Method 6 - Determination of Sulfur Dioxide Emissions from Stationary Sources

1. PRINCIPLE AND APPLICABILITY

1.1 Principle. A gas sample is extracted from the sampling point in the stack. The sulfuric acid mist (including sulfur trioxide) and the sulfur dioxide (SO_2) are separated. The SO_2 fraction is measured by the barium-thorin titration method.

1.2 Applicability.

1.2.1 This method is applicable for the determination of SO_2 emissions from stationary sources. The minimum detectable limit of the method has been determined to be 3.4 mg of SO_2/m^3 (2.12 x 10^{-7} lb/ft³). Although no upper limit has been established, tests have shown that concentrations as high as 80,000 mg/m³ of SO_2 can be collected efficiently in two midget impingers, each containing 15 ml of 3 percent hydrogen peroxide, at a rate of 1.0 liter/min for 20 minutes. Based on theoretical calculations, the upper concentration limit in a 20-liter sample is about 93,300 mg/m³.

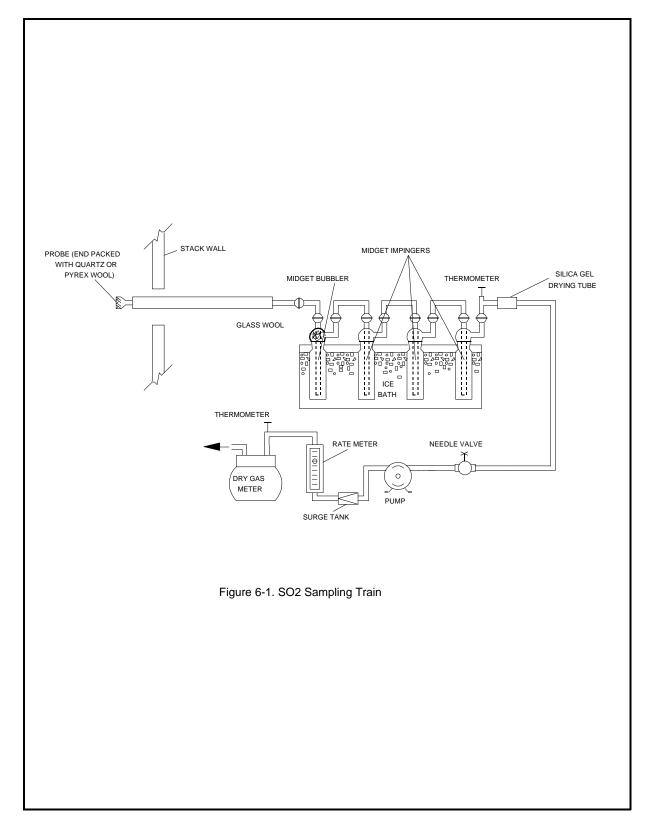
1.2.2 Possible interferants are free ammonia, water-soluble cations, and fluorides. The cations and fluorides are removed by glass wool filters and an isopropanol bubbler, and hence do not affect the SO_2 analysis. When samples are being taken from a gas stream with high concentrations of very fine metallic fumes (such as found in inlets to control devices), 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 interferants.

1.2.3 Free ammonia interferes by reacting with SO_2 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 noticing white particulate matter in the probe and isopropanol bubbler), alternative methods, subject to the approval of the Administrator, U.S. Environmental Protection Agency, are required.

2. APPARATUS

2.1 Sampling.

2.1.1 The sampling train is shown in Figure 6-1, and component parts are discussed below. The tester has the option of substituting sampling equipment described in Method 8 in place of the midget 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.



2.1.2 The tester also has the option of determining SO_2 simultaneously with particulate matter and moisture determinations by (1) replacing the water in a Method 5 impinger system with 3 percent peroxide solution, or (2) by replacing the Method 5 water impinger system with a Method 8 isopropanol-filter-peroxide system. The analysis for SO_2 must be consistent with the procedure of Method 8.

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

2.1.2 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 bubbler and midget impingers must be connected in series with leak-free glass connectors. Silicone grease may be used, if necessary, to prevent leakage.

2.1.2.1 At the option of the tester, a midget impinger may be used in place of the midget bubbler.

2.1.2.2 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 SO_2 .

2.1.3 Glass Wool. Borosilicate or quartz.

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

2.1.5 Temperature Gauge. Dial thermometer, or equivalent, to measure temperature of gas leaving impinger train to within $1^{\circ}C$ (2°F).

2.1.6 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. See also the note in Method 5, Section 3.1.2.

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

2.1.8 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 eliminate the pulsation effect of the diaphragm pump on the rotameter.

2.1.9 Rate Meter. Rotameter, or equivalent, capable of measuring flow rate to within 2 percent of the selected flow rate of about 1000 cc/min.

2.1.10 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 gauge (dial thermometer, or equivalent) capable of measuring temperature accurately to within $3^{\circ}C$ (5.4°F).

2.1.11 Barometer. Mercury, aneroid, or other barometer capable of measuring atmospheric pressure to within 2.5 mm (0.1 in.) Hg. See the note in Method 5, Section 2.1.9.

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

2.2 Sample Recovery.

2.2.1 Wash Bottles. Polyethylene or glass, 500-ml, two.

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

2.3 Analysis.

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

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

2.3.3 Burettes. 5- and 50-ml sizes.

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

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

2.3.6 Graduated Cylinder. 100-ml size.

2.3.7 Spectrophotometer. To measure absorbance at 352 nanometers.

3. REAGENTS

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.

3.1 Sampling.

3.1.1 Water. Deionized distilled to conform to ASTM Specification D 1193-77, Type 3. At the option of the analyst, the $KMn0_4$ test for oxidizable organic

matter may be omitted when high concentrations of organic matter are not expected to be present.

3.1.2 Isopropanol, 80 Percent. Mix 80 ml of isopropanol with 20 ml of water.

3.1.2.1 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 nanometers on a spectrophotometer, using a 1-cm path length. If absorbance exceeds 0.1, reject alcohol for use.

3.1.2.2 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.

3.1.3 Hydrogen Peroxide, 3 Percent. Dilute 30 percent hydrogen peroxide 1:9 (v/v) with water (30 ml is needed per sample). Prepare fresh daily.

3.1.4 Potassium Iodide Solution, 10 Percent. Dissolve 10.0 g of KI in water, and dilute to 100 ml. Prepare when needed.

3.2 Sample Recovery.

3.2.1 Water. Same as in Section 3.1.1.

3.2.2 Isopropanol, 80 Percent. Same as in Section 3.1.2.

3.3 Analysis.

3.3.1 Water. Same as in Section 3.1.1.

3.3.2 Isopropanol, 100 Percent.

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

3.3.4 Barium Standard Solution, 0.0100 N. Dissolve 1.95 g of barium perchlorate trihydrate $[Ba(Cl0_4)_2 \cdot 3H_20]$ in 200 ml water, and dilute to 1 liter with isopropanol. Alternatively, 1.22 g of barium chloride dihydrate $[BaCl_2 \cdot 2H_20]$ may be used instead of the perchlorate. Standardize as in Section 5.5.

3.3.5 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).

3.3.6 Quality Assurance Audit Samples. Sulfate samples in glass vials prepared by EPA's Atmospheric Research and Exposure Assessment Laboratory, Quality Assurance Division, Source Branch, Mail Drop 77A, Research Triangle Park, North Carolina 27711. Each set will consist of two vials having solutions of unknown concentrations. Only when making compliance determinations, obtain an audit

sample set from the Quality Assurance Management Office at each EPA regional office or the responsible enforcement agency. (Note: The tester should notify the quality assurance office or the responsible enforcement agency at least 30 days prior to the test date to allow sufficient time for sample delivery.)

4. PROCEDURE

4.1 Sampling.

4.1.1 Preparation of Collection Train. Measure 15 ml of 80 percent isopropanol into the midget bubbler and 15 ml of 3 percent hydrogen peroxide into each of the first two midget impingers. Leave the final midget impinger dry. Assemble the train as shown in Figure 6-1. Adjust probe heater to a temperature sufficient to prevent water condensation. Place crushed ice and water around the impingers.

4.1.2 Leak-Check Procedure. A leak-check prior to the sampling run is optional;

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

4.1.2.1 Temporarily attach a suitable (e.g., 0- to 40-cc/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 (10 in.) Hg, and note the flow rate as indicated by the rotameter. A leakage rate not in excess of 2 percent of the average sampling rate is acceptable. <u>Note</u>: Carefully release the probe inlet plug before turning off the pump.

4.1.2.2 It is suggested (not mandatory) that the pump be leak-checked separately, either prior to or after the sampling run. If done prior to the sampling run, the pump leak-check shall precede the leak-check of the sampling train described immediately above; if done after the sampling run, the pump leak-check shall follow the train leak-check. 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 (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.

4.1.2.3 Other leak-check procedures may be used, subject to the approval of the Administrator, U.S. Environmental Protection Agency.

4.1.3 Sample Collection.

4.1.3.1 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 rotameter. Maintain this constant rate (±10 percent) during the entire sampling run. Take readings (DGM, temperatures at DGM and at impinger outlet, and rate meter) 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. At the conclusion of each run, turn off the pump, remove probe from the stack, and record the final readings. Conduct a leak-check as in Section 4.1.2. (This leak-check is mandatory.) If a leak is found, void the test run or use procedures acceptable to the Administrator to adjust the sample volume for the leakage. 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.

4.1.3.2 Clean ambient air can be provided by passing air through a charcoal filter or through an extra midget impinger with 15 ml of 3 percent H_2O_2 . The tester may opt to use simply ambient air without purification.

4.2 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 connecting tubes with water, and add the washings to the same storage container. Mark the fluid level. Seal and identify the sample container.

4.3 Sample Analysis.

4.3.1 Note level of liquid in container, and confirm whether any sample was lost during shipment; note this on 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.

4.3.2 Transfer the contents of the 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 80 ml of 100 percent isopropanol and two to four drops of thorin indicator, and titrate to a pink endpoint using 0.0100 N barium standard solution. Repeat, 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.

4.3.3 <u>Note</u>: Protect the 0.0100 N barium standard solution from evaporation at all times.

4.4 Audit Sample Analysis.

4.4.1 Concurrently analyze the two audit samples and a set of compliance samples (Section 4.3) 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 analysis to optimize the system accuracy and precision. One source of these samples is the Source Branch listed in Section 3.3.6.) The same analysts, analytical reagents, and analytical system shall be used both for compliance samples and the EPA audit samples; if this condition is met, auditing of subsequent compliance analyses for the same enforcement agency within 30 days is not required. An audit sample set may not be used to validate different sets of compliance samples under the jurisdiction of different enforcement agencies, unless prior arrangements are made with both enforcement agencies.

4.4.2 Calculate the concentrations in mg/dscm using the specified sample volume in the audit instructions. (<u>Note</u>: Indication of acceptable results may be obtained immediately by reporting the audit results in mg/dscm and compliance results in total mg SO_2 /sample by telephone to the responsible enforcement agency.) Include the results of both audit samples, their identification numbers, and the analyst's name with the results of the compliance determination samples in appropriate reports to the EPA regional office or the appropriate enforcement agency. Include this information with subsequent compliance analyses for the same enforcement agency during the 30-day period.

4.4.3 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 samples and audit samples, and include initial and reanalysis values in the test report (see <u>Note</u> in first paragraph of this section).

4.4.4 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.

5. CALIBRATION

5.1 Metering System.

5.1.1 Initial Calibration.

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

5.1.1.2 Next, 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 drying tube. Make three independent calibrations 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. If any Y-value deviates by more than 2 percent from the average, the metering system is unacceptable for use. Otherwise, use the average as the calibration factor for subsequent test runs.

5.1.2 Post-Test Calibration Check. After each field test series, conduct a calibration check as in Section 5.1.1 above, except for the following variations: (a) the leak-check is not to be conducted, (b) three, or more revolutions of the DGM may be used, and (c) only two independent runs need be made. If the calibration factor does not deviate by more than 5 percent from the initial calibration factor (determined in Section 5.1.1), then the DGM volumes obtained during the test series are acceptable. If the calibration factor deviates by more than 5 percent, recalibrate the metering system as in Section 5.1.1, and for the calculations, use the calibration factor (initial or recalibration) that yields the lower gas volume for each test run.

5.2 Thermometers. Calibrate against mercury-in-glass thermometers.

5.3 Rotameter. The rotameter need not be calibrated, but should be cleaned and maintained according to the manufacturer's instruction.

5.4 Barometer. Calibrate against a mercury barometer.

5.5 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 a pair of duplicate analyses where the titrations agree within 1 percent or 0.2 ml, whichever is larger.

6. CALCULATIONS

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

6.1 Nomenclature.

- C_{SO2} = Concentration of SO2, dry basis corrected to standard conditions, mg/dsm^3 (lb/dscf).
 - N = Normality of barium standard titrant, meq./ml.

 P_{bar} = Barometric pressure at the exit orifice of the DGM, mm Hg (in. Hg).

 P_{std} = Standard absolute pressure, 760 mm Hg (29.92 in. Hg).

- T_m = Average DGM absolute temperature, °K (°R).
- T_{std} = Standard absolute temperature, 293°K (528°R).
- V_a = Volume of sample aliquot titrated, ml.
- V_m = Dry gas volume as measured by the DGM, dcm (dcf).
- $V_{m(std)}$ = Dry gas volume measured by the DGM, corrected to standard conditions, dscm (dscf).
- $V_{\rm soln}$ = Total volume of solution in which the $_2\,\text{SO}$ sample is contained, 100 ml.
 - $V_{\rm t}$ = Volume of barium standard titrant used for the sample (average of replicate titrations), ml.
 - V_{tb} = Volume of barium standard titrant used for the blank, ml.
 - Y = DGM calibration factor.

 $32.03 = Equivalent weight of SO_2$.

6.2 Dry Sample Gas Volume, Corrected to Standard Conditions.

$$V_{m(std)} = V_{m}Y\left(\frac{T_{std}}{T_{m}}\right)\left(\frac{P_{bar}}{P_{std}}\right) = K_{1}YV_{m}\frac{P_{bar}}{T_{m}}$$
 Eq.6-1

Where:

 $K_1 = 0.3858$ °K/mm Hg for metric units,

= 17.64 °R/in. Hg for English units.

6.3 SO₂ Concentration.

$$C_{SO_{2}} = K_{2} \frac{\left(V_{t} - V_{tb}\right) N\left(\frac{V_{soln}}{V_{a}}\right)}{V_{m(std)}}$$
 Eq.6-2

 $K_2 = 32.03 \text{ mg/meq.}$ for metric units,

= 7.061 x 10^{-5} lb/meq. for English units.

6.4 Relative Error (RE) for QA Audit Samples, Percent.

$$RE = \frac{C_d - C_a}{C_a} \quad (100) \qquad Eq$$

.6-3

C_d = Determined audit sample concentration, mg/dscm.

C_a = Actual audit sample concentration, mg/dscm.

7. ALTERNATIVE PROCEDURES

7.1 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 5.1, provided that it is calibrated initially and recalibrated periodically according to the same procedures outlined in Method 5, Section 7.1, with the following exceptions: (1) the DGM is calibrated against a wet test meter having a capacity of 1 liter/rev or 3 liters/rev and having the capability of measuring volume to within 1 percent; (2) the DGM is calibrated at 1 liter/min (2 cfh); and (3) the meter box of the Method 6 sampling train is calibrated at the same flow rate.

7.2 Critical Orifices for Volume and Rate Measurements. A critical orifice may be used in place of the DGM specified in Section 2.1.10, provided that it is selected, calibrated, and used as follows:

7.2.1 Preparation of Collection Train. Prepare the sampling train as shown in Figure 6-2. The rotameter 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.)

7.2.2 Selection of Critical Orifices.

7.2.2.1 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 below give the following approximate flow rates.

Gauge/cm	Flow rate, cc/min	Gauge/cm	Flow rate, cc/min
21/7.6	1100	23/3.8	500
22/2.9	1000	23/5.1	450
22/3.8	900	24/3.2	400

7.2.2.2 Determine the suitability and the appropriate operating vacuum of the critical orifice as follows: If applicable, temporarily attach a rotameter and

surge tank to the outlet of the sampling train. Turn on the pump, and adjust the valve to give an outlet vacuum reading corresponding to about half of the atmospheric pressure. Observe the rotameter reading. Slowly increase the vacuum until a stable reading is obtained on the rotameter. Record the critical vacuum, which is the outlet vacuum when the rotameter first reaches a stable value. Orifices that do not reach a critical value shall not be used.

7.2.3 Field Procedure.

7.2.3.1 Leak-Check Procedure. A leak-check before the sampling run is recommended, but is optional. The leak-check procedure is as follows: Temporarily attach a suitable (e.g., 0-40 cc/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 254 mm Hg (10 in. Hg), and note the flow rate as indicated by the rotameter or bubble meter. A leakage rate not in excess of 2 percent of the average sampling rate ($Q_{std(avg)}$ is acceptable. Carefully release the probe inlet plug before turning off the pump.

7.2.3.2 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.

7.2.3.3 Critical Orifice Calibration. Prior to testing, at the sampling location, calibrate the entire sampling train using a 500-cc soap bubble meter which is attached to the inlet of the probe and 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:

$$V_{sb(std)} = V_{sb} \left(\frac{T_{std}}{T_{amb}} \right) \left(\frac{P_{bar}}{P_{std}} \right)$$
 Eq.6-4

$$Q_{std} = \frac{V_{sb(std)}}{2}$$
 Eq.6-5

Where:

 \mathbf{P}_{bar} = Barometric pressure, mm Hg (in. Hg).

 P_{std} = Standard absolute pressure, 760 mm Hg (29.92 in. Hg).

- Q_{std} = Volumetric flow rate through critical orifice, scm/min (scf/min).
- T_{amb} = Ambient absolute temperature of air, °K (°R).
- T_{std} = Standard absolute temperature, 273°K (528°R).
- V_{sb} = Volume of gas as measured by the soap bubble meter, m^3 (ft³).

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

2 = Time, min.

7.2.3.4 Sampling.

7.2.3.4.1 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.

7.2.3.4.2 Conduct a post-test calibration run using the calibration procedure outlined in Section 7.2.3.3. 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, $V_{m(std)}$, using Equation 6-6 and the average of Q_{std} of both runs, as follows:

$$V_{m(std)} = \bar{Q}_{std} \mathbf{2}_{s} (1 - B_{wa}) \left(\frac{P_{bar} + P_{sr}}{P_{bar} + P_{c}} \right)$$
 Eq. 6-6

Where:

- $V_{\rm m(std)}$ = Dry gas volume measured with the critical orifice, corrected to standard conditions, dscm (dscf).
- $Q_{std(avg)}$ = Average flow rate of pretest and post-test calibration runs, scm/min (scf/min).
 - B_{wa} = Water vapor in ambient air, proportion by volume.
 - $\mathbf{2}_{s}$ = Sampling time, min.
 - P_c = Inlet vacuum reading obtained during the calibration run, mm Hg (in. Hg).
 - $P_{\rm sr}$ = Inlet vacuum reading obtained during the sampling run, mm Hg (in. Hg).

7.2.3.4.3 If the percent difference between the molecular weight of the ambient air at saturated conditions and the sample gas is more that ±3 percent, then the molecular weight of the gas sample must be considered in the calculations using the following equation:

$$V_{m(std)} = \bar{Q}_{std} \, \mathbf{2}_{s} \, (1 - B_{wa}) \, \sqrt{\frac{M_{a}}{M_{s}}} \left(\frac{P_{bar} + P_{sr}}{P_{bar} + P_{c}} \right)$$
 Eq. 6-7

Where:

- M_a = Molecular weight of the ambient air saturated at impinger temperature, g/g-mole (lb/lb-mole).
- M_s = Molecular weight of the sample gas saturated at impinger temperature, g/g-mole (lb/lb-mole).

7.2.3.4.4 <u>Note</u>: A post-test leak-check is not necessary because the post-test calibration run results will indicate whether there is any leakage.

7.2.3.4.5 Drain the ice bath, and purge the sampling train using the procedure described in Section 4.1.3.

BIBLIOGRAPHY

- Atmospheric Emissions from Sulfuric Acid Manufacturing Processes. U.S DHEW, PHS, Division of Air Pollution. Public Health Service Publication No. 999-AP-13. Cincinnati, OH. 1965.
- 2. Corbett, P.F. The Determination of SO_2 and SO_3 in Flue Gases. Journal of the Institute of Fuel. <u>24</u>:237-243. 1961.
- 3. Matty, R.E. and E.K. Diehl. Measuring Flue-Gas SO_2 and SO_2 . Power. <u>101</u>:94-97. November 1957.
- Patton, W.F. and J.A. Brink, Jr. New Equipment and Techniques for Sampling Chemical Process Gases. J. Air Pollution Control Association. <u>13</u>:162. 1963.
- Rom, J.J. Maintenance, Calibration, and Operation of Isokinetic Source-Sampling Equipment. Office of Air Programs, Environmental Protection Agency. Research Triangle Park, NC. APTD-0576. March 1972.
- Hamil, H.F. and D.E. Camann. Collaborative Study of Method for the Determination of Sulfur Dioxide Emissions from Stationary Sources (Fossil-Fuel Fired Steam Generators). Environmental Protection Agency, Research Triangle Park, NC. EPA-650/4-74-024. December 1973.
- Annual Book of ASTM Standards. Part 31; Water, Atmospheric Analysis. American Society for Testing and Materials. Philadelphia, PA. 1974. pp. 40-42.
- Knoll, J.E. and M.R. Midgett. The Application of EPA Method 6 to High Sulfur Dioxide Concentrations. Environmental Protection Agency. Research Triangle Park, NC. EPA-600/4-76-038. July 1976.
- 9. Westlin, P. R. and R. T. Shigehara. Procedure for Calibrating and Using Dry Gas Volume Meters as Calibration Standards. Source Evaluation Society Newsletter. <u>3</u>(1):17-30. February 1978.
- 10. Yu, K. K. Evaluation of Moisture Effect on Dry Gas Meter Calibration. Source Evaluation Society Newsletter. 5(1):24-28. February 1980.
- Lodge, J.P., Jr., J.B. Pate, B.E. Ammons, and G.A. Swanson. The Use of Hypodermic Needles as Critical Orifices in Air Sampling. J. Air Pollution Control Association. <u>16</u>:197-200. 1966.

12. Shigehara, R.T., and Candace B. Sorrell. Using Critical Orifices as Method 5 Calibration Standards. Source Evaluation Society Newsletter. <u>10</u>:4-15. August 1985.

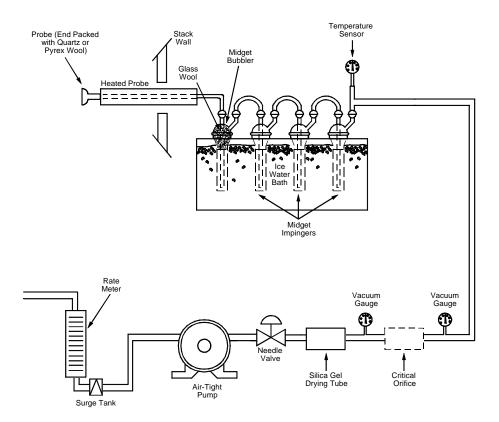


Figure 6-2. SO_2 sampling train using a critical orifice.

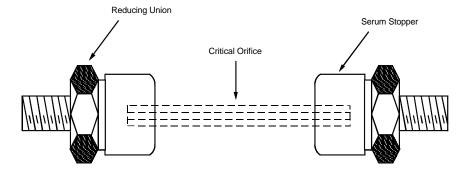


Figure 6-3. Critical orifice adaptation for Method 6 sampling train.

Date Train ID Critical orifice size Critical vacuum	-		
		<u>Pretest</u>	<u>Post-test</u>
Soap bubble meter volume, $\rm V_{sb}$	cc		
	m ³ (ft ³)		
Time, $oldsymbol{2}$	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)		
$V_{\tt sb(std)}$	m ³ (ft ³)		
Flow rate, Q_{std}	$\frac{\mathrm{m}^{3}}{\mathrm{min}}\left(\frac{\mathrm{ft}^{3}}{\mathrm{min}}\right)$		

Figure 6-4. Critical Orifice Calibration Data Sheet.