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

1.0 Scope and Application

What is Method 16C?

Method 16C is a procedure for measuring total reduced sulfur (TRS) in stationary source emissions using a continuous instrumental analyzer. Quality assurance and quality control requirements are included to assure that you, the tester, collect data of known quality. You must document your adherence to these specific requirements for equipment, supplies, sample collection and analysis, calculations, and data analysis. This method does not completely describe all equipment, supplies, and sampling and analytical procedures you will need but refers to other methods for some of the details. Therefore, to obtain reliable results, you should also have a thorough knowledge of these additional test methods which are found in appendix A to this part:

- (a) Method 6C—Determination of Sulfur Dioxide Emissions from Stationary Sources (Instrumental Analyzer Procedure)
- (b) Method 7E—Determination of Nitrogen Oxides Emissions from Stationary Sources (Instrumental Analyzer Procedure)
- (c) Method 16A—Determination of Total Reduced Sulfur Emissions from Stationary Sources (Impinger Technique)

1.1 Analytes. What does Method 16C determine?

Analyte	CAS No.
Total reduced sulfur 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.

1.3 Data Quality Objectives. Adherence to the requirements described in Method 16C will enhance the quality of the data obtained.

2.0 Summary of Method

2.1 An integrated 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 determined as SO₂ by an instrumental analyzer. This method is a combination of the sampling procedures of Method 16A and the analytical procedures of Method 6C (referenced in Method 7E), with minor modifications to facilitate their use together.

3.0 Definitions

Analyzer calibration error, Calibration curve, Calibration gas, Low-level gas, Mid-level gas, High-level gas, Calibration drift, Calibration span, Data recorder, Direct calibration mode, Gas analyzer, Interference check, Measurement system, Response time, Run, System calibration mode, System performance check, and Test are the same as used in Methods 16A and 6C.

4.0 Interferences

4.1 Reduced sulfur compounds other than those defined as TRS, if present, may be measured by this method. Compounds like carbonyl sulfide, which is partially oxidized to SO₂ and may be present in a lime kiln exit stack, would be a positive interferent. Interferences may vary among instruments, and instrument-specific interferences must be evaluated through the interference check.

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.

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 to establish appropriate safety and health practices before performing this test method.

5.2 Hydrogen Sulfide. Hydrogen sulfide is a flammable, poisonous gas with the odor of rotten eggs. Hydrogen sulfide 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. It is the responsibility of the user of this test method to establish appropriate safety and health practices.

6.0 Equipment and Supplies

What do I need for the measurement system?

The measurement system is similar to those applicable components in Methods 16A and 6C. Modifications to the apparatus are accepted provided the performance criteria in section 13.0 are met.

6.1 Probe. Teflon tubing, 6.4-mm ($\frac{1}{4}$ in.) diameter, sequentially wrapped with heat-resistant fiber strips, a rubberized heat tape (plug at one end), and heat-resistant adhesive tape. A flexible thermocouple or other suitable temperature measuring device must be placed between the Teflon tubing and the fiber strips so that the temperature can be monitored to prevent softening of the probe. The probe must 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 moisture and particulate from entering between the probe and sheath. A 6.4-mm ($\frac{1}{4}$ in.) Teflon elbow (bored out) must be attached to the inlet of the probe, and a 2.54 cm (1 in.) piece of Teflon tubing must be attached at the open end of the elbow to permit the opening of the probe to be turned away from the particulate stream; this will reduce the amount of particulate drawn into the sampling train. The probe is depicted in Figure 16A-2 of Method 16A.

6.2 Probe Brush. Nylon bristle brush with handle inserted into a 3.2-mm ($\frac{1}{8}$ in.) Teflon tubing. The Teflon tubing should be long enough to pass the brush through the length of the probe.

6.3 Particulate Filter. 50-mm Teflon filter holder and a 1- to 2- μ m porosity, Teflon filter (may be available through Savillex Corporation, 5325 Highway 101, Minnetonka, Minnesota 55343, or other suppliers of filters). The filter holder must be maintained in a hot box at a temperature sufficient to prevent moisture condensation. A temperature of 121 °C (250 °F) was found to be sufficient when testing a lime kiln under sub-freezing ambient conditions.

6.4 SO₂ Scrubber. Three 300-ml Teflon segmented impingers connected in series with flexible, thick-walled, Teflon tubing. (Impinger parts and tubing may be available through Savillex or other suppliers.) 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 ($\frac{1}{8}$ in.) ID and should be immersed to a depth of at least 5 cm (2 in.).

6.5 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 ($\frac{1}{4}$ 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. Alternative combustion tubes are acceptable provided they are shown to combust TRS at concentrations encountered during tests.

6.6 Furnace. A furnace of sufficient size to enclose the combustion chamber of the combustion tube with a temperature regulator capable of maintaining the temperature at 800 \pm 100 °C (1472

±180 °F). The furnace operating temperature should be checked with a thermocouple to ensure accuracy.

6.7 Sampling Pump. A leak-free pump is required to pull the sample gas through the system at a flow rate sufficient to minimize the response time of the measurement system and must be constructed of material that is non-reactive to the gas it contacts. For dilution-type measurement systems, an eductor pump may be used to create a vacuum that draws the sample through a critical orifice at a constant rate.

6.8 Calibration Gas Manifold. The calibration gas manifold must allow the introduction of calibration gases either directly to the gas analyzer in direct calibration mode or into the measurement system, at the probe, in system calibration mode, or both, depending upon the type of system used. In system calibration mode, the system must be able to flood the sampling probe and vent excess gas. Alternatively, calibration gases may be introduced at the calibration valve following the probe. Maintain a constant pressure in the gas manifold. For in-stack dilution-type systems, a gas dilution subsystem is required to transport large volumes of purified air to the sample probe, and a probe controller is needed to maintain the proper dilution ratio.

6.9 Sample Gas Manifold. The sample gas manifold diverts a portion of the sample to the analyzer, delivering the remainder to the by-pass discharge vent. The manifold should also be able to introduce calibration gases directly to the analyzer. The manifold must be made of material that is non-reactive to SO₂ and be configured to safely discharge the bypass gas.

6.10 SO₂ Analyzer. You must use an instrument that uses an ultraviolet, non-dispersive infrared, fluorescence, or other detection principle to continuously measure SO₂ in the gas stream provided it meets the performance specifications in section 13.0.

6.11 Data Recording. A strip chart recorder, computerized data acquisition system, digital recorder, or data logger for recording measurement data must be used.

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 must be used.

7.1 Water. Deionized distilled water must conform to ASTM Specification D 1193-77 or 91 Type 3 (incorporated by reference—see §60.17). The KMnO₄ test for oxidizable organic matter may be omitted when high concentrations of organic matter are not expected to be present.

7.2 Citrate Buffer. Dissolve 300 g of potassium citrate (or 284 g of sodium citrate) and 41 g of anhydrous citric acid in 1 liter of water (200 ml is needed per test). Adjust the pH to between 5.4 and 5.6 with potassium citrate or citric acid, as required.

7.3 Calibration Gas. Refer to section 7.1 of Method 7E (as applicable) for the calibration gas requirements. Example calibration gas mixtures are listed below.

- (a) SO₂ in nitrogen (N₂).
- (b) SO₂ in air.
- (c) SO₂ and carbon dioxide (CO₂) in N₂.
- (d) SO₂ and oxygen (O₂) in N₂.
- (e) SO₂/CO₂/O₂ gas mixture in N₂.
- (f) CO₂/NO_x gas mixture in N₂.
- (g) CO₂/SO₂/NO_x gas mixture in N₂.

For fluorescence-based analyzers, the O₂ and CO₂ concentrations of the calibration gases as introduced to the analyzer must be within 1.0 percent (absolute) O₂ and 1.0 percent (absolute) CO₂ of the O₂ and CO₂ concentrations of the effluent samples as introduced to the analyzer. Alternatively, for fluorescence-based analyzers, use calibration blends of SO₂ in air and the nomographs provided by the vendor to determine the quenching correction factor (the effluent O₂ and CO₂ concentrations must be known). This requirement does not apply to ambient-level fluorescence analyzers that are used in conjunction with sample dilution systems. Alternatively, H₂S in O₂ or air may be used to calibrate the analyzer through the tube furnace.

7.4 System Performance Check Gas. You must use H₂S (100 ppmv or less) stored in aluminum cylinders with the concentration certified by the manufacturer. Hydrogen sulfide in nitrogen is more stable than H₂S in air, but air may be used as the balance gas.

NOTE: Alternatively, H₂S recovery gas generated from a permeation device gravimetrically calibrated and certified at some convenient operating temperature may be used. The permeation rate of the device must be such that at the appropriate dilution gas flow rate, an H₂S concentration can be generated in the range of the stack gas or within 20 percent of the emission standard.

7.5 Interference Check. Examples of test gases for the interference check are listed in Table 7E-3 of Method 7E.

8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Pre-sampling Tests. Before measuring emissions, perform the following procedures:

- (a) Calibration gas verification,
- (b) Calibration error test,
- (c) System performance check,

(d) Verification that the interference check has been satisfied.

8.1.1 Calibration Gas Verification. Obtain a certificate from the gas manufacturer documenting the quality of the gas. Confirm that the manufacturer certification is complete and current. Ensure that your calibration gas certifications have not expired. This documentation should be available on-site for inspection. To the extent practicable, select a high-level gas concentration that will result in the measured emissions being between 20 and 100 percent of the calibration span.

8.1.2 Analyzer Calibration Error Test. After you have assembled, prepared, and calibrated your sampling system and analyzer, you must conduct a 3-point analyzer calibration error test before the first run and again after any failed system performance check or failed drift test to ensure the calibration is acceptable. Introduce the low-, mid-, and high-level calibration gases sequentially to the analyzer in direct calibration mode. For each calibration gas, calculate the analyzer calibration error using Equation 16C-1 in section 12.2. The calibration error for the low-, mid-, and high-level gases must not exceed 5.0 percent or 0.5 ppmv. If the calibration error specification is not met, take corrective action and repeat the test until an acceptable 3-point calibration is achieved.

8.1.3 System Performance Check. A system performance check is done (1) to validate the sampling train components and procedure (prior to testing), and (2) to validate a test run (after a run). You must conduct a performance check in the field prior to testing, and after each 3-hour run or after three 1-hour runs. A performance check consists of sampling and analyzing a known concentration of H₂S (system performance check gas) and comparing the analyzed concentration to the known concentration. To conduct the system performance check, mix the system performance check gas (Section 7.4) and ambient air, that has been conditioned to remove moisture and sulfur-containing gases, in a dilution system such as that shown in Figure 16A-3 of Method 16A. Alternatively, ultra-high purity (UHP) grade air may be used. Adjust the gas flow rates to generate an H₂S concentration in the range of the stack gas or within 20 percent of the applicable standard and an oxygen concentration greater than 1 percent at a total flow rate of at least 2.5 liters/min (5.3 ft³/hr). Use Equation 16A-3 from Method 16A to calculate the concentration of system performance check gas generated. Calibrate the flow rate from both gas sources with a soap bubble flow meter so that the diluted concentration of H₂S can be accurately calculated. Alternatively, mass flow controllers with documented calibrations may be used if UHP grade air is being used. Sample duration should be sufficiently long to ensure a stable response from the analyzer. Analyze in the same manner as the emission samples. Collect the sample through the probe of the sampling train using a manifold or other suitable device that will ensure extraction of a representative sample. The TRS sample concentration measured between system performance checks is corrected by the average of the pre- and post-system performance checks.

8.1.4 Interference Check. Same as in Method 7E, section 8.2.7.

8.2 Measurement System Preparation.

8.2.1 For the SO₂ scrubber, measure 100 ml of citrate buffer into the first and second impingers; leave the third impinger empty. Immerse the impingers in an ice bath, and locate them as close as possible to the filter heat box. The connecting tubing should be free of loops. Maintain the probe and filter temperatures sufficiently high to prevent moisture condensation, and monitor with a suitable temperature sensor. Prepare the oxidation furnace and maintain at 800 ±100 °C (1472 ±180 °F).

8.2.2 Citrate Scrubber Conditioning Procedure. Condition the citrate buffer scrubbing solution by pulling stack gas through the Teflon impingers as described in section 8.4.1.

8.3 Pretest Procedures. After the complete measurement system has been set up at the site and deemed to be operational, the following procedures must be completed before sampling is initiated.

8.3.1 Leak-Check. Appropriate leak-check procedures must be employed to verify the integrity of all components, sample lines, and connections. 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.

8.3.2 Initial System Performance Check. A system performance check using the test gas (Section 7.4) is performed prior to testing to validate the sampling train components and procedure.

8.4 Sample Collection and Analysis.

8.4.1 After performing the required pretest procedures described in section 8.1, insert the sampling probe into the test port ensuring that no dilution air enters the stack through the port. Condition the sampling system and citrate buffer solution for a minimum of 15 minutes before beginning analysis. Begin sampling and analysis. A source test consists of three test runs. A test run shall consist of a single sample collected over a 3-hour period or three separate 1-hour samples collected over a period not to exceed six hours.

8.5 Post-Run Evaluations.

8.5.1 System Performance Check. Perform a post-run system performance check before replacing the citrate buffer solution and particulate filter and before the probe is cleaned. The check results must not exceed the 100 ±20 percent limit set forth in section 13.2. If this limit is exceeded, the intervening run is considered invalid. However, if the recovery efficiency is not in the 100 ±20 percent range, but the 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.

8.5.2 Calibration Drift. After a run or series of runs, not to exceed a 24-hour period after initial calibration, perform a calibration drift test using a calibration gas (preferably the level that best approximates the sample concentration) in direct calibration mode. This drift must not differ

from the initial calibration error percent by more than 3.0 percent or 0.5 ppm. If the drift exceeds this limit, the intervening run or runs are considered valid, but a new analyzer calibration error test must be performed and passed before continuing sampling.

9.0 Quality Control

Section	Quality control measure	Effect
8.1.2	Analyzer calibration error test	Establishes initial calibration accuracy within 5.0%.
8.1.3, 8.5.1	System performance check	Ensures accuracy of sampling/analytical procedure to 100 ±20%.
8.5.2	Calibration drift test	Ensures calibration drift is within 3.0%.
8.1.4	Interference check	Checks for analytical interferences.
8.3	Sampling equipment leak-check	Ensures accurate measurement of sample gas flow rate, sample volume.

10.0 Calibration

10.1 Calibrate the system using the gases described in section 7.3. Perform the initial 3-point calibration error test as described in section 8.1.2 before you start the test. The specification in section 13 must be met. Conduct an initial system performance test described in section 8.1.3 as well before the test to validate the sampling components and procedures before sampling. After the test commences, a system performance check is required after each run. You must include a copy of the manufacturer's certification of the calibration gases used in the testing as part of the test report. This certification must include the 13 documentation requirements in the EPA Traceability Protocol for Assay and Certification of Gaseous Calibration Standards, September 1997, as amended August 25, 1999.

11.0 Analytical Procedure

Because sample collection and analysis are performed together (see section 8.0), additional discussion of the analytical procedure is not necessary.

12.0 Calculations and Data Analysis

12.1 Nomenclature.

ACE = Analyzer calibration error, percent of calibration span.

CD = Calibration drift, percent.

C_{Dir} = Measured concentration of a calibration gas (low, mid, or high) when introduced in direct calibration mode, ppmv.

C_{H₂S} = Concentration of the system performance check gas, ppmv H₂S.

C_S = Measured concentration of the system performance gas when introduced in system calibration mode, ppmv H₂S.

C_V = Manufacturer certified concentration of a calibration gas (low, mid, or high), ppmv SO₂.

C_{SO_2} = Unadjusted sample SO₂ concentration, ppmv.

C_{TRS} = Total reduced sulfur concentration corrected for system performance, ppmv.

DF = Dilution system (if used) dilution factor, dimensionless.

SP = System performance, percent.

12.2 Analyzer Calibration Error. Use Equation 16C-1 to calculate the analyzer calibration error for the low-, mid-, and high-level calibration gases.

$$ACE = \frac{C_{Dir} - C_V}{C_V} \times 100 \quad \text{Eq. 16C-1}$$

12.3 System Performance Check. Use Equation 16C-2 to calculate the system performance.

$$SP = \frac{C_S - C_{H_2S}}{C_{H_2S}} \times 100 \quad \text{Eq. 16C-2}$$

12.4 Calibration Drift. Use Equation 16C-3 to calculate the calibration drift at a single concentration level after a run or series of runs (not to exceed a 24-hr period) from initial calibration. Compare the single-level calibration gas error (ACE_n) to the original error obtained for that gas in the initial analyzer calibration error test (ACE_i).

$$CD = |ACE_i - ACE_n| \quad \text{Eq. 16C-3}$$

12.5 TRS Concentration as SO₂. For each sample or test run, calculate the arithmetic average of SO₂ concentration values (e.g., 1-minute averages). Then calculate the sample TRS concentration by adjusting the average value of C_{SO_2} for system performance using Equation 16C-4.

$$C_{TRS} = \frac{\overline{C_{SO_2}}}{1 - |SP|} \quad \text{Eq. 16C-4}$$

13.0 Method Performance

13.1 Analyzer Calibration Error. At each calibration gas level (low, mid, and high), the calibration error must either not exceed 5.0 percent of the calibration gas concentration or $|C_{Dir} - C_V|$ must be ≤ 0.5 ppmv.

13.2 System Performance. Each system performance check must not deviate from the system performance gas concentration by more than 20 percent. Alternatively, the results are acceptable if $|C_s - C_{H2S}|$ is ≤ 0.5 ppmv.

13.3 Calibration Drift. The calibration drift at the end of any run or series of runs within a 24-hour period must not differ by more than 3.0 percent from the original ACE at the test concentration level or $|ACE_i - ACE_n|$ must not exceed 0.5 ppmv.

13.4 Interference Check. For the analyzer, the total interference response (i.e., the sum of the interference responses of all tested gaseous components) must not be greater than 2.5 percent of the calibration span. Any interference is also acceptable if the sum of the responses does not exceed 0.5 ppmv for a calibration span of 5 to 10 ppmv, or 0.2 ppmv for a calibration span < 5 ppmv.

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

1. The references are the same as in section 16.0 of Method 16, section 17.0 of Method 16A, and section 17.0 of Method 6C.

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 [Reserved]