State of California
Air Resources Board

Method 16

Semicontinuous Determination of Sulfur Emissions from Stationary Sources

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Amended: ______________

Note: this document consists of the text of the proposed amendment to Method 16. Proposed deletions are noted by graphic screen and proposed additions are noted by underline.

Method 16 Semicontinuous Determination of Sulfur Emissions From Stationary Sources

Introduction

The method described below uses the principle of gas chromatographic separation and flame photometric detection (FPD). Since there are many systems or sets of operating conditions that represent useable methods of determining sulfur emissions, all systems which employ this principle, but differ only in details of equipment and operation, may be used as alternative methods, provided that criteria below calibration precision and sample line loss criteria are met.

1. Principle and Applicability

1.1 Principle. A gas sample is extracted from the emission source and diluted with clean dry air. Aan aliquot of the diluted sample is then analyzed for hydrogen sulfide (H_2S), methyl mercaptan (MeSH), dimethyl sulfide (DMS), and dimethyl disulfide (DMDS) by gas chromatographic (GC) separation and flame photometric detection (FPD). These four compounds are know collectively as total reduced sulfur (TRS).

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.

1.2 Applicability. This method is applicable for determination of TRS compounds from recovery furnaces, lime kilns, and smelt dissolving tanks at kraft pulp mills.

2. Range and Sensitivity

2.1 Range. The analytical range will vary with the sample loop size. Typically, the analytical range may extend from 0.1 to 100 ppm using 10 to 0.1-ml sample loop sizes. This eliminates the need for sample dilution in most cases. Coupled with a gas chromatographic system utilizing a ten milliliter sample size, the maximum limit of the FPD for each sulfur compound is approximately 1 ppm. This limit is expanded by dilution of the sample before analysis. Kraft mill gas samples are normally diluted tenfold (9:1), resulting in an upper limit of about 10 ppm for each sample.

For sources with emission levels between 10 and 100 ppm, the measuring range can be best extended by reducing the sample size to 1 milliliter.

2.2 Sensitivity. Using the 10-ml sample size, the minimum detectable concentration is approximately 50 ppb.

3. Interferences

3.1 Moisture Condensation. Moisture condensation in the sample delivery system, the analytical column, or the FPD burner block can cause losses or interferences. This is prevented by maintaining the probe, filter box, and connections at a temperature of at least 120°C (248°F). Moisture is removed in the SO_2 scrubber and heating the sample beyond this point is not necessary provided the ambient temperature is above 0°C. Alternatively, moisture may be eliminated by heating the sample line, and by conditioning the sample with dry dilution air to lower its dew point below the operating temperature of the GC/FPD analytical system prior to analysis. This potential is eliminated by heating the sample line, and by conditioning the sample with dry dilution air to lower it's dew point below the operating temperature of the GC/FPD analytical system prior to analysis.

3.2 Carbon Monoxide and Carbon Dioxide. CO and CO_2 have a substantial desensitizing effect on the flame photometric detector even after 9:1 dilution. Acceptable systems must demonstrate that they have eliminated this interference by some procedure such as eluting these compounds before any of the compounds to be measured. Compliance with this requirement can be demonstrated by submitting chromatograms of calibration gases with and without CO_2 in the diluent gas. The CO_2 level should be approximately 10 percent for the case with CO_2 present. The two chromatograms chromatographs should show agreement within the precision limits of Section 4.1.

3.3 Particulate Matter. Particulate matter in gas samples can cause interference by eventual clogging of the analytical system. This interference must be is eliminated by using the Teflon filter after the probe.

3.4 Sulfur Dioxide (SO_2). Sulfur dioxide is not a specific interferent but may be present in such large amounts that it cannot be effectively separated from the other compounds of interest. The SO_2 scrubber described in Section 5.1.3 will effectively remove SO_2 from the sample. The procedure must be designed to eliminate this problem either by the choice of separation columns or by removal of SO_2 from the sample. In the example system, SO_2 is removed by a citrate buffer solution prior to GC injection. This scrubber will be used when SO_2 levels are high enough to prevent baseline separation from the reduced sulfur compounds.

Compliance with this section can be demonstrated by submitting chromatographs of calibration gases with SO_2 present in the same quantities expected from the emission source to be tested.

Acceptable systems shall show baseline separation with the amplifier attenuation set so that the reduced sulfur compound of concern is at least 50 percent of full scale. Baseline separation is defined as a return to zero ±5 percent in the interval between peaks.

4. Precision and Accuracy

4.1 GC/FPD 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.

4.2 Calibration Drift. The calibration drift determined from the mean of three injections made at the beginning and end of any 8 hour period run or series of runs within a 24-hour period shall not exceed ±10 percent 5 percent.

4.3 System Calibration Accuracy. Losses through the sample transport system must be measured and a correction factor developed to adjust the calibration accuracy to 100 percent.

5. Apparatus (See Figure 16-1)

5.1. Sampling.

5.1.1 Probe. The probe must be made of inert material such as stainless steel or glass. It should be designed to incorporate a filter and to allow calibration gas to enter the probe at or near the sample entry point. Any portion of the probe not exposed to the stack gas must be heated to prevent moisture condensation.

5.1.1.1 Teflon or Teflon-lined stainless steel. The probe must be heated to prevent moisture condensation. It shall be designed to allow calibration gas to enter the probe at or near the sample point entry. Any portion of the probe that contacts the stack gas must be heated to prevent moisture condensation.

5.1.1.2 Figure 16-1 illustrates the probe used in lime kilns and other sources where significant amounts of particulate matter are present. The probe is designed with the deflector shield placed between the sample and the gas inlet holes to reduce clogging of the filter and possible adsorption of sample gas. As an alternative, the probe described in Section 2.1.1 of Methods 16A having a nozzle directed away from the gas stream may be used at sources having significant amounts of particulate matter.

Note: Mention of trade names or specific products does not constitute an endorsement by the Air Resources Board.

5.1.2 Particulate Filter. 50-mm Teflon filter holder and a 1- to 2-micron porosity Teflon filter (available through Savillex Corporation, 5325 Highway 101, Minnetonka, Minnesota 55343). The filter holder must be maintained in a hot box at a temperature of at least 120°C (248°F).

5.1.3 SO_2 Scrubber.

5.1.3.1 Three 300-ml Teflon segmented impingers connected in series with flexible, thick-walled, Teflon tubing. (Impinger parts and tubing available through Savillex.) The first two impingers contain 100 ml of citrate buffer and the third impinger is initially dry. The tip of the tube inserted into the solution should be constricted to less than 3-mm (1/8-in.) ID and should be immersed to a depth of at least 5 cm (2 in.). Immerse the impingers in an ice water bath and maintain near 0°C. The scrubber solution will normally last for a 3-hour run before needing replacement. This will depend upon the effects of moisture and particulate matter on the solution strength and pH.

5.1.3.2 Connections between the probe, particulate filter, and SO_2 scrubber shall be made of Teflon and as short in length as possible. All portions of the probe, particulate filter, and connections prior to the SO_2 scrubber (or alternative point of moisture removal) shall be maintained at a temperature of at least 120°C (248°F).

5.1.2 5.1.4 Sample Line. The sample line must be made of Teflon, no greater than

1.3 cm 1.3-cm (1/2-in.) inside diameter ID. All parts from the probe to the dilution system must be thermostatically heated to 120°C. Alternative materials, such as virgin Nylon, may be used provided the line loss test is acceptable.

5.1.3 5.1.5 Sample Pump. The sample pump shall be leakless Teflon-coated diaphragm type or equivalent. If the pump is upstream of the dilution system, the pump head must be heated to 120°C.

5.2 Dilution System. The dillution system must be constructed such that all sample contacts are made of inert material (e.g., stainless steel, or Teflon). It must be heated to 120°C and be capable of approximately a 9:1 dilution of the sample. Needed only for high sample concentrations. The dilution system must be constructed such that all sample contacts are made of Teflon, glass, or stainless steel.

5.3 SO_2 Scrubber. The SO_2 scrubber is a midget impinger packed with glass wool to eliminate entrained mist and charged with potassium citrate buffer.

5.4 5.3 Gas Chromatograph. The gas chromatograph must have at least the following components:

5.43.1 Oven. Capable of maintaining the separation column at the proper operating temperature ±1 °C.

5.43.2 Temperature Gauge. To monitor column oven, detector, and exhaust temperature ±1 °C.

5.43.3 Flow System. Gas metering system to measure sample, fuel, combustion gas, and carrier gas flows.

5.43.4 Flame Photometric Detector.

5.43.4.1 Electrometer. Capable of full scale amplification of linear ranges of 10^{-9} to 10^{-4} amperes full scale.

5.43.4.2 Power Supply. Capable of delivering up to 750 volts.

5.43.4.3 Recorder. Compatible with the output voltage range of the electrometer.

5.3.4.4 Rotary Gas Valves. Multiport Teflon-lined valves equipped with sample loop. Sample loop volumes shall be chosen to provide the needed analytical range. Teflon tubing and fittings shall be used throughout to present an inert surface for sample gas. The gas chromatograph shall be calibrated with the sample loop used for sample analysis.

5.5 5.4 Gas Chromatograph Columns. The column system must be demonstrated to be capable of resolving the four major reduced sulfur compounds: H_2S, MeSH, DMS, and DMDS. It must also demonstrate freedom from known interferences.

To demonstrate that adequate resolution has been achieved, the tester must submit a chromatograph chromatogram of a calibration gas containing all four of the TRS compounds in the concentration range of the applicable standard. Adequate resolution will be defined as base line separation of adjacent peaks when the amplifier attenuation is set so that the smaller peak is at least 50 percent of full scale. Baseline separation is defined in Section 3.4 as a return to zero ±5 percent in the interval between peaks. Systems not meeting this criteria may be considered alternate methods subject to the approval of the Control Agency's authorized representativeExecutive Officer.

5.6 5.5 Calibration System. The calibration system must contain the following components. (Figure 16-2)

5.65.1 Tube Chamber. Chamber of glass or Teflon of sufficient dimensions to house permeation tubes.

5.65.2 Flow System. To measure air flow over permeation tubes at ±2 percent. Each flowmeter shall be calibrated after a complete test series with a wet test meter. If the flow measuring device differs from the wet test meter by 5 percent, the completed test shall be discarded. Alternatively, the tester may elect to use the flow data that would yield the lower flow measurement. Calibration with a wet test meter before a test is optional. Flow over the permeation device may also be determined using a soap bubble flowmeter.

5.65.3 Constant Temperature Bath. Device capable of maintaining the permeation tubes at the calibration temperature within ±0.1 ^{o}C.

5.65.4 Temperature Gauge. Thermometer or equivalent to monitor bath temperature within ±1 ^{o}C ±0.1^{o}C.

6. Reagents

6.1 Fuel. Hydrogen (H_2), prepurified grade or better.

6.2 Combustion Gas. Oxygen (O_2) or air, research purity or better.

6.3 Carrier Gas. Prepurified grade or better.

6.4 Diluent (If required). Air containing less than 50 ppb total sulfur compounds and less than 10 ppm each of moisture and total hydrocarbons. This gas must be heated prior to mixing with the sample to avoid water condensation at the point of contact

6.5 Calibration Gases. Permeation tubes, one each of H_2S, MeSH, DMS, and DMDS, 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.

6.6 Citrate Buffer. Dissolve 300 grams of potassium citrate and 41 grams of anhydrous citric acid in 1 liter of deionized water. Two hundred eightyfour 284 grams 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.

6.7 Sample Line Loss Gas (Optional). As an alternative to permeation gas, H_2S cylinder gas may be used for the sample line loss test. The gas shall be calibrated against permeation devices having known permeation rates or by the procedure in Section 7 of Method 16A.

7. Pretest Procedures

The following procedures are optional but would be helpful in preventing any problem which might occur later and invalidate the entire test.

7.1 After the complete measurement system has been set up at the site and deemed to be operational, the following procedures are to should be completed before sampling is initiated.

7.1.1 Leak Test. Appropriate leak test procedures should be employed to verify the integrity of all components, sample lines, and connections. The following leak test 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 greater than 50 mm (2 in.) Hg vacuum, 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 10.1 may be performed to verify the integrity of components.

7.1.2 System Performance. Since the complete system is calibrated following each test, the precise calibration of each component is not critical. However, these components should be verified to be operating 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 and ascertaining the response to be within predicted limits. In any component, or if 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. Calibration

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. The calibration must, however, be verified as prescribed in Section 10, after the last run made within the 24-hour period.)

8.1 General Considerations. This section outlines steps to be followed for use of the GC/FPD and the dilution system (if applicable). The 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 citations in the Bibliography at the end of this method are recommended for review for this purpose.

8.2 Calibration Procedure. 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 ^{o}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 the precision limits of Section 4.1.

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 parts per million generated by a tube containing a specific permeant can be calculated as follows:

$$C = \frac{KP_r}{ML} \qquad \text{Eq. 16-1}$$

Where:
C = Concentration of permeant producesd in ppm.
Pr = Permeation rate of the tube in µg/min.
M = Molecular weight of the permeant (g/g-mole).
L = Flow rate, l/min, of air over permeant @ 20 ^{o}C, 760 mm Hg.
K = Gas constant at 20 ^{o}C and 760 mm Hg
= 24.04 l /g mole.

8.3 Calibration of Analysis System. Generate a series of three or more known concentrations spanning the linear range of the FPD (approximately 0.05 to 1.0 0.5 to 10 ppm for a 1-ml sample) for each of the four major sulfur compounds. Bypassing the dilution system but using the SO2 scrubber, inject Inject these standards into the GC/FPD analyzers and monitor the responses. Three injects injections for each concentration must yield the precision specified in Section 4.1 not vary by more than 5 percent from the mean of the three injections. Failure to attain this precision is an indication of a problem in the calibration or analytical system. Any such problem must be identified and corrected before proceeding.

8.4 Calibration Curves. Plot the GC/FPD response in current (amperes) versus their causative concentrations in ppm 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.

8.5 Calibration of Dilution System. Generate a known concentration of hydrogen sulfide 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 and monitor its response. Three injections for each dilution must yield the precision described in Section 4.1. 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 H_2S (developed under 8.3) determine the diluted calibration gas concentration in ppm. Then calculate the dilution factor as the ratio of the calibration gas concentration before dilution to the diluted calibration gas concentration determined under this paragraph. 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. This 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 of Section 4.1 are still applicable.

9. Sampling and Analysis Procedure

9.1 Sampling. Insert the sampling probe into the test port making certain 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 that which is determined in paragraph 8.5. Condition the entire system with sample for a minimum of 15 minutes prior to commencing analysis.

9.2 Analysis. Aliquots of diluted sample pass through the SO2 scrubber and are then are injected into the GC/FPD analyzer for analysis.

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

9.2.2 Observation for Clogging of Probe or Filter. 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 sample probe or filter is clogged with particulate matter. If the probe either is found to be clogged, the test must be stopped and the results up to that point discarded. Testing may resume after cleaning the probe or replacing it with a clean one the probe and filter. After each run, the sample probe and filter shall must be inspected and, if necessary, dismantled and cleaned replaced.

10. Post-Test Procedures

10.1 Sample line loss. A known concentration of hydrogen sulfide 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 normal manner. (See figure 16-1). The resulting measured concentration should be compared to the known value to determine the sampling system loss.

For sampling losses greater than 20 percent in a sample run, the sample run is not to be used when determining the arithmetic mean of the performance test. For sampling losses of 0-20 percent, the sample concentration must be corrected by dividing the sample concentration by the fraction of recovery. The fraction of recovery is equal to one minus the ratio of the measured concentration to the known concentration of hydrogen sulfide in the sample line loss procedure. The known gas sample may be generated using permeation tubes. Alternatively, cylinders of hydrogen sulfide mixed in air nitrogen and certified according to section 6.7 may be used provided they are traceable to permeation tubes. The optional pretest procedures provide a good guideline for determining if there are leaks in the sampling system.

10.2 Recalibration. After each run, or after a series of runs made within a 24-hour period, perform a partial recalibration using the procedures in Section 8. Only H_2S (or other permeant calibration gas) need be used to recalibrate the GC/FPD analysis system (Section 8.3) and the dilution system (Section 8.5).

10.3 Determination of Calibration Drift. Compare the calibration curves obtained prior to the runs, to the calibration curves obtained under paragraph 10.1 Section 10.2. The calibration drift should not exceed the limits set forth in subsection Section 4.2. If the drift exceeds this limit, the intervening run or runs should be considered not valid. The tester, however, may instead have the option of choosing the calibration data set which would give the highest sample values.

11. Calculations

11.1 Determine the concentrations of each reduced sulfur compound detected directly from the calibration curves. Alternatively, the concentrations may be calculated using the equation for the least squares line.

11.2 Calculation of TRS. Total reduced sulfur will be determined for each analysis made by summing the concentrations of each reduced sulfur compound resolved during a given analysis.

$$TRS = \Sigma(H_2S,\ MeSH,\ DMS,\ 2DMDS)\ d \qquad \text{Eq. 16-2}$$

Where:
TRS = Total reduced sulfur in ppm, wet dry basis.
H_2S = Hydrogen sulfide, ppm.
MeSH = Methyl mercaptan, ppm.
DMS = Dimethyl sulfide, ppm.
DMDS = Dimethyl disulfide, ppm.
d = Dilution factor, dimensionless.

11.3 Average TRS. The average TRS will be determined as follows:

$$\text{Average TRS} = \frac{\sum_{i=1}^{N} TRS_i}{N(1-B_{wo})} \qquad \text{Eq. 16-3}$$

Where:
Average TRS = Average total reduced sulfur in ppm, dry basis.
TRS_i = Total reduced sulfur in ppm as determined by Equation 16-2.
N = Number of samples.

B_{wo} = Fraction of volume of water vapor in the gas stream as determined by reference Method 1-4 Method 4 - Determination of Moisture in Stack Gases.

11.4 Average Concentration of Individual Reduced Sulfur Compounds.

$$C = \frac{\sum_{i=1}^{N} S_i}{N} \qquad \text{Eq. 16-4}$$

Where:
S_i = Concentration of any reduced sulfur compound from the ith sample injection, ppm.
C = Average concentration of any one of the reduced sulfur compounds for the entire run, ppm.
N = Number of injections in any run period.

12 Example System

12.1 Apparatus

12.1.1 Sample System

12.1.1.1 Probe. Figure 16-1 illustrates the probe used in lime kilns and other sources where significant amounts of particulate matter are present. The probe is designed with the deflector shield placed between the sample and the gas inlet holes and the glass wool plugs to reduce clogging of the filter and possible desorption of sample gas. The exposed portion of the probe between the sampling point and the sample line is heated with heating tape.

12.1.1.2 Sample Line. 3/16 inch inside diameter Teflon tubing heated to 120°C. This temperature is controled by a thermostatic heater.

12.1.1.3 Sample Pump. Leakless Teflon coated diaphragm type or equivalent. The pump head is heated to 120°C by enclosing it in the sample dilution box (12.2.4 below).

12.1.2 Dilution System. A schematic of the dynamic dilution system is given in Figure 16-2. The dilution system is constructed such that all sample contacts are made of inert materials. The dilution system which is heated to 120°C must be capable of a minimum of 9:1 dilution of sample. Equipment used in the dilution system is listed below:

12.1.2.1 Dilution Pump. Model A-150 Kohmyhr Teflon positive displacement type, nonadjustable 150 cc/mon.± 2.0 percent, or equivalent, per dilution stage. A 9:1 dilution of sample is accomplished by combining

150 cc of sample with 1350 cc of clean dry air as shown in figure 16-2.

12.1.2.2 Valves. Three-way Teflon solenoid or manual type.

12.1.2.3 Tubing. Teflon tubing and fittings are used throughout from the sample probe to the GC/FPD to present an inert surface for sample gas.

12.1.2.4 Box. Insulated box, heated and maintained at 120°C , of sufficient dimensions to house dilution apparatus.

12.2.3.5 Flowmeters. Rotameters or equivalent to measure flow from 0 to 1500 ml/min. ±1 percent per dilution stage.

12.1.3 SO_2 Scrubber. Midget impinger with15 ml of potassium citrate buffer to absorb SO_2 in the sample.

12.1.4 Gas Chromatograph Columns. Two types of columns are used for separation of low and high molecular weight sulfur compounds:

12.1.4.1 Low Molecular Weight Sulfur Compounds Column (GC/FPD-I)

12.1.4.1.1 Separation Column. 11m by 2.16 mm (36 ft by 0.085 in.) Inside diameter Teflon tubing packed with 30/60 mesh Teflon coated with 5 percent polyphenyl ether and 0.05 percent orthophosphoric acid, or equivalent (see figure 16-3).

12.1.4.1.2 Stripper or Precolumn. 0.06 m by 2.16 mm (2 ft by 0.085 in.) Inside diameter Teflon tubing.

12.1.4.1.3 Sample Valve. Teflon 10-port gas sampling valve, equipped with a 10 ml sampling loop, actuated by compressed air (Figure 16-3).

12.1.4.1.4 Oven. For containing sample valve, stripper column, and separation column. The oven should be capable of maintaining an elevated temperature ranging from ambient to 100°C, constant within ±1°C.

12.1.4.1.5 Temperature Monitor. Thermocouple pyrometer to measure column oven, detector and exhaust temperature ±1°C.

12.1.4.1.6 Flow System. Gas metering system to measure sample flow, hydrogen flow and oxygen flow (and nitrogen carrier gas flow).

12.1.4.1.7 Detector. Flame photometric detector.

12.1.4.1.8 Electrometer. Capable of full scale amplification of linear ranges of 10^{-9} to 10^{-4} amperes full scale.

12.1.4.1.9 Power supply. Capable of delivering up to 750 volts.

12.1.4.1.10 Recorder. Compatible with the output voltage of the electrometer.

12.1.4.2 High Molecular Weight Compounds Column (GC/FPD-II).

12.1.4.2.1 Separation Column. 3.05 m by 2.16 mm (10 ft 0.085 in.) Inside diameter Teflon tubing packed with 30/60 mesh Teflon coated with 10 percent Triton X-305, or equivalent.

12.1.4.2.2 Sample Valve. Teflon 6-port gas sampling valve, equipped with a 10 ml sample loop, actuated by compressed air (Figure 16-3).

12.1.4.2.3 Other Components. All components same as in 12.1.4.1.4 to 12.1.4.1.10.

12.1.5 Calibration. Permeation Tube System (Figure 16-4).

12.1.5.1 Tube Chamber. Glass chamber of sufficient dimensions to house permeation tubes.

12.1.5.2 Mass Flowmeters. Two mass flowmeters in the range of 0-3 l/min. And 0-10 l/min. To measure air flow over permeation tubes at ±2 percent. These flowmeters shall be cross-calibrated at the beginning of each test. Using a convenient flow rate in the measuring range of both flowmeters, set and monitor the flow of gas over the permeation tubes. Injection of calibration gas generated at this flow rate as measured by one flowmeter followed by injection of calibration gas at the same flow rate as measured by the other flowmeter should agree within the specified precision limits. If they do not, then there is a problem with the mass flow measurement. Each mass flowmeter shall be calibrated prior to the first test with a wet test meter and therafter at least once each year.

12.1.5.3 Constant Temperature Bath. Capable of maintaining permeation tubes at certification temperature of 30^{o}C within ±0.1^{o}C.

12.2 Reagents.

12.2.1 Fuel. Hydrogen (H_2) prepurified grade or better.

12.2.2 Combustion Gas. Oxygen (O_2) research purity or better.

12.2.3 Carrier Gas. Nitrogen (N_2) prepurified grade or better.

12.2.4 Diluent. Air containing less than 0.5 ppb total sulfur compounds and less than 10 ppm each of moisture, and total hydrocarbons, and filtered using MSA filters 46727 and 79030, or equivalent. Removal of sulfur compounds can be verified by injecting dilution air only, described in section 8.3.

12.2.5 Compressed Air. 60 psig for GC valve actuation.

12.2.6 Calibration Gases. Permeation tubes gravimetrically calibrated and certified at 30.0^{o}C.

12.2.7 Citrate Buffer. Dissolve 300 grams of potassium citrate and 400 grams of anhydrous citric acid in 1 liter of deionized water..

12.3 Operating parameters.

12.3.1 Low Molecular Weight Sulfur Compounds. The operating parameters for the GC/FPD system used for low molecular weight compounds are as follows: nitrogen carrier gas flow rate of 50 cc/min., exhaust temperature of 110^{o}C, detector temperature of 105^{o}C, oven temperature of 40^{o}C, hydrogen flow rate of 80 cc/minute, oxygen flow rate of 20 cc/minute, and sample flow rate between 20 and 80 cc/minute.

12.3.2 High Molecular Weight Sulfur Compounds. The operating parameters for the GC/FPD system for high molecular weight compounds are the same as 12.3.1 except: oven temperature of 70^{o}C, and nitrogen carrier gas flow of 100 cc/min.

12.4 Analysis Procedure.

12.4.1 Analysis. Aliquots of diluted sample are injected simultaneously into both GC/FPD analyzers for analysis. GC/FPD is used to measure the low molecular weight reduced sulfur compounds. The low molecular weight compounds include hydrogen sulfide, methyl mercaptan, and dimethyl sulfide. GC/FPD-II is used to resolve the high molecular weight compound. The high molecular weight compound is dimethyl disulfide.

12.4.1.1 Analysis of Low-Molecular Weight Compounds. The sample valve is actuated for 3 minutes in which time an aliquot of diluted sample is injected onto the stripper column and analytical column. The valve is then deactivated for approximately 12 minutes in which time the analytical column continues to be foreflushed, the stripper column is backflushed, and the sample loop is refilled. Monitor the responses. The elution time for each compound will be determined during calibration.

12.4.1.2 Analysis of High-Molecular Weight Compounds. The procedure is essentially the same as above except that no stripper column is needed.

1312. Bibliography

1. EPA Method 16, Semicontinuous Determination of Sulfur Emissions from Stationary Sources, CFR40, Part 60, Appendix A

2. ARB Method 16A, Determination of Total Reduced Sulfur Emissions from Stationary Sources

(Impinger Method)

3. ARB Method 4, Determination of Moisture Content in Stack Gases

1. O'Keeffe, A. E. and G. C. Ortman. "Primary Standards for Trace Gas Analysis." Analytical Chemical Journal, 38,760 (1966).

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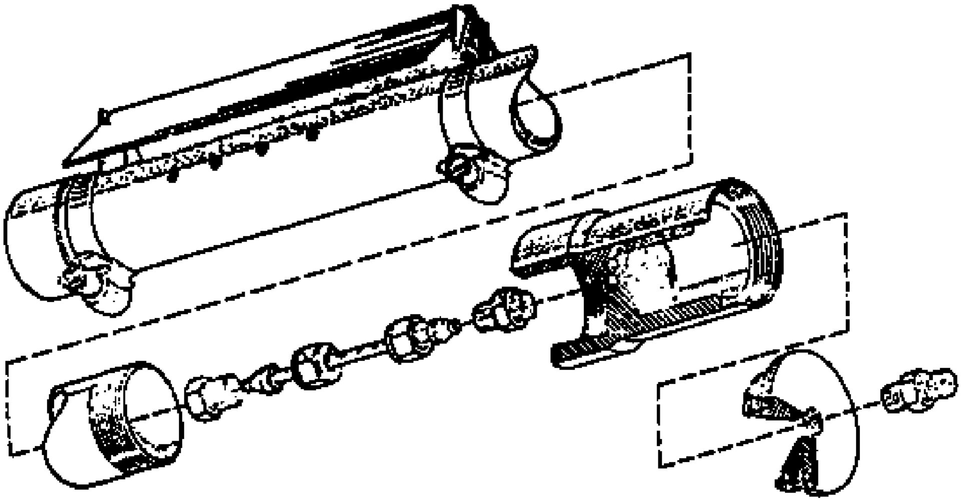

Figure 16-1. Probe Used for Sample Gas Containing High Particulate Loadings.

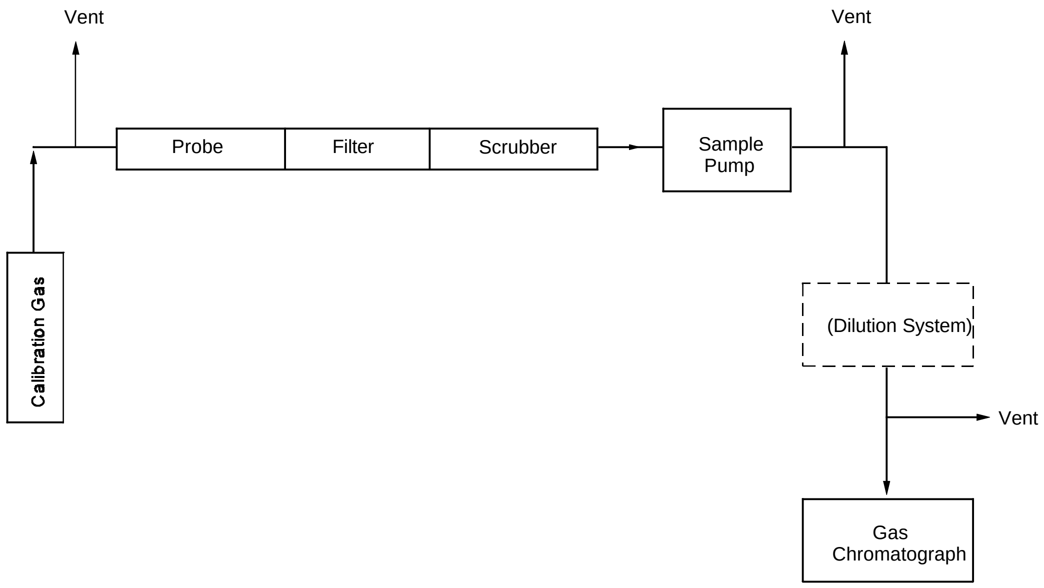

Figure 16-2. Determination of Sample Line Loss.