



Figure 6A-2. CO₂ Absorber

METHOD 6B—DETERMINATION OF SULFUR DIOXIDE AND CARBON DIOXIDE DAILY AVERAGE EMISSIONS FROM FOSSIL FUEL COMBUSTION 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 thorough knowledge of at least the following additional test methods: Method 1, Method 2, Method 3, Method 5, Method 6, and Method 6A.

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS No.	Sensitivity
Sulfur dioxide (SO ₂)	7449-09-05	3.4 mg SO ₂ /m ³ (2.12 × 10 ⁻⁷ lb/ft ³)
Carbon dioxide (CO ₂)	124-38-9	N/A

1.2 **Applicability.** This method is applicable for the determination of SO₂ emissions from combustion sources in terms of concentration (ng/dscm or lb/dscf) and emission rate (ng/J or lb/10⁶ Btu), and for the determination of CO₂ concentration (percent) on a daily (24 hours) basis.

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 sampling point in the stack intermittently over a 24-hour or other specified time period. The SO₂ fraction is measured by the bariumthorin titration method. Moisture and CO₂ fractions are collected in the same sampling train, and are determined gravimetrically.

3.0 Definitions. [Reserved]

4.0 Interferences

Same as Method 6, Section 4.0.

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 to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to performing this test method.

5.2 **Corrosive Reagents.** Same as Method 6, Section 5.2.

6.0 Equipment and Supplies

Same as Method 6A, Section 6.0, with the following exceptions and additions:

6.1 The isopropanol bubbler is not used. An empty bubbler for the collection of liquid droplets, that does not allow direct contact between the collected liquid and the gas sample, may be included in the sampling train.

6.2 For intermittent operation, include an industrial timer-switch designed to operate in the "on" position at least 2 minutes continuously and "off" the remaining period over a repeating cycle. The cycle of operation is designated in the applicable regulation. At a minimum, the sampling operation should include at least 12, equal, evenly-spaced periods per 24 hours.

6.3 Stainless steel sampling probes, type 316, are not recommended for use with Method 6B because of potential sample contami-

nation due to corrosion. Glass probes or other types of stainless steel, *e.g.*, Hasteloy or Carpenter 20, are recommended for long-term use.

NOTE: For applications downstream of wet scrubbers, a heated out-of-stack filter (either borosilicate glass wool or glass fiber mat) is necessary. Probe and filter heating systems capable of maintaining a sample gas temperature of between 20 and 120 °C (68 and 248 °F) at the filter are also required in these cases. The electric supply for these heating systems should be continuous and separate from the timed operation of the sample pump.

7.0 Reagents and Standards

Same as Method 6A, Section 7.0, with the following exceptions:

7.1 Isopropanol is not used for sampling.

7.2 The hydrogen peroxide absorbing solution shall be diluted to no less than 6 percent by volume, instead of 3 percent as specified in Methods 6 and 6A.

7.3 If the Method 6B sampling train is to be operated in a low sample flow condition (less than 100 ml/min or 0.21 ft³/hr), molecular sieve material may be substituted for Ascarite II as the CO₂ absorbing material. The recommended molecular sieve material is Union Carbide 1/16 inch pellets, 5 A°, or equivalent. Molecular sieve material need not be discarded following the sampling run, provided that it is regenerated as per the manufacturer's instruction. Use of molecular sieve material at flow rates higher than 100 ml/min (0.21 ft³/hr) may cause erroneous CO₂ results.

8.0 Sample Collection, Preservation, Transport, and Storage

8.1 **Preparation of Sampling Train.** Same as Method 6A, Section 8.1, with the addition of the following:

8.1.1 The sampling train is assembled as shown in Figure 6A-1 of Method 6A, except that the isopropanol bubbler is not included.

8.1.2 Adjust the timer-switch to operate in the "on" position from 2 to 4 minutes on a 2-hour repeating cycle or other cycle specified in the applicable regulation. Other timer sequences may be used with the restriction that the total sample volume collected is between 25 and 60 liters (0.9 and 2.1 ft³) for the amounts of sampling reagents prescribed in this method.

8.1.3 Add cold water to the tank until the impingers and bubblers are covered at least two-thirds of their length. The impingers and bubbler tank must be covered and protected from intense heat and direct sunlight. If freezing conditions exist, the impinger solution and the water bath must be protected.

NOTE: Sampling may be conducted continuously if a low flow-rate sample pump [20

to 40 ml/min (0.04 to 0.08 ft³/hr) for the reagent volumes described in this method] is used. If sampling is continuous, the timer-switch is not necessary. In addition, if the sample pump is designed for constant rate sampling, the rate meter may be deleted. The total gas volume collected should be between 25 and 60 liters (0.9 and 2.1 ft³) for the amounts of sampling reagents prescribed in this method.

8.2 Sampling Train Leak-Check Procedure. Same as Method 6, Section 8.2.

8.3 Sample Collection.

8.3.1 The probe and filter (either in-stack, out-of-stack, or both) must be heated to a temperature sufficient to prevent water condensation.

8.3.2 Record the initial dry gas meter reading. To begin sampling, position the tip of the probe at the sampling point, connect the probe to the first impinger (or filter), and start the timer and the sample pump. Adjust the sample flow to a constant rate of approximately 1.0 liter/min (0.035 cfm) as indicated by the rotameter. Observe the operation of the timer, and determine that it is operating as intended (*i.e.*, the timer is in the "on" position for the desired period, and the cycle repeats as required).

8.3.3 One time between 9 a.m. and 11 a.m. during the 24-hour sampling period, record the dry gas meter temperature (T_m) and the barometric pressure (P_{bar}).

8.3.4 At the conclusion of the run, turn off the timer and the sample pump, remove the probe from the stack, and record the final gas meter volume reading. Conduct a leak-check as described in Section 8.2. If a leak is found, void the test run or use procedures acceptable to the Administrator to adjust the sample volume for leakage. Repeat the steps in Sections 8.3.1 to 8.3.4 for successive runs.

8.4 Sample Recovery. The procedures for sample recovery (moisture measurement, peroxide solution, and CO₂ absorber) are the same as those in Method 6A, Section 8.3.

9.0 Quality Control

Same as Method 6, Section 9.0., with the exception of the isopropanol-check.

10.0 Calibration and Standardization

Same as Method 6, Section 10.0, with the addition of the following:

10.1 Periodic Calibration Check. After 30 days of operation of the test train, conduct a calibration check according to the same procedures as the post-test calibration check (Method 6, Section 10.1.2). If the deviation between initial and periodic calibration factors exceeds 5 percent, use the smaller of the two factors in calculations for the preceding 30 days of data, but use the most recent calibration factor for succeeding test runs.

11.0 Analytical Procedures

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

11.2 Quality Assurance (QA) Audit Samples. Analysis of QA audit samples is required only when this method is used for compliance determinations. Obtain an audit sample set as directed in Section 7.3.6 of Method 6. Analyze the audit samples at least once for every 30 days of sample collection, and report the results as directed in Section 11.3 of Method 6. The analyst performing the sample analyses shall perform the audit analyses. If more than one analyst performs the sample analyses during the 30-day sampling period, each analyst shall perform the audit analyses and all audit results shall be reported. Acceptance criteria for the audit results are the same as those in Method 6.

12.0 Data Analysis and Calculations

Same as Method 6A, Section 12.0, except that P_{bar} and T_m correspond to the values recorded in Section 8.3.3 of this method. The values are as follows:

P_{bar} = Initial barometric pressure for the test period, mm Hg.

T_m = Absolute meter temperature for the test period, °K.

13.0 Method Performance

13.1 Range.

13.1.1 Sulfur Dioxide. Same as Method 6.

13.1.2 Carbon Dioxide. Not determined.

13.2 Repeatability and Reproducibility. EPA-sponsored collaborative studies were undertaken to determine the magnitude of repeatability and reproducibility achievable by qualified testers following the procedures in this method. The results of the studies evolve from 145 field tests including comparisons with Methods 3 and 6. For measurements of emission rates from wet, flue gas desulfurization units in (ng/J), the repeatability (intra-laboratory precision) is 8.0 percent and the reproducibility (inter-laboratory precision) is 11.1 percent.

14.0 Pollution Prevention. [Reserved]

15.0 Waste Management. [Reserved]

16.0 Alternative Methods

Same as Method 6A, Section 16.0, except that the timer is needed and is operated as outlined in this method.

17.0 References

Same as Method 6A, Section 17.0, with the addition of the following:

1. Butler, Frank E., et. al. The Collaborative Test of Method 6B: Twenty-Four-Hour Analysis of SO₂ and CO₂. JAPCA. Vol. 33, No. 10. October 1983.

18.0 Tables, Diagrams, Flowcharts, and Validation Data. [Reserved]

METHOD 6C—DETERMINATION OF SULFUR DIOXIDE EMISSIONS FROM STATIONARY SOURCES (INSTRUMENTAL ANALYZER PROCEDURE)

1. *Applicability and Principle*

1.1 *Applicability.* This method is applicable to the determination of sulfur dioxide (SO₂) concentrations in controlled and uncontrolled emissions from stationary sources only when specified within the regulations.

1.2 *Principle.* A gas sample is continuously extracted from a stack, and a portion of the sample is conveyed to an instrumental analyzer for determination of SO₂ gas concentration using an ultraviolet (UV), non-dispersive infrared (NDIR), or fluorescence analyzer. Performance specifications and test procedures are provided to ensure reliable data.

2. *Range and Sensitivity*

2.1 *Analytical Range.* The analytical range is determined by the instrumental design. For this method, a portion of the analytical range is selected by choosing the span of the monitoring system. The span of the monitoring system shall be selected such that the pollutant gas concentration equivalent to the emission standard is not less than 30 percent of the span. If at any time during a run the measured gas concentration exceeds the span, the run shall be considered invalid.

2.2 *Sensitivity.* The minimum detectable limit depends on the analytical range, span, and signal-to-noise ratio of the measurement system. For a well designed system, the minimum detectable limit should be less than 2 percent of the span.

3. *Definitions*

3.1 *Measurement System.* The total equipment required for the determination of gas concentration. The measurement system consists of the following major subsystems:

3.1.1 *Sample Interface.* That portion of a system used for one or more of the following: sample acquisition, sample transport, sample conditioning, or protection of the analyzers from the effects of the stack effluent.

3.1.2 *Gas Analyzer.* That portion of the system that senses the gas to be measured and generates an output proportional to its concentration.

3.1.3 *Data Recorder.* A strip chart recorder, analog computer, or digital recorder for recording measurement data from the analyzer output.

3.2 *Span.* The upper limit of the gas concentration measurement range displayed on the data recorder.

3.3 *Calibration Gas.* A known concentration of a gas in an appropriate diluent gas.

3.4 *Analyzer Calibration Error.* The difference between the gas concentration exhib-

ited by the gas analyzer and the known concentration of the calibration gas when the calibration gas is introduced directly to the analyzer.

3.5 *Sampling System Bias.* The difference between the gas concentrations exhibited by the measurement system when a known concentration gas is introduced at the outlet of the sampling probe and when the same gas is introduced directly to the analyzer.

3.6 *Zero Drift.* The difference in the measurement system output reading from the initial calibration response at the zero concentration level after a stated period of operation during which no unscheduled maintenance, repair, or adjustment took place.

3.7 *Calibration Drift.* The difference in the measurement system output reading from the initial calibration response at a mid-range calibration value after a stated period of operation during which no unscheduled maintenance, repair, or adjustment took place.

3.8 *Response Time.* The amount of time required for the measurement system to display 95 percent of a step change in gas concentration on the data recorder.

3.9 *Interference Check.* A method for detecting analytical interferences and excessive biases through direct comparison of gas concentrations provided by the measurement system and by a modified Method 6 procedure. For this check, the modified Method 6 samples are acquired at the sample by-pass discharge vent.

3.10 *Calibration Curve.* A graph or other systematic method of establishing the relationship between the analyzer response and the actual gas concentration introduced to the analyzer.

4. *Measurement System Performance Specifications*

4.1 *Analyzer Calibration Error.* Less than ± 2 percent of the span for the zero, mid-range, and high-range calibration gases.

4.2 *Sampling System Bias.* Less than ± 5 percent of the span for the zero, and mid- or high-range calibration gases.

4.3 *Zero Drift.* Less than ± 3 percent of the span over the period of each run.

4.4 *Calibration Drift.* Less than ± 3 percent of the span over the period of each run.

4.5 *Interference Check.* Less than ± 7 percent of the modified Method 6 result for each run.

5. *Apparatus and Reagents*

5.1 *Measurement System.* Any measurement system for SO₂ that meets the specifications of this method. A schematic of an acceptable measurement system is shown in Figure 6C-1. The essential components of the measurement system are described below:

5.1.1 *Sample Probe.* Glass, stainless steel, or equivalent, of sufficient length to traverse the sample points. The sampling probe shall be heated to prevent condensation.