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METHOD 16B—DETERMINATION OF TOTAL REDUCED SULFUR EMISSIONS FROM STATIONARY SOURCES

NOTE: This method does not include all of the specifications (*e.g.*, equipment and supplies) and procedures (*e.g.*, sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a knowledge of at least the following additional test methods: Method 6C, Method 16, and Method 16A.

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS No.
Total reduced sulfur (TRS) including:	N/A
Dimethyl disulfide (DMDS), [(CH ₃) ₂ S ₂]	62-49-20
Dimethyl sulfide (DMS), [(CH ₃) ₂ S]	75-18-3
Hydrogen sulfide (H ₂ S)	7783-06-4
Methyl mercaptan (MeSH), [CH ₄ S]	74-93-1
Reported as: Sulfur dioxide (SO ₂)	7449-09-5

1.2 Applicability. This method is applicable for determining TRS emissions from recovery furnaces (boilers), lime kilns, and smelt dissolving tanks at kraft pulp mills, and from other sources when specified in an applicable subpart of the regulations. The flue gas must contain at least 1 percent oxygen for complete oxidation of all TRS to SO₂.

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 A gas sample is extracted from the stack. The SO₂ is removed selectively from the sample using a citrate buffer solution. The TRS compounds are then thermally oxidized to SO₂ and analyzed as SO₂ by gas chromatography (GC) using flame photometric detection (FPD).

3.0 Definitions [Reserved]

4.0 Interferences

4.1 Reduced sulfur compounds other than those regulated by the emission standards, if present, may be measured by this method. Therefore, carbonyl sulfide, which is partially oxidized to SO₂ and may be present in a lime kiln exit stack, would be a positive interferant.

4.2 Particulate matter from the lime kiln stack gas (primarily calcium carbonate) can cause a negative bias if it is allowed to enter the citrate scrubber; the particulate matter will cause the pH to rise and H₂S to be absorbed before oxidation. Proper use of the particulate filter, described in section 6.1.3 of Method 16A, will eliminate this interference.

4.3 Carbon monoxide (CO) and carbon dioxide (CO₂) have substantial desensitizing effects on the FPD even after dilution. Acceptable systems must demonstrate that they have eliminated this interference by some procedure such as eluting these compounds before the SO₂. Compliance with this requirement can be demonstrated by submitting chromatograms of calibration gases with and without CO₂ in diluent gas. The CO₂ level should be approximately 10 percent for the case with CO₂ present. The two chromatograms should show agreement within the precision limits of section 13.0.

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 Hydrogen Sulfide (H₂S). A flammable, poisonous gas with the odor of rotten eggs. H₂S is extremely hazardous and can cause collapse, coma, and death within a few seconds of one or two inhalations at sufficient concentrations. Low concentrations irritate the mucous membranes and may cause nausea, dizziness, and headache after exposure.

6.0 Equipment and Supplies

6.1 Sample Collection. The sampling train is shown in Figure 16B-1. Modifications to the apparatus are accepted provided the system performance check in section 8.3.1 is met.

6.1.1 Probe, Probe Brush, Particulate Filter, SO₂ Scrubber, Combustion Tube, and Furnace. Same as in Method 16A, sections 6.1.1 to 6.1.6.

6.1.2 Sampling Pump. Leakless Teflon-coated diaphragm type or equivalent.

6.2 Analysis.

6.2.1 Dilution System (optional), Gas Chromatograph, Oven, Temperature Gauges, Flow System, Flame Photometric Detector, Electrometer, Power Supply, Recorder, Calibration

System, Tube Chamber, Flow System, and Constant Temperature Bath. Same as in Method 16, sections 6.2.1, 6.2.2, and 6.3.

6.2.2 Gas Chromatograph Columns. Same as in Method 16, section 6.2.3. Other columns with demonstrated ability to resolve SO₂ and be free from known interferences are acceptable alternatives. Single column systems such as a 7-ft Carbsorb B HT 100 column have been found satisfactory in resolving SO₂ from CO₂.

7.0 Reagents and Standards

Same as in Method 16, section 7.0, except for the following:

7.1 Calibration Gas. SO₂ permeation tube gravimetrically calibrated and certified at some convenient operating temperature. These tubes consist of hermetically sealed FEP Teflon tubing in which a liquefied 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. In place of SO₂ permeation tubes, cylinder gases containing SO₂ in nitrogen may be used for calibration. The cylinder gas concentration must be verified according to section 8.2.1 of Method 6C. The calibration gas is used to calibrate the GC/FPD system and the dilution system.

7.2 Recovery Check Gas.

7.2.1 Hydrogen sulfide [100 parts per million by volume (ppmv) or less] in nitrogen, stored in aluminum cylinders. Verify the concentration by Method 11, the procedure discussed in section 16.0 of Method 16A, or gas chromatography where the instrument is calibrated with an H₂S permeation tube as described below. For the wet-chemical methods, the standard deviation should not exceed 5 percent on at least three 20-minute runs.

7.2.2 Hydrogen sulfide recovery gas generated from a permeation device gravimetrically calibrated and certified at some convenient operation temperature may be used. The permeation rate of the device must be such that at a dilution gas flow rate of 3 liters/min (64 ft³/hr), an H₂S concentration in the range of the stack gas or within 20 percent of the emission standard can be generated.

7.3 Combustion Gas. Gas containing less than 50 ppbv reduced sulfur compounds and less than 10 ppmv total hydrocarbons. The gas may be generated from a clean-air system that purifies ambient air and consists of the following components: diaphragm pump, silica gel drying tube, activated charcoal tube, and flow rate measuring device. Gas from a compressed air cylinder is also acceptable.

8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Pretest Procedures. Same as in Method 15, section 8.1.

8.2 Sample Collection. Before any source sampling is performed, conduct a system performance check as detailed in section 8.3.1 to validate the sampling train components and procedures. Although this test is optional, it would significantly reduce the possibility of rejecting tests as a result of failing the post-test performance check. At the completion of the pretest system performance check, insert the sampling probe into the test port making certain that no dilution air enters the stack through the port. Condition the entire system with sample for a minimum of 15 minutes before beginning analysis. If the sample is diluted, determine the dilution factor as in section 10.4 of Method 15.

8.3 Analysis. Inject aliquots of the sample into the GC/FPD analyzer for analysis. Determine the concentration of SO₂ directly from the calibration curves or from the equation for the least-squares line.

8.4. Post-Test Procedures

8.4.1 System Performance Check. Same as in Method 16A, section 8.5. A sufficient number of sample injections should be made so that the precision requirements of section 13.2 are satisfied.

8.4.2 Determination of Calibration Drift. Same as in Method 15, section 8.3.2.

9.0 Quality Control

Section	Quality control measure	Effect
8.2, 8.3	System performance check	Ensure validity of sampling train components and analytical procedure.
8.1	Sampling equipment leak-check and calibration	Ensure accurate measurement of stack gas flow rate, sample volume.
10.0	Analytical calibration	Ensure precision of analytical results within 5 percent.

10.0 Calibration

Same as in Method 16, section 10, except SO₂ is used instead of H₂S.

11.0 Analytical Procedure

11.1 Sample collection and analysis are concurrent for this method (see section 8.3).

12.0 Data Analysis and Calculations

12.1 Nomenclature.

C_{SO₂} = Sulfur dioxide concentration, ppmv.

C_{TRS} = Total reduced sulfur concentration as determined by Equation 16B-1, ppmv.

d = Dilution factor, dimensionless.

N = Number of samples.

12.2 SO₂ Concentration. Determine the concentration of SO₂, C_{SO₂}, directly from the calibration curves. Alternatively, the concentration may be calculated using the equation for the least-squares line.

12.3 TRS Concentration.

$$C_{TRS} = C_{SO_2} d \quad \text{Eq. 16B-1}$$

12.4 Average TRS Concentration

$$Avg. C_{TRS} = \frac{\sum_{i=1}^n C_{TRS}}{N} \quad \text{Eq. 16B-2}$$

13.0 Method Performance.

13.1 Range and Sensitivity. Coupled with a GC using a 1-ml sample size, the maximum limit of the FPD for SO₂ is approximately 10 ppmv. This limit is extended by diluting the sample gas before analysis or by reducing the sample aliquot size. For sources with emission levels between 10 and 100 ppm, the measuring range can be best extended by reducing the sample size.

13.2 GC/FPD Calibration and Precision. A series of three consecutive injections of the sample calibration gas, at any dilution, must produce results which do not vary by more than 5 percent from the mean of the three injections.

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

13.4 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.

13.5 Field tests between this method and Method 16A showed an average difference of less than 4.0 percent. This difference was not determined to be significant.

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

1. Same as in Method 16, section 16.0.

2. National Council of the Paper Industry for Air and Stream Improvement, Inc, A Study of TRS Measurement Methods. Technical Bulletin No. 434. New York, NY. May 1984. 12p.

3. Margeson, J.H., J.E. Knoll, and M.R. Midgett. A Manual Method for TRS Determination. Draft available from the authors. Source Branch, Quality Assurance Division, U.S. Environmental Protection Agency, Research Triangle Park, NC 27711.

17.0 Tables, Diagrams, Flowcharts, and Validation Data

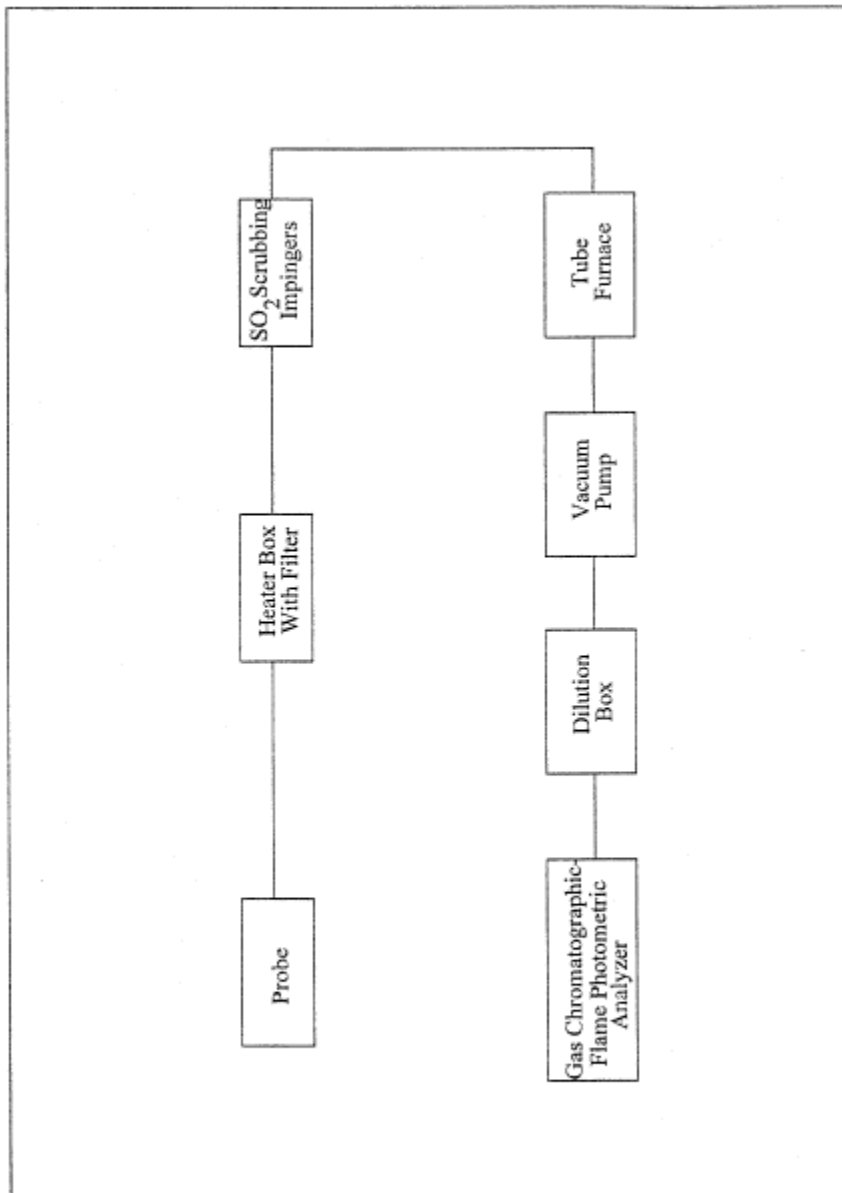


Figure 16B-1. Method 16B Sampling Train.