

**State of California
Air Resources Board**

Method 8

Determination of Sulfuric Acid Mist and Sulfur Dioxide Emissions from Stationary Sources

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Method 8 - Determination of Sulfuric Acid Mist and Sulfur Emissions from Stationary Sources

1. PRINCIPLE AND APPLICABILITY

1.1 Principle.

A gas sample is extracted isokinetically from the stack. The sulfuric acid mist (including sulfur trioxide) and the sulfur dioxide are separated, and both fractions are measured separately by the barium-thorin titration method.

1.2 Applicability.

This method is applicable for the determination of sulfuric acid mist (including sulfur trioxide (SO₃) in the absence of other particulate matter) and sulfur dioxide (SO₂) emissions from stationary sources. Collaborative tests have shown that the minimum detectable limits of the method are 0.05 mg/m³ (0.03 x 10^{C7} lb/ft³) for SO₃ and 1.2 mg/m³ (0.74 x 10⁻⁷ lb/ft³) for SO₂. No upper limits have been established. Based on theoretical calculations for 200 ml of 3 percent hydrogen peroxide solution, the upper concentration limit for SO₂ in a 1.0 m³ (35.3 ft³) gas sample is about 12,500 mg/m³ (7.7 x 10^{C4} lb/ft³). The upper limit can be extended by increasing the quantity of peroxide solution in the impingers.

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

Any modification of this method beyond those expressly permitted shall be considered a major modification subject to the approval of the Executive Officer. The term Executive Officer as used in this document shall mean the Executive Officer of the Air Resources Board (ARB), or his or her authorized representative.

Filterable particulate matter may be determined along with SO₃ and SO₂ (subject to the approval of the Executive Officer) by inserting a heated glass fiber filter between the probe and isopropanol impinger (see Section 2.1 of Method 6). If this option is chosen, particulate analysis is gravimetric only; H₂SO₄ acid mist is not determined separately.

2. APPARATUS

2.1 Sampling.

A schematic of the sampling train used in this method is shown in Figure 8-1; it is similar to the Method 5 train, except that the filter position is different, and the filter holder does not have to be heated. Commercial models of this train are available. For those who desire to build their own, however, complete construction details are described in APTD-0581 (*Construction Details of Isokinetic Source-Sampling Equipment*, EPA, 1971, document #PB-203-060, available from NTIS). Changes from the APTD-0581 document and allowable modifications to figure 8-1 are discussed in the following subsections.

The operating and maintenance procedures for the sampling train are described in APTD-0576 (*Maintenance, Calibration and Operation of Isokinetic Source Sampling Equipment*, EPA, 1972, document #PB-209-022, available from NTIS). Since correct usage is

important in obtaining valid results, all users should read the APTD-0576 document and adopt the operating and maintenance procedures outlined in it, unless otherwise specified herein. Further details and guidelines on operation and maintenance are given in Method 5 and should be read and followed whenever they are applicable.

2.1.1 Probe Nozzle.

Same as Method 5, Section 2.1.1.

2.1.2 Probe Liner.

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

2.1.3 Pitot Tube.

Same as Method 5, Section 2.1.3.

2.1.4 Differential Pressure Gauge.

Same as Method 5, Section 2.1.4.

2.1.5 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 Executive Officer. 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. Note: Do not heat the filter holder.

2.1.6 Impingers.

Four, as shown in Figure 8-1. The first and third shall be of Greenburg-Smith design with standard tips. The second and fourth shall be of Greenburg-Smith design modified by replacing the insert with an approximately 13-mm (0.5-in.) ID glass tube, having an unstricted tip located 13 mm (0.5 in.) from the bottom of the flask. Similar collection systems, subject to the approval of the Executive Officer, may be used.

2.1.7 Metering System.

Same as Method 5, Section 2.1.8.

2.1.8 Barometer.

Same as Method 5, Section 2.1.9.

2.1.9 Gas Density Determination Equipment.

Same as Method 5, Section 2.1.10.

2.1.10 Temperature Gauge.

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

2.2 Sample Recovery.

2.2.1 Wash Bottles.

Polyethylene or glass, 500-ml (two).

2.2.2 Graduated Cylinders.

250-ml, 1-liter. (Volumetric flasks may also be used.)

2.2.3 Storage Bottles.

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

2.2.4 Trip Balance.

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

2.3 Analysis.**2.3.1 Pipettes.**

Volumetric 25-ml, 100-ml.

2.3.2 Burette.

50-ml.

2.3.3 Erlenmeyer Flask.

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

2.3.4 Graduated Cylinder.

100-ml.

2.3.5 Trip Balance.

500 g capacity, to measure to ± 0.5 g.

2.3.6 Dropping Bottle.

To add indicator solution, 125-ml size.

3. REAGENTS

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.

3.1 Sampling.**3.1.1 Filters.**

Same as in Method 5, Sections 3.1.1.

3.1.2 Silica Gel.

Same as Method 5, Section 3.1.2.

3.1.3 Water.

Deionized, distilled to conform to ASTM Specification D1193-77, Type 3. At the option of the analyst, the KMnO_4 test for oxidizable organic matter may be omitted when high concentrations of organic matter are not expected to be present.

3.1.4 Isopropanol, 80 Percent.

Mix 800 ml of isopropanol with 200 ml of deionized, distilled water.

Note: Experience has shown that only A.C.S. grade isopropanol is satisfactory. Tests have shown that isopropanol obtained from commercial sources occasionally has peroxide impurities that will cause erroneously high sulfuric acid mist measurement. Use the following test for detecting peroxides in each lot of isopropanol: Shake 10 ml of the isopropanol with 10 ml of freshly prepared 10 percent potassium iodide solution. Prepare a blank by similarly treating 10 ml of distilled water. After 1 minute, read the absorbance on a spectrophotometer at 352 nanometers. If the absorbance exceeds 0.1, the isopropanol shall not be used. 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 is readily available from commercial sources; therefore, rejection of contaminated lots may be more efficient than following the peroxide removal procedure.

3.1.5 Hydrogen Peroxide, 3 Percent.

Dilute 100 ml of 30 percent hydrogen peroxide to 1 liter with deionized, distilled water. Prepare fresh daily.

3.1.6 Crushed Ice.

3.2 Sample Recovery.

3.2.1 Water.

Same as in Section 3.1.3.

3.2.2 Isopropanol, 80 Percent.

Same as in Section 3.1.4.

3.3 Analysis.

3.3.1 Water.

Same as 3.1.3.

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 deionized, distilled water.

3.3.4 Barium Perchlorate (0.0100 Normal).

Dissolve 1.95 g of barium perchlorate trihydrate ($\text{Ba}(\text{ClO}_4)_2 \cdot 3\text{H}_2\text{O}$) in 200 ml deionized, distilled water, and dilute to 1 liter with isopropanol; 1.22 g of barium chloride dihydrate ($\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$) may be used instead of the barium perchlorate. Standardize with sulfuric acid as in Section 5.2. This solution must be protected against evaporation at all times.

3.3.5 Sulfuric Acid Standard (0.0100 N).

Purchase or standardize to ± 0.0002 N against 0.0100 N NaOH that has previously

been standardized against primary standard potassium acid phthalate.

3.3.6 Quality Assurance Audit Samples.

Same as in Method 6, Section 3.3.6.

4. PROCEDURE

4.1 Sampling.

4.1.1 Pretest Preparation.

Follow the procedure in Method 5, Section 4.1.1; 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.

4.1.2 Preliminary Determinations.

Follow the procedure in Method 5, Section 4.1.2.

4.1.3 Preparation of Collection Train.

Follow the procedure in Method 5, Section 4.1.3 (except for the second paragraph regarding impinger solutions and other obviously inapplicable parts), and use Figure 8-1 instead of Figure 5-1. Replace the second paragraph with: Place 100 ml of 80 percent isopropanol in the first impinger, 100 ml of 3 percent hydrogen peroxide 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.

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.

4.1.4 Pretest Leak-Check Procedure.

Follow the basic procedure in Method 5, Section 4.1.4.1, noting that the probe heater shall be adjusted to the minimum temperature required to prevent condensation, and also that verbiage such as "...plugging the inlet to the filter holder...." shall be replaced by "...plugging the inlet to the first impinger...." The pretest leak-check is optional.

4.1.5 Train Operation.

Follow the basic procedures in Method 5, Section 4.1.5, in conjunction with the following special instructions. Record the data on a sheet similar to the one in Figure 8-2.(or use Figure 5-2 in Method 5) 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 it 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 done immediately before each change, according to the procedure outlined in Section 4.1.4.2 of Method 5 (with appropriate modifications, as mentioned in Section 4.1.4 of this method); record all leak rates. If the leakage rate(s) exceeds the specified rate, the tester shall either void the run or shall plan to correct the sample volume as outlined in Section 6.3 of Method 5. Immediately after

component changes, leak-checks are optional. If these leak-checks are done, the procedure in Section 4.1.4.1 of Method 5 (with appropriate modifications) shall be used.

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 in Section 4.1.4.3 of Method 5 (with appropriate modifications), and record the leak rate. If the post-test leakage rate exceeds the specified acceptable rate, the tester shall either correct the sample volume, as in Section 6.3 of Method 5, or shall void the run.

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. At the option of the tester, ambient air (without cleaning) may be used.)

4.1.6 Calculation of Percent Isokinetic.

Follow the procedure in Method 5, Section 4.1.6.

4.2 Sample Recovery.

4.2.1 Container No. 1.

If a moisture content analysis is to be done, weigh the first impinger plus contents to the nearest 0.5 g, and record this weight.

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 Rinse Solution to the cylinder. Dilute to 250 ml with 80 percent isopropanol. Add the filter to the solution, mix, and transfer to the storage container. Protect the solution against evaporation. Mark the level of liquid on the container, and identify the sample container.

4.2.2 Container No. 2.

If a moisture content analysis is to be done, 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.

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 to 1 liter with water. Transfer the solution to a storage container. Mark the level of liquid on the container. Seal and identify the sample container.

4.3 Analysis.

Note the level of the liquid in Containers No. 1 and 2, 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 Executive Officer, to correct the final results.

4.3.1 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. 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 perchlorate. 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.

4.3.2 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 perchlorate. 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.

4.3.3 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.

4.4 Quality Control Procedures.

Same as in Method 5, Section 4.4.

4.5 Audit Sample Analysis.

Same as in Method 6, Section 4.4.

5. CALIBRATION

5.1

Calibrate equipment using the procedures specified in the following sections of Method 5: Section 5.3 (metering system), Section 5.5 (temperature gauges), and Section 5.7 (barometer). Note that the recommended leak-check of the metering system, described in Section 5.6 of Method 5, also applies to this method.

5.2

Standardize the barium perchlorate solution with 25 ml of standard sulfuric acid, to which 100 ml of 100 percent isopropanol has been added.

6. CALCULATIONS

NOTE: 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.

A_n	=	Cross-sectional area of nozzle, m^2 (ft^2).
B_{ws}	=	Water vapor in the gas stream, proportion by volume.
$C_{H_2SO_4}$	=	Sulfuric acid (including SO_3) concentration, g/dscm (lb/dscf).
C_{SO_2}	=	Sulfur dioxide concentration, g/dscm (lb/dscf).

- I = Percent of isokinetic sampling.
- N = Normality of barium perchlorate titrant, g-equivalents/liter.
- P_{bar} = Barometric pressure at the sampling site, mm Hg (in. Hg).
- P_s = Absolute stack gas pressure, mm Hg (in. Hg).
- P_{std} = Standard absolute pressure, 760 mm Hg (29.92 in. Hg).
- T_m = Average absolute dry gas meter temperature, (see Figure 8-2), °K (°R).
- T_s = Average absolute stack gas temperature, (see Figure 8-2), °K (°R).
- T_{std} = Standard absolute temperature, 293°K (528°R).
- V_a = Volume of sample aliquot titrated, 100 ml for H₂SO₄ and 10 ml for SO₂.
- V_{1c} = Total volume of liquid collected in impingers and silica gel, ml.
- V_m = Volume of gas sample as measured by dry gas meter, dcm (dcf).
- V_{m(std)} = Volume of gas sample measured by the dry gas meter corrected to standard conditions, dscm (dscf).
- v_s = Average stack gas velocity, calculated by Method 2, equation 2-9, using data obtained from Method 8, m/sec (ft/sec).
- V_{soln} = Total volume of solution in which the H₂SO₄ or SO₂ sample is contained, 250 ml or 1000 ml, respectively.
- 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.
- Y = Dry gas meter calibration factor.
- ΔH = Average pressure drop across orifice meter, mm (in.)H₂O.
- θ = Total sampling time, min.
- 13.6 = Specific gravity of Mercury.
- 60 = sec/min.
- 100 = Conversion to percent.

6.2 Average Dry Gas Meter Temperature and Average Orifice Pressure Drop.

See data sheet (Figure 8-2).

6.3 Dry Gas Volume.

Correct the sample volume measured by the dry gas meter to standard conditions (20°C and 760 mm Hg or 68°F and 29.92 in. Hg) by using Equation 8-1.

$$\begin{aligned}
 V_{m(std)} &= V_m Y \left(\frac{T_{std}}{T_m} \right) \frac{P_{bar} + \left(\frac{\Delta H}{13.6} \right)}{P_{std}} \\
 &= K_1 V_m Y \frac{P_{bar} + \left(\frac{\Delta H}{13.6} \right)}{T_m}
 \end{aligned}
 \tag{Eq. 8-1}$$

Where:

- K₁ = 0.3858 °K/mm Hg for metric units.
- = 17.65 °R/in. Hg for English units.

Note: If the leak rate observed during any mandatory leak-checks exceeds the specified acceptable rate, the tester shall either correct the value of V_m in Equation 8-1 (as described in Section 6.3 of Method 5), or shall invalidate the test run.

6.4 Volume of Water Vapor 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, using Equation 5-3 of Method 5. The Note in Section 6.5 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.

6.5 Sulfuric Acid Mist (Including SO₃) Concentration.

$$C_{\text{H}_2\text{SO}_4} = K_2 \frac{N(V_t - V_{tb}) \left(\frac{V_{\text{soln}}}{V_a} \right)}{V_{m(\text{std})}} \quad \text{Eq. 8-2}$$

Where:

$$\begin{aligned} K_2 &= 0.04904 \text{ g/milliequivalent for metric units,} \\ &= 1.081 \times 10^{-4} \text{ lb/meq for English units.} \end{aligned}$$

6.6 Sulfur Dioxide Concentration.

$$C_{\text{SO}_2} = K_3 \frac{N(V_t - V_{tb}) \left(\frac{V_{\text{soln}}}{V_a} \right)}{V_{m(\text{std})}} \quad \text{Eq. 8-3}$$

Where:

$$\begin{aligned} K_3 &= 0.03203 \text{ g/meq for metric units,} \\ &= 7.061 \times 10^{-5} \text{ lb/meq for English units.} \end{aligned}$$

6.7 Isokinetic Variation.

6.7.1 Calculation from raw data.

$$I = \frac{100 T_s \left(K_4 V_{ic} + \left(\frac{V_m Y}{T_m} \right) \left(P_{\text{bar}} + \frac{\Delta H}{13.6} \right) \right)}{60 \dot{v}_s P_s A_n} \quad \text{Eq. 8-4}$$

Where:

$$\begin{aligned} K_4 &= 0.003464 \text{ mm Hg} \cdot \text{m}^3/\text{ml} \cdot ^\circ\text{K for metric units.} \\ &= 0.002676 \text{ in. Hg} \cdot \text{ft}^3/\text{ml} \cdot ^\circ\text{R for English units.} \end{aligned}$$

6.7.2 Calculation from intermediate values.

$$\begin{aligned} I &= \frac{T_s V_{m(\text{std})} P_{\text{std}} 100}{T_{\text{std}} \dot{v}_s \dot{e} A_n P_s 60 (1 - B_{ws})} \\ &= K_5 \frac{T_s V_{m(\text{std})}}{P_s \dot{v}_s A_n \dot{e} (1 - B_{ws})} \end{aligned} \quad \text{Eq. 8-5}$$

Where:

K_5 = 4.320 for metric units.
= 0.09450 for English units.

6.8 Acceptable Results.

If 90 percent < I < 110 percent, the results are acceptable. If the results are low in comparison to the standards and I is beyond the acceptable range, the Executive Officer may opt to accept the results. Otherwise, reject the results and repeat the test.

6.9 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 equations in Sections 5.2 and 5.3 of Method 2.

6.10 Relative Error (RE) for QA Audit Samples.

Same as in Method 6, Section 6.4.

7. BIBLIOGRAPHY

1. EPA Method 8, Determination of Sulfuric Acid Mist and Sulfur Dioxide Emissions from Stationary Sources, CFR40, Part 60, Appendix A
2. ARB Method 5, Determination of Particulate Matter Emissions from Stationary Sources
3. ARB Method 6, Determination of Sulfur Dioxide Emissions from Stationary Sources
4. ARB Method 2, Determination of Stack Gas Velocity and Volumetric Flow Rate (Type S Pitot Tube)

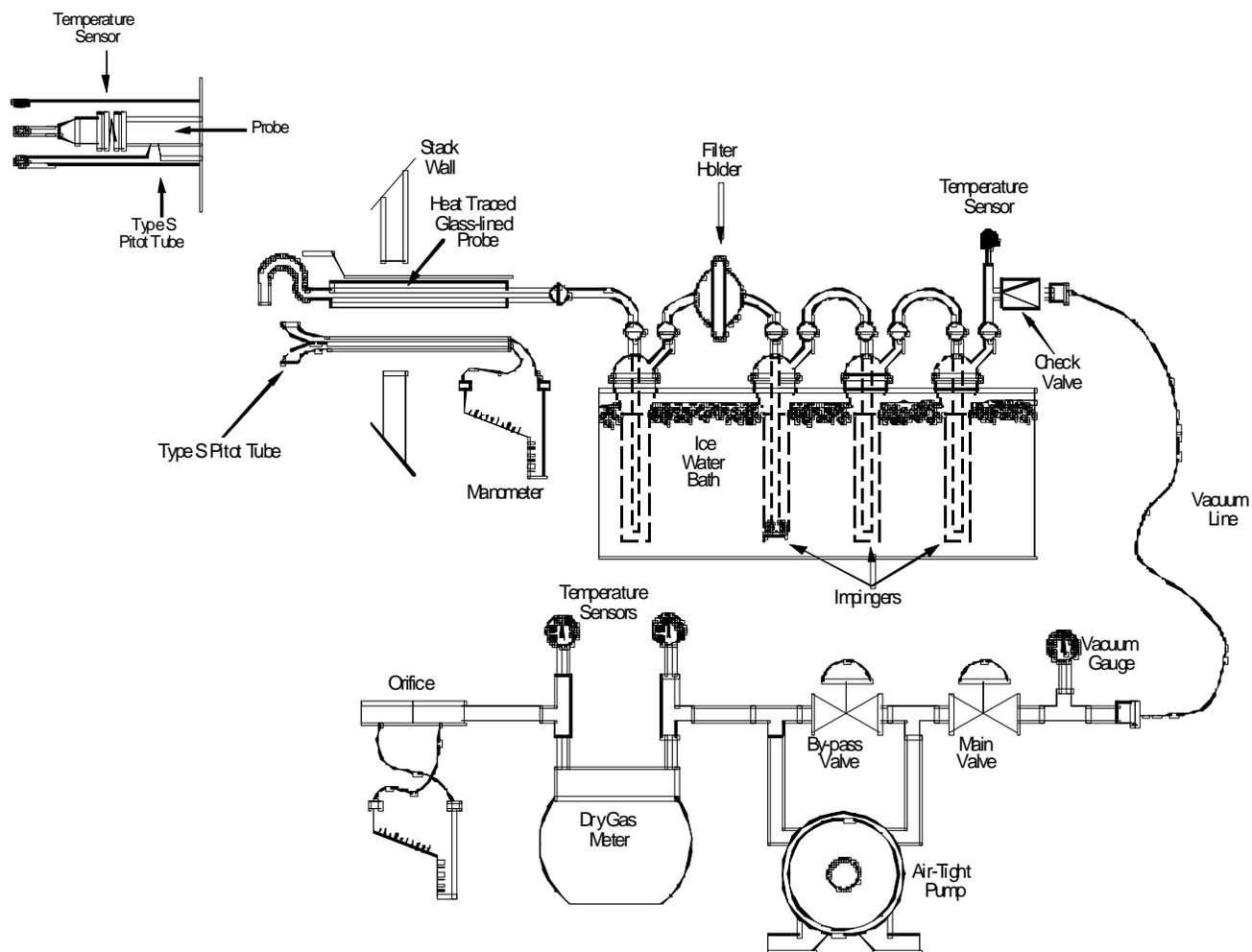


Figure 8-1 Sample Train Schematic

