immediately flush with copious amounts of water at least 15 minutes. Remove clothing under shower and decontaminate. Treat residual chemical burns as thermal burns.

5.2.1 Hydrogen Peroxide (H<sub>2</sub>O<sub>2</sub>). Irritating to eyes, skin, nose, and lungs.

5.2.2 Sulfuric Acid (H<sub>2</sub>SO<sub>4</sub>). Rapidly destructive to body tissue. Will cause third degree burns. Eye damage may result in blindness. Inhalation may be fatal from spasm of the larynx, usually within 30 minutes. May

cause lung tissue damage with edema. 8 mg/m<sup>3</sup> will cause lung damage in uninitiated. 1 mg/m<sup>3</sup> for 8 hours will cause lung damage or, in higher concentrations, death. Provide ventilation to limit inhalation. Reacts violently with metals and organics.

#### 6.0 Equipment and Supplies

6.1 Sample Collection. Same as in Method 7, section 6.1.

6.2 Sample Recovery. Same as in Method 7, section 6.2, except the stirring rod and pH paper are not needed.

6.3 Analysis. For the analysis, the following equipment and supplies are required. Alternative instrumentation and procedures will be allowed provided the calibration precision requirement in section 10.1.2 can be met.

6.3.1 Volumetric Pipets. Class A: 1-, 2-, 4-, 5-ml (two for the set of standards and one per sample), 6-, 10-, and graduated 5-ml sizes.

6.3.2 Volumetric Flasks. 50-ml (two per sample and one per standard), 200-ml, and 1-liter sizes.

6.3.3 Analytical Balance. To measure to within 0.1 mg.

6.3.4 Ion Chromatograph. The ion chromatograph should have at least the following components:

6.3.4.1 Columns. An anion separation or other column capable of resolving the nitrate ion from sulfate and other species present and a standard anion suppressor column (optional). Suppressor columns are produced as proprietary items; however, one can be produced in the laboratory using the resin available from BioRad Company, 32nd and Griffin Streets, Richmond, California. Peak resolution can be optimized by varying the eluent strength or column flow rate, or by experimenting with alternative columns that may offer more efficient separation. When using guard columns with the stronger reagent to protect the separation column, the analyst should allow rest periods between injection intervals to purge possible sulfate buildup in the guard column.

6.3.4.2 Pump. Capable of maintaining a steady flow as required by the system.

6.3.4.3 Flow Gauges. Capable of measuring the specified system flow rate.

6.3.4.4 Conductivity Detector.

6.3.4.5 Recorder. Compatible with the output voltage range of the detector.

7.0 Reagents and Standards

Unless otherwise indicated, it is intended that all reagents conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available; otherwise, use the best available grade.

7.1 Sample Collection. Same as Method 7, section 7.1.

7.2 Sample Recovery. Same as Method 7, section 7.1.1.

7.3 Analysis. The following reagents and standards are required for analysis:

7.3.1 Water. Same as Method 7, section 7.1.1.

7.3.2 Stock Standard Solution, 1 mg NO<sub>2</sub>/ml. Dry an adequate amount of sodium nitrate (NaNO<sub>3</sub>) at 105 to 110 °C (221 to 230 °F) for a minimum of 2 hours just before preparing the standard solution. Then dissolve exactly 1.847 g of dried NaNO<sub>3</sub> in water, and dilute to 1 liter in a volumetric flask. Mix well. This solution is stable for 1 month and should not be used beyond this time.

7.3.3 Working Standard Solution, 25 µg/ml. Dilute 5 ml of the standard solution to 200 ml with water in a volumetric flask, and mix well.

7.3.4 Eluent Solution. Weigh 1.018 g of sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>) and 1.008 g of sodium bicarbonate (NaHCO<sub>3</sub>), and dissolve in 4 liters of water. This solution is 0.0024 M Na<sub>2</sub>CO<sub>3</sub>/0.003 M NaHCO<sub>3</sub>. Other eluents appropriate to the column type and capable of resolving nitrate ion from sulfate and other species present may be used.

8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Sampling. Same as in Method 7, section 8.1.

8.2 Sample Recovery. Same as in Method 7, section 8.2, except delete the steps on adjusting and checking the pH of the sample. Do not store the samples more than 4 days between collection and analysis.

9.0 Quality Control

Section	Quality control measure	Effect
10.1	Ion chromatograph calibration	Ensure linearity of ion chromatograph response to standards.

10.0 Calibration and Standardizations

10.1 Ion Chromatograph.

10.1.1 Determination of Ion Chromatograph Calibration Factor S. Prepare a series of five standards by adding 1.0, 2.0, 4.0, 6.0, and 10.0 ml of working standard solution (25 µg/ml) to a series of five 50-ml volumetric flasks. (The standard masses will equal 25, 50, 100, 150, and 250 µg.) Dilute each flask to the mark with water, and mix well. Analyze with the samples as described in section 11.2, and subtract the blank from each value. Prepare or calculate a linear regression plot of the standard masses in µg (x-axis) versus their peak height responses in millimeters (y-axis). (Take peak height measurements with symmetrical peaks; in all other cases, calculate peak areas.) From this curve, or equation, determine the slope, and calculate its reciprocal to denote as the calibration factor, S.

10.1.2 Ion Chromatograph Calibration Quality Control. If any point on the calibration curve deviates from the line by more than 7 percent of the concentration at that point, remake and reanalyze that standard. This deviation can be determined by multiplying S times the peak height response for each standard. The resultant concentrations must not differ by more than 7 percent from each known standard mass (i.e., 25, 50, 100, 150, and 250 µg).

10.2 Conductivity Detector. Calibrate according to manufacturer's specifications prior to initial use.

10.3 Barometer. Calibrate against a mercury barometer.

10.4 Temperature Gauge. Calibrate dial thermometers against mercury-in-glass thermometers. An alternative mercury-free thermometer may be used if the thermometer is, at a minimum, equivalent in terms of performance or suitably effective for the specific temperature measurement application.

10.5 Vacuum Gauge. Calibrate mechanical gauges, if used, against a mercury manometer such as that specified in section 6.1.6 of Method 7.

10.6 Analytical Balance. Calibrate against standard weights.

11.0 Analytical Procedures

11.1 Sample Preparation.

11.1.1 Note on the analytical data sheet, the level of the liquid in the container, and whether any sample was lost during shipment. If a noticeable amount of leakage has occurred, either void the sample or use methods, subject to the approval of the Administrator, to correct the final results. Immediately before analysis, transfer the contents of the shipping container to a 50-ml volumetric flask, and rinse the container twice with 5 ml portions of water. Add the rinse water to the flask, and dilute to the mark with water. Mix thoroughly.

11.1.2 Pipet a 5-ml aliquot of the sample into a 50-ml volumetric flask, and dilute to the mark with water. Mix thoroughly. For each set of determinations, prepare a reagent



blank by diluting 5 ml of absorbing solution to 50 ml with water. (Alternatively, eluent solution may be used instead of water in all sample, standard, and blank dilutions.)

11.2 Analysis.

11.2.1 Prepare a standard calibration curve according to section 10.1.1. Analyze the set of standards followed by the set of samples using the same injection volume for both standards and samples. Repeat this analysis sequence followed by a final analysis of the standard set. Average the results. The two sample values must agree within 5 percent of their mean for the analysis to be valid. Perform this duplicate analysis sequence on the same day. Dilute any sample and the blank with equal volumes of water if the concentration exceeds that of the highest standard.

11.2.2 Document each sample chromatogram by listing the following analytical parameters: injection point, injection volume, nitrate and sulfate retention times, flow rate, detector sensitivity setting, and recorder chart speed.

12.0 Data Analysis and Calculations

Carry out the calculations, retaining at least one extra significant figure beyond that of the acquired data. Round off figures after final calculations.

12.1 Sample Volume. Calculate the sample volume  $V_{sc}$  (in ml), on a dry basis, corrected to standard conditions, using Equation 7-2 of Method 7.

12.2 Sample Concentration of  $NO_x$  as  $NO_2$ .

12.2.1 Calculate the sample concentration  $C$  (in mg/dscm) as follows:

$$C = (H)(S)(F)(10^4)/V_{sc} \quad \text{Eq. 7A-1}$$

Where:

- H = Sample peak height, mm.
- S = Calibration factor,  $\mu\text{g}/\text{mm}$ .
- F = Dilution factor (required only if sample dilution was needed to reduce the concentration into the range of calibration), dimensionless.
- $10^4$  = 1:10 dilution times conversion factor of:  $(\text{mg}/10^3 \mu\text{g})(10^6 \text{ ml}/\text{m}^3)$ .

12.2.2 If desired, the concentration of  $NO_2$  may be calculated as ppm  $NO_2$  at standard conditions as follows:

$$\text{ppm } NO_2 = 0.5228C \quad \text{Eq. 7A-2}$$

Where:

0.5228 = ml/mg  $NO_2$ .

13.0 Method Performance

13.1 Range. The analytical range of the method is from 125 to 1250 mg  $NO_x/\text{m}^3$  as  $NO_2$  (65 to 655 ppmv), and higher concentrations may be analyzed by diluting the sample. The lower detection limit is approximately 19 mg/ $\text{m}^3$  (10 ppmv), but may vary among instruments.

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

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17.0 Tables, Diagrams, Flowcharts, and Validation Data [Reserved]

METHOD 7B—DETERMINATION OF NITROGEN OXIDE EMISSIONS FROM STATIONARY SOURCES (ULTRAVIOLET SPECTROPHOTOMETRIC METHOD)

NOTE: This method does not include all of the specifications (e.g., equipment and supplies) and procedures (e.g., sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 1, Method 5, and Method 7.

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS No.	Sensitivity
Nitrogen oxides ( $NO_x$ ), as $NO_2$ , including:		

Analyte	CAS No.	Sensitivity
Nitric oxide (NO) .....	10102-43-9	30-786 ppmv
Nitrogen dioxide (NO <sub>2</sub> ) .....	10102-44-0	

1.2 Applicability. This method is applicable for the determination of NO<sub>x</sub> emissions from nitric acid plants.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

#### 2.0 Summary of Method

2.1 A grab sample is collected in an evacuated flask containing a dilute sulfuric acid-hydrogen peroxide absorbing solution; the NO<sub>x</sub>, excluding nitrous oxide (N<sub>2</sub>O), are measured by ultraviolet spectrophotometry.

#### 3.0 Definition [Reserved]

#### 4.0 Interferences [Reserved]

#### 5.0 Safety

5.1 This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and to determine the applicability of regulatory limitations prior to performing this test method.

5.2 Corrosive reagents. The following reagents are hazardous. Personal protective equipment and safe procedures are useful in preventing chemical splashes. If contact occurs, immediately flush with copious amounts of water at least 15 minutes. Remove clothing under shower and decontaminate. Treat residual chemical burn as thermal burn.

5.2.1 Hydrogen Peroxide (H<sub>2</sub>O<sub>2</sub>). Irritating to eyes, skin, nose, and lungs.

5.2.2 Sodium Hydroxide (NaOH). Causes severe damage to eyes and skin. Inhalation causes irritation to nose, throat, and lungs. Reacts exothermically with limited amounts of water.

5.2.3 Sulfuric Acid (H<sub>2</sub>SO<sub>4</sub>). Rapidly destructive to body tissue. Will cause third degree burns. Eye damage may result in blindness. Inhalation may be fatal from spasm of the larynx, usually within 30 minutes. May cause lung tissue damage with edema. 3 mg/m<sup>3</sup> will cause lung damage in uninitiated. 1 mg/m<sup>3</sup> for 8 hours will cause lung damage or, in higher concentrations, death. Provide ventilation to limit inhalation. Reacts violently with metals and organics.

#### 6.0 Equipment and Supplies

6.1 Sample Collection. Same as Method 7, section 6.1.

6.2 Sample Recovery. The following items are required for sample recovery:

6.2.1 Wash Bottle. Polyethylene or glass.

6.2.2 Volumetric Flasks. 100-ml (one for each sample).

6.3 Analysis. The following items are required for analysis:

6.3.1 Volumetric Pipettes. 5-, 10-, 15-, and 20-ml to make standards and sample dilutions.

6.3.2 Volumetric Flasks. 1000- and 100-ml for preparing standards and dilution of samples.

6.3.3 Spectrophotometer. To measure ultraviolet absorbance at 210 nm.

6.3.4 Analytical Balance. To measure to within 0.1 mg.

#### 7.0 Reagents and Standards

NOTE: Unless otherwise indicated, all reagents are to conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Otherwise, use the best available grade.

7.1 Sample Collection. Same as Method 7, section 7.1. It is important that the amount of hydrogen peroxide in the absorbing solution not be increased. Higher concentrations of peroxide may interfere with sample analysis.

7.2 Sample Recovery. Same as Method 7, section 7.2.

7.3 Analysis. Same as Method 7, sections 7.3.1, 7.3.3, and 7.3.4, with the addition of the following:

7.3.1 Working Standard KNO<sub>3</sub> Solution. Dilute 10 ml of the standard solution to 1000 ml with water. One milliliter of the working standard is equivalent to 10 µg NO<sub>2</sub>.

#### 8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Sample Collection. Same as Method 7, section 8.1.

8.2 Sample Recovery.

8.2.1 Let the flask sit for a minimum of 16 hours, and then shake the contents for 2 minutes.

8.2.2 Connect the flask to a mercury filled U-tube manometer. Open the valve from the flask to the manometer, and record the flask temperature (T<sub>f</sub>), the barometric pressure, and the difference between the mercury levels in the manometer. The absolute internal pressure in the flask (P<sub>f</sub>) is the barometric pressure less the manometer reading.

8.2.3 Transfer the contents of the flask to a leak-free wash bottle. Rinse the flask three times with 10-ml portions of water, and add

to the bottle. Mark the height of the liquid level so that the container can be checked for leakage after transport. Label the con-

tainer to identify clearly its contents. Seal the container for shipping.

9.0 Quality Control

Section	Quality control measure	Effect
10.1 .....	Spectrophotometer calibration .....	Ensures linearity of spectrophotometer response to standards.

10.0 Calibration and Standardizations

Same as Method 7, sections 10.2 through 10.5, with the addition of the following:

10.1 Determination of Spectrophotometer Standard Curve. Add 0 ml, 5 ml, 10 ml, 15 ml, and 20 ml of the KNO<sub>3</sub> working standard solution (1 ml = 10 µg NO<sub>2</sub>) to a series of five 100-ml volumetric flasks. To each flask, add 5 ml of absorbing solution. Dilute to the mark with water. The resulting solutions contain 0.0, 50, 100, 150, and 200 µg NO<sub>2</sub>, respectively. Measure the absorbance by ultraviolet spectrophotometry at 210 nm, using the blank as a zero reference. Prepare a standard curve plotting absorbance vs. µg NO<sub>2</sub>.

NOTE: If other than a 20-ml aliquot of sample is used for analysis, then the amount of absorbing solution in the blank and standards must be adjusted such that the same

amount of absorbing solution is in the blank and standards as is in the aliquot of sample used.

10.1.1 Calculate the spectrophotometer calibration factor as follows:

$$K_c = \frac{\sum_{i=1}^n M_i A_i}{\sum_{i=1}^n A_i^2} \quad \text{Eq. 7B-1}$$

Where:

- M<sub>i</sub> = Mass of NO<sub>2</sub> in standard i, µg.
- A<sub>i</sub> = Absorbance of NO<sub>2</sub> standard i.
- n = Total number of calibration standards.

10.1.2 For the set of calibration standards specified here, Equation 7B-1 simplifies to the following:

$$K_c = 50 \frac{A_1 + 2A_2 + 3A_3 + 4A_4}{A_1^2 + A_2^2 + A_3^2 + A_4^2} \quad \text{Eq. 7B-2}$$

10.2 Spectrophotometer Calibration Quality Control. Multiply the absorbance value obtained for each standard by the K<sub>c</sub> factor (reciprocal of the least squares slope) to determine the distance each calibration point lies from the theoretical calibration line. The difference between the calculated concentration values and the actual concentrations (i.e., 50, 100, 150, and 200 µg NO<sub>2</sub>) should be less than 7 percent for all standards.

11.0 Analytical Procedures

11.1 Sample Loss Check. Note the level of the liquid in the container, and confirm whether any sample was lost during shipment. Note this on the analytical data sheet. If a noticeable amount of leakage has occurred, either void the sample or use methods, subject to the approval of the Administrator, to correct the final results.

11.2 Sample Preparation. Immediately prior to analysis, transfer the contents of the shipping container to a 100-ml volumetric flask, and rinse the container twice with 5-ml portions of water. Add the rinse

water to the flask, and dilute to mark with water.

11.3 Sample Analysis. Mix the contents of the flask thoroughly and pipette a 20 ml-aliquot of sample into a 100-ml volumetric flask. Dilute to the mark with water. Using the blank as zero reference, read the absorbance of the sample at 210 nm.

11.4 Audit Sample Analysis. Same as Method 7, section 11.4, except that a set of audit samples must be analyzed with each set of compliance samples or once per analysis day, or once per week when averaging continuous samples.

12.0 Data Analysis and Calculations

Same as Method 7, section 12.0, except replace section 12.3 with the following:

12.1 Total µg NO<sub>2</sub> Per Sample.

$$m = 5 K_c A F \quad \text{Eq. 7B-3}$$

Where:

5 = 100/20, the aliquot factor.

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NOTE: If other than a 20-ml aliquot is used for analysis, the factor 5 must be replaced by a corresponding factor.

Spectrophotometry. *Analyst*, 104:837. September 1979.

*13.0 Method Performance*

13.1 Range. The analytical range of the method as outlined has been determined to be 57 to 1500 milligrams NO<sub>x</sub> (as NO<sub>2</sub>) per dry standard cubic meter, or 30 to 786 parts per million by volume (ppmv) NO<sub>x</sub>.

*17.0 Tables, Diagrams, Flowcharts, and Validation Data [Reserved]*

**METHOD 7C—DETERMINATION OF NITROGEN OXIDE EMISSIONS FROM STATIONARY SOURCES (ALKALINE PERMANGANATE/COLORIMETRIC METHOD)**

*14.0 Pollution Prevention [Reserved]*

NOTE: This method does not include all of the specifications (e.g., equipment and supplies) and procedures (e.g., sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 1, Method 3, Method 6 and Method 7.

*15.0 Waste Management [Reserved]*

*16.0 References*

1. National Institute for Occupational Safety and Health. Recommendations for Occupational Exposure to Nitric Acid. In: Occupational Safety and Health Reporter. Washington, D.C. Bureau of National Affairs, Inc. 1976. p. 149.
2. Rennie, P.J., A.M. Sumner, and F.B. Basketter. Determination of Nitrate in Raw, Potable, and Waste Waters by Ultraviolet

*1.0 Scope and Application*

1.1 Analytes.

Analyte	CAS no.	Sensitivity
Nitrogen oxides (NO <sub>x</sub> ), as NO <sub>2</sub> , including:		
Nitric oxide (NO) .....	10102-43-9	
Nitrogen dioxide (NO <sub>2</sub> ) .....	10102-44-07	ppmv

1.2 Applicability. This method applies to the measurement of NO<sub>x</sub> emissions from fossil-fuel fired steam generators, electric utility plants, nitric acid plants, or other sources as specified in the regulations.

cent if all the SO<sub>2</sub> is consumed in the first impinger.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

4.2 Ammonia (NH<sub>3</sub>) is slowly oxidized to NO<sub>3</sub><sup>-</sup> by the absorbing solution. At 100 ppm NH<sub>3</sub> in the gas stream, an interference of 6 ppm NO<sub>x</sub> (11 mg NO<sub>2</sub>/m<sup>3</sup>) was observed when the sample was analyzed 10 days after collection. Therefore, the method may not be applicable to plants using NH<sub>3</sub> injection to control NO<sub>x</sub> emissions unless means are taken to correct the results. An equation has been developed to allow quantification of the interference and is discussed in Reference 5 of section 16.0.

*2.0 Summary of Method*

An integrated gas sample is extracted from the stack and passed through impingers containing an alkaline potassium permanganate solution; NO<sub>x</sub> (NO + NO<sub>2</sub>) emissions are oxidized to NO<sub>2</sub><sup>-</sup> and NO<sub>3</sub><sup>-</sup>. Then NO<sub>3</sub><sup>-</sup> is reduced to NO<sub>2</sub><sup>-</sup> with cadmium, and the NO<sub>2</sub><sup>-</sup> is analyzed colorimetrically.

*5.0 Safety*

*3.0 Definitions [Reserved]*

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and to determine the applicability of regulatory limitations prior to performing this test method.

*4.0 Interferences*

Possible interferents are sulfur dioxides (SO<sub>2</sub>) and ammonia (NH<sub>3</sub>).

5.2 Corrosive Reagents. The following reagents are hazardous. Personal protective equipment and safe procedures are useful in preventing chemical splashes. If contact occurs, immediately flush with copious amounts of water for at least 15 minutes. Remove clothing under shower and decontaminate. Treat residual chemical burns as thermal burns.

4.1 High concentrations of SO<sub>2</sub> could interfere because SO<sub>2</sub> consumes MnO<sub>4</sub><sup>-</sup> (as does NO<sub>x</sub>) and, therefore, could reduce the NO<sub>x</sub> collection efficiency. However, when sampling emissions from a coal-fired electric utility plant burning 2.1 percent sulfur coal with no control of SO<sub>2</sub> emissions, collection efficiency was not reduced. In fact, calculations show that sampling 3000 ppm SO<sub>2</sub> will reduce the MnO<sub>4</sub><sup>-</sup> concentration by only 5 per-

5.2.1 Hydrochloric Acid (HCl). Highly toxic and corrosive. Causes severe damage to skin. Vapors are highly irritating to eyes, skin, nose, and lungs, causing severe damage. May cause bronchitis, pneumonia, or edema of lungs. Exposure to vapor concentrations of 0.13 to 0.2 percent can be lethal in minutes. Will react with metals, producing hydrogen.

5.2.2 Oxalic Acid (COOH)<sub>2</sub>. Poisonous. Irritating to eyes, skin, nose, and throat.

5.2.3 Sodium Hydroxide (NaOH). Causes severe damage to eye tissues and to skin. Inhalation causes irritation to nose, throat, and lungs. Reacts exothermically with small amounts of water.

5.2.4 Potassium Permanganate (KMnO<sub>4</sub>). Caustic, strong oxidizer. Avoid bodily contact with.

#### 6.0 Equipment and Supplies

6.1 Sample Collection and Sample Recovery. A schematic of the Method 7C sampling train is shown in Figure 7C-1, and component parts are discussed below. Alternative apparatus and procedures are allowed provided acceptable accuracy and precision can be demonstrated to the satisfaction of the Administrator.

6.1.1 Probe. Borosilicate glass tubing, sufficiently heated to prevent water condensation and equipped with an in-stack or heated out-of-stack filter to remove particulate matter (a plug of glass wool is satisfactory for this purpose). Stainless steel or Teflon tubing may also be used for the probe.

6.1.2 Impingers. Three restricted-orifice glass impingers, having the specifications given in Figure 7C-2, are required for each sampling train. The impingers must be connected in series with leak-free glass connectors. Stopcock grease may be used, if necessary, to prevent leakage. (The impingers can be fabricated by a glass blower if not available commercially.)

6.1.3 Glass Wool, Stopcock Grease, Drying Tube, Valve, Pump, Barometer, and Vacuum Gauge and Rotameter. Same as in Method 6, sections 6.1.1.3, 6.1.1.4, 6.1.1.6, 6.1.1.7, 6.1.1.8, 6.1.2, and 6.1.3, respectively.

6.1.4 Rate Meter. Rotameter, or equivalent, accurate to within 2 percent at the selected flow rate of between 400 and 500 ml/min (0.014 to 0.018 cfm). For rotameters, a range of 0 to 1 liter/min (0 to 0.035 cfm) is recommended.

6.1.5 Volume Meter. Dry gas meter (DGM) capable of measuring the sample volume under the sampling conditions of 400 to 500 ml/min (0.014 to 0.018 cfm) for 60 minutes within an accuracy of 2 percent.

6.1.6 Filter. To remove NO<sub>x</sub> from ambient air, prepared by adding 20 g of 5-angstrom molecular sieve to a cylindrical tube (e.g., a polyethylene drying tube).

6.1.7 Polyethylene Bottles. 1-liter, for sample recovery.

6.1.8 Funnel and Stirring Rods. For sample recovery.

6.2 Sample Preparation and Analysis.

6.2.1 Hot Plate. Stirring type with 50- by 10-mm Teflon-coated stirring bars.

6.2.2 Beakers. 400-, 600-, and 1000-ml capacities.

6.2.3 Filtering Flask. 500-ml capacity with side arm.

6.2.4 Buchner Funnel. 75-mm ID, with spout equipped with a 13-mm ID by 90-mm long piece of Teflon tubing to minimize possibility of aspirating sample solution during filtration.

6.2.5 Filter Paper. Whatman GF/C, 7.0-cm diameter.

6.2.6 Stirring Rods.

6.2.7 Volumetric Flasks. 100-, 200- or 250-, 500-, and 1000-ml capacity.

6.2.8 Watch Glasses. To cover 600- and 1000-ml beakers.

6.2.9 Graduated Cylinders. 50- and 250-ml capacities.

6.2.10 Pipettes. Class A.

6.2.11 pH Meter. To measure pH from 0.5 to 12.0.

6.2.12 Burette. 50-ml with a micrometer type stopcock. (The stopcock is Catalog No. 8225-t-05, Ace Glass, Inc., Post Office Box 996, Louisville, Kentucky 50201.) Place a glass wool plug in bottom of burette. Cut off burette at a height of 43 cm (17 in.) from the top of plug, and have a blower attach a glass funnel to top of burette such that the diameter of the burette remains essentially unchanged. Other means of attaching the funnel are acceptable.

6.2.13 Glass Funnel. 75-mm ID at the top.

6.2.14 Spectrophotometer. Capable of measuring absorbance at 540 nm; 1-cm cells are adequate.

6.2.15 Metal Thermometers. Bimetallic thermometers, range 0 to 150 °C (32 to 300 °F).

6.2.16 Culture Tubes. 20-by 150-mm, Kimax No. 45048.

6.2.17 Parafilm "M." Obtained from American Can Company, Greenwich, Connecticut 06830.

6.2.18 CO<sub>2</sub> Measurement Equipment. Same as in Method 3, section 6.0.

#### 7.0 Reagents and Standards

Unless otherwise indicated, it is intended that all reagents conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available; otherwise, use the best available grade.

7.1 Sample Collection.

7.1.1 Water. Deionized distilled to conform to ASTM Specification D 1193-77 or 91 Type 3 (incorporated by reference—see §60.17).

7.1.2 Potassium Permanganate, 4.0 Percent (w/w), Sodium Hydroxide, 2.0 Percent (w/w) solution (KMnO<sub>4</sub>/NaOH solution). Dissolve 40.0 g of KMnO<sub>4</sub> and 20.0 g of NaOH in 940 ml of water.

7.2 Sample Preparation and Analysis.

7.2.1 Water. Same as in section 7.1.1.

7.2.2 Oxalic Acid Solution. Dissolve 48 g of oxalic acid [(COOH)<sub>2</sub>·2H<sub>2</sub>O] in water, and dilute to 500 ml. Do not heat the solution.

7.2.3 Sodium Hydroxide, 0.5 N. Dissolve 20 g of NaOH in water, and dilute to 1 liter.

7.2.4 Sodium Hydroxide, 10 N. Dissolve 40 g of NaOH in water, and dilute to 100 ml.

7.2.5 Ethylenediamine Tetraacetic Acid (EDTA) Solution, 6.5 percent (w/v). Dissolve 6.5 g of EDTA (disodium salt) in water, and dilute to 100 ml. Dissolution is best accomplished by using a magnetic stirrer.

7.2.6 Column Rinse Solution. Add 20 ml of 6.5 percent EDTA solution to 960 ml of water, and adjust the pH to between 11.7 and 12.0 with 0.5 N NaOH.

7.2.7 Hydrochloric Acid (HCl), 2 N. Add 86 ml of concentrated HCl to a 500 ml-volumetric flask containing water, dilute to volume, and mix well. Store in a glass-stoppered bottle.

7.2.8 Sulfanilamide Solution. Add 20 g of sulfanilamide (melting point 165 to 167 °C (329 to 333 °F)) to 700 ml of water. Add, with mixing, 50 ml concentrated phosphoric acid (85 percent), and dilute to 1000 ml. This solution is stable for at least 1 month, if refrigerated.

7.2.9 N-(1-Naphthyl)-Ethylenediamine Dihydrochloride (NEDA) Solution. Dissolve 0.5 g of NEDA in 500 ml of water. An aqueous solution should have one absorption peak at 320 nm over the range of 260 to 400 nm. NEDA that shows more than one absorption peak over this range is impure and should not be used. This solution is stable for at least 1 month if protected from light and refrigerated.

7.2.10 Cadmium. Obtained from Matheson Coleman and Bell, 2909 Highland Avenue, Norwood, Ohio 45212, as EM Laboratories Catalog No. 2001. Prepare by rinsing in 2 N HCl for 5 minutes until the color is silver-grey. Then rinse the cadmium with water until the rinsings are neutral when tested with pH paper. CAUTION: H<sub>2</sub> is liberated during preparation. Prepare in an exhaust hood away from any flame or combustion source.

7.2.11 Sodium Sulfite (NaNO<sub>2</sub>) Standard Solution. Nominal Concentration, 1000 µg NO<sub>2</sub><sup>-</sup>/ml. Desiccate NaNO<sub>2</sub> overnight. Accurately weigh 1.4 to 1.6 g of NaNO<sub>2</sub> (assay of 97 percent NaNO<sub>2</sub> or greater), dissolve in water, and dilute to 1 liter. Calculate the exact NO<sub>2</sub><sup>-</sup> concentration using Equation 7C-1 in section 12.2. This solution is stable for at least 6 months under laboratory conditions.

7.2.12 Potassium Nitrate (KNO<sub>3</sub>) Standard Solution. Dry KNO<sub>3</sub> at 110 °C (230 °F) for 2 hours, and cool in a desiccator. Accurately weigh 9 to 10 g of KNO<sub>3</sub> to within 0.1 mg, dissolve in water, and dilute to 1 liter. Calculate the exact NO<sub>3</sub><sup>-</sup> concentration using Equation 7C-2 in section 12.3. This solution is stable for 2 months without preservative under laboratory conditions.

7.2.13 Spiking Solution. Pipette 7 ml of the KNO<sub>3</sub> standard into a 100-ml volumetric flask, and dilute to volume.

7.2.14 Blank Solution. Dissolve 2.4 g of KMnO<sub>4</sub> and 1.2 g of NaOH in 96 ml of water. Alternatively, dilute 60 ml of KMnO<sub>4</sub>/NaOH solution to 100 ml.

#### 8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Preparation of Sampling Train. Add 200 ml of KMnO<sub>4</sub>/NaOH solution (Section 7.1.2) to each of three impingers, and assemble the train as shown in Figure 7C-1. Adjust the probe heater to a temperature sufficient to prevent water condensation.

8.2 Leak-Checks. Same as in Method 6, section 8.2.

#### 8.3 Sample Collection.

8.3.1 Record the initial DGM reading and barometric pressure. Determine the sampling point or points according to the appropriate regulations (e.g., §60.46(b)(5) of 40 CFR Part 60). Position the tip of the probe at the sampling point, connect the probe to the first impinger, and start the pump. Adjust the sample flow to a value between 400 and 500 ml/min (0.014 and 0.018 cfm). CAUTION: DO NOT EXCEED THESE FLOW RATES. Once adjusted, maintain a constant flow rate during the entire sampling run. Sample for 60 minutes. For relative accuracy (RA) testing of continuous emission monitors, the minimum sampling time is 1 hour, sampling 20 minutes at each traverse point.

NOTE: When the SO<sub>2</sub> concentration is greater than 1200 ppm, the sampling time may have to be reduced to 30 minutes to eliminate plugging of the impinger orifice with MnO<sub>2</sub>. For RA tests with SO<sub>2</sub> greater than 1200 ppm, sample for 30 minutes (10 minutes at each point).

8.3.2 Record the DGM temperature, and check the flow rate at least every 5 minutes. At the conclusion of each run, turn off the pump, remove the probe from the stack, and record the final readings. Divide the sample volume by the sampling time to determine the average flow rate. Conduct the mandatory post-test leak-check. If a leak is found, void the test run, or use procedures acceptable to the Administrator to adjust the sample volume for the leakage.

8.4 CO<sub>2</sub> Measurement. During sampling, measure the CO<sub>2</sub> content of the stack gas near the sampling point using Method 3. The single-point grab sampling procedure is adequate, provided the measurements are made at least three times (near the start, midway, and before the end of a run), and the average CO<sub>2</sub> concentration is computed. The Orsat or Fyrite analyzer may be used for this analysis.

8.5 Sample Recovery. Disconnect the impingers. Pour the contents of the impingers into a 1-liter polyethylene bottle

using a funnel and a stirring rod (or other means) to prevent spillage. Complete the quantitative transfer by rinsing the impingers and connecting tubes with water until the rinsings are clear to light pink, and

add the rinsings to the bottle. Mix the sample, and mark the solution level. Seal and identify the sample container.

9.0 Quality Control

Section	Quality control measure	Effect
8.2, 10.1-10.3	Sampling equipment leak-check and calibration.	Ensure accurate measurement of sample volume.
10.4	Spectrophotometer calibration	Ensure linearity of spectrophotometer response to standards
11.3	Spiked sample analysis.	Ensure reduction efficiency of column.

10.0 Calibration and Standardizations

10.1 Volume Metering System. Same as Method 6, section 10.1. For detailed instructions on carrying out these calibrations, it is suggested that section 3.5.2 of Reference 4 of section 16.0 be consulted.

10.2 Temperature Sensors and Barometer. Same as in Method 6, sections 10.2 and 10.4, respectively.

10.3 Check of Rate Meter Calibration Accuracy (Optional). Disconnect the probe from the first impinger, and connect the filter. Start the pump, and adjust the rate meter to read between 400 and 500 ml/min (0.014 and 0.018 cfm). After the flow rate has stabilized, start measuring the volume sampled, as recorded by the dry gas meter and the sampling time. Collect enough volume to measure accurately the flow rate. Then calculate the flow rate. This average flow rate must be less than 500 ml/min (0.018 cfm) for the sample to be valid; therefore, it is recommended that the flow rate be checked as above prior to each test.

10.4 Spectrophotometer.

10.4.1 Dilute 5.0 ml of the NaNO<sub>2</sub> standard solution to 200 ml with water. This solution nominally contains 25 µg NO<sub>2</sub><sup>-</sup>/ml. Use this solution to prepare calibration standards to cover the range of 0.25 to 3.00 µg NO<sub>2</sub><sup>-</sup>/ml. Prepare a minimum of three standards each for the linear and slightly nonlinear (described below) range of the curve. Use pipettes for all additions.

10.4.2 Measure the absorbance of the standards and a water blank as instructed in section 11.5. Plot the net absorbance vs. µg NO<sub>2</sub><sup>-</sup>/ml. Draw a smooth curve through the points. The curve should be linear up to an absorbance of approximately 1.2 with a slope of approximately 0.53 absorbance units/µg NO<sub>2</sub><sup>-</sup>/ml. The curve should pass through the origin. The curve is slightly nonlinear from an absorbance of 1.2 to 1.6.

11.0 Analytical Procedures

11.1 Sample Stability. Collected samples are stable for at least four weeks; thus, analysis must occur within 4 weeks of collection.

11.2 Sample Preparation.

11.2.1 Prepare a cadmium reduction column as follows: Fill the burette with water. Add freshly prepared cadmium slowly, with tapping, until no further settling occurs. The height of the cadmium column should be 39 cm (15 in). When not in use, store the column under rinse solution.

NOTE: The column should not contain any bands of cadmium fines. This may occur if regenerated cadmium is used and will greatly reduce the column lifetime.

11.2.2 Note the level of liquid in the sample container, and determine whether any sample was lost during shipment. If a noticeable amount of leakage has occurred, the volume lost can be determined from the difference between initial and final solution levels, and this value can then be used to correct the analytical result. Quantitatively transfer the contents to a 1-liter volumetric flask, and dilute to volume.

11.2.3 Take a 100-ml aliquot of the sample and blank (unexposed KMnO<sub>4</sub>/NaOH) solutions, and transfer to 400-ml beakers containing magnetic stirring bars. Using a pH meter, add concentrated H<sub>2</sub>SO<sub>4</sub> with stirring until a pH of 0.7 is obtained. Allow the solutions to stand for 15 minutes. Cover the beakers with watch glasses, and bring the temperature of the solutions to 50 °C (122 °F). Keep the temperature below 60 °C (140 °F). Dissolve 4.8 g of oxalic acid in a minimum volume of water, approximately 50 ml, at room temperature. Do not heat the solution. Add this solution slowly, in increments, until the KMnO<sub>4</sub> solution becomes colorless. If the color is not completely removed, prepare some more of the above oxalic acid solution, and add until a colorless solution is obtained. Add an excess of oxalic acid by dissolving 1.6 g of oxalic acid in 50 ml of water, and add 6 ml of this solution to the colorless solution. If suspended matter is present, add concentrated H<sub>2</sub>SO<sub>4</sub> until a clear solution is obtained.

11.2.4 Allow the samples to cool to near room temperature, being sure that the samples are still clear. Adjust the pH to between 11.7 and 12.0 with 10 N NaOH. Quantitatively transfer the mixture to a Buchner funnel containing GF/C filter paper, and filter the

precipitate. Filter the mixture into a 500-ml filtering flask. Wash the solid material four times with water. When filtration is complete, wash the Teflon tubing, quantitatively transfer the filtrate to a 500-ml volumetric flask, and dilute to volume. The samples are now ready for cadmium reduction. Pipette a 50-ml aliquot of the sample into a 150-ml beaker, and add a magnetic stirring bar. Pipette in 1.0 ml of 6.5 percent EDTA solution, and mix.

11.3 Determine the correct stopcock setting to establish a flow rate of 7 to 9 ml/min of column rinse solution through the cadmium reduction column. Use a 50-ml graduated cylinder to collect and measure the solution volume. After the last of the rinse solution has passed from the funnel into the burette, but before air entrapment can occur, start adding the sample, and collect it in a 250-ml graduated cylinder. Complete the quantitative transfer of the sample to the column as the sample passes through the column. After the last of the sample has passed from the funnel into the burette, start adding 60 ml of column rinse solution, and collect the rinse solution until the solution just disappears from the funnel. Quantitatively transfer the sample to a 200-ml volumetric flask (a 250-ml flask may be required), and dilute to volume. The samples are now ready for NO<sub>2</sub>-analysis.

NOTE: Two spiked samples should be run with every group of samples passed through the column. To do this, prepare two additional 50-ml aliquots of the sample suspected to have the highest NO<sub>2</sub>-concentration, and add 1 ml of the spiking solution to these aliquots. If the spike recovery or column efficiency (see section 12.2) is below 95 percent, prepare a new column, and repeat the cadmium reduction.

11.5 Sample Analysis. Pipette 10 ml of sample into a culture tube. Pipette in 10 ml of sulfanilamide solution and 1.4 ml of NEDA solution. Cover the culture tube with parafilm, and mix the solution. Prepare a blank in the same manner using the sample from treatment of the unexposed KMnO<sub>4</sub>/NaOH solution. Also, prepare a calibration standard to check the slope of the calibration curve. After a 10-minute color develop-

ment interval, measure the absorbance at 540 nm against water. Read μg NO<sub>2</sub><sup>-</sup>/ml from the calibration curve. If the absorbance is greater than that of the highest calibration standard, use less than 10 ml of sample, and repeat the analysis. Determine the NO<sub>2</sub><sup>-</sup> concentration using the calibration curve obtained in section 10.4.

NOTE: Some test tubes give a high blank NO<sub>2</sub><sup>-</sup> value but culture tubes do not.

11.6 Audit Sample Analysis. Same as in Method 7, section 11.4.

#### 12.0 Data Analysis and Calculations

Carry out calculations, retaining at least one extra significant figure beyond that of the acquired data. Round off figures after final calculation.

##### 12.1 Nomenclature.

B = Analysis of blank, μg NO<sub>2</sub><sup>-</sup>/ml.

C = Concentration of NO<sub>x</sub> as NO<sub>2</sub>, dry basis, mg/dsm<sup>3</sup>.

E = Column efficiency, dimensionless

K<sub>2</sub> = 10<sup>-3</sup> mg/μg.

m = Mass of NO<sub>x</sub>, as NO<sub>2</sub>, in sample, μg.

P<sub>bar</sub> = Barometric pressure, mm Hg (in. Hg).

P<sub>std</sub> = Standard absolute pressure, 760 mm Hg (29.92 in. Hg).

s = Concentration of spiking solution, μg NO<sub>2</sub>/ml.

S = Analysis of sample, μg NO<sub>2</sub><sup>-</sup>/ml.

T<sub>m</sub> = Average dry gas meter absolute temperature, °K.

T<sub>std</sub> = Standard absolute temperature, 293 °K (528 °R).

V<sub>m(std)</sub> = Dry gas volume measured by the dry gas meter, corrected to standard conditions, dscm (dscf).

V<sub>m</sub> = Dry gas volume as measured by the dry gas meter, scm (scf).

x = Analysis of spiked sample, μg NO<sub>2</sub><sup>-</sup>/ml.

X = Correction factor for CO<sub>2</sub> collection = 100/(100 - %CO<sub>2</sub>(V/V)).

y = Analysis of unspiked sample, μg NO<sub>2</sub><sup>-</sup>/ml.

Y = Dry gas meter calibration factor.

1.0 ppm NO = 1.247 mg NO/m<sup>3</sup> at STP.

1.0 ppm NO<sub>2</sub> = 1.912 mg NO<sub>2</sub>/m<sup>3</sup> at STP.

1 ft<sup>3</sup> = 2.832 × 10<sup>-2</sup> m<sup>3</sup>.

12.2 NO<sub>2</sub> Concentration. Calculate the NO<sub>2</sub> concentration of the solution (see section 7.2.11) using the following equation:

$$\frac{\mu\text{g NO}_2^-}{\text{ml}} = \text{g NaNO}_2 \times \frac{\text{purity, \%}}{100} \times 10^3 \times \frac{46.01}{69.01} \quad \text{Eq. 7C-1}$$

12.3 NO<sub>3</sub> Concentration. Calculate the NO<sub>3</sub> concentration of the KNO<sub>3</sub> solution (see section 7.2.12) using the following equation:



$$\frac{\mu\text{g NO}_3^-}{\text{ml}} = \text{g KNO}_3 \times (10^3) \times \frac{62.01}{101.10} \quad \text{Eq. 7C-2}$$

12.4 Sample Volume, Dry Basis, Corrected to Standard Conditions.

$$V_{m(\text{std})} = V_m \times Y \frac{T_{\text{std}}}{T_m} \frac{P_{\text{bar}}}{P_{\text{std}}} \quad \text{Eq. 7C-3}$$

$$= K_1 \times Y \times V_m \frac{P_{\text{bar}}}{T_m}$$

Where:

$K_1 = 0.3855 \text{ }^\circ\text{K/mm Hg}$  for metric units.

$K_1 = 17.65 \text{ }^\circ\text{R/in. Hg}$  for English units.

12.5 Efficiency of Cadmium Reduction Column. Calculate this value as follows:

$$E = \frac{200}{1.0 \text{ s}} \frac{(x-y)}{46.01} = \frac{269.6(x-y)}{s} \quad \text{Eq. 7C-4}$$

Where:

200 = Final volume of sample and blank after passing through the column, ml.

1.0 = Volume of spiking solution added, ml.

46.01 =  $\mu\text{g NO}_2^-/\mu\text{mole}$ .

62.01 =  $\mu\text{g NO}_3^-/\mu\text{mole}$ .

12.6 Total  $\mu\text{g NO}_2$ .

$$m = 200 \left( \frac{500}{50} \right) \left( \frac{1000}{100} \right) \left( \frac{S-B}{E} \right) = \frac{(2 \times 10^4)(S-B)}{E} \quad \text{Eq. 7C-5}$$

Where:

500 = Total volume of prepared sample, ml.

50 = Aliquot of prepared sample processed through cadmium column, ml.

100 = Aliquot of  $\text{KMnO}_4/\text{NaOH}$  solution, ml.

1000 = Total volume of  $\text{KMnO}_4/\text{NaOH}$  solution, ml.

12.7 Sample Concentration.

$$C = K_2 \frac{m}{V_{m(\text{std})}} \quad \text{Eq. 7C-6}$$

### 13.0 Method Performance

13.1 Precision. The intra-laboratory relative standard deviation for a single measurement is 2.8 and 2.9 percent at 201 and 268 ppm  $\text{NO}_x$ , respectively.

13.2 Bias. The method does not exhibit any bias relative to Method 7.

13.3 Range. The lower detectable limit is 13 mg  $\text{NO}_x/\text{m}^3$ , as  $\text{NO}_2$  (7 ppm  $\text{NO}_x$ ) when sampling at 500 ml/min for 1 hour. No upper limit has been established; however, when using the recommended sampling conditions, the method has been found to collect  $\text{NO}_x$  emis-

sions quantitatively up to 1782 mg  $\text{NO}_x/\text{m}^3$ , as  $\text{NO}_2$  (932 ppm  $\text{NO}_x$ ).

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

### 16.0 References

1. Margeson, J.H., W.J. Mitchell, J.C. Suggs, and M.R. Midgett. Integrated Sampling and Analysis Methods for Determining  $\text{NO}_x$  Emissions at Electric Utility Plants. U.S. Environmental Protection Agency, Research Triangle Park, NC. Journal of the Air Pollution Control Association. 32:1210-1215. 1982.

2. Memorandum and attachment from J.H. Margeson, Source Branch, Quality Assurance Division, Environmental Monitoring Systems Laboratory, to The Record, EPA, March 30, 1983.  $\text{NH}_3$  Interference in Methods 7C and 7D.

3. Margeson, J.H., J.C. Suggs, and M.R. Midgett. Reduction of Nitrate to Nitrite with Cadmium. Anal. Chem. 52:1955-57. 1980.

4. Quality Assurance Handbook for Air Pollution Measurement Systems. Volume III—Stationary Source Specific Methods. U.S.

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Environmental Protection Agency, Research Triangle Park, NC. Publication No. EPA-600/4-77-027b. August 1977.

Nitric Acid Plants. Analytical Chemistry. 47 (11):1801. 1975.

5. Margeson, J.H., *et al.* An Integrated Method for Determining NO<sub>x</sub> Emissions at

17.0 Tables, Diagrams, Flowcharts, and Validation Data

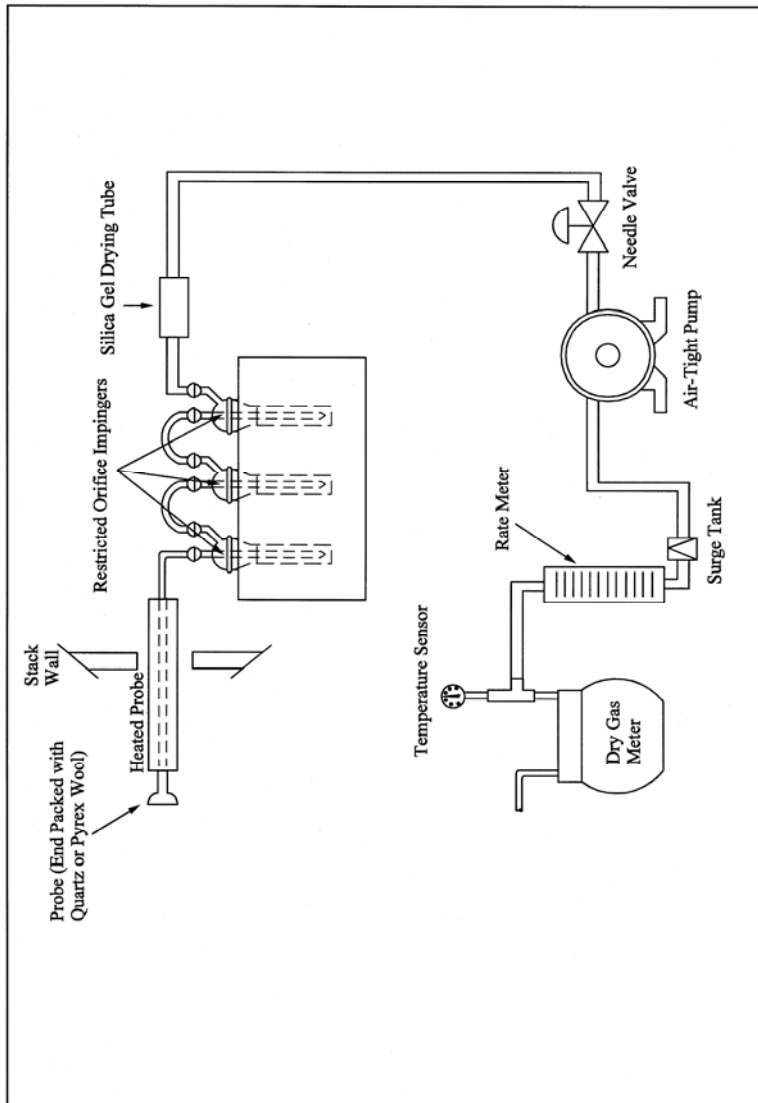


Figure 7C-1. NO<sub>x</sub> Sampling Train.

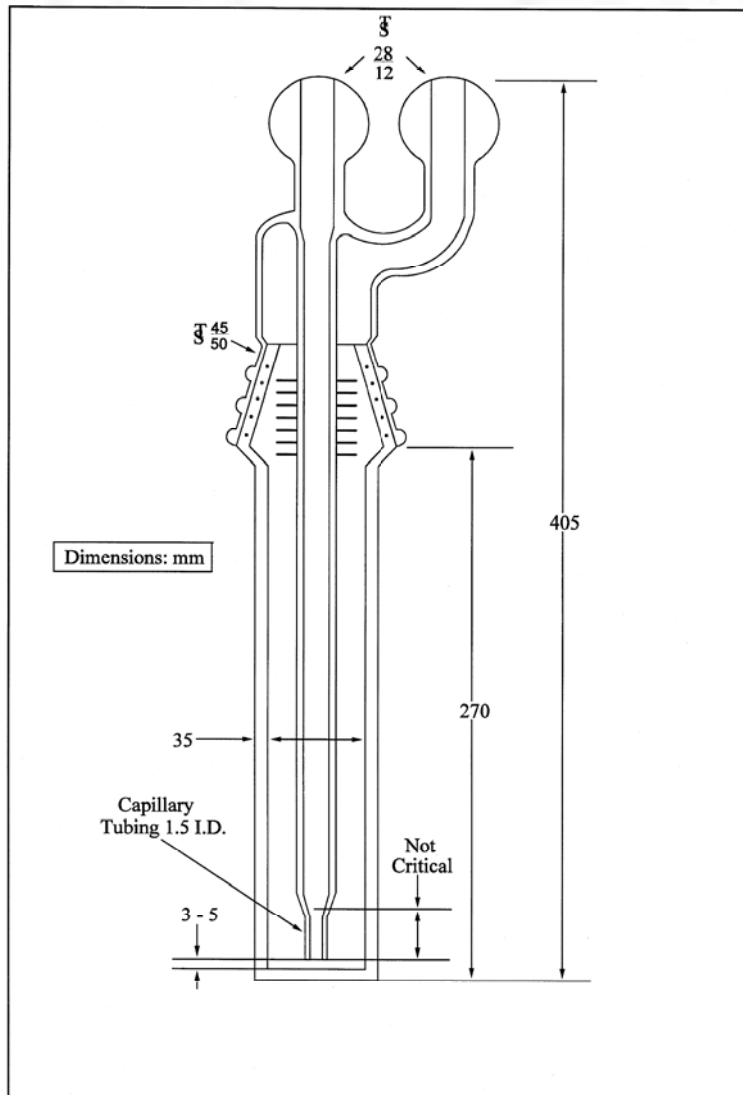


Figure 7C-2. Restricted-Orifice Impinger.

METHOD 7D—DETERMINATION OF NITROGEN OXIDE EMISSIONS FROM STATIONARY SOURCES (ALKALINE-PERMANGANATE/ION CHROMATOGRAPHIC METHOD)

NOTE: This method is not inclusive with respect to specifications (*e.g.*, equipment and supplies) and procedures (*e.g.*, sampling and analytical) essential to its performance. Some material is incorporated by reference

from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 1, Method 3, Method 6, Method 7, and Method 7C.

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS No.	Sensitivity
Nitrogen oxides (NO <sub>x</sub> ), as NO <sub>2</sub> , including:		
Nitric oxide (NO) .....	10102-43-9	
Nitrogen dioxide (NO <sub>2</sub> ) .....	10102-44-0	7 ppmv

1.2 Applicability. This method applies to the measurement of NO<sub>x</sub> emissions from fossil-fuel fired steam generators, electric utility plants, nitric acid plants, or other sources as specified in the regulations.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

#### 2.0 Summary of Method

An integrated gas sample is extracted from the stack and passed through impingers containing an alkaline-potassium permanganate solution; NO<sub>x</sub> (NO + NO<sub>2</sub>) emissions are oxidized to NO<sub>3</sub><sup>-</sup>. Then NO<sub>3</sub><sup>-</sup> is analyzed by ion chromatography.

#### 3.0 Definitions [Reserved]

#### 4.0 Interferences

Same as in Method 7C, section 4.0.

#### 5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and to determine the applicability of regulatory limitations prior to performing this test method.

5.2 Corrosive reagents. The following reagents are hazardous. Personal protective equipment and safe procedures are useful in preventing chemical splashes. If contact occurs, immediately flush with copious amounts of water for at least 15 minutes. Remove clothing under shower and decontaminate. Treat residual chemical burns as thermal burns.

5.2.1 Hydrogen Peroxide (H<sub>2</sub>O<sub>2</sub>). Irritating to eyes, skin, nose, and lungs. 30% H<sub>2</sub>O<sub>2</sub> is a strong oxidizing agent; avoid contact with skin, eyes, and combustible material. Wear gloves when handling.

5.2.2 Sodium Hydroxide (NaOH). Causes severe damage to eye tissues and to skin. Inhalation causes irritation to nose, throat, and lungs. Reacts exothermically with limited amounts of water.

5.2.3 Potassium Permanganate (KMnO<sub>4</sub>). Caustic, strong oxidizer. Avoid bodily contact with.

#### 6.0 Equipment and Supplies

6.1 Sample Collection and Sample Recovery. Same as Method 7C, section 6.1. A sche-

matic of the sampling train used in performing this method is shown in Figure 7C-1 of Method 7C.

#### 6.2 Sample Preparation and Analysis.

6.2.1 Magnetic Stirrer. With 25- by 10-mm Teflon-coated stirring bars.

6.2.2 Filtering Flask. 500-ml capacity with sidearm.

6.2.3 Buchner Funnel. 75-mm ID, with spout equipped with a 13-mm ID by 90-mm long piece of Teflon tubing to minimize possibility of aspirating sample solution during filtration.

6.2.4 Filter Paper. Whatman GF/C, 7.0-cm diameter.

6.2.5 Stirring Rods.

6.2.6 Volumetric Flask. 250-ml.

6.2.7 Pipettes. Class A.

6.2.8 Erlenmeyer Flasks. 250-ml.

6.2.9 Ion Chromatograph. Equipped with an anion separator column to separate NO<sub>3</sub><sup>-</sup>, H<sub>3</sub><sup>+</sup> suppressor, and necessary auxiliary equipment. Nonsuppressed and other forms of ion chromatography may also be used provided that adequate resolution of NO<sub>3</sub><sup>-</sup> is obtained. The system must also be able to resolve and detect NO<sub>2</sub><sup>-</sup>.

#### 7.0 Reagents and Standards

NOTE: Unless otherwise indicated, it is intended that all reagents conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available; otherwise, use the best available grade.

#### 7.1 Sample Collection.

7.1.1 Water. Deionized distilled to conform to ASTM specification D 1193-77 or 91 Type 3 (incorporated by reference—see § 60.17).

7.1.2 Potassium Permanganate, 4.0 Percent (w/w), Sodium Hydroxide, 2.0 Percent (w/w). Dissolve 40.0 g of KMnO<sub>4</sub> and 20.0 g of NaOH in 940 ml of water.

#### 7.2 Sample Preparation and Analysis.

7.2.1 Water. Same as in section 7.1.1.

7.2.2 Hydrogen Peroxide (H<sub>2</sub>O<sub>2</sub>), 5 Percent. Dilute 30 percent H<sub>2</sub>O<sub>2</sub> 1:5 (v/v) with water.

7.2.3 Blank Solution. Dissolve 2.4 g of KMnO<sub>4</sub> and 1.2 g of NaOH in 96 ml of water. Alternatively, dilute 60 ml of KMnO<sub>4</sub>/NaOH solution to 100 ml.

7.2.4 KNO<sub>3</sub> Standard Solution. Dry KNO<sub>3</sub> at 110 °C for 2 hours, and cool in a desiccator. Accurately weigh 9 to 10 g of KNO<sub>3</sub> to within 0.1 mg, dissolve in water, and dilute to 1 liter. Calculate the exact NO<sub>3</sub><sup>-</sup> concentration using Equation 7D-1 in section 12.2. This

solution is stable for 2 months without preservative under laboratory conditions.

7.2.5 Eluent. 0.003 M NaHCO<sub>3</sub>/0.0024 M Na<sub>2</sub>CO<sub>3</sub>. Dissolve 1.008 g NaHCO<sub>3</sub> and 1.018 g Na<sub>2</sub>CO<sub>3</sub> in water, and dilute to 4 liters. Other eluents capable of resolving nitrate ion from sulfate and other species present may be used.

8.0 Sample Collection, Preservation, Transport, and Storage.

8.1 Sampling. Same as in Method 7C, section 8.1.

8.2 Sample Recovery. Same as in Method 7C, section 8.2.

8.3 Sample Preparation for Analysis.

NOTE: Samples must be analyzed within 28 days of collection.

8.3.1 Note the level of liquid in the sample container, and determine whether any sample was lost during shipment. If a noticeable amount of leakage has occurred, the volume lost can be determined from the difference between initial and final solution levels, and this value can then be used to correct the analytical result. Quantitatively transfer the contents to a 1-liter volumetric flask, and dilute to volume.

8.3.2 Sample preparation can be started 36 hours after collection. This time is necessary to ensure that all NO<sub>2</sub><sup>-</sup> is converted to NO<sub>3</sub><sup>-</sup> in the collection solution. Take a 50-ml ali-

quot of the sample and blank, and transfer to 250-ml Erlenmeyer flasks. Add a magnetic stirring bar. Adjust the stirring rate to as fast a rate as possible without loss of solution. Add 5 percent H<sub>2</sub>O<sub>2</sub> in increments of approximately 5 ml using a 5-ml pipette. When the KMnO<sub>4</sub> color appears to have been removed, allow the precipitate to settle, and examine the supernatant liquid. If the liquid is clear, the H<sub>2</sub>O<sub>2</sub> addition is complete. If the KMnO<sub>4</sub> color persists, add more H<sub>2</sub>O<sub>2</sub>, with stirring, until the supernatant liquid is clear.

NOTE: The faster the stirring rate, the less volume of H<sub>2</sub>O<sub>2</sub> that will be required to remove the KMnO<sub>4</sub>. Quantitatively transfer the mixture to a Buchner funnel containing GF/C filter paper, and filter the precipitate. The spout of the Buchner funnel should be equipped with a 13-mm ID by 90-mm long piece of Teflon tubing. This modification minimizes the possibility of aspirating sample solution during filtration. Filter the mixture into a 500-ml filtering flask. Wash the solid material four times with water. When filtration is complete, wash the Teflon tubing, quantitatively transfer the filtrate to a 250-ml volumetric flask, and dilute to volume. The sample and blank are now ready for NO<sub>3</sub><sup>-</sup> analysis.

9.0 Quality Control

Section	Quality control measure	Effect
8.2, 10.1-10.3	Sampling equipment leak-check and calibration	Ensure accurate measurement of sample volume.
10.4	Spectrophotometer calibration	Ensure linearity of spectrophotometer response to standards.
11.3	Spiked sample analysis	Ensure reduction efficiency of column.

10.0 Calibration and Standardizations

10.1 Dry Gas Meter (DGM) System.

10.1.1 Initial Calibration. Same as in Method 6, section 10.1.1. For detailed instructions on carrying out this calibration, it is suggested that section 3.5.2 of Citation 4 in section 16.0 of Method 7C be consulted.

10.1.2 Post-Test Calibration Check. Same as in Method 6, section 10.1.2.

10.2 Thermometers for DGM and Barometer. Same as in Method 6, sections 10.2 and 10.4, respectively.

10.3 Ion Chromatograph.

10.3.1 Dilute a given volume (1.0 ml or greater) of the KNO<sub>3</sub> standard solution to a convenient volume with water, and use this solution to prepare calibration standards. Prepare at least four standards to cover the range of the samples being analyzed. Use pipettes for all additions. Run standards as instructed in section 11.2. Determine peak height or area, and plot the individual values versus concentration in µg NO<sub>3</sub><sup>-</sup>/ml.

10.3.2 Do not force the curve through zero. Draw a smooth curve through the points. The curve should be linear. With the linear curve, use linear regression to determine the calibration equation.

11.0 Analytical Procedures

11.1 The following chromatographic conditions are recommended: 0.003 M NaHCO<sub>3</sub>/0.0024 Na<sub>2</sub>CO<sub>3</sub> eluent solution (Section 7.2.5), full scale range, 3 µMHO; sample loop, 0.5 ml; flow rate, 2.5 ml/min. These conditions should give a NO<sub>3</sub><sup>-</sup> retention time of approximately 15 minutes (Figure 7D-1).

11.2 Establish a stable baseline. Inject a sample of water, and determine whether any NO<sub>3</sub><sup>-</sup> appears in the chromatogram. If NO<sub>3</sub><sup>-</sup> is present, repeat the water load/injection procedure approximately five times; then re-inject a water sample and observe the chromatogram. When no NO<sub>3</sub><sup>-</sup> is present, the instrument is ready for use. Inject calibration standards. Then inject samples and a blank. Repeat the injection of the calibration

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standards (to compensate for any drift in response of the instrument). Measure the  $\text{NO}_3^-$  peak height or peak area, and determine the sample concentration from the calibration curve.

### 12.0 Data Analysis and Calculations

Carry out calculations, retaining at least one extra significant figure beyond that of

the acquired data. Round off figures after final calculation.

12.1 Nomenclature. Same as in Method 7C, section 12.1.

12.2  $\text{NO}_3^-$  concentration. Calculate the  $\text{NO}_3^-$  concentration in the  $\text{KNO}_3$  standard solution (see section 7.2.4) using the following equation:

$$\frac{\mu\text{g NO}_3^-}{\text{ml}} = \text{g of KNO}_3 \times 10^3 \times \frac{62.01}{101.10} \quad \text{Eq. 7D-1}$$

12.3 Sample Volume, Dry Basis, Corrected to Standard Conditions. Same as in Method 7C, section 12.4.

12.4 Total  $\mu\text{g NO}_2$  Per Sample.

$$\begin{aligned} m &= 250 \left( \frac{1000}{50} \right) \left( \frac{46.01}{62.01} \right) (S-B) \quad \text{Eq. 7D-2} \\ &= 3710 (S-B) \end{aligned}$$

Where:

250 = Volume of prepared sample, ml.

1000 = Total volume of  $\text{KMnO}_4$  solution, ml.

50 = Aliquot of  $\text{KMnO}_4/\text{NaOH}$  solution, ml.

46.01 = Molecular weight of  $\text{NO}_3^-$ .

62.01 = Molecular weight of  $\text{NO}_2^-$ .

12.5 Sample Concentration. Same as in Method 7C, section 12.7.

### 13.0 Method Performance

13.1 Precision. The intra-laboratory relative standard deviation for a single measurement is approximately 6 percent at 200 to 270 ppm  $\text{NO}_x$ .

13.2 Bias. The method does not exhibit any bias relative to Method 7.

13.3 Range. The lower detectable limit is similar to that of Method 7C. No upper limit has been established; however, when using the recommended sampling conditions, the method has been found to collect  $\text{NO}_x$  emissions quantitatively up to 1782 mg  $\text{NO}_x/\text{m}^3$ , as  $\text{NO}_2$  (932 ppm  $\text{NO}_x$ ).

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

### 16.0 References

Same as Method 7C, section 16.0, References 1, 2, 4, and 5.

17.0 Tables, Diagrams, Flowcharts, and Validation Data

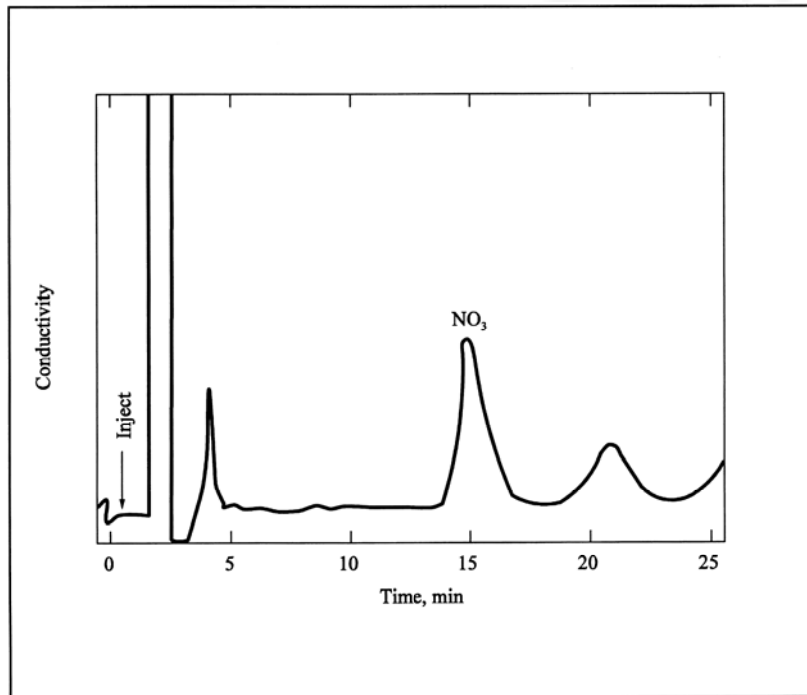


Figure 7D-1. Ion Chromatogram of a Prepared Sample.

**METHOD 7E—DETERMINATION OF NITROGEN OXIDES EMISSIONS FROM STATIONARY SOURCES (INSTRUMENTAL ANALYZER PROCEDURE)**

*1.0 Scope and Application*

*What is Method 7E?*

Method 7E is a procedure for measuring nitrogen oxides (NO<sub>x</sub>) in stationary source emissions using a continuous instrumental analyzer. Quality assurance and quality control requirements are included to assure that you, the tester, collect data of known quality. You must document your adherence to these specific requirements for equipment, supplies, sample collection and analysis, cal-

culations, and data analysis. This method does not completely describe all equipment, supplies, and sampling and analytical procedures you will need but refers to other methods for some of the details. Therefore, to obtain reliable results, you should also have a thorough knowledge of these additional test methods which are found in appendix A to this part:

- (a) Method 1—Sample and Velocity Traverses for Stationary Sources.
- (b) Method 4—Determination of Moisture Content in Stack Gases.

*1.1 Analytes. What does this method determine?* This method measures the concentration of nitrogen oxides as NO<sub>2</sub>.

Analyte	CAS No.	Sensitivity
Nitric oxide (NO) .....	10102-43-9	Typically <2% of Calibration Span <sub>1</sub>
Nitrogen dioxide (NO <sub>2</sub> ) .....	10102-44-0	

*1.2 Applicability. When is this method required?* The use of Method 7E may be required by specific New Source Performance Standards, Clean Air Marketing rules, State Implementation Plans, and permits where

measurement of NO<sub>x</sub> concentrations in stationary source emissions is required, either to determine compliance with an applicable

emissions standard or to conduct performance testing of a continuous monitoring system (CEMS). Other regulations may also require the use of Method 7E.

**1.3 Data Quality Objectives (DQO).** *How good must my collected data be?* Method 7E is designed to provide high-quality data for determining compliance with Federal and State emission standards and for relative accuracy testing of CEMS. In these and other applications, the principal objective is to ensure the accuracy of the data at the actual emission levels encountered. To meet this objective, the use of EPA traceability protocol calibration gases and measurement system performance tests are required.

**1.4 Data Quality Assessment for Low Emitters.** *Is performance relief granted when testing low-emission units?* Yes. For low-emitting sources, there are alternative performance specifications for analyzer calibration error, system bias, drift, and response time. Also, the alternative dynamic spiking procedure in section 16 may provide performance relief for certain low-emitting units.

#### 2.0 Summary of Method

In this method, a sample of the effluent gas is continuously sampled and conveyed to the analyzer for measuring the concentration of NO<sub>x</sub>. You may measure NO and NO<sub>2</sub> separately or simultaneously together but, for the purposes of this method, NO<sub>x</sub> is the sum of NO and NO<sub>2</sub>. You must meet the performance requirements of this method to validate your data.

#### 3.0 Definitions

**3.1 Analyzer Calibration Error,** for non-dilution systems, means the difference between the manufacturer certified concentration of a calibration gas and the measured concentration of the same gas when it is introduced into the analyzer in direct calibration mode.

**3.2 Calibration Curve** means the relationship between an analyzer's response to the injection of a series of calibration gases and the actual concentrations of those gases.

**3.3 Calibration Gas** means the gas mixture containing NO<sub>x</sub> at a known concentration and produced and certified in accordance with "EPA Traceability Protocol for Assay and Certification of Gaseous Calibration Standards," September 1997, as amended August 25, 1999, EPA-600/R-97/121 or more recent updates. The tests for analyzer calibration error, drift, and system bias require the use of calibration gas prepared according to this protocol. If a zero gas is used for the low-level gas, it must meet the requirements under the definition for "zero air material" in 40 CFR 72.2 in place of being prepared by the traceability protocol.

**3.3.1 Low-Level Gas** means a calibration gas with a concentration that is less than 20 per-

cent of the calibration span and may be a zero gas.

**3.3.2 Mid-Level Gas** means a calibration gas with a concentration that is 40 to 60 percent of the calibration span.

**3.3.3 High-Level Gas** means a calibration gas with a concentration that is equal to the calibration span.

**3.4 Calibration Span** means the upper limit of the analyzer's calibration that is set by the choice of high-level calibration gas. No valid run average concentration may exceed the calibration span. To the extent practicable, the measured emissions should be between 20 to 100 percent of the selected calibration span. This may not be practicable in some cases of low-concentration measurements or testing for compliance with an emission limit when emissions are substantially less than the limit. In such cases, calibration spans that are practicable to achieving the data quality objectives without being excessively high should be chosen.

**3.5 Centroidal Area** means the central area of the stack or duct that is no greater than 1 percent of the stack or duct cross section. This area has the same geometric shape as the stack or duct.

**3.6 Converter Efficiency Gas** means a calibration gas with a known NO or NO<sub>2</sub> concentration and of Traceability Protocol quality.

**3.7 Data Recorder** means the equipment that permanently records the concentrations reported by the analyzer.

**3.8 Direct Calibration Mode** means introducing the calibration gases directly into the analyzer (or into the assembled measurement system at a point downstream of all sample conditioning equipment) according to manufacturer's recommended calibration procedure. This mode of calibration applies to non-dilution-type measurement systems.

**3.9 Drift** means the difference between the pre- and post-run system bias (or system calibration error) checks at a specific calibration gas concentration level (*i.e.* low-, mid- or high-).

**3.10 Gas Analyzer** means the equipment that senses the gas being measured and generates an output proportional to its concentration.

**3.11 Interference Check** means the test to detect analyzer responses to compounds other than the compound of interest, usually a gas present in the measured gas stream, that is not adequately accounted for in the calibration procedure and may cause measurement bias.

**3.12 Low-Concentration Analyzer** means any analyzer that operates with a calibration span of 20 ppm NO<sub>x</sub> or lower. Each analyzer model used routinely to measure low NO<sub>x</sub> concentrations must pass a manufacturer's stability test (MST). An MST subjects the analyzer to a range of line voltages and temperatures that reflect potential field conditions to demonstrate its stability following



procedures similar to those provided in 40 CFR 53.23. Ambient-level analyzers are exempt from the MST requirements of section 16.3. A copy of this information must be included in each test report. Table 7E-5 lists the criteria to be met.

**3.13 Measurement System** means all of the equipment used to determine the NO<sub>x</sub> concentration. The measurement system comprises six major subsystems: Sample acquisition, sample transport, sample conditioning, calibration gas manifold, gas analyzer, and data recorder.

**3.14 Response Time** means the time it takes the measurement system to respond to a change in gas concentration occurring at the sampling point when the system is operating normally at its target sample flow rate or dilution ratio.

**3.15 Run** means a series of gas samples taken successively from the stack or duct. A test normally consists of a specific number of runs.

**3.16 System Bias** means the difference between a calibration gas measured in direct calibration mode and in system calibration mode. System bias is determined before and after each run at the low- and mid- or high-concentration levels. For dilution-type systems, pre- and post-run system calibration error is measured rather than system bias.

**3.17 System Calibration Error** applies to dilution-type systems and means the difference between the measured concentration of low-, mid-, or high-level calibration gas and the certified concentration for each gas when introduced in system calibration mode. For dilution-type systems, a 3-point system calibration error test is conducted in lieu of the analyzer calibration error test, and 2-point system calibration error tests are conducted in lieu of system bias tests.

**3.18 System Calibration Mode** means introducing the calibration gases into the measurement system at the probe, upstream of the filter and all sample conditioning components.

**3.19 Test** refers to the series of runs required by the applicable regulation.

#### 4.0 Interferences

Note that interferences may vary among instruments and that instrument-specific interferences must be evaluated through the interference test.

#### 5.0 Safety

*What safety measures should I consider when using this method?* This method may require you to work with hazardous materials and in hazardous conditions. We encourage you to establish safety procedures before using the method. Among other precautions, you should become familiar with the safety recommendations in the gas analyzer user's manual, Occupational Safety and Health Ad-

ministration (OSHA) regulations concerning cylinder and noxious gases may apply. Nitric oxide and NO<sub>2</sub> are toxic and dangerous gases. Nitric oxide is immediately converted to NO<sub>2</sub> upon reaction with air. Nitrogen dioxide is a highly poisonous and insidious gas. Inflammation of the lungs from exposure may cause only slight pain or pass unnoticed, but the resulting edema several days later may cause death. A concentration of 100 ppm is dangerous for even a short exposure, and 200 ppm may be fatal. Calibration gases must be handled with utmost care and with adequate ventilation. Emission-level exposure to these gases should be avoided.

#### 6.0 Equipment and Supplies

The performance criteria in this method will be met or exceeded if you are properly using equipment designed for this application.

**6.1** What do I need for the measurement system? You may use any equipment and supplies meeting the following specifications:

(1) Sampling system components that are not evaluated in the system bias or system calibration error test must be glass, Teflon, or stainless steel. Other materials are potentially acceptable, subject to approval by the Administrator.

(2) The interference, calibration error, and system bias criteria must be met.

(3) Sample flow rate must be maintained within 10 percent of the flow rate at which the system response time was measured.

(4) All system components (excluding sample conditioning components, if used) must maintain the sample temperature above the moisture dew point. Ensure minimal contact between any condensate and the sample gas. Section 6.2 provides example equipment specifications for a NO<sub>x</sub> measurement system. Figure 7E-1 is a diagram of an example dry-basis measurement system that is likely to meet the method requirements and is provided as guidance. For wet-basis systems, you may use alternative equipment and supplies as needed (some of which are described in Section 6.2), provided that the measurement system meets the applicable performance specifications of this method.

#### 6.2 Measurement System Components

**6.2.1 Sample Probe.** Glass, stainless steel, or other approved material, of sufficient length to traverse the sample points.

**6.2.2 Particulate Filter.** An in-stack or out-of-stack filter. The filter must be made of material that is non-reactive to the gas being sampled. The filter media for out-of-stack filters must be included in the system bias test. The particulate filter requirement may be waived in applications where no significant particulate matter is expected (e.g., for emission testing of a combustion turbine firing natural gas).

**6.2.3 Sample Line.** The sample line from the probe to the conditioning system/sample pump should be made of Teflon or other material that does not absorb or otherwise alter the sample gas. For a dry-basis measurement system (as shown in Figure 7E-1), the temperature of the sample line must be maintained at a sufficiently high level to prevent condensation before the sample conditioning components. For wet-basis measurement systems, the temperature of the sample line must be maintained at a sufficiently high level to prevent condensation before the analyzer.

**6.2.4 Conditioning Equipment.** For dry basis measurements, a condenser, dryer or other suitable device is required to remove moisture continuously from the sample gas. Any equipment needed to heat the probe or sample line to avoid condensation prior to the sample conditioning component is also required.

For wet basis systems, you must keep the sample above its dew point either by: (1) Heating the sample line and all sample transport components up to the inlet of the analyzer (and, for hot-wet extractive systems, also heating the analyzer) or (2) by diluting the sample prior to analysis using a dilution probe system. The components required to do either of the above are considered to be conditioning equipment.

**6.2.5 Sampling Pump.** For systems similar to the one shown in Figure 7E-1, a leak-free pump is needed to pull the sample gas through the system at a flow rate sufficient to minimize the response time of the measurement system. The pump may be constructed of any material that is non-reactive to the gas being sampled. For dilution-type measurement systems, an ejector pump (eductor) is used to create a vacuum that draws the sample through a critical orifice at a constant rate.

**6.2.6 Calibration Gas Manifold.** Prepare a system to allow the introduction of calibration gases either directly to the gas analyzer in direct calibration mode or into the measurement system, at the probe, in system calibration mode, or both, depending upon the type of system used. In system calibration mode, the system should be able to flood the sampling probe and vent excess gas. Alternatively, calibration gases may be introduced at the calibration valve following the probe. Maintain a constant pressure in the gas manifold. For in-stack dilution-type systems, a gas dilution subsystem is required to transport large volumes of purified air to the sample probe and a probe controller is needed to maintain the proper dilution ratio.

**6.2.7 Sample Gas Manifold.** For the type of system shown in Figure 7E-1, the sample gas manifold diverts a portion of the sample to the analyzer, delivering the remainder to the by-pass discharge vent. The manifold should also be able to introduce calibration gases

directly to the analyzer (except for dilution-type systems). The manifold must be made of material that is non-reactive to the gas sampled or the calibration gas and be configured to safely discharge the bypass gas.

**6.2.8 NO<sub>x</sub> Analyzer.** An instrument that continuously measures NO<sub>x</sub> in the gas stream and meets the applicable specifications in section 13.0. An analyzer that operates on the principle of chemiluminescence with an NO<sub>2</sub> to NO converter is one example of an analyzer that has been used successfully in the past. Analyzers operating on other principles may also be used provided the performance criteria in section 13.0 are met.

**6.2.8.1 Dual Range Analyzers.** For certain applications, a wide range of gas concentrations may be encountered, necessitating the use of two measurement ranges. Dual-range analyzers are readily available for these applications. These analyzers are often equipped with automated range-switching capability, so that when readings exceed the full-scale of the low measurement range, they are recorded on the high range. As an alternative to using a dual-range analyzer, you may use two segments of a single, large measurement scale to serve as the low and high ranges. In all cases, when two ranges are used, you must quality-assure both ranges using the proper sets of calibration gases. You must also meet the interference, calibration error, system bias, and drift checks. However, we caution that when you use two segments of a large measurement scale for dual range purposes, it may be difficult to meet the performance specifications on the low range due to signal-to-noise ratio considerations.

**6.2.8.2 Low Concentration Analyzer.** When an analyzer is routinely calibrated with a calibration span of 20 ppmv or less, the manufacturer's stability test (MST) is required. See Table 7E-5 for test parameters.

**6.2.9 Data Recording.** A strip chart recorder, computerized data acquisition system, digital recorder, or data logger for recording measurement data may be used.

## 7.0 Reagents and Standards

**7.1 Calibration Gas.** What calibration gases do I need? Your calibration gas must be NO in N<sub>2</sub> and certified (or recertified) within an uncertainty of 2.0 percent in accordance with "EPA Traceability Protocol for Assay and Certification of Gaseous Calibration Standards" September 1997, as amended August 25, 1999, EPA-600/R-97/121. Blended gases meeting the Traceability Protocol are allowed if the additional gas components are shown not to interfere with the analysis. If a zero gas is used for the low-level gas, it must meet the requirements under the definition for "zero air material" in 40 CFR 72.2. The calibration gas must not be used after its expiration date. Except for applications under part 75 of

this chapter, it is acceptable to prepare calibration gas mixtures from EPA Traceability Protocol gases in accordance with Method 205 in appendix M to part 51 of this chapter. For part 75 applications, the use of Method 205 is subject to the approval of the Administrator. The goal and recommendation for selecting calibration gases is to bracket the sample concentrations. The following calibration gas concentrations are required:

**7.1.1 High-Level Gas.** This concentration is chosen to set the calibration span as defined in Section 3.4.

**7.1.2 Mid-Level Gas.** 40 to 60 percent of the calibration span.

**7.1.3 Low-Level Gas.** Less than 20 percent of the calibration span.

**7.1.4 Converter Efficiency Gas.** *What reagents do I need for the converter efficiency test?* The converter efficiency gas is a manufacturer-certified gas with a concentration sufficient to show NO<sub>2</sub> conversion at the concentrations encountered in the source. A test gas concentration in the 40 to 60 ppm range is suggested, but other concentrations may be more appropriate to specific sources. For the test described in section 8.2.4.1, NO<sub>2</sub> is required. For the alternative converter efficiency tests in section 16.2, NO is required.

**7.2 Interference Check.** *What reagents do I need for the interference check?* Use the appropriate test gases listed in Table 7E-3 or others not listed that can potentially interfere (as indicated by the test facility type, instrument manufacturer, etc.) to conduct the interference check. These gases should be manufacturer certified but do not have to be prepared by the EPA traceability protocol.

### 8.0 Sample Collection, Preservation, Storage, and Transport

#### Emission Test Procedure

Since you are allowed to choose different options to comply with some of the performance criteria, it is your responsibility to identify the specific options you have chosen, to document that the performance criteria for that option have been met, and to identify any deviations from the method.

**8.1 What sampling site and sampling points do I select?**

**8.1.1** Unless otherwise specified in an applicable regulation or by the Administrator, when this method is used to determine compliance with an emission standard, conduct a stratification test as described in section 8.1.2 to determine the sampling traverse points to be used. For performance testing of continuous emission monitoring systems, follow the sampling site selection and traverse point layout procedures described in the appropriate performance specification or applicable regulation (e.g., Performance Specification 2 in appendix B to this part).

**8.1.2 Determination of Stratification.** Perform a stratification test at each test site to

determine the appropriate number of sample traverse points. If testing for multiple pollutants or diluents at the same site, a stratification test using only one pollutant or diluent satisfies this requirement. A stratification test is not required for small stacks that are less than 4 inches in diameter. To test for stratification, use a probe of appropriate length to measure the NO<sub>x</sub> (or pollutant of interest) concentration at 12 traverse points located according to Table 1-1 or Table 1-2 of Method 1. Alternatively, you may measure at three points on a line passing through the centroidal area. Space the three points at 16.7, 50.0, and 83.3 percent of the measurement line. Sample for a minimum of twice the system response time (see section 8.2.6) at each traverse point. Calculate the individual point and mean NO<sub>x</sub> concentrations. If the concentration at each traverse point differs from the mean concentration for all traverse points by no more than: ±5.0 percent of the mean concentration; or ±0.5 ppm (whichever is less restrictive), the gas stream is considered unstratified, and you may collect samples from a single point that most closely matches the mean. If the 5.0 percent or 0.5 ppm criterion is not met, but the concentration at each traverse point differs from the mean concentration for all traverse points by not more than: ±10.0 percent of the mean concentration; or ±1.0 ppm (whichever is less restrictive), the gas stream is considered to be minimally stratified and you may take samples from three points. Space the three points at 16.7, 50.0, and 83.3 percent of the measurement line. Alternatively, if a 12-point stratification test was performed and the emissions were shown to be minimally stratified (all points within ± 10.0 percent of their mean or within ±1.0 ppm), and if the stack diameter (or equivalent diameter, for a rectangular stack or duct) is greater than 2.4 meters (7.8 ft), then you may use 3-point sampling and locate the three points along the measurement line exhibiting the highest average concentration during the stratification test at 0.4, 1.2 and 2.0 meters from the stack or duct wall. If the gas stream is found to be stratified because the 10.0 percent or 1.0 ppm criterion for a 3-point test is not met, locate 12 traverse points for the test in accordance with Table 1-1 or Table 1-2 of Method 1.

**8.2 Initial Measurement System Performance Tests.** *What initial performance criteria must my system meet before I begin collecting samples?* Before measuring emissions, perform the following procedures:

- (a) Calibration gas verification,
- (b) Measurement system preparation,
- (c) Calibration error test,
- (d) NO<sub>2</sub> to NO conversion efficiency test, if applicable,
- (e) System bias check,
- (f) System response time test, and
- (g) Interference check

**8.2.1 Calibration Gas Verification.** How must I verify the concentrations of my calibration gases? Obtain a certificate from the gas manufacturer documenting the quality of the gas. Confirm that the manufacturer certification is complete and current. Ensure that your calibration gas certifications have not expired. This documentation should be available on-site for inspection. To the extent practicable, select a high-level gas concentration that will result in the measured emissions being between 20 and 100 percent of the calibration span.

**8.2.2 Measurement System Preparation.** How do I prepare my measurement system? Assemble, prepare, and precondition the measurement system according to your standard operating procedure. Adjust the system to achieve the correct sampling rate or dilution ratio (as applicable).

**8.2.3 Calibration Error Test.** How do I confirm my analyzer calibration is correct? After you have assembled, prepared and calibrated your sampling system and analyzer, you must conduct a 3-point analyzer calibration error test (or a 3-point system calibration error test for dilution systems) before the first run and again after any failed system bias test (or 2-point system calibration error test for dilution systems) or failed drift test. Introduce the low-, mid-, and high-level calibration gases sequentially. For non-dilution-type measurement systems, introduce the gases in direct calibration mode. For dilution-type measurement systems, introduce the gases in system calibration mode.

(1) For non-dilution systems, you may adjust the system to maintain the correct flow rate at the analyzer during the test, but you may not make adjustments for any other purpose. For dilution systems, you must operate the measurement system at the appropriate dilution ratio during all system calibration error checks, and may make only the adjustments necessary to maintain the proper ratio.

(2) Record the analyzer's response to each calibration gas on a form similar to Table 7E-1. For each calibration gas, calculate the analyzer calibration error using Equation 7E-1 in section 12.2 or the system calibration error using Equation 7E-3 in section 12.4 (as applicable). The calibration error specification in section 13.1 must be met for the low-, mid-, and high-level gases. If the calibration error specification is not met, take corrective action and repeat the test until an acceptable 3-point calibration is achieved.

**8.2.4 NO<sub>2</sub> to NO Conversion Efficiency Test.** Before or after each field test, you must conduct an NO<sub>2</sub> to NO conversion efficiency test if your system converts NO<sub>2</sub> to NO before analyzing for NO<sub>x</sub>. You may risk testing multiple facilities before performing this test provided you pass this test at the conclusion of the final facility test. A failed final conversion efficiency test in this case

will invalidate all tests performed subsequent to the test in which the converter efficiency test was passed. Follow the procedures in section 8.2.4.1, or 8.2.4.2. If desired, the converter efficiency factor derived from this test may be used to correct the test results for converter efficiency if the NO<sub>2</sub> fraction in the measured test gas is known. Use Equation 7E-8 in section 12.8 for this correction.

**8.2.4.1** Introduce NO<sub>2</sub> converter efficiency gas to the analyzer in direct calibration mode and record the NO<sub>x</sub> concentration displayed by the analyzer. Calculate the converter efficiency using Equation 7E-7 in section 12.7. The specification for converter efficiency in section 13.5 must be met. The user is cautioned that state-of-the-art NO<sub>2</sub> calibration gases may have limited shelf lives, and this could affect the ability to pass the 90-percent conversion efficiency requirement.

**8.2.4.2** Alternatively, either of the procedures for determining conversion efficiency using NO in section 16.2 may be used.

**8.2.5 Initial System Bias and System Calibration Error Checks.** Before sampling begins, determine whether the high-level or mid-level calibration gas best approximates the emissions and use it as the upscale gas. Introduce the upscale gas at the probe upstream of all sample conditioning components in system calibration mode. Record the time it takes for the measured concentration to increase to a value that is at least 95 percent or within 0.5 ppm (whichever is less restrictive) of a stable response for both the low-level and upscale gases. Continue to observe the gas concentration reading until it has reached a final, stable value. Record this value on a form similar to Table 7E-2.

(1) Next, introduce the low-level gas in system calibration mode and record the time required for the concentration response to decrease to a value that is within 5.0 percent or 0.5 ppm (whichever is less restrictive) of the certified low-range gas concentration. If the low-level gas is a zero gas, use the procedures described above and observe the change in concentration until the response is 0.5 ppm or 5.0 percent of the upscale gas concentration (whichever is less restrictive).

(2) Continue to observe the low-level gas reading until it has reached a final, stable value and record the result on a form similar to Table 7E-2. Operate the measurement system at the normal sampling rate during all system bias checks. Make only the adjustments necessary to achieve proper calibration gas flow rates at the analyzer.

(3) From these data, calculate the measurement system response time (see section 8.2.6) and then calculate the initial system bias using Equation 7E-2 in section 12.3. For dilution systems, calculate the system calibration error in lieu of system bias using

equation 7E-3 in section 12.4. See section 13.2 for acceptable performance criteria for system bias and system calibration error. If the initial system bias (or system calibration error) specification is not met, take corrective action. Then, you must repeat the applicable calibration error test from section 8.2.3 and the initial system bias (or 2-point system calibration error) check until acceptable results are achieved, after which you may begin sampling.

(NOTE: For dilution-type systems, data from the 3-point system calibration error test described in section 8.2.3 may be used to meet the initial 2-point system calibration error test requirement of this section, if the calibration gases were injected as described in this section, and if response time data were recorded).

**8.2.6 Measurement System Response Time.** As described in section 8.2.5, you must determine the measurement system response time during the initial system bias (or 2-point system calibration error) check. Observe the times required to achieve 95 percent of a stable response for both the low-level and upscale gases. The longer interval is the response time.

**8.2.7 Interference Check.** Conduct an interference response test of the gas analyzer prior to its initial use in the field. If you have multiple analyzers of the same make and model, you need only perform this alternative interference check on one analyzer. You may also meet the interference check requirement if the instrument manufacturer performs this or a similar check on an analyzer of the same make and model of the analyzer that you use and provides you with documented results.

(1) You may introduce the appropriate interference test gases (that are potentially encountered during a test; see examples in Table 7E-3) into the analyzer separately or as mixtures. Test the analyzer with the interference gas alone at the highest concentration expected at a test source and again with the interference gas and NO<sub>x</sub> at a representative NO<sub>x</sub> test concentration. For analyzers measuring NO<sub>x</sub> greater than 20 ppm, use a calibration gas with a NO<sub>x</sub> concentration of 80 to 100 ppm and set this concentration equal to the calibration span. For analyzers measuring less than 20 ppm NO<sub>x</sub>, select an NO concentration for the calibration span that reflects the emission levels at the sources to be tested, and perform the interference check at that level. Measure the total interference response of the analyzer to these gases in ppmv. Record the responses and determine the interference using Table 7E-4. The specification in section 13.4 must be met.

(2) A copy of this data, including the date completed and signed certification, must be available for inspection at the test site and

included with each test report. This interference test is valid for the life of the instrument unless major analytical components (*e.g.*, the detector) are replaced with different model parts. If major components are replaced with different model parts, the interference gas check must be repeated before returning the analyzer to service. If major components are replaced, the interference gas check must be repeated before returning the analyzer to service. The tester must ensure that any specific technology, equipment, or procedures that are intended to remove interference effects are operating properly during testing.

**8.3 Dilution-Type Systems—Special Considerations.** When a dilution-type measurement system is used, there are three important considerations that must be taken into account to ensure the quality of the emissions data. First, the critical orifice size and dilution ratio must be selected properly so that the sample dew point will be below the sample line and analyzer temperatures. Second, a high-quality, accurate probe controller must be used to maintain the dilution ratio during the test. The probe controller should be capable of monitoring the dilution air pressure, eductor vacuum, and sample flow rates. Third, differences between the molecular weight of calibration gas mixtures and the stack gas molecular weight must be addressed because these can affect the dilution ratio and introduce measurement bias.

#### **8.4 Sample Collection.**

(1) Position the probe at the first sampling point. Purge the system for at least two times the response time before recording any data. Then, traverse all required sampling points, sampling at each point for an equal length of time and maintaining the appropriate sample flow rate or dilution ratio (as applicable). You must record at least one valid data point per minute during the test run.

(2) Each time the probe is removed from the stack and replaced, you must recondition the sampling system for at least two times the system response time prior to your next recording. If the average of any run exceeds the calibration span value, that run is invalid.

(3) You may satisfy the multipoint traverse requirement by sampling sequentially using a single-hole probe or a multi-hole probe designed to sample at the prescribed points with a flow within 10 percent of mean flow rate. Notwithstanding, for applications under part 75 of this chapter, the use of multi-hole probes is subject to the approval of the Administrator.

#### **8.5 Post-Run System Bias Check and Drift Assessment.**

How do I confirm that each sample I collect is valid? After each run, repeat the system bias check or 2-point system calibration error check (for dilution systems) to validate

the run. Do not make adjustments to the measurement system (other than to maintain the target sampling rate or dilution ratio) between the end of the run and the completion of the post-run system bias or system calibration error check. Note that for all post-run system bias or 2-point system calibration error checks, you may inject the low-level gas first and the upscale gas last, or vice-versa. You may risk sampling for multiple runs before performing the post-run bias or system calibration error check provided you pass this test at the conclusion of the group of runs. A failed final test in this case will invalidate all runs subsequent to the last passed test.

(1) If you do not pass the post-run system bias (or system calibration error) check, then the run is invalid. You must diagnose and fix the problem and pass another calibration error test (Section 8.2.3) and system bias (or 2-point system calibration error) check (Section 8.2.5) before repeating the run. Record the system bias (or system calibration error) results on a form similar to Table 7E-2.

(2) After each run, calculate the low-level and upscale drift, using Equation 7E-4 in section 12.5. If the post-run low- and upscale bias (or 2-point system calibration error) checks are passed, but the low-or upscale drift exceeds the specification in section 13.3, the run data are valid, but a 3-point calibration error test and a system bias (or 2-point system calibration error) check must be performed and passed before any more test runs are done.

(3) For dilution systems, data from a 3-point system calibration error test may be used to met the pre-run 2-point system calibration error requirement for the first run in a test sequence. Also, the post-run bias (or 2-point calibration error) check data may be used as the pre-run data for the next run in

the test sequence at the discretion of the tester.

**8.6 Alternative Interference and System Bias Checks (Dynamic Spike Procedure).** *If I want to use the dynamic spike procedure to validate my data, what procedure should I follow?* Except for applications under part 75 of this chapter, you may use the dynamic spiking procedure and requirements provided in section 16.1 during each test as an alternative to the interference check and the pre- and post-run system bias checks. The calibration error test is still required under this option. Use of the dynamic spiking procedure for Part 75 applications is subject to the approval of the Administrator.

**8.7 Moisture correction.** You must determine the moisture content of the flue gas and correct the measured gas concentrations to a dry basis using Method 4 or other appropriate methods, subject to the approval of the Administrator, when the moisture basis (wet or dry) of the measurements made with this method is different from the moisture basis of either: (1) The applicable emissions limit; or (2) the CEMS being evaluated for relative accuracy. Moisture correction is also required if the applicable limit is in lb/mmBtu and the moisture basis of the Method 7E NO<sub>x</sub> analyzer is different from the moisture basis of the Method 3A diluent gas (CO<sub>2</sub> or O<sub>2</sub>) analyzer.

9.0 Quality Control

What quality control measures must I take?

The following table is a summary of the mandatory, suggested, and alternative quality assurance and quality control measures and the associated frequency and acceptance criteria. All of the QC data, along with the sample run data, must be documented and included in the test report.

SUMMARY TABLE OF AQ/QC

Status	Process or element	QA/QC specification	Acceptance criteria	Checking frequency
S .....	Identify Data User .....		Regulatory Agency or other primary end user of data.	Before designing test.
S .....	Analyzer Design .....	Analyzer resolution or sensitivity.	<2.0% of full-scale range .....	Manufacturer design.
M .....		Interference gas check.	Sum of responses ≤2.5% of calibration span Alternatively, sum of responses: ≤0.5 ppmv for calibration spans of 5 to 10 ppmv. ≤0.2 ppmv for calibration spans <5 ppmv. See Table 7E-3.	
M .....	Calibration Gases .....	Traceability protocol (G1, G2).	Valid certificate required Uncertainty ≤2.0% of tag value.	
M .....		High-level gas .....	Equal to the calibration span .....	Each test.
M .....		Mid-level gas .....	40 to 60% of calibration span .....	Each test.
M .....		Low-level gas .....	<20% of calibration span .....	Each test.
S .....	Data Recorder Design.	Data resolution .....	≤0.5% of full-scale range .....	Manufacturer design.
S .....	Sample Extraction .....	Probe material .....	SS or quartz if stack >500 °F .....	East test.
M .....	Sample Extraction .....	Probe, filter and sample line temperature.	For dry-basis analyzers, keep sample above the dew point by heating, prior to sample conditioning.	Each run.