

**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:		0.05 mg/m ³
Sulfuric acid	7664-93-9	(0.03 × 10 ⁻⁷
(H ₂ SO ₄) mist	7449-11-9	lb/ft ³)
Sulfur trioxide		
(SO 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 H_2SO_4 and the SO_2 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 Liner. Borosilicate or quartz glass, with a heating system to prevent visible condensation during sampling. Do not use metal probe liners.

6.1.1.2 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.

6.1.1.3 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.

6.1.1.4 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.

7.3.1 Quality Assurance Audit Samples. When making compliance determinations, and upon availability, audit samples may be obtained from the appropriate EPA Regional Office or from the responsible enforcement authority.

NOTE: The responsible enforcement authority should be notified at least 30 days prior to the test date to allow sufficient time for sample delivery.

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 H₂O₂ 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
11.3	Audit sample analysis	Evaluate analyst's technique and standards preparation

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.

11.3 Audit Sample Analysis.

11.3.1 When the method is used to analyze samples to demonstrate compliance with a source emission regulation, EPA audit samples must be analyzed, subject to availability.

11.3.2 Concurrently analyze audit samples and the compliance samples in the same manner to evaluate the technique of the analyst and the standards preparation.

NOTE: It is recommended that known quality control samples be analyzed prior to the compliance and audit sample analyses to optimize the system accuracy and precision. These quality control samples may be obtained by contacting the appropriate EPA regional Office or the responsible enforcement authority.

11.3.3 The same analyst, analytical reagents, and analytical system shall be used for the compliance samples and the EPA audit samples. If this condition is met, duplicate auditing of subsequent compliance analyses for the same enforcement agency within a 30-day period is waived. Audit samples may not be used to validate different compliance samples under the jurisdiction of separate enforcement agencies, unless prior arrangements have been made with both enforcement agencies.

11.4 Audit Sample Results.

11.4.1 Calculate the audit sample concentrations in mg/dscm and submit results using the instructions provided with the audit samples.

11.4.2 Report the results of the audit samples and the compliance determination samples along with their

identification numbers, and the analyst's name to the responsible enforcement authority. Include this information with reports of any subsequent compliance analyses for the same enforcement authority during the 30-day period.

11.4.3 The concentrations of the audit samples obtained by the analyst shall agree within 5 percent of the actual concentrations. If the 5 percent specification is not met, reanalyze the compliance and audit samples, and include initial and reanalysis values in the test report.

11.4.4 Failure to meet the 5 percent specification may require retests until the audit problems are resolved. However, if the audit results do not affect the compliance or noncompliance status of the affected facility, the Administrator may waive the reanalysis requirement, further audits, or retests and accept the results of the compliance test. While steps are being taken to resolve audit analysis problems, the Administrator may also choose to use the data to determine the compliance or noncompliance status of the affected facility.

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_a = Actual concentration of SO_2 in audit sample, mg/dscm.
- C_d = Determined concentration of SO_2 in audit sample, mg/dscm.
- $C_{H_2SO_4}$ = 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.
- RE = Relative error of QA audit sample analysis, percent
- 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, 250 ml for the SO_2 sample and 1000 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.

$$C_{H_2SO_4} = K_3 [N (V_t - V_{tb}) (V_{soln}/V_a)]/V_{m(std)} \quad \text{Eq. 8-1}$$

where:

$$\begin{aligned} K_3 &= 0.04904 \text{ g/meq for metric units,} \\ &= 1.081 \times 10^{-4} \text{ lb/meq for English units.} \end{aligned}$$

12.6 Sulfur Dioxide Concentration.

$$C_{SO_2} = K_4 [N (V_t - V_{tb}) (V_{soln}/V_a)]/V_{m(std)} \quad \text{Eq. 8-2}$$

where:

$$\begin{aligned} K_4 &= 0.03203 \text{ g/meq for metric units,} \\ &= 7.061 \times 10^{-5} \text{ lb/meq for English units.} \end{aligned}$$

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.

12.9 Relative Error (RE) for QA Audit Samples. Same as Method 6, Section 12.4.

13.0 Method Performance.

13.1 Analytical Range. Collaborative tests have shown that the minimum detectable limits of the method are 0.06 mg/m³ (4×10^{-9} lb/ft³) for H₂SO₄ and 1.2 mg/m³ (74×10^{-9} lb/ft³) for SO₂. No upper limits have been established. Based on theoretical calculations for 200 ml of 3 percent H₂O₂ solution, the upper concentration limit for SO₂ in a 1.0 m³ (35.3 ft³) gas sample is about 12,000 mg/m³ (7.7×10^{-4} lb/ft³). 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.

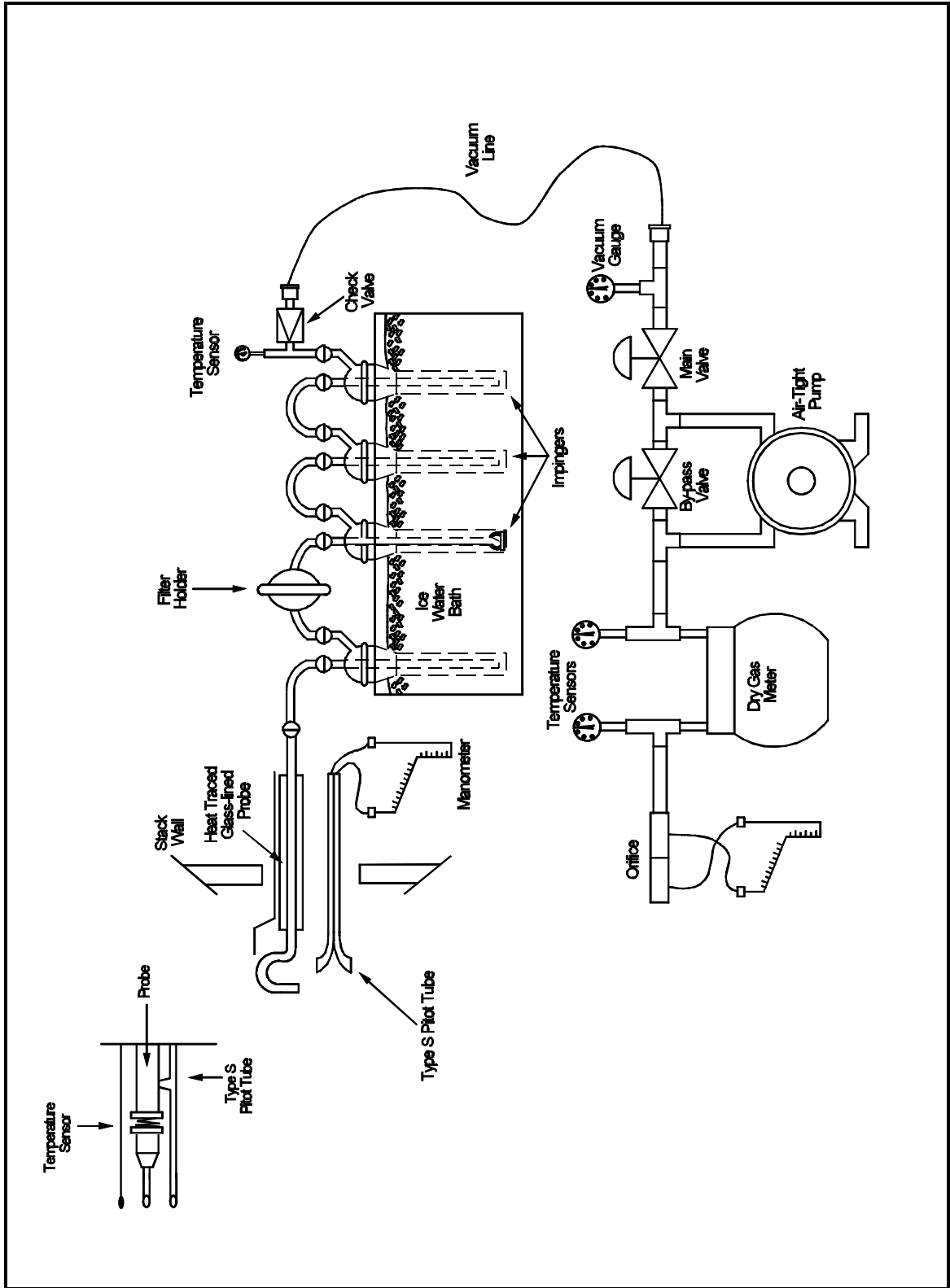


Figure 8-1. Sulfuric Acid Sampling Train.

Plant _____ Location _____ Operator _____ Date _____ Run No. _____ Sample box No. _____ Meter box No. _____ Meter ID# _____ C factor _____ Pitot tube coefficient, C p _____	<div style="border: 1px solid black; width: 150px; height: 100px; margin: 0 auto;"></div>	Ambient temperature _____ Barometric pressure _____ Assumed moisture, % _____ Probe length, (ft) _____ Nozzle identification No. _____ Average calibrated nozzle diameter, (in.) _____ Probe heater setting _____ Leak rate, (cfm) _____ Static pressure, (in. Hg) _____ Probe liner material _____ Filter No. _____	SCHEMATIC OF STACK CROSS SECTION						
Traverse point number	Sampling time	Vacuum	Stack temperature	Velocity/head	Pressure differential across orifice meter	Gas meter reading	Gas sample temperature at dry gas meter	Filter temperature	Temperature of gas leaving condenser or last impinger
	min.	(in.Hg)	(T _g) (°F)	(ΔP) (in. H ₂ O ₂)	(in. H ₂ O)	(ft)	Inlet (°F)	(°F)	(°F)
Total						Avg	Avg		
Average						Avg	Avg		

Figure 8-2. Field Data Sheet.

