

6.3.3 Temperature Sensor. Thermometer or equivalent to monitor bath temperature within 0.1 °C.

7.0 Reagents and Standards

7.1 Fuel, Hydrogen gas (H₂). Prepurified grade or better.

7.2 Combustion Gas. Oxygen (O₂) or air, research purity or better.

7.3 Carrier Gas. Prepurified grade or better.

7.4 Diluent. Air containing less than 0.5 ppmv total sulfur compounds and less than 10 ppmv each of moisture and total hydrocarbons.

7.5 Calibration Gases.

7.5.1 Permeation Devices. One each of H₂S, COS, and CS₂, gravimetrically calibrated and certified at some convenient operating temperature. These tubes consist of hermetically sealed FEP Teflon tubing in which a liquified gaseous substance is enclosed. The enclosed gas permeates through the tubing wall at a constant rate. When the temperature is constant, calibration gases covering a wide range of known concentrations can be generated by varying and accurately measuring the flow rate of diluent gas passing over the tubes. These calibration gases are used to calibrate the GC/FPD system and the dilution system.

7.5.2 Cylinder Gases. Cylinder gases may be used as alternatives to permeation devices. The gases must be traceable to a primary standard (such as permeation tubes) and not used beyond the certification expiration date.

7.6 Citrate Buffer. Dissolve 300 g of potassium citrate and 41 g of anhydrous citric acid in 1 liter of water. Alternatively, 284 g of sodium citrate may be substituted for the potassium citrate. Adjust the pH to between 5.4 and 5.6 with potassium citrate or citric acid, as required.

8.0 Sample Collection, Preservation, Transport, and Storage

8.1 Pretest Procedures. After the complete measurement system has been set up at the site and deemed to be operational, the following procedures should be completed before sampling is initiated. These procedures are not required, but would be helpful in preventing any problem which might occur later to invalidate the entire test.

8.1.1 Leak-Check. Appropriate leak-check procedures should be employed to verify the integrity of all components, sample lines, and connections. The following procedure is suggested: For components upstream of the sample pump, attach the probe end of the sample line to a manometer or vacuum gauge, start the pump and pull a vacuum greater than 50 mm (2 in.) Hg, close off the pump outlet, and then stop the pump and ascertain that there is no leak for 1 minute. For components after the pump, apply a slight positive pressure and check for leaks by applying a liquid (detergent in water, for

example) at each joint. Bubbling indicates the presence of a leak. As an alternative to the initial leak-test, the sample line loss test described in section 8.3.1 may be performed to verify the integrity of components.

8.1.2 System Performance. Since the complete system is calibrated at the beginning and end of each day of testing, the precise calibration of each component is not critical. However, these components should be verified to operate properly. This verification can be performed by observing the response of flowmeters or of the GC output to changes in flow rates or calibration gas concentrations, respectively, and ascertaining the response to be within predicted limits. If any component or the complete system fails to respond in a normal and predictable manner, the source of the discrepancy should be identified and corrected before proceeding.

8.2 Sample Collection and Analysis

8.2.1 After performing the calibration procedures outlined in section 10.0, insert the sampling probe into the test port ensuring that no dilution air enters the stack through the port. Begin sampling and dilute the sample approximately 9:1 using the dilution system. Note that the precise dilution factor is the one determined in section 10.4. Condition the entire system with sample for a minimum of 15 minutes before beginning the analysis. Inject aliquots of the sample into the GC/FPD analyzer for analysis. Determine the concentration of each reduced sulfur compound directly from the calibration curves or from the equation for the least-squares line.

8.2.2 If reductions in sample concentrations are observed during a sample run that cannot be explained by process conditions, the sampling must be interrupted to determine if the probe or filter is clogged with particulate matter. If either is found to be clogged, the test must be stopped and the results up to that point discarded. Testing may resume after cleaning or replacing the probe and filter. After each run, the probe and filter shall be inspected and, if necessary, replaced.

8.2.3 A sample run is composed of 16 individual analyses (injects) performed over a period of not less than 3 hours or more than 6 hours.

8.3 Post-Test Procedures.

8.3.1 Sample Line Loss. A known concentration of H₂S at the level of the applicable standard, ±20 percent, must be introduced into the sampling system at the opening of the probe in sufficient quantities to ensure that there is an excess of sample which must be vented to the atmosphere. The sample must be transported through the entire sampling system to the measurement system in the same manner as the emission samples. The resulting measured concentration is compared to the known value to determine

the sampling system loss. For sampling losses greater than 20 percent, the previous sample run is not valid. Sampling losses of 0-20 percent must be corrected by dividing the resulting sample concentration by the fraction of recovery. The known gas sample may be calibration gas as described in section 7.5. Alternatively, cylinder gas containing H₂S mixed in nitrogen and verified according to section 7.1.4 of Method 16A may be used. The optional pretest procedures provide a good guideline for determining if there are leaks in the sampling system.

8.3.2 Determination of Calibration Drift. After each run, or after a series of runs made within a 24-hour period, perform a partial recalibration using the procedures in section 10.0. Only H₂S (or other permeant) need be

used to recalibrate the GC/FPD analysis system and the dilution system. Partial recalibration may be performed at the mid-level calibration gas concentration or at a concentration measured in the samples but not less than the lowest calibration standard used in the initial calibration. Compare the calibration curves obtained after the runs to the calibration curves obtained under section 10.3. The calibration drift should not exceed the limits set forth in section 13.4. If the drift exceeds this limit, the intervening run or runs should be considered invalid. As an option, the calibration data set that gives the highest sample values may be chosen by the tester.

9.0 Quality Control

Section	Quality control measure	Effect
8.3.1	Sample line loss check	Ensures that uncorrected negative bias introduced by sample loss is no greater than 20 percent, and provides for correction of bias of 20 percent or less.
8.3.2	Calibration drift test	Ensures that bias introduced by drift in the measurement system output during the run is no greater than 5 percent.
10.0	Analytical calibration	Ensures precision of analytical results within 5 percent.

10.0 Calibration and Standardization

Prior to any sampling run, calibrate the system using the following procedures. (If more than one run is performed during any 24-hour period, a calibration need not be performed prior to the second and any subsequent runs. However, the calibration drift must be determined as prescribed in section 8.3.2 after the last run is made within the 24-hour period.)

NOTE: This section outlines steps to be followed for use of the GC/FPD and the dilution system. The calibration procedure does not include detailed instructions because the operation of these systems is complex, and it requires an understanding of the individual system being used. Each system should include a written operating manual describing in detail the operating procedures associated with each component in the measurement system. In addition, the operator should be familiar with the operating principles of the components, particularly the GC/FPD. The references in section 16.0 are recommended for review for this purpose.

10.1 Calibration Gas Permeation Tube Preparation.

10.1.1 Insert the permeation tubes into the tube chamber. Check the bath temperature to assure agreement with the calibration temperature of the tubes within 0.1 °C. Allow 24 hours for the tubes to equilibrate. Alternatively, equilibration may be verified by injecting samples of calibration gas at 1-hour intervals. The permeation tubes can be assumed to have reached equilibrium when

consecutive hourly samples agree within 5 percent of their mean.

10.1.2 Vary the amount of air flowing over the tubes to produce the desired concentrations for calibrating the analytical and dilution systems. The air flow across the tubes must at all times exceed the flow requirement of the analytical systems. The concentration in ppmv generated by a tube containing a specific permeant can be calculated using Equation 15-1 in section 12.2.

10.2 Calibration of Analytical System. Generate a series of three or more known concentrations spanning the linear range of the FPD (approximately 0.5 to 10 ppmv for a 1-ml sample) for each of the three major sulfur compounds. Bypassing the dilution system, inject these standards into the GC/FPD and monitor the responses until three consecutive injections for each concentration agree within 5 percent of their mean. Failure to attain this precision indicates a problem in the calibration or analytical system. Any such problem must be identified and corrected before proceeding.

10.3 Calibration Curves. Plot the GC/FPD response in current (amperes) versus their causative concentrations in ppmv on log-log coordinate graph paper for each sulfur compound. Alternatively, a least-squares equation may be generated from the calibration data using concentrations versus the appropriate instrument response units.

10.4 Calibration of Dilution System. Generate a known concentration of H₂S using the permeation tube system. Adjust the flow rate of diluent air for the first dilution stage

so that the desired level of dilution is approximated. Inject the diluted calibration gas into the GC/FPD system until the results of three consecutive injections for each dilution agree within 5 percent of their mean. Failure to attain this precision in this step is an indication of a problem in the dilution system. Any such problem must be identified and corrected before proceeding. Using the calibration data for H₂S (developed under section 10.3), determine the diluted calibration gas concentration in ppmv. Then calculate the dilution factor as the ratio of the calibration gas concentration before dilution to the diluted calibration gas concentration determined under this section. Repeat this procedure for each stage of dilution required. Alternatively, the GC/FPD system may be calibrated by generating a series of three or more concentrations of each sulfur compound and diluting these samples before injecting them into the GC/FPD system. These data will then serve as the calibration data for the unknown samples and a separate determination of the dilution factor will not be necessary. However, the precision requirements are still applicable.

11.0 Analytical Procedure

Sample collection and analysis are concurrent for this method (see section 8.0).

12.0 Data Analysis and Calculations

12.1 Nomenclature.

C = Concentration of permeant produced, ppmv.
 COS = Carbonyl sulfide concentration, ppmv.
 CS₂ = Carbon disulfide concentration, ppmv.
 d = Dilution factor, dimensionless.
 H₂S = Hydrogen sulfide concentration, ppmv.
 K = 24.04 L/g mole. (Gas constant at 20 °C and 760 mm Hg)
 L = Flow rate, L/min. of air over permeant 20 °C, 760 mm Hg.
 M = Molecular weight of the permeant, g/mole.
 N = Number of analyses performed.
 P_r = Permeation rate of the tube, µg/min.

12.2 Permeant Concentration. Calculate the concentration generated by a tube containing a specific permeant (see section 10.1) using the following equation:

$$C = \frac{KP_r}{ML} \quad \text{Eq. 15-1}$$

12.3 Calculation of SO₂ Equivalent. SO₂ equivalent will be determined for each analysis made by summing the concentrations of

each reduced sulfur compound resolved during the given analysis. The SO₂ equivalent is expressed as SO₂ in ppmv.

$$\text{SO}_2 \text{ equivalent}_i = \sum (\text{H}_2\text{S}, \text{COS}, 2\text{CS}_2) d \quad \text{Eq. 15-2}$$

12.4 Average SO₂ Equivalent. This is determined using the following equation. Systems that do not remove moisture from the sample but condition the gas to prevent condensation must correct the average SO₂

equivalent for the fraction of water vapor present. This is not done under applications where the emission standard is not specified on a dry basis.

$$\text{Avg SO}_2 \text{ equivalent} = \frac{\sum_{i=1}^n \text{SO}_2 \text{ equivalent}_i}{N} \quad \text{Eq. 15-3}$$

Where:

Avg SO₂ equivalent = Average SO₂ equivalent in ppmv, dry basis.

Average SO₂ equivalent_i = SO₂ in ppmv as determined by Equation 15-2.

13.0 Method Performance

13.1 Range. Coupled with a GC system using a 1-ml sample size, the maximum limit of the FPD for each sulfur compound is approximately 10 ppmv. It may be necessary to

dilute samples from sulfur recovery plants a hundredfold (99:1), resulting in an upper limit of about 1000 ppmv for each compound.

13.2 Sensitivity. The minimum detectable concentration of the FPD is also dependent on sample size and would be about 0.5 ppmv for a 1-ml sample.

13.3 Calibration Precision. A series of three consecutive injections of the same calibration gas, at any dilution, shall produce results which do not vary by more than 5 percent from the mean of the three injections.

13.4 Calibration Drift. The calibration drift determined from the mean of three injections made at the beginning and end of any run or series of runs within a 24-hour period shall not exceed 5 percent.

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References.

1. O'Keeffe, A.E., and G.C. Ortman. "Primary Standards for Trace Gas Analysis." *Anal. Chem.* 38,760. 1966.
2. Stevens, R.K., A.E. O'Keeffe, and G.C. Ortman. "Absolute Calibration of a Flame Photometric Detector to Volatile Sulfur Compounds at Sub-Part-Per-Million Levels."

Environmental Science and Technology 3:7. July 1969.

3. Mulik, J.D., R.K. Stevens, and R. Baumgardner. "An Analytical System Designed to Measure Multiple Malodorous Compounds Related to Kraft Mill Activities." Presented at the 12th Conference on Methods in Air Pollution and Industrial Hygiene Studies, University of Southern California, Los Angeles, CA, April 6-8, 1971.

4. Devonald, R.H., R.S. Serenius, and A.D. McIntyre. "Evaluation of the Flame Photometric Detector for Analysis of Sulfur Compounds." *Pulp and Paper Magazine of Canada*, 73,3, March 1972.

5. Grimley, K.W., W.S. Smith, and R.M. Martin. "The Use of a Dynamic Dilution System in the Conditioning of Stack Gases for Automated Analysis by a Mobile Sampling Van." Presented at the 63rd Annual APCA Meeting in St. Louis, MO. June 14-19, 1970.

6. General Reference. *Standard Methods of Chemical Analysis* Volume III-A and III-B: *Instrumental Analysis*. Sixth Edition. Van Nostrand Reinhold Co.

17.0 Tables, Diagrams, Flowcharts, and Validation Data

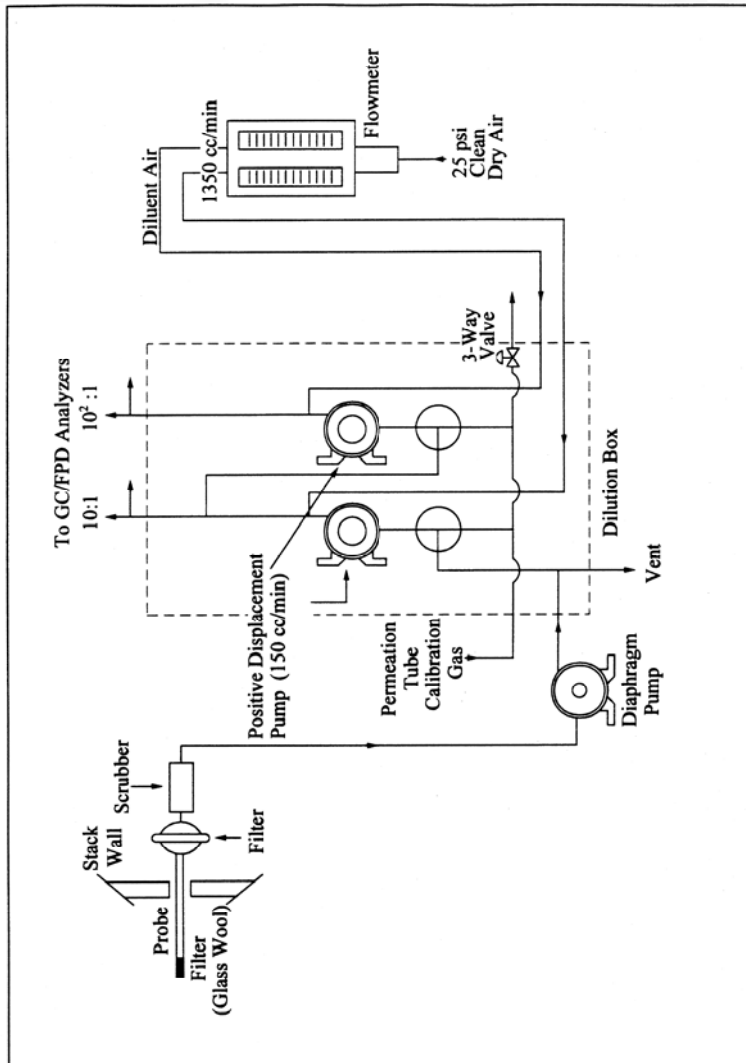


Figure 15-1. Sampling and Dilution Apparatus.

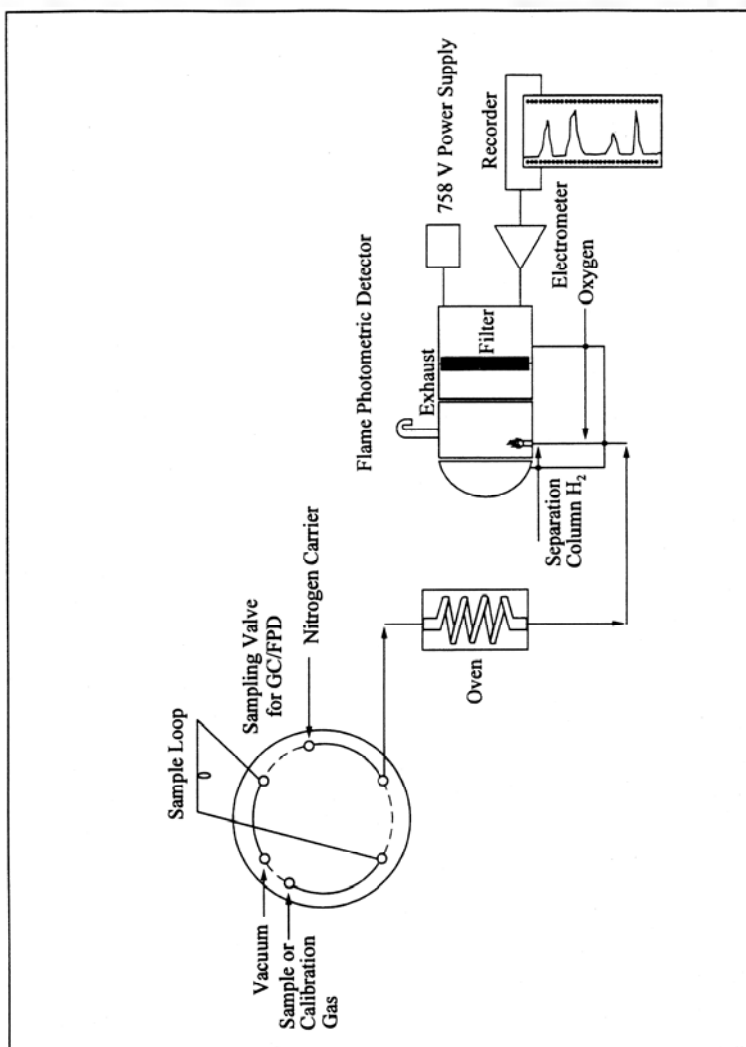


Figure 15-2. Gas Chromatographic Flame Photometric Analyzer.

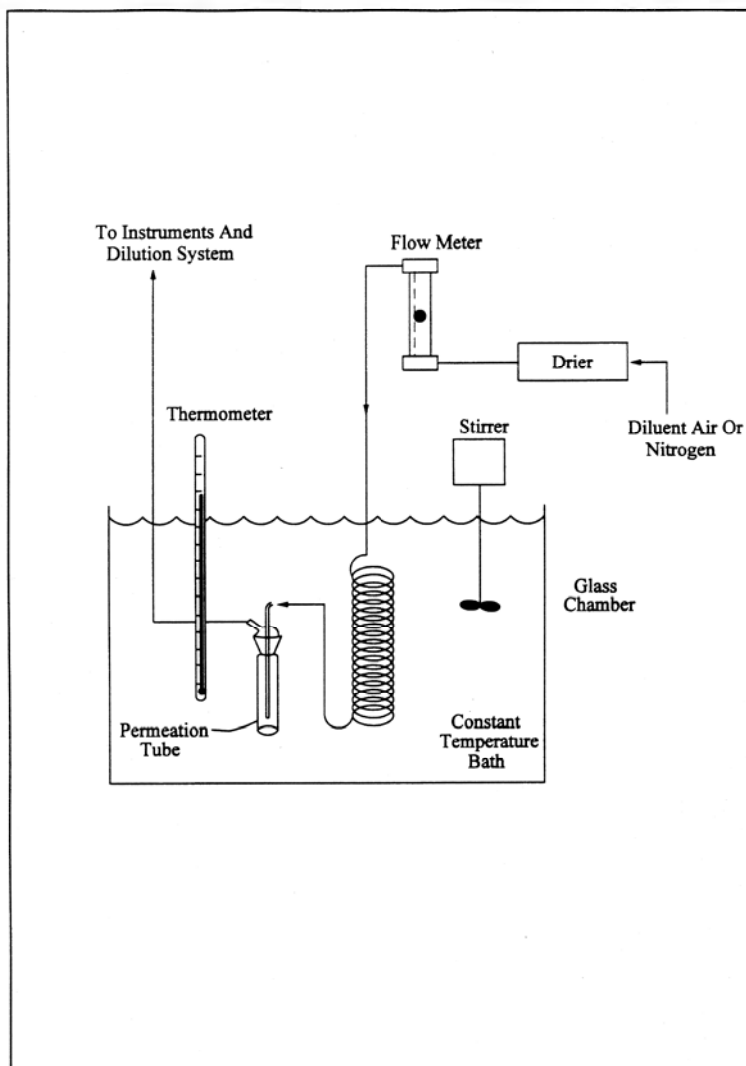


Figure 15-3. Apparatus for Field Calibration.

METHOD 15A—DETERMINATION OF TOTAL REDUCED SULFUR EMISSIONS FROM SULFUR RECOVERY PLANTS IN PETROLEUM REFINERIES

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 6, Method 15, and Method 16A.

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS No.	Sensitivity
Reduced sulfur compounds	None assigned	Not determined.

1.2 **Applicability.** This method is applicable for the determination of emissions of reduced sulfur compounds from sulfur recovery plants where the emissions are in a reducing atmosphere, such as in Stretford units.

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

2.0 Summary of Method

2.1 An integrated gas sample is extracted from the stack, and combustion air is added to the oxygen (O₂)-deficient gas at a known rate. The reduced sulfur compounds [including carbon disulfide (CS₂), carbonyl sulfide (COS), and hydrogen sulfide (H₂S)] are thermally oxidized to sulfur dioxide (SO₂), which is then collected in hydrogen peroxide as sulfate ion and analyzed according to the Method 6 barium-thorin titration procedure.

3.0 Definitions [Reserved]

4.0 Interferences

4.1 Reduced sulfur compounds, other than CS₂, COS, and H₂S, that are present in the emissions will also be oxidized to SO₂, causing a positive bias relative to emission standards that limit only the three compounds listed above. For example, thiophene has been identified in emissions from a Stretford unit and produced a positive bias of 30 percent in the Method 15A result. However, these biases may not affect the outcome of the test at units where emissions are low relative to the standard.

4.2 Calcium and aluminum have been shown to interfere in the Method 6 titration procedure. Since these metals have been identified in particulate matter emissions from Stretford units, a Teflon filter is required to minimize this interference.

4.3 Dilution of the hydrogen peroxide (H₂O₂) absorbing solution can potentially reduce collection efficiency, causing a negative bias. When used to sample emissions containing 7 percent moisture or less, the mid-gel impingers have sufficient volume to contain the condensate collected during sampling. Dilution of the H₂O₂ does not affect the collection of SO₂. At higher moisture contents, the potassium citrate-citric acid buffer system used with Method 16A should be used to collect the condensate.

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

5.2.1 **Hydrogen Peroxide (H₂O₂).** Irritating to eyes, skin, nose, and lungs.

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

5.2.3 **Sulfuric Acid (H₂SO₄).** Rapidly destructive to body tissue. Will cause third degree burns. Eye damage may result in blindness. Inhalation may be fatal from spasm of the larynx, usually within 30 minutes. May cause lung tissue damage with edema. 3 mg/m³ will cause lung damage in uninitiated. 1 mg/m³ for 8 hours will cause lung damage or, in higher concentrations, death. Provide ventilation to limit inhalation. Reacts violently with metals and organics.

6.0 Equipment and Supplies

6.1 **Sample Collection.** The sampling train used in performing this method is shown in Figure 15A-1, and component parts are discussed below. Modifications to this sampling train are acceptable provided that the system performance check is met.

6.1.1 **Probe.** 6.4-mm (¼-in.) OD Teflon tubing sequentially wrapped with heat-resistant fiber strips, a rubberized heating tape (with a plug at one end), and heat-resistant adhesive tape. A flexible thermocouple or some other suitable temperature-measuring device shall be placed between the Teflon tubing and the fiber strips so that the temperature can be monitored. The probe should be sheathed in stainless steel to provide in-stack rigidity. A series of bored-out stainless steel fittings placed at the front of the sheath will prevent flue gas from entering between the probe and sheath. The sampling probe is depicted in Figure 15A-2.

6.1.2 **Particulate Filter.** A 50-mm Teflon filter holder and a 1- to 2-mm porosity Teflon filter (available through Savillex Corporation, 5325 Highway 101, Minnetonka, Minnesota 55345). The filter holder must be

maintained in a hot box at a temperature high enough to prevent condensation.

6.1.3 Combustion Air Delivery System. As shown in the schematic diagram in Figure 15A-3. The rate meter should be selected to measure an air flow rate of 0.5 liter/min (0.02 ft³/min).

6.1.4 Combustion Tube. Quartz glass tubing with an expanded combustion chamber 2.54 cm (1 in.) in diameter and at least 30.5 cm (12 in.) long. The tube ends should have an outside diameter of 0.6 cm (¼ in.) and be at least 15.3 cm (6 in.) long. This length is necessary to maintain the quartz-glass connector near ambient temperature and thereby avoid leaks. Alternatively, the outlet may be constructed with a 90 degree glass elbow and socket that would fit directly onto the inlet of the first peroxide impinger.

6.1.5 Furnace. Of sufficient size to enclose the combustion tube. The furnace must have a temperature regulator capable of maintaining the temperature at 1100 ±50 °C (2,012 ±90 °F). The furnace operating temperature must be checked with a thermocouple to ensure accuracy. Lindberg furnaces have been found to be satisfactory.

6.1.6 Peroxide Impingers, Stopcock Grease, Temperature Sensor, Drying Tube, Valve, Pump, and Barometer. Same as in Method 6, sections 6.1.1.2, 6.1.1.4, 6.1.1.5, 6.1.1.6, 6.1.1.7, 6.1.1.8, and 6.1.2, respectively, except that the midjet bubbler of Method 6, section 6.1.1.2 is not required.

6.1.7 Vacuum Gauge and Rate Meter. At least 760 mm Hg (30 in. Hg) gauge and rotameter, or equivalent, capable of measuring flow rate to ±5 percent of the selected flow rate and calibrated as in section 10.2.

6.1.8 Volume Meter. Dry gas meter capable of measuring the sample volume under the particular sampling conditions with an accuracy of 2 percent.

6.1.9 U-tube manometer. To measure the pressure at the exit of the combustion gas dry gas meter.

6.2 Sample Recovery and Analysis. Same as Method 6, sections 6.2 and 6.3, except a 10-ml buret with 0.05-ml graduations is required for titrant volumes of less than 10.0 ml, and the spectrophotometer is not needed.

7.0 Reagents and Standards

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

7.1 Sample Collection. The following reagents and standards are required for sample analysis:

7.1.1 Water. Same as Method 6, section 7.1.1.

7.1.2 Hydrogen Peroxide (H₂O₂), 3 Percent by Volume. Same as Method 6, section 7.1.3 (40 ml is needed per sample).

7.1.3 Recovery Check Gas. Carbonyl sulfide in nitrogen [100 parts per million by volume (ppmv) or greater, if necessary] in an aluminum cylinder. Concentration certified by the manufacturer with an accuracy of ±2 percent or better, or verified by gas chromatography where the instrument is calibrated with a COS permeation tube.

7.1.4 Combustion Gas. Air, contained in a gas cylinder equipped with a two-stage regulator. The gas shall contain less than 50 ppb of reduced sulfur compounds and less than 10 ppm total hydrocarbons.

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

8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Preparation of Sampling Train. For the Method 6 part of the train, measure 20 ml of 3 percent H₂O₂ into the first and second midjet impingers. Leave the third midjet impinger empty and add silica gel to the fourth impinger. Alternatively, a silica gel drying tube may be used in place of the fourth impinger. Place crushed ice and water around all impingers. Maintain the oxidation furnace at 1100 ±50 °C (2,012 ±90 °F) to ensure 100 percent oxidation of COS. Maintain the probe and filter temperatures at a high enough level (no visible condensation) to prevent moisture condensation and monitor the temperatures with a thermocouple.

8.2 Leak-Check Procedure. Assemble the sampling train and leak-check as described in Method 6, section 8.2. Include the combustion air delivery system from the needle valve forward in the leak-check.

8.3 Sample Collection. Adjust the pressure on the second stage of the regulator on the combustion air cylinder to 10 psig. Adjust the combustion air flow rate to 0.5 ±0.05 L/min (1.1 ±0.1 ft³/hr) before injecting combustion air into the sampling train. Then inject combustion air into the sampling train, start the sample pump, and open the stack sample gas valve. Carry out these three operations within 15 to 30 seconds to avoid pressurizing the sampling train. Adjust the total sample flow rate to 2.0 ±0.2 L/min (4.2 ±0.4 ft³/hr). These flow rates produce an O₂ concentration of 5.0 percent in the stack gas, which must be maintained constantly to allow oxidation of reduced sulfur compounds to SO₂. Adjust these flow rates during sampling as necessary. Monitor and record the combustion air manometer reading at regular intervals during the sampling period. Sample for 1 or 3 hours. At the end of sampling, turn off the sample pump and combustion air simultaneously (within 30 seconds of each other). All other procedures are the same as in Method 6, section 8.3, except that the sampling train should not be purged. After collecting the

sample, remove the probe from the stack and conduct a leak-check according to the procedures outlined in section 8.2 of Method 6 (mandatory). After each 3-hour test run (or after three 1-hour samples), conduct one system performance check (see section 8.5). After this system performance check and before the next test run, it is recommended that the probe be rinsed and brushed and the filter replaced.

NOTE: In Method 15, a test run is composed of 16 individual analyses (injects) performed over a period of not less than 3 hours or more than 6 hours. For Method 15A to be consistent with Method 15, the following may be used to obtain a test run: (1) Collect three 60-minute samples or (2) collect one 3-hour sample. (Three test runs constitute a test.)

8.4 Sample Recovery. Recover the hydrogen peroxide-containing impingers as detailed in Method 6, section 8.4.

8.5 System Performance Check.

8.5.1 A system performance check is done (1) to validate the sampling train components and procedure (before testing, optional) and (2) to validate a test run (after a run, mandatory). Perform a check in the field before testing consisting of at least two samples (optional), and perform an additional check after each 3-hour run or after three 1-hour samples (mandatory).

8.5.2 The checks involve sampling a known concentration of COS and comparing the analyzed concentration with the known con-

centration. Mix the recovery gas with N₂ as shown in Figure 15A-4 if dilution is required. Adjust the flow rates to generate a COS concentration in the range of the stack gas or within 20 percent of the applicable standard at a total flow rate of at least 2.5 L/min (5.3 ft³/hr). Use Equation 15A-4 (see section 12.5) to calculate the concentration of recovery gas generated. Calibrate the flow rate from both sources with a soap bubble flow tube so that the diluted concentration of COS can be accurately calculated. Collect 30-minute samples, and analyze in the same manner as the emission samples. Collect the samples through the probe of the sampling train using a manifold or some other suitable device that will ensure extraction of a representative sample.

8.5.3 The recovery check must be performed in the field before replacing the particulate filter and before cleaning the probe. A sample recovery of 100 ±20 percent must be obtained for the data to be valid and should be reported with the emission data, but should not be used to correct the data. However, if the performance check results do not affect the compliance or noncompliance status of the affected facility, the Administrator may decide to accept the results of the compliance test. Use Equation 15A-5 (see section 12.6) to calculate the recovery efficiency.

9.0 Quality Control

Section	Quality control measure	Effect
8.5	System performance check	Ensures validity of sampling train components and analytical procedure.
8.2, 10.0	Sampling equipment leak-check and calibration.	Ensures accurate measurement of stack gas flow rate, sample volume.
10.0	Barium standard solution standardization	Ensures precision of normality determination.
11.1	Replicate titrations	Ensures precision of titration determinations.

10.0 Calibration and Standardization

10.1 Metering System, Temperature Sensors, Barometer, and Barium Perchlorate Solution. Same as Method 6, sections 10.1, 10.2, 10.4, and 10.5, respectively.

10.2 Rate Meter. Calibrate with a bubble flow tube.

11.0 Analytical Procedure

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

12.0 Data Analysis and Calculations

In the calculations, retain at least one extra decimal figure beyond that of the acquired data. Round off figures after final calculations.

12.1 Nomenclature.

- C_{COS} = Concentration of COS recovery gas, ppm.
- C_{RC(Act)} = Actual concentration of recovery check gas (after dilution), ppm.
- C_{RC(Ins)} = Measured concentration of recovery check gas generated, ppm.
- C_{RS} = Concentration of reduced sulfur compounds as SO₂, dry basis, corrected to standard conditions, ppm.
- N = Normality of barium perchlorate titrant, milliequivalents/ml.
- P_{bar} = Barometric pressure at exit orifice of the dry gas meter, mm Hg.
- P_{std} = Standard absolute pressure, 760 mm Hg.
- Q_{COS} = Flow rate of COS recovery gas, liters/min.
- Q_N = Flow rate of diluent N₂, liters/min.
- R = Recovery efficiency for the system performance check, percent.
- T_m = Average dry gas meter absolute temperature, °K.

Environmental Protection Agency

Pt. 60, App. A-5, Meth. 15A

- T_{std} = Standard absolute temperature, 293 °K.
- V_a = Volume of sample aliquot titrated, ml.
- V_{ms} = Dry gas volume as measured by the sample train dry gas meter, liters.
- V_{mc} = Dry gas volume as measured by the combustion air dry gas meter, liters.
- V_{ms(std)} = Dry gas volume measured by the sample train dry gas meter, corrected to standard conditions, liters.
- V_{mc(std)} = Dry gas volume measured by the combustion air dry gas meter, corrected to standard conditions, liters.
- V_{soln} = Total volume of solution in which the sulfur dioxide sample is contained, 100 ml.
- V_t = Volume of barium perchlorate titrant used for the sample (average of replicate titrations), ml.
- V_{tb} = Volume of barium perchlorate titrant used for the blank, ml.
- Y = Calibration factor for sampling train dry gas meter.
- Y_c = Calibration factor for combustion air dry gas meter.
- 32.03 = Equivalent weight of sulfur dioxide, mg/meq.

$$12025 \frac{\mu\text{l}}{\text{meq}} = \frac{(32.03 \text{ mg})}{\text{meq}} \frac{(24.051)}{\text{mole}} \frac{(\text{mole})(\text{lg})(10^3 \text{ ml})(10^3 \mu\text{l})}{(64.06 \text{ g})(10^3 \text{ mg})(1)(\text{ml})}$$

12.2 Dry Sample Gas Volume, Corrected to Standard Conditions.

$$\begin{aligned} V_{m(\text{std})} &= V_{ms} Y \frac{T_{\text{std}} P_{\text{bar}}}{T_m P_{\text{std}}} && \text{Eq. 15A-1} \\ &= K_1 Y \frac{V_m P_{\text{bar}}}{T_m} \end{aligned}$$

Where:
 K₁ = 0.3855 °K/mm Hg for metric units,
 = 17.65 °R/in. Hg for English units.

12.3 Combustion Air Gas Volume, corrected to Standard Conditions.

$$V_{mc(\text{std})} = k_1 Y_c \frac{(V_{mc})(P_{\text{bar}})}{T_m} \quad \text{Eq. 15A-2}$$

NOTE: Correct P_{bar} for the average pressure of the manometer during the sampling period.

12.4 Concentration of reduced sulfur compounds as ppm SO₂.

$$C_{RS} = K_2 N \frac{(V_t - V_{tb})(V_{\text{soln}}/V_a)}{V_{ms(\text{std})} - V_{mc(\text{std})}} \quad \text{Eq. 15A-3}$$

Where:

$$K_2 = 32.03 \frac{\text{mg}}{\text{meq}} \frac{24.05 \text{ l}}{\text{mole}} \frac{1 \text{ mole}}{64.06 \text{ g}} \frac{1 \text{ g}}{10^3 \text{ mg}} \frac{10^3 \text{ ml}}{1} \frac{10^3 \mu\text{l}}{1 \text{ ml}}$$

$$= \frac{12025 \text{ ml}}{\text{meq}}$$

12.5 Concentration of Generated Recovery Gas.

$$C_{\text{RG}} = \frac{(C_{\text{cos}})(Q_{\text{cos}})}{Q_{\text{cos}} + Q_{\text{N}_2}} \quad \text{Eq. 15A-4}$$

12.6 Recovery Efficiency for the System Performance Check.

$$R = \frac{C_{\text{RG(m)}}}{C_{\text{RG(act)}}} \times 100 \quad \text{Eq. 15A-5}$$

13.0 Method Performance

13.1 Analytical Range. The lower detectable limit is 0.1 ppmv when sampling at 2 lpm for 3 hours or 0.3 ppmv when sampling at 2 lpm for 1 hour. The upper concentration limit of the method exceeds concentrations of reduced sulfur compounds generally encountered in sulfur recovery plants.

13.2 Precision. Relative standard deviations of 2.8 and 6.9 percent have been obtained when sampling a stream with a reduced sulfur compound concentration of 41 ppmv as SO₂ for 1 and 3 hours, respectively.

13.3 Bias. No analytical bias has been identified. However, results obtained with this method are likely to contain a positive bias relative to emission regulations due to the presence of nonregulated sulfur compounds (that are present in petroleum) in the emissions. The magnitude of this bias varies accordingly, and has not been quantified.

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

1. American Society for Testing and Materials Annual Book of ASTM Standards, Part 31: Water, Atmospheric Analysis. Philadelphia, Pennsylvania, 1974, pp. 40-42.
2. Blosser, R.O., H.S. Oglesby, and A.K. Jain. A Study of Alternate SO₂ Scrubber Designs Used for TRS Monitoring. National Council of the Paper Industry for Air and Stream Improvement, Inc., New York, New York. Special Report 77-05, July 1977.
3. Curtis, F., and G.D. McAlister. Development and Evaluation of an Oxidation/Method 6 TRS Emission Sampling Procedure. Emission Measurement Branch, Emission Standards and Engineering Division, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, February 1980.
4. Gellman, I. A Laboratory and Field Study of Reduced Sulfur Sampling and Monitoring Systems. National Council of the Paper Industry for Air and Stream Improvement, Inc., New York, New York. Atmospheric Quality Improvement Technical Bulletin No. 81, October 1975.
5. Margeson, J.H., et al. A Manual Method for TRS Determination. Journal of Air Pollution Control Association, 35:1280-1286, December 1985.

17.0 Tables, Diagrams, Flowcharts, and Validation Data

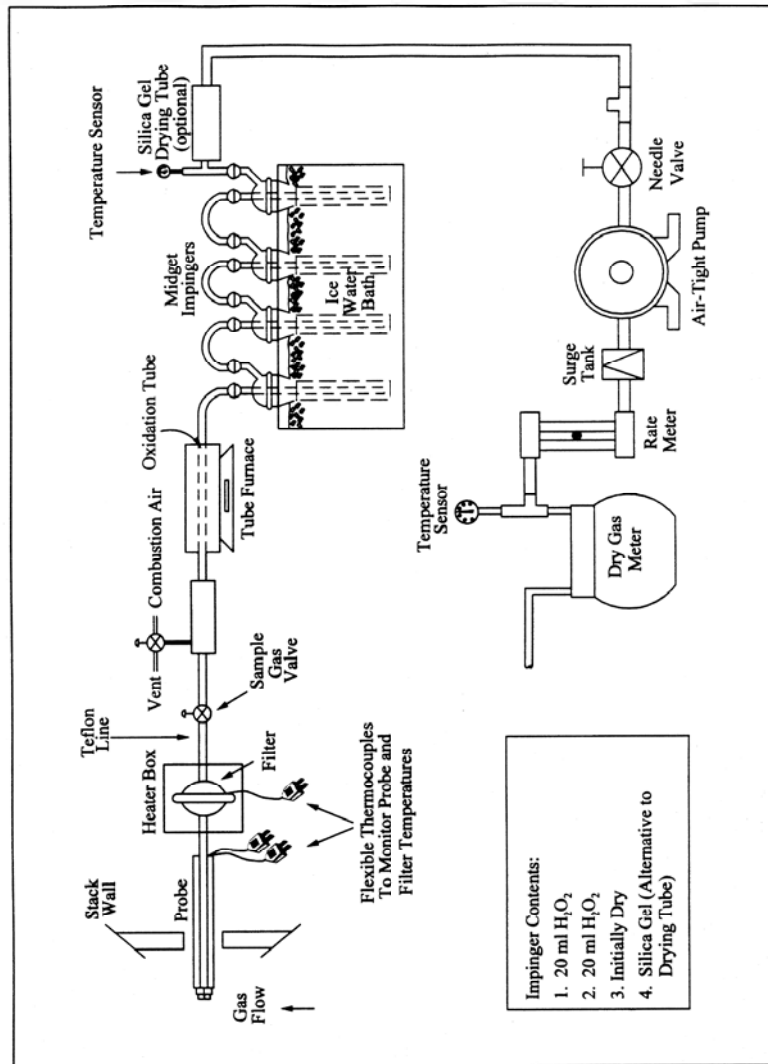


Figure 15A-1. Method 15A Sampling Train.

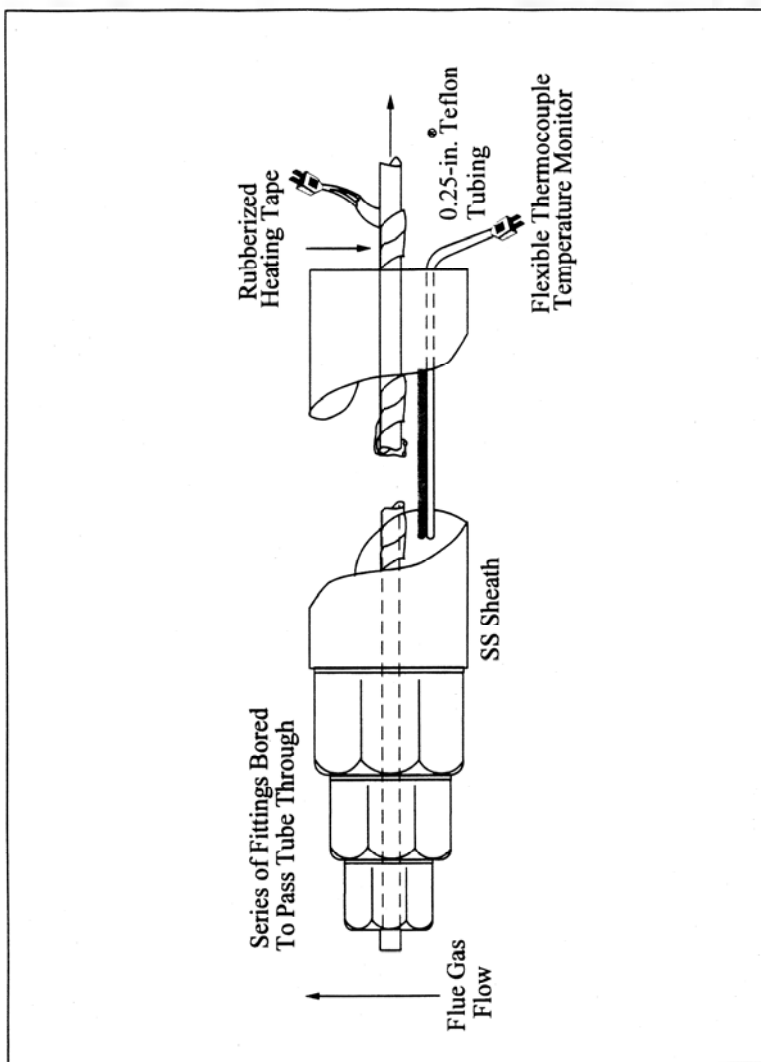


Figure 15A-2. Method 15A Sampling Probe.

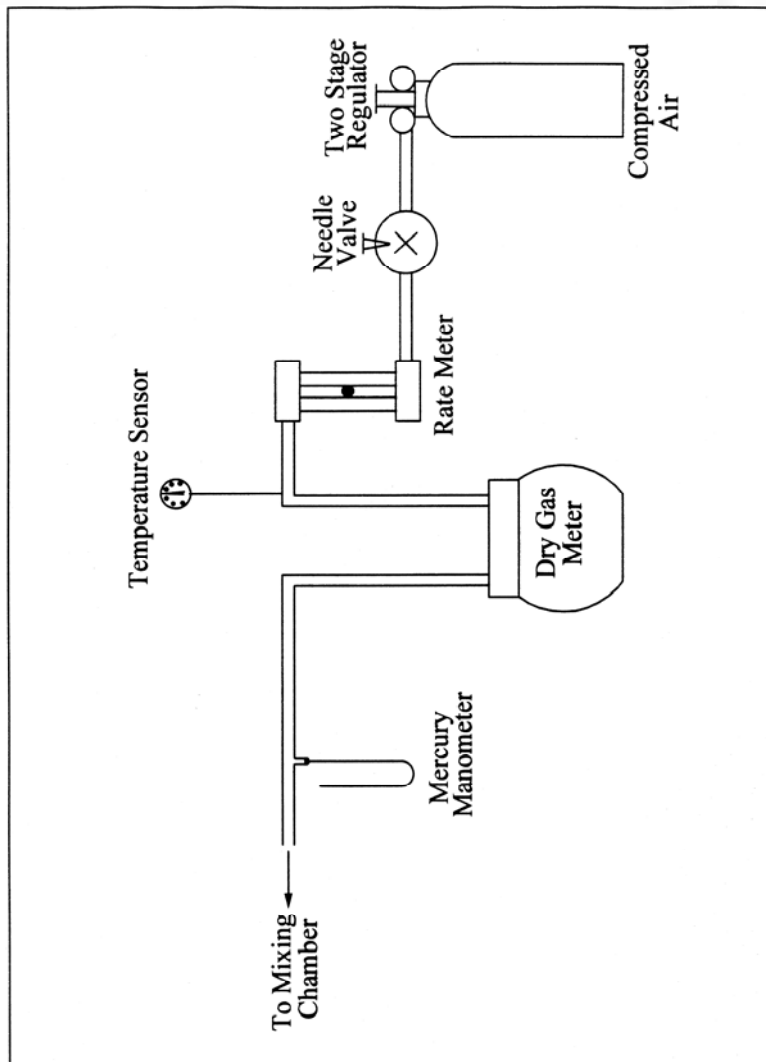


Figure 15A-3. Combustion Air Delivery System.

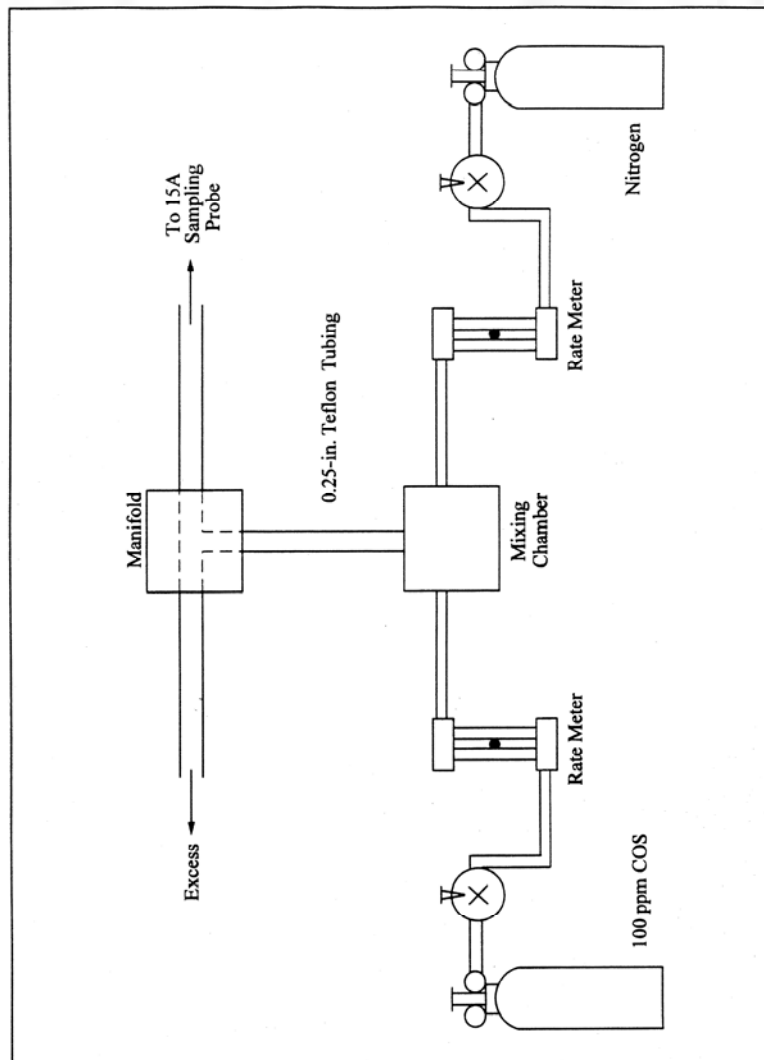


Figure 15A-4. Recovery Gas Generator System.

[36 FR 24877, Dec. 23, 1971]

EDITORIAL NOTE: For FEDERAL REGISTER citations affecting appendix A-5 to part 60, see the List of CFR sections Affected, which appears in the Finding Aids section of the printed volume and at www.fdsys.gov.