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 (SO_2) 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 SO_2 gas concentration using an ultraviolet (UV), nondispersive 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.

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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 exhibited 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-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. Use any measurement system for SO_2 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.

5.1.2 Sample Line. Heated (sufficient to prevent condensation) stainless steel or Teflon tubing, to transport the sample gas to the moisture removal system.

5.1.3 Sample Transport Lines. Stainless steel or Teflon tubing, to transport the sample from the moisture removal system to the sample pump, sample flow rate control, and sample gas manifold.

5.1.4 Calibration Valve Assembly. A three-way valve assembly, or equivalent, for blocking the sample gas flow and introducing calibration gases to the measurement system at the outlet of the sampling probe when in the calibration mode.

5.1.5 Moisture Removal System. A refrigerator-type condenser or similar device (e.g., permeation dryer), to remove condensate continuously from the sample gas while maintaining minimal contact between the condensate and the sample gas. The moisture removal system is not necessary for analyzers that can measure gas concentrations on a wet basis; for these analyzers, (1) heat the sample line and all interface components up to the inlet of the analyzer sufficiently to prevent condensation, and (2) determine the moisture content and correct the measured gas concentrations to a dry basis using appropriate methods, subject to the approval of the Administrator. The determination of sample moisture content is not necessary for pollutant analyzers that measure concentrations on a wet basis when (1) a wet basis CO_2 analyzer operated according to Method 3A is used to obtain simultaneous measurements, and (2) the pollutant/ CO_2 measurements are used to determine emissions in units of the standard.

5.1.6 Particulate Filter. An in-stack or heated (sufficient to prevent water condensation) out-of-stack filter. The filter shall be borosilicate or quartz glass wool, or glass fiber mat. Additional filters at the inlet or outlet of the moisture removal system and inlet of the analyzer may be used to prevent accumulation of particulate material in the measurement system and extend the useful life of the components. All filters shall be fabricated of materials that are nonreactive to the gas being sampled.

5.1.7 Sample Pump. A leak-free pump, to pull the sample gas through the system at a flow rate sufficient to minimize the response time of the measurement system. The pump may be constructed of any material that is nonreactive to the gas being sampled.

5.1.8 Sample Flow Rate Control. A sample flow rate control valve and rotameter, or equivalent, to maintain a constant sampling rate within 10 percent. (<u>Note</u>: The tester may elect to install a back-pressure regulator to maintain the sample gas manifold at a constant pressure in order to protect the analyzer(s) from overpressurization, and to minimize the need for flow rate adjustments.)

5.1.9 Sample Gas Manifold. A sample gas manifold, to divert a portion of the sample gas stream to the analyzer and the remainder to the by-pass discharge vent. The sample gas manifold should also include provisions for introducing calibration gases directly to the analyzer. The manifold may be constructed of any material that is nonreactive to the gas being sampled.

5.1.10 Gas Analyzer. A UV or NDIR absorption or fluorescence analyzer, to determine continuously the SO_2 concentration in the sample gas stream. The analyzer shall meet the applicable performance specifications of Section 4. A

means of controlling the analyzer flow rate and a device for determining proper sample flow rate (e.g., precision rotameter, pressure gauge downstream of all flow controls, etc.) shall be provided at the analyzer. (<u>Note</u>: Housing the analyzer(s) in a clean, thermally-stable, vibration-free environment will minimize drift in the analyzer calibration.)

5.1.11 Data Recorder. A strip chart recorder, analog computer, or digital recorder, for recording measurement data. The data recorder resolution (i.e., readability) shall be 0.5 percent of span. Alternatively, a digital or analog meter having a resolution of 0.5 percent of span may be used to obtain the analyzer responses and the readings may be recorded manually. If this alternative is used, the readings shall be obtained at equally spaced intervals over the duration of the sampling run. For sampling run durations of less than 1 hour, measurements at 1-minute intervals or a minimum of 30 measurements, whichever is less restrictive, shall be obtained. For sampling run durations of 96 measurements, whichever is less restrictive, shall be obtained.

5.2 Method 6 Apparatus and Reagents. The apparatus and reagents described in Method 6 and shown by the schematic of the sampling train in Figure 6C-2 are used to conduct the interference check.

5.3 SO₂ Calibration Gases. The calibration gases for the gas analyzer shall be SO_2 in N_2 or SO_2 in air. Alternatively, SO_2/CO_2 , SO_2/O_2 , or $SO_2/CO_2/O_2$ gas mixtures in N_2 may be used. For fluorescence-based analyzers, the Q and CO concentrations of the calibration gases as introduced to the analyzer shall be within 1 percent (absolute) O_2 and 1 percent (absolute) CQ of the Q and QO concentrations of the effluent samples introduced to the analyzer. Alternatively, for fluorescence-based analyzers, use calibration blends of SO_2 in air and the nomographs provided by the vendor to determine the quenching correction factor (the effluent O_2 and CO_2 concentrations must be known). Use three calibration gases as specified below:

5.3.1 High-Range Gas. Concentration equivalent to 80 to 100 percent of the span.

5.3.2 Mid-Range Gas. Concentration equivalent to 40 to 60 percent of the span.

5.3.3 Zero Gas. Concentration of less than 0.25 percent of the span. Purified ambient air may be used for the zero gas by passing air through a charcoal filter or through one or more impingers containing a solution of 3 percent H_2O_2 .

6. MEASUREMENT SYSTEM PERFORMANCE TEST PROCEDURES

Perform the following procedures before measurement of emissions (Section 7).

6.1 Calibration Gas Concentration Verification. There are two alternatives for establishing the concentrations of calibration gases. Alternative No. 1 is preferred.

6.1.1 Alternative No. 1--Use of calibration gases that are analyzed following the Environmental Protection Agency Traceability Protocol No. 1 (see Citation 1 in Bibliography). Obtain a certification from the gas manufacturer that Protocol No. 1 was followed.

6.1.2 Alternative No. 2--Use of calibration gases not prepared according to Protocol No. 1. If this alternative is chosen, obtain gas mixtures with a manufacturer's tolerance not to exceed ±2 percent of the tag value. Within

6 months before the emission test, analyze each of the calibration gases in triplicate using Method 6. Citation 2 in the Bibliography describes procedures and techniques that may be used for this analysis. Record the results on a data sheet (example is shown in Figure 6C-3). Each of the individual SO_2 analytical results for each calibration gas shall be within 5 percent (or 5 ppm, whichever is greater) of the triplicate set average; otherwise, discard the entire set and repeat the triplicate analyses. If the average of the triplicate analyses is within 5 percent of the calibration gas manufacturer's cylinder tag value, use the tag value; otherwise, conduct at least three additional analyses until the results of six consecutive runs agree within 5 percent (or 5 ppm, whichever is greater) of the average. Then use this average for the cylinder value.

6.2 Measurement System Preparation. Assemble the measurement system by following the manufacturer's written instructions for preparing and preconditioning the gas analyzer and, as applicable, the other system components. Introduce the calibration gases in any sequence, and make all necessary adjustments to calibrate the analyzer and the data recorder. Adjust system components to achieve correct sampling rates.

6.3 Analyzer Calibration Error. Conduct the analyzer calibration error check by introducing calibration gases to the measurement system at any point upstream of the gas analyzer as follows:

6.3.1 After the measurement system has been prepared for use, introduce the zero, mid-range, and high-range gases to the analyzer. During this check, make no adjustments to the system except those necessary to achieve the correct calibration gas flow rate at the analyzer. Record the analyzer responses to each calibration gas on a form similar to Figure 6C-4. Note: A calibration curve established prior to the analyzer calibration error check may be used to convert the analyzer response to the equivalent gas concentration introduced to the analyzer. However, the same correction procedure shall be used for all effluent and calibration measurements obtained during the test.

6.3.2 The analyzer calibration error check shall be considered invalid if the gas concentration displayed by the analyzer exceeds ±2 percent of the span for any of the calibration gases. If an invalid calibration is exhibited, take corrective action and repeat the analyzer calibration error check until acceptable performance is achieved.

6.4 Sampling System Bias Check. Perform the sampling system bias check by introducing calibration gases at the calibration valve installed at the outlet of the sampling probe. A zero gas and either the mid-range or high-range gas, whichever most closely approximates the effluent concentrations, shall be used for this check as follows:

6.4.1 Introduce the upscale calibration gas, and record the gas concentration displayed by the analyzer on a form similar to Figure 6C-5. Then introduce zero gas, and record the gas concentration displayed by the analyzer. During the sampling system bias check, operate the system at the normal sampling rate, and make no adjustments to the measurement system other than those necessary to achieve proper calibration gas flow rates at the analyzer. Alternately introduce the zero and upscale gases until a stable response is achieved. The tester shall determine the measurement system response time by observing the times required to achieve a stable response for both the zero and upscale gases. Note the longer of the two times as the response time.

6.4.2 The sampling system bias check shall be considered invalid if the difference between the gas concentrations displayed by the measurement system for

the analyzer calibration error check and for the sampling system bias check exceeds ±5 percent of the span for either the zero or upscale calibration gases. If an invalid calibration is exhibited, take corrective action, and repeat the sampling system bias check until acceptable performance is achieved. If adjustment to the analyzer is required, first repeat the analyzer calibration error check, then repeat the sampling system bias check.

7. EMISSION TEST PROCEDURE

7.1 Selection of Sampling Site and Sampling Points. Select a measurement site and sampling points using the same criteria that are applicable to Method 6.

7.2 Interference Check Preparation. For each individual analyzer, conduct an interference check for at least three runs per during the initial field test on a particular source category. Retain the results, and report them with each test performed on that source category. If an interference check is being performed, assemble the modified Method 6 train (flow control valve, two midget impingers containing 3 percent H_2O_2 , and dry gas meter) as shown in Figure 6C-2. Install the sampling train to obtain a sample at the measurement system sample by-pass discharge vent. Record the initial dry gas meter reading.

7.3 Sample Collection. Position the sampling probe at the first measurement point, and begin sampling at the same rate as used during the sampling system bias check. Maintain constant rate sampling (i.e., ±10 percent) during the entire run. The sampling time per run shall be the same as for Method 6 plus twice the average system response time. For each run, use only those measurements obtained after twice the response time of the measurement system has elapsed to determine the average effluent concentration. If an interference check is being performed, open the flow control valve on the modified Method 6 train concurrent with the initiation of the sampling period, and adjust the flow to 1 liter per minute (±10 percent). (<u>Note</u>: If a pump is not used in the modified Method 6 train, caution should be exercised in adjusting the flow rate since over-pressurization of the impingers may cause leakage in the impinger train, resulting in positively biased results).

7.4 Zero and Calibration Drift Tests. Immediately preceding and following each run, or if adjustments are necessary for the measurement system during the run, repeat the sampling system bias check procedure described in Section 6.4. (Make no adjustments to the measurement system until after the drift checks are completed.) Record the analyzer's responses on a form similar to Figure 6C-5.

7.4.1 If either the zero or upscale calibration value exceeds the sampling system bias specification, then the run is considered invalid. Repeat both the analyzer calibration error check procedure (Section 6.3) and the sampling system bias check procedure (Section 6.4) before repeating the run.

7.4.2 If both the zero and upscale calibration values are within the sampling system bias specification, then use the average of the initial and final bias check values to calculate the gas concentration for the run. If the zero or upscale calibration drift value exceeds the drift limits, based on the difference between the sampling system bias check responses immediately before and after the run, repeat both the analyzer calibration error check procedure (Section 6.3) and the sampling system bias check procedure (Section 6.4) before conducting additional runs.

7.5 Interference Check (if performed). After completing the run, record the final dry gas meter reading, meter temperature, and barometric pressure. Recover and analyze the contents of the midget impingers, and determine the SO_2 gas

concentration using the procedures of Method 6. (It is not necessary to analyze EPA performance audit samples for Method 6.) Determine the average gas concentration exhibited by the analyzer for the run. If the gas concentrations provided by the analyzer and the modified Method 6 differ by more than 7 percent of the modified Method 6 result, the run is invalidated.

8. EMISSION CALCULATION

The average gas effluent concentration is determined from the average gas concentration displayed by the gas analyzer and is adjusted for the zero and upscale sampling system bias checks, as determined in accordance with Section 7.4. The average gas concentration displayed by the analyzer may be determined by integration of the area under the curve for chart recorders, or by averaging all of the effluent measurements. Alternatively, the average may be calculated from measurements recorded at equally spaced intervals over the entire duration of the run. For sampling run durations of less than 1 hour, measurements at 1-minute intervals or a minimum of 30 measurements, whichever is less restrictive, shall be used. For sampling run durations greater than 1 hour, measurements at 2-minute intervals or a minimum of 96 measurements, whichever is less restrictive, shall be used. Calculate the effluent gas concentration using Equation 6C-1.

$$C_{gas} = (\overline{C} - C_{o}) \frac{C_{ma}}{C_{m} - C_{o}}$$

Eq. 6C-1

Where:

- C_{gas} = Effluent gas concentration, dry basis, ppm.
- C_{avg} = Average gas concentration indicated by gas analyzer, dry basis, ppm.
- $\rm C_{\circ}$ = Average of initial and final system calibration bias check responses for the zero gas, ppm.
- C_m = Average of initial and final system calibration bias check responses for the upscale calibration gas, ppm.
- $C_{\mbox{\scriptsize ma}}$ = Actual concentration of the upscale calibration gas, ppm.

BIBLIOGRAPHY

- Traceability Protocol for Establishing True Concentrations of Gases Used for Calibrations and Audits of Continuous Source Emission Monitors: Protocol Number 1. U. S. Environmental Protection Agency, Quality Assurance Division. Research Triangle Park, N.C. June 1978.
- Westlin, Peter R. and John W. Brown. Methods for Collecting and Analyzing Gas Cylinder Samples. Source Evaluation Society Newsletter. <u>3</u>(3):5-15. September 1978.



Figure 6C-1. Measurement System Schematic.



Figure 6C-2. Interference Check Sampling Train.

Figure 6C-3. Analysis of Calibration Gases.

Date				
Analytic Method Used				
	Gas Concentration (indicate units)			
	Zero ^a	Mid- Range ^b	High- range ^c	
Sample Run:				
1				
2				
3				
Average				
Maximum Percent Deviation				

 $^{\rm a}$ Average must be less than 0.25 percent of span.

^b Average must be 50 to 60 percent of span.

 $^{\rm c}$ Average must be 80 to 90 percent of span.

Figure 6C-4. Analyzer Calibration Data.

Source Identification:	Runs:
Test Personnel:	Span:

Date:

Analyzer Calibration Data for Sampling

	Cylinder Value (indicate units)	Analyzer Calibration Response (indicate units)	Absolute Difference (indicate units)	Difference (percent of span)
Zero Gas				
Mid-Range Gas				
High-Range Gas				

Source Identification:			Run Number:			
Test Personnel:			Span:			
Date:						
		Initial	l Values	Final Values		
	Analyzer Calibrat ion Response	System Calibrat ion Response	System cal. bias (percent of span)	System Calibrat ion Response	System Cal. Bias (percen t of span)	Drift (percen t of span)
Zero Gas						
Upscale Gas						

Figure 6C-5. System Calibration Bias and Drift Data.

SystemCalibrationBias = SystemCal.Response - AnalyzerCal.Response ×100 Span

Drift = FinalSystemCal.Response - InitialSystemCal.Response ×100 Span