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METHOD 8—DETERMINATION OF SULFURIC ACID AND 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 6.

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS No.	Sensitivity
Sulfuric acid, including: Sulfuric acid (H ₂ SO ₄) mist, Sulfur trioxide (SO ₃)	7664-93-9, 7449-11-9	0.05 mg/m ³ (0.03 × 10 ⁻⁷ lb/ft ³).
Sulfur dioxide (SO ₂)	7449-09-5	1.2 mg/m ³ (3 × 10 ⁻⁹ lb/ft ³).

1.2 Applicability. This method is applicable for the determination of H₂SO₄ (including H₂SO₄ mist and SO₃) and gaseous SO₂ emissions from stationary sources.

NOTE: Filterable particulate matter may be determined along with H₂SO₄ and SO₂ (subject to the approval of the Administrator) by inserting a heated glass fiber filter between the probe and isopropanol impinger (see section 6.1.1 of Method 6). If this option is chosen, particulate analysis is gravimetric only; sulfuric acid is not determined separately.

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 gas sample is extracted isokinetically from the stack. The H₂SO₄ and the SO₂ are separated, and both fractions are measured separately by the barium-thorin titration method.

3.0 Definitions [Reserved]

4.0 Interferences

4.1 Possible interfering agents of this method are fluorides, free ammonia, and dimethyl aniline. If any of these interfering agents is present (this can be determined by knowledge of the process), alternative methods, subject to the approval of the Administrator, are required.

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 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 5, section 6.1, with the following additions and exceptions:

6.1.1 Sampling Train. A schematic of the sampling train used in this method is shown in Figure 8-1; it is similar to the Method 5 sampling train, except that the filter position is different, and the filter holder does not have to be heated. See Method 5, section 6.1.1, for details and guidelines on operation and maintenance.

6.1.1.1 Probe Nozzle. Borosilicate or quartz glass with a sharp, tapered leading edge and coupled to the probe liner using a polytetrafluoroethylene (PTFE) or glass-lined union (*e.g.*, fused silica, Slico, or equivalent). When the stack temperature exceeds 210 °C (410 °F), a leak-free ground glass fitting or other leak free, non-contaminating fitting must be used to couple the nozzle to the probe liner. It is also acceptable to use a one-piece glass nozzle/liner assembly. The angle of the taper shall be $\leq 30^\circ$, and the taper shall be on the outside to preserve a constant internal diameter. The probe nozzle shall be of the button-hook or elbow design, unless otherwise specified by the Administrator. Other materials of construction may be used, subject to the approval of the Administrator. A range of nozzle sizes suitable for isokinetic sampling should be available. Typical nozzle sizes range from 0.32 to 1.27 cm ($\frac{1}{8}$ to $\frac{1}{2}$ in) inside diameter (ID) in increments of 0.16 cm ($\frac{1}{16}$ in). Larger nozzle sizes are also available if higher volume sampling trains are used.

6.1.1.2 Probe Liner. Borosilicate or quartz glass, with a heating system to prevent visible condensation during sampling. Do not use metal probe liners.

6.1.1.3 Filter Holder. Borosilicate glass, with a glass frit filter support and a silicone rubber gasket. Other gasket materials (*e.g.*, Teflon or Viton) may be used, subject to the approval of the Administrator. The holder design shall provide a positive seal against leakage from the outside or around the filter. The filter holder shall be placed between the first and second impingers. Do not heat the filter holder.

6.1.1.4 Impingers. Four, of the Greenburg-Smith design, as shown in Figure 8-1. The first and third impingers must have standard tips. The second and fourth impingers must be modified by replacing the insert with an approximately 13-mm ($\frac{1}{2}$ -in.) ID glass tube, having an unstricted tip located 13 mm ($\frac{1}{2}$ in.) from the bottom of the impinger. Similar collection systems, subject to the approval of the Administrator, may be used.

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

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

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

6.2.2 Graduated Cylinders. Two graduated cylinders (volumetric flasks may be used), 250-ml, 1-liter.

6.2.3 Storage Bottles. Leak-free polyethylene bottles, 1-liter size (two for each sampling run).

6.2.4 Trip Balance. 500-g capacity, to measure to ± 0.5 g (necessary only if a moisture content analysis is to be done).

6.3 Analysis. The following items are required for sample analysis:

6.3.1 Pipettes. Volumetric 10-ml, 100-ml.

6.3.2 Burette. 50-ml.

6.3.3 Erlenmeyer Flask. 250-ml (one for each sample, blank, and standard).

6.3.4 Graduated Cylinder. 100-ml.

6.3.5 Dropping Bottle. To add indicator solution, 125-ml size.

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. The following reagents are required for sample collection:

7.1.1 Filters and Silica Gel. Same as in Method 5, sections 7.1.1 and 7.1.2, respectively.

7.1.2 Water. Same as in Method 6, section 7.1.1.

7.1.3 Isopropanol, 80 Percent by Volume. Mix 800 ml of isopropanol with 200 ml of water.

NOTE: Check for peroxide impurities using the procedure outlined in Method 6, section 7.1.2.1.

7.1.4 Hydrogen Peroxide (H_2O_2), 3 Percent by Volume. Dilute 100 ml of 30 percent H_2O_2 to 1 liter with water. Prepare fresh daily.

7.1.5 Crushed Ice.

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

7.2.1 Water. Same as in section 7.1.2.

7.2.2 Isopropanol, 80 Percent. Same as in section 7.1.3.

7.3 Sample Analysis. Same as Method 6, section 7.3.

8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Pretest Preparation. Same as Method 5, section 8.1, except that filters should be inspected but need not be desiccated, weighed, or identified. If the effluent gas can be considered dry (i.e., moisture-free), the silica gel need not be weighed.

8.2 Preliminary Determinations. Same as Method 5, section 8.2.

8.3 Preparation of Sampling Train. Same as Method 5, section 8.3, with the following exceptions:

8.3.1 Use Figure 8-1 instead of Figure 5-1.

8.3.2 Replace the second sentence of Method 5, section 8.3.1 with: Place 100 ml of 80 percent isopropanol in the first impinger, 100 ml of 3 percent H_2O_2 in both the second and third impingers; retain a portion of each reagent for use as a blank solution. Place about 200 g of silica gel in the fourth impinger.

8.3.3 Ignore any other statements in section 8.3 of Method 5 that are obviously not applicable to the performance of Method 8.

NOTE: If moisture content is to be determined by impinger analysis, weigh each of the first three impingers (plus absorbing solution) to the nearest 0.5 g, and record these weights. Weigh also the silica gel (or silica gel plus container) to the nearest 0.5 g, and record.)

8.4 Metering System Leak-Check Procedure. Same as Method 5, section 8.4.1.

8.5 Pretest Leak-Check Procedure. Follow the basic procedure in Method 5, section 8.4.2, noting that the probe heater shall be adjusted to the minimum temperature required to prevent condensation, and also that verbage such as “* * * plugging the inlet to the filter holder * * *”

found in section 8.4.2.2 of Method 5 shall be replaced by “ * * * plugging the inlet to the first impinger * * * ”. The pretest leak-check is recommended, but is not required.

8.6 Sampling Train Operation. Follow the basic procedures in Method 5, section 8.5, in conjunction with the following special instructions:

8.6.1 Record the data on a sheet similar to that shown in Figure 8-2 (alternatively, Figure 5-2 in Method 5 may be used). The sampling rate shall not exceed 0.030 m³/min (1.0 cfm) during the run. Periodically during the test, observe the connecting line between the probe and first impinger for signs of condensation. If condensation does occur, adjust the probe heater setting upward to the minimum temperature required to prevent condensation. If component changes become necessary during a run, a leak-check shall be performed immediately before each change, according to the procedure outlined in section 8.4.3 of Method 5 (with appropriate modifications, as mentioned in section 8.5 of this method); record all leak rates. If the leakage rate(s) exceeds the specified rate, the tester shall either void the run or plan to correct the sample volume as outlined in section 12.3 of Method 5. Leak-checks immediately after component changes are recommended, but not required. If these leak-checks are performed, the procedure in section 8.4.2 of Method 5 (with appropriate modifications) shall be used.

8.6.2 After turning off the pump and recording the final readings at the conclusion of each run, remove the probe from the stack. Conduct a post-test (mandatory) leak-check as outlined in section 8.4.4 of Method 5 (with appropriate modifications), and record the leak rate. If the post-test leakage rate exceeds the specified acceptable rate, either correct the sample volume, as outlined in section 12.3 of Method 5, or void the run.

8.6.3 Drain the ice bath and, with the probe disconnected, purge the remaining part of the train by drawing clean ambient air through the system for 15 minutes at the average flow rate used for sampling.

NOTE: Clean ambient air can be provided by passing air through a charcoal filter. Alternatively, ambient air (without cleaning) may be used.

8.7 Calculation of Percent Isokinetic. Same as Method 5, section 8.6.

8.8 Sample Recovery. Proper cleanup procedure begins as soon as the probe is removed from the stack at the end of the sampling period. Allow the probe to cool. Treat the samples as follows:

8.8.1 Container No. 1.

8.8.1.1 If a moisture content analysis is to be performed, clean and weigh the first impinger (plus contents) to the nearest 0.5 g, and record this weight.

8.8.1.2 Transfer the contents of the first impinger to a 250-ml graduated cylinder. Rinse the probe, first impinger, all connecting glassware before the filter, and the front half of the filter holder with 80 percent isopropanol. Add the isopropanol rinse solution to the cylinder. Dilute the contents of the cylinder to 225 ml with 80 percent isopropanol, and transfer the cylinder contents

to the storage container. Rinse the cylinder with 25 ml of 80 percent isopropanol, and transfer the rinse to the storage container. Add the filter to the solution in the storage container and mix. Seal the container to protect the solution against evaporation. Mark the level of liquid on the container, and identify the sample container.

8.8.2 Container No. 2.

8.8.2.1 If a moisture content analysis is to be performed, clean and weigh the second and third impingers (plus contents) to the nearest 0.5 g, and record the weights. Also, weigh the spent silica gel (or silica gel plus impinger) to the nearest 0.5 g, and record the weight.

8.8.2.2 Transfer the solutions from the second and third impingers to a 1-liter graduated cylinder. Rinse all connecting glassware (including back half of filter holder) between the filter and silica gel impinger with water, and add this rinse water to the cylinder. Dilute the contents of the cylinder to 950 ml with water. Transfer the solution to a storage container. Rinse the cylinder with 50 ml of water, and transfer the rinse to the storage container. Mark the level of liquid on the container. Seal and identify the sample container.

9.0 Quality Control

9.1 Miscellaneous Quality Control Measures.

Section	Quality control measure	Effect
7.1.3	Isopropanol check	Ensure acceptable level of peroxide impurities in isopropanol.
8.4, 8.5, 10.1	Sampling equipment leak-check and calibration	Ensure accurate measurement of stack gas flow rate, sample volume.
10.2	Barium standard solution standardization	Ensure normality determination.
11.2	Replicate titrations	Ensure precision of titration determinations.

9.2 Volume Metering System Checks. Same as Method 5, section 9.2.

10.0 Calibration and Standardization

10.1 Sampling Equipment. Same as Method 5, section 10.0.

10.2 Barium Standard Solution. Same as Method 6, section 10.5.

11.0 Analytical Procedure

11.1. Sample Loss. Same as Method 6, section 11.1.

11.2. Sample Analysis.

11.2.1 Container No. 1. Shake the container holding the isopropanol solution and the filter. If the filter breaks up, allow the fragments to settle for a few minutes before removing a sample aliquot. Pipette a 100-ml aliquot of this solution into a 250-ml Erlenmeyer flask, add 2 to 4 drops of thorin indicator, and titrate to a pink endpoint using 0.0100 N barium standard solution. Repeat the titration with a second aliquot of sample, and average the titration values. Replicate titrations must agree within 1 percent or 0.2 ml, whichever is greater.

11.2.2 Container No. 2. Thoroughly mix the solution in the container holding the contents of the second and third impingers. Pipette a 10-ml aliquot of sample into a 250-ml Erlenmeyer flask. Add 40 ml of isopropanol, 2 to 4 drops of thorin indicator, and titrate to a pink endpoint using 0.0100 N barium standard solution. Repeat the titration with a second aliquot of sample, and average the titration values. Replicate titrations must agree within 1 percent or 0.2 ml, whichever is greater.

11.2.3 Blanks. Prepare blanks by adding 2 to 4 drops of thorin indicator to 100 ml of 80 percent isopropanol. Titrate the blanks in the same manner as the samples.

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 Method 5, section 12.1, with the following additions and exceptions:

$C_{H_2SO_4}$ = Sulfuric acid (including SO_3) concentration, g/dscm (lb/dscf).

C_{SO_2} = Sulfur dioxide concentration, g/dscm (lb/dscf).

N = Normality of barium perchlorate titrant, meq/ml.

V_a = Volume of sample aliquot titrated, 100 ml for H_2SO_4 and 10 ml for SO_2 .

V_{soln} = Total volume of solution in which the sample is contained, 1000 ml for the SO_2 sample and 250 ml for the H_2SO_4 sample.

V_t = Volume of barium standard solution titrant used for the sample, ml.

V_{tb} = Volume of barium standard solution titrant used for the blank, ml.

12.2 Average Dry Gas Meter Temperature and Average Orifice Pressure Drop. See data sheet (Figure 8-2).

12.3 Dry Gas Volume. Same as Method 5, section 12.3.

12.4 Volume of Water Vapor Condensed and Moisture Content. Calculate the volume of water vapor using Equation 5-2 of Method 5; the weight of water collected in the impingers and silica gel can be converted directly to milliliters (the specific gravity of water is 1 g/ml). Calculate the

moisture content of the stack gas (B_{ws}) using Equation 5-3 of Method 5. The note in section 12.5 of Method 5 also applies to this method. Note that if the effluent gas stream can be considered dry, the volume of water vapor and moisture content need not be calculated.

12.5 Sulfuric Acid Mist (Including SO_3) Concentration.

$$C_{H_2SO_4} = K_3 \left[N (V_t - V_{t0}) (V_{soh} / V_a) \right] / V_{m(std)} \quad Eq. 8-1$$

Where:

$K_3 = 0.04904$ g/meq for metric units,

$K_3 = 1.081 \times 10^{-4}$ lb/meq for English units.

12.6 Sulfur Dioxide Concentration.

$$C_{SO_2} = K_4 \left[N (V_t - V_{t0}) (V_{soh} / V_a) \right] / V_{m(std)} \quad Eq. 8-2$$

Where:

$K_4 = 0.03203$ g/meq for metric units,

$K_4 = 7.061 \times 10^{-5}$ lb/meq for English units.

12.7 Isokinetic Variation. Same as Method 5, section 12.11.

12.8 Stack Gas Velocity and Volumetric Flow Rate. Calculate the average stack gas velocity and volumetric flow rate, if needed, using data obtained in this method and the equations in sections 12.6 and 12.7 of Method 2.

13.0 Method Performance

13.1 Analytical Range. Collaborative tests have shown that the minimum detectable limits of the method are 0.06 mg/m^3 ($4 \times 10^{-9} \text{ lb/ft}^3$) for H_2SO_4 and 1.2 mg/m^3 ($74 \times 10^{-9} \text{ lb/ft}^3$) for SO_2 . No upper limits have been established. Based on theoretical calculations for 200 ml of 3 percent H_2O_2 solution, the upper concentration limit for SO_2 in a 1.0 m^3 (35.3 ft^3) gas sample is about $12,000 \text{ mg/m}^3$ ($7.7 \times 10^{-4} \text{ lb/ft}^3$). The upper limit can be extended by increasing the quantity of peroxide solution in the impingers.

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

Same as section 17.0 of Methods 5 and 6.

17.0 Tables, Diagrams, Flowcharts, and Validation Data

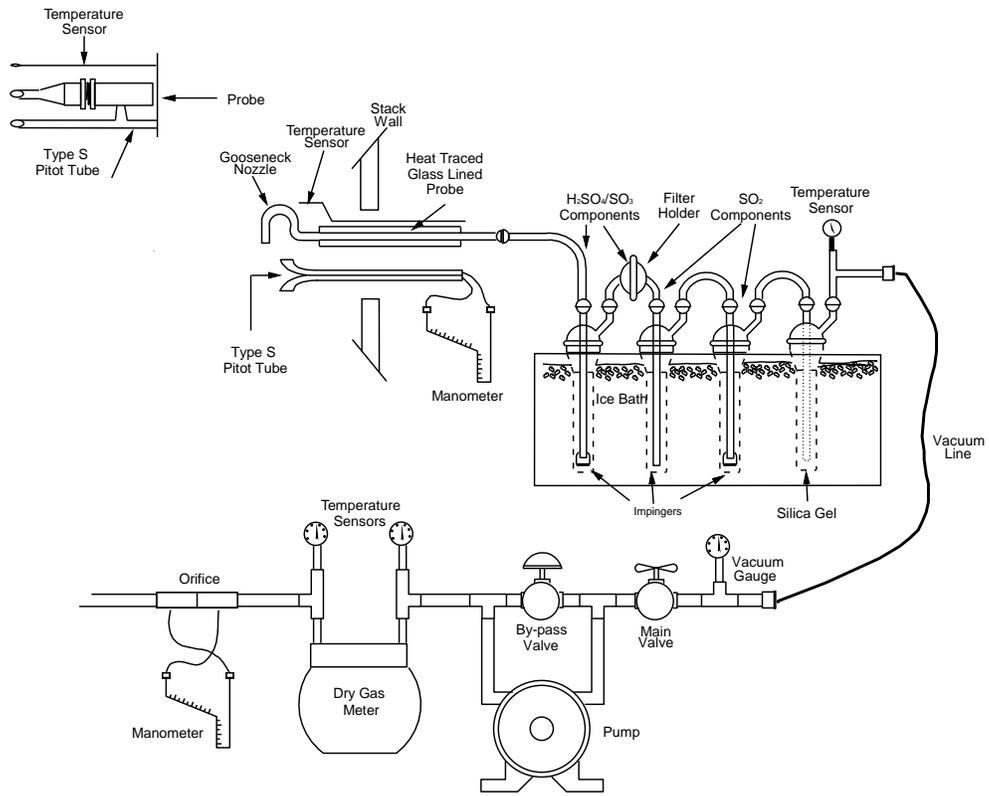


Figure 8-1. Sulfuric Acid Sampling Train

