



Quality Assurance Handbook for Air Pollution Measurement Systems: Volume III. Stationary Sources Specific Methods

**Sections 3.0.5, 3.0.6,
3.0.8, and 3.13**

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5.0 SPECIFIC PROCEDURES TO ASSESS ACCURACY OF REFERENCE METHODS USED FOR STANDARDS OF PERFORMANCE FOR NEW STATIONARY SOURCES

On May 30, 1979, the EPA Administrator stated in a memo "the EPA must have a comprehensive quality assurance (QA) effort to provide for the generation, storage, and use of environmental data which are of known quality." The memo further stated that participation in the QA effort was mandatory for all EPA supported or required monitoring activities. In a subsequent memo (dated June 14, 1979), it was stated that the mandatory QA program included all EPA grants, contracts, cooperative agreements, and interagency agreements. On November 24, 1980, the EPA Administrator approved a strategy to implement the QA program. As part of this strategy, each Project Officer must develop and obtain approval for a QA Project Plan if he/she determines the project will result in "environmentally related measurements." All source emission tests conducted for compliance or enforcement purposes are considered "environmentally related measurements." Guidelines for the development of a QA Project Plan are discussed in Section 1.4.23 and Appendix M of Volume I of this Handbook. The most important part of any QA Project Plan is a description of specific procedures to routinely assess and document data precision, accuracy, and completeness of specific measurement parameters involved.

The purpose of this Section is to briefly describe specific procedures to routinely assess and document the accuracy of reference and alternative methods for source test data under SPNSS (Standards of Performance for New Stationary Sources). Procedures for assessment of precision and completeness are not given because compliance or enforcement tests are short-term (only a few hours duration) and additional duplicate tests to obtain precision data are costly. Accuracy is determined from results of performance audits (i.e., measurements made by the routine operator or analyst). The routine operator or analyst must not know the concentration or value of the audit standard used, and the results must be submitted to an immediate supervisor or QA coordinator who does know the audit value.

Audit samples must have known or true values. They must be prepared with materials similar to field samples and/or calibration standards. Meticulous procedures and programs must also be established to ensure audit sample values (1) are correct as stated, (2) remain stable until used, (3) are properly coded and recorded, and (4) are of the proper concentration range to be audited.

Since a high degree of experience and planning is required for audit sample preparation, and EPA has mandated that quality assurance be an integral part of the agency measurement programs, the EPA's Environmental Monitoring Systems Laboratory (EMSL) in Research Triangle Park, North Carolina has been delegated the

responsibility for preparation of audit samples and materials for air measurements. Federal, State, and local agency personnel can obtain audit samples and materials for any enforcement and compliance measurement program directly from the Quality Assurance Coordinator in each EPA Regional Office unless otherwise directed in the following Reference Method subsections. When audit materials are unavailable from EPA or needed for nonagency use, commercial suppliers should be sought. Table 5.1 lists the address and telephone number for the Quality Assurance Coordinator in each of the ten EPA Regional Offices.

Several of the EPA Reference Methods have no performance audits because (1) they are specification methods or (2) no reliable or low cost procedures are currently available. The EPA Reference Methods for which audits are recommended are shown in Table 5.2 with their corresponding subsection number.

The specific assessment procedure for each promulgated Reference Method is approximately three pages in length. This brief description of the assessment procedure includes the following:

1. Method description.
2. References for details on the method.
3. Performance audit program to assess the accuracy of sampling and analytical procedures.
4. Recommended frequency for performance audits of compliance and enforcement tests. A frequency less than that recommended for enforcement purposes may be acceptable when testing for other purposes.
5. Recommended standards and levels for establishing audit values.
6. Procedure to calculate accuracy.
7. Availability of audit materials.
8. Cost of the recommended audit.

The philosophy of these assessments is that relative error calculations will be made of the accuracy (1) to determine errors in the testers'/analysts' techniques and systems, (2) when possible, to correct errors in these techniques and systems, and (3) for interpretation of the final reported emission test results by the data user. The reported emissions test data should not be corrected on the basis of these relative error calculations.

The general approach that has been developed for these audits follow those already described in the Reference Methods

TABLE 5.1. REGIONAL QUALITY ASSURANCE COORDINATORS (AIR)

Quality Assurance Coordinator (Air) Central Regional Laboratory Environmental Services Division US EPA, Region 1 60 Westview Street Lexington, MA 02173 FTS: 861-6700; COML: 617-861-6700	Quality Assurance Coordinator (Air) Environmental Services Div. US EPA, Region 6 First International Bldg. 1201 Elm Street Dallas, TX 75270 FTS: 729-0728, COML: 214-767-0728
Quality Assurance Coordinator (Air) Environmental Services Division USEPA, Region 2 Edison, NJ 08837 FTS: 340-6766; COML: 201-321-6766	Quality Assurance Coordinator (Air) USEPA, Region 7 25 Funston Road Kansas City, KS 66115 FTS: 926-3881; COML: 913-236-3881
Quality Assurance Coordinator (Air) Environmental Services Division USEPA, Region 3 841 Chestnut Building, 8th Floor Philadelphia, PA 19107 FTS: 597-6445; COML: 215-597-6445	Quality Assurance Coordinator (Air) Environmental Services Div. 1860 Lincoln Street Denver, CO 80295 FTS: 776-5064; COML: 303-564-5064
Quality Assurance Coordinator (Air) Environmental Services Division USEPA, Region 4 College Station Road Athens, GA 30613 FTS: 250-3390; COML: 404-546-3390	Quality Assurance Coordinator (Air) USEPA, Region 9 215 Fremont Street San Francisco, CA 94105 FTS: 454-7480; COML: 415-974-0922
Quality Assurance Coordinator (Air) Environmental Services Division USEPA, Region 5 536 South Clark Street Chicago, IL 60605 FTS: 353-9317; COML: 312-353-9317	Quality Assurance Coordinator (Air) Environmental Services Div. US EPA, Region 10 1200 Sixth Ave., Mail Stop 337 Seattle, WA 98101 FTS: 399-1675; COML: 206-442-1675

TABLE 5.2. EPA REFERENCE METHODS INCLUDED IN SECTION 3.0.5

Method number	Description	Subsection number
2	Volumetric Flow Rate	5.1
3	Carbon Dioxide and Oxygen	5.2
5, 5A, & 5D	Particulate Matter	5.3
6, 6A, & 6B	Sulfur Dioxide	5.4
7, 7A, 7C, & 7D	Oxides of Nitrogen	5.5
8	Sulfuric Acid and Sulfur Dioxide	5.6
10	Carbon Monoxide	5.7
11	Hydrogen Sulfide	5.8
12	Inorganic Lead	5.9
13A & 13B	Total Fluoride	5.10
15	Hydrogen Sulfide, Carbonyl Sulfide, and Carbon Disulfide	5.11
16	Hydrogen Sulfide, Methylmercaptan, Dimethyl Sulfide, and Dimethyl Disulfide	5.12
16A	Alternate Method for TRS	5.13
17	Instack Filterable Particulate	5.14
18	VOC, General GC Method	5.15
19	Sulfur Dioxide Removal Efficiency and Particulate, Sulfur Dioxide, and Nitrogen Oxide	5.16
20	Nitrogen Oxide, Sulfur Dioxide, and Oxygen for Stationary Gas Turbines	5.17
25	Total Gaseous Nonmethane Organics	5.18
25A & 25B	Total Gaseous Organics	5.19

for EPA Method 6 and 7 (see Reference 1) and/or Method 18 (see Reference 2). These audit procedures require the tester/analyst to provide the auditor with the audit results, either prior to the field sample analysis or prior to including the field sample results in the test report. When large relative errors are identified, the tester/analyst is allowed to correct his system. If possible, this is accomplished prior to the taking of the field samples or performing the final analysis on the field samples; this approach works quite well when the auditor is present for an on-site analysis. However, in the absence of the auditor the tester/analyst must telephone the auditor with results of the audit sample analysis in order to make necessary corrections prior to analyzing the field samples. If the auditor feels that is unwarranted, or if the tester/analyst does not wish to take the possible opportunity to correct an error in the system and/or techniques, the audit sample(s) would then be prepared and analyzed in the same manner and at the same time as the field samples. The approach of notifying the auditor prior to field sample analysis can provide the source and agency with a greater chance of more accurate data, may require the rejection of less test results, and may improve the techniques and system of the tester and/or analyst.

For compliance determination, the audit sample values should be within the range of the allowable emission limit. The audit sample concentration or value should be within 40 to 200 percent of the value of interest for audits containing a single audit sample. For audits containing two audit samples, the low concentration sample should be between 25 and 100 percent of the value of interest and the high concentration between 100 and 250 percent.

5.1 Method 2 (Stack Gas Velocity and Volumetric Flow Rate)

5.1.1 Method Description - Method 2 is applicable for measurement of the average velocity of a gas stream and for quantifying gas flow. This procedure is not applicable at measurement sites which fail to meet the criteria of Method 1. Also, the Method cannot be used for direct measurement in cyclonic or swirling gas streams. Method 1 shows how to determine cyclonic or swirling flow conditions. Therefore, when unacceptable conditions exist, alternative procedures subject to the approval of the Administrator, U.S. Environmental Protection Agency, must be employed to make accurate flow rate determinations; examples of such alternative procedures are: (1) to install straightening vanes; (2) to calculate the total volumetric flow rate stoichiometrically; or (3) to move to another measurement site at which the flow is acceptable.

The average gas velocity in a stack is determined from the gas density and from measurement of the average velocity head with a Type S (Stauscheibe or reverse type) pitot tube.

Section 3.1.10 of this Handbook contains a detailed description of Method 2 (40 CFR 60, Appendix A, Method 2).

5.1.2 Audits to Assess Accuracy of Sampling and Analytical Procedures -

5.1.2.1 Sampling Accuracy - When an inclined manometer that meets the specifications shown in Section 2.2 of Method 2 is used to measure the velocity pressure of the stack gas velocity, no audit is recommended. When another differential pressure gauge is used (e.g., Magnahelic[®] gauge), the gauge should be assessed for accuracy against an inclined manometer for each test series. The auditor should use an inclined manometer that meets the specifications shown in Section 2.2 of Method 2, Appendix A, 40 CFR 60.

The following items are provided as guidance for a proper audit and should be performed only when a differential pressure gauge other than an inclined manometer is used. When an inclined manometer that meets the specifications in Method 2 is used as the differential pressure gauge, no audit is recommended.

1. The pitot tube/differential pressure system should have been leak checked, leveled and zeroed.

2. After the velocity measurement system has been checked and prepared for testing, the differential pressure gauge should be audited by attaching an inclined manometer and "T" connections and tubing to the measurement system as explained in Method 2, Subsection 3.1.2 of this Handbook. The tubing may be slipped over the end of the pitot tube if a leakless connection can be made.

3. Prior to the testing series, the differential pressure gauge's accuracy must be checked at a value close to the average Δp obtained from the preliminary velocity traverse. Check both the negative and positive side. The readings should agree within 5 percent. If this agreement cannot be met, try to determine the problem and repeat the audit.

4. The auditor should compute the % relative error (RE) for each of the audits:

$$RE = \frac{C_M - C_A}{C_A} \times 100$$

where:

C_M = Pressure measured by differential pressure gauge, in. H_2O , and

C_A = Pressure measured by inclined manometer, in. H_2O .

5. When the initial and repeat audit does not meet the 5 percent relative error, the auditor may take actions deemed appropriate, or may inform the tester that if the post-test calibration of the differential pressure gauge does not meet the 5 percent agreement, the test may be voided.

6. The calculated RE should be included in the emission test report as an assessment of the accuracy of Method 2.

The difference between the measured values is used to assess the sampling accuracy. The significance of the error in the final velocity measurement will be the square root of $1 + \frac{RE}{100}$.

5.1.2.2 Analytical Accuracy - No analysis is in this Method.

5.1.3 Audit Frequency - When Method 2 is used for SPNSS purposes, the following audit frequency is recommended for the compliance and enforcement test. No audits are recommended for sampling or analysis if an inclined manometer is used that meets the specifications of Method 2. If a differential pressure gauge other than an inclined manometer is used, the gauge should be audited prior to the field test series (one audit per entire test series). An additional audit should be performed when (1) the differential pressure gauge is replaced or (2) the differential pressure gauge is altered to the point that the mechanical workings may be changed. A lesser frequency may be accepted when Method 2 is used for other applications depending on the purpose of the test.

5.1.4 Availability of Audit Materials - The inclined manometers are available commercially. The purchaser should ensure that the manometer meets the specifications explained in Method 2, Subsection 2.2.

5.1.5 Cost of Audit - The audit for Method 2 should require less than one additional technical hour of effort to complete. This would generally represent less than 10 percent of the total effort to conduct, calculate, and report the Method 2 testing.

5.2 Method 3 (Carbon Dioxide and Oxygen)

Method 3 should be audited using the quality assurance requirements in Method 3 (see Reference 3 for details).

5.2.1 Method Description* - This Method is used for determining CO_2 and O_2 concentrations > 0.2 percent by volume and for calculating² excess air and the dry molecular weight of gas streams from combustion sources. The Method may also be applicable to other processes where it has been determined that compounds other than CO_2 , O_2 , CO , and nitrogen (N_2) are not present in concentrations sufficient to affect the results. Section 3.2.11 of this Handbook contains a detailed description of Method 3 (Method 3 is found in 40 CFR 60, Appendix A). Limitations to the use of Method 3 are cited in the NOTE below.

5.2.2 Audits to Assess Accuracy of Sampling and Analytical Procedures -

5.2.2.1 Sampling Accuracy - No audit is recommended for sampling procedures at this time .

5.2.2.2 Analytical Accuracy - If the data are to be used only for molecular weight determination, no audit is recommended for the analytical procedures. If the data are to be used for excess air determination, concentration correction or F-factor calculation, an audit is recommended. This is the same audit that is suggested by EPA Reference Method 3. No additional requirements were included.

Although in most instances only CO_2 or O_2 is required, it is recommended that both CO_2 and O_2 be measured to provide a check on the quality of the data. The following performance audit is suggested.

* NOTE: Since the Method for validating CO_2 and O_2 analyses is based on combustion of organic and fossil fuels and² dilution of the gas stream with air, this Method does not apply to sources that (1) remove CO_2 or O_2 through processes other than combustion, (2) add O_2 (e.g., oxygen enrichment) and N_2 in proportions different² from that of air, (3) add CO_2 (e.g., cement or lime kilns), or (4) have no fuel factor, F_o ² values obtainable (e.g., extremely variable waste mixtures⁸). This Method validates the measured proportions of CO_2 and O_2 for the fuel type, but the Method does not detect sample² dilution resulting from leaks during or after sample collection. The Method is applicable for samples collected downstream of most lime or lime flue-gas desulfurization units as the CO_2 added or removed from the gas stream is not significant in relation to the total CO_2 concentration. The CO_2 concentrations from other types of scrubbers using only water or basic slurry can be significantly affected and would render the F_o check minimally useful.

Calculate a fuel factor, F_o , using the following equation:

$$F_o = \frac{20.9 - \%O_2}{\%CO_2}$$

where:

$\% O_2$ = Percent O_2 by volume (dry basis).
 $\% CO_2$ = Percent CO_2 by volume (dry basis).
 20.9 = Percent O_2 by volume in ambient air.

If CO is present in quantities measurable by this Method, adjust the O_2 and CO_2 values before performing the calculation for F_o as follows:

$$\begin{aligned} \%CO_2(\text{adj}) &= \%CO_2 + \%CO \\ \%O_2(\text{adj}) &= \%O_2 - 0.5 \%CO \end{aligned}$$

where: $\%CO$ = Percent CO volume (dry basis).

Compare the calculated F_o factor with the expected F_o values. The following table may be used in establishing acceptable ranges for the expected F_o if the fuel being burned is known. When fuels are burned in combination, calculate the combined fuel F_d and F_c factors (as defined in EPA Reference Method 19) according to the procedure in Method 19 Section 5.2.3. Then calculate the F_o factor as follows:

$$F_o = \frac{0.209 F_d}{F_c}$$

where:

F_d and F_c have the units of scm/J or scf/million Btu; $\%H$, $\%C$, $\%S$, $\%N$, $\%O$, and $\%H_2O$ are the concentrations by weight (expressed in percent) of hydrogen, carbon, sulfur, nitrogen, oxygen, and water from an ultimate analysis of the fuel; and GCV is the gross calorific value of the fuel in kJ/kg or Btu/lb and is consistent with the ultimate analysis. Follow ASTM 2015 for solid fuels, D 240 for liquid fuels, and D 1826 for gaseous fuels as applicable in determining GCV.

<u>Fuel Type</u>	<u>F_o Range</u>
Coal:	
Anthracite and lignite	1.016 - 1.130
Bituminous	1.083 - 1.230
Oil:	
Distillate	1.260 - 1.413
Residual	1.210 - 1.370

<u>Fuel Type</u>	<u>F_O Range</u>
Gas:	
Natural	1.600 - 1.836
Propane	1.434 - 1.586
Butane	1.405 - 1.553
Wood:.....	1.000 - 1.120
Wood bark:	1.003 - 1.130

Calculated F_O values beyond the acceptable ranges shown in this table should be investigated before accepting the test results. For example, the strength of the solutions in the gas analyzer and the analyzing technique should be checked by sampling and analyzing a known concentration, such as air; the fuel factor should then be reviewed and verified. An acceptability range of +12 percent is appropriate for the F_O factor of mixed fuels with variable fuel ratios. The level of the emission rate relative to the compliance level should be considered in determining if a retest is appropriate, i.e., if the measured emissions are much lower or much greater than the compliance limit, repetition of the test would not significantly change the compliance status of the source and would be unnecessarily time-consuming and costly.

It should be noted that this audit only checks the accuracy relative to the ratio of CO₂ to O₂. If the sampling system had a leak, this check would not detect the bias in the results.

5.2.3 Audit Frequency - When Method 3 is used for SPNSS purposes, the following audit frequency is recommended for the compliance and enforcement test. An audit for accuracy should be conducted after each analysis. A lesser frequency may be acceptable when Method 3 is used for other applications depending on the purposes of the test (i.e., no audit would be recommended if the data are to be used only to determine stack gas molecular weight).

5.2.4 Availability of Audit Materials - No audit materials are required.

5.2.5 Cost of Audit - The audit of Method 3 is a calculation audit of the field sample analytical results. No additional samples or analysis is required. The audit for Method 3 should require less than one technical man hour of effort to complete. This effort would generally represent less than 10 percent of the total effort to conduct, calculate, and report Method 3 sampling and analysis.

5.3 Method 5, 5A and 5D (Particulate Matter)

Methods 5, 5A, and 5D should be audited using the quality assurance requirements in Method 5 (see Reference 4 for details).

5.3.1 Method Description - These Methods, when used in conjunction with Methods 1, 2, 3, and 4, are applicable for the determination of particulate emissions from stationary sources.

A gas sample is extracted isokinetically from the stack. Particulate matter is collected on an out-of-stack, glass fiber filter maintained at $120^{\circ} + 14^{\circ}\text{C}$ ($248^{\circ} + 25^{\circ}\text{F}$) for Methods 5 and 5D and $42^{\circ} + 10^{\circ}\text{C}$ ($108^{\circ} + 18^{\circ}\text{F}$) for Method 5A, or at another temperature specified by an applicable subpart of the standard or approved by the Administrator. The mass of particulate matter, which includes any material that condenses at or above the specified filter temperature, is measured gravimetrically after removal of uncombined water. Section 3.4.10 of this Handbook contains a detailed description of Method 5. Method 5 is found in 40 CFR 60, Appendix A. Method 5A can be found in the Federal Register Vol. 47, page 34137, August 6, 1982.

5.3.2 Audits to Assess Accuracy of Sampling and Analytical Procedures

5.3.2.1 Sampling Accuracy - The audit procedure for the sampling phase is to determine the accuracy of the flow totalizing system (dry gas meter) which is described below in this subsection and the accuracy of any differential pressure gauge used to measure velocity that does not meet the specifications in Section 2.2 of Method 2, 40 CFR 60, Appendix A. The audit of the differential pressure gauge is described in Subsection 5.1.2 (Method 2) in this Section.

The audit of the flow totalizing system may be conducted by two methods. The first method compares it to the flow rate system (orificemeter) in the sample train as described in the Reference Method and described below. The second method is with the use of a calibrated orifice that has been certified by EPA.

The following items are provided to conduct a proper audit of the flow totalizing system using the flow rate system. Using the calibration data obtained during the calibration procedure described in Section 5.3 of Method 5, determine the $\Delta H_{\text{orifice}}$ for the metering system orifice. The $\Delta H_{\text{orifice}}$ is the orifice pressure differential that correlates to 0.75 cfm of air at 528°R and 29.92 in. Hg in units of in. H_2O . The $\Delta H_{\text{orifice}}$ is calculated as follows:

$$\Delta H_{\theta} = 0.0319 \Delta H \left(\frac{T_m}{P_{\text{bar}}} \right) \left(\frac{\theta^2}{Y^2 V_m^2} \right)$$

where:

ΔH = Pressure drop reading from orifice meter, in. H_2O .
 T_m = Absolute average dry gas meter temperature, $^{\circ}R$.
 P_{bar} = Barometric pressure, in. Hg.
 θ = Total sampling time, min.
 Y = Dry gas meter calibration factor, dimensionless.
 V_m = Volume of gas sample as measured by dry gas meter, dcf.
 $0.0319 = (0.0567 \text{ in. Hg}/^{\circ}R) \times (0.75 \text{ dscfm})^2$

Before beginning the field test (a set of three runs usually constitutes a field test), operate the metering system (i.e., pump, volume meter, and orifice) at the H_{θ} pressure differential for 10 minutes. Record the volume collected, the dry gas meter temperatures and the barometric pressure. Calculate the average dry gas meter temperature. Calculate a dry gas meter calibration check value, Y_c , as follows:

$$Y_c = \frac{10}{V_m} \left| \frac{0.0319 T_m}{P_{\text{bar}}} \right|^{1/2}$$

where:

Y = Dry gas meter calibration check value, dimensionless.
 10 = 10 minutes of run time.

Compare the Y_c value with the dry gas meter calibration factor Y to determine that :

$$0.97Y < Y_c < 1.03Y .$$

If the Y_c value is not within this range, the volume metering system should be investigated before beginning the test and the audit repeated. If the initial and repeat audit do not agree with the range, the auditor may take actions deemed appropriate or inform the tester that if the post test calibration does not agree within the range stated by the Method, that the results may affect the acceptability of the test.

Alternatively, the dry gas meter may be audited using a calibrated flow orifice housed in a quick-connect coupling certified by the EPA. The following recommendations are provided as guidance:

1. Remove the calibrated orifice from its case and insert it into the gas inlet quick-connect coupling on the source

sampling meter box. Turn on the pump and adjust until 19 in. Hg vacuum is being pulled on the calibrated orifice based on the sampling meter box vacuum gauge.

2. Make the quality assurance check prior to the start of the field test. Record the initial and the final dry gas meter volumes, the dry gas meter inlet and outlet temperatures, the internal orifice pressure drop (ΔH), the ambient temperature, and the barometric pressure. The duration of the run should be slightly >15 min. The following procedure is recommended for each quality assurance run: 15 min. after a run is started, watch the dry gas meter needle closely. As the needle reaches the zero (12 o'clock) position stop the pump and stopwatch simultaneously. Record the dry gas meter volume and the time.

3. Calculate the corrected dry gas volume for the run using the equation below. Record the collected dry gas volume (V_m), the sampling time in decimal minutes, the barometric pressure (P_{bar}) the average temperature (T_m), the internal orifice pressure drop (ΔH) and the dry gas meter calibration factor (Y).

$$V_{m(std)} = V_m Y \left(\frac{T_{std}}{T_m} \right) \left(\frac{P_{bar} + \frac{\Delta H}{13.6}}{P_{std}} \right)$$

$$= K_1 V_m Y \left(\frac{P_{bar} + \frac{\Delta H}{13.6}}{T_m} \right)$$

where:

$$K_1 = 0.3858^\circ K/mm \text{ Hg for metric units, or}$$

$$= 17.64^\circ R/in. \text{ Hg for English units.}$$

The auditor should then calculate the percent relative error (RE) between the measured standard volume and the audit or given standard volume (calibrated orifice calculated volume). The percent relative error is a measure of the bias of the volume measurement in the sampling phase of Method 5. Calculate RE using the equation below.

$$RE = \frac{V_M - V_A}{V_A} \times 100$$

where:

V_M = Volume measured by the field crew, corrected to standard conditions, m^3 , and
 V_A = Audit or given volume of the audit device, corrected to standard conditions, m^3 .

4. The results of the calculated RE should be included in the emission test report as an assessment of the accuracy of the sampling phase of the Method 5 test.

Since the calibrated orifice is not a primary standard, the auditor should always have at least two orifices available. When the first orifice audit results deviate by more than +10 percent, the second orifice should be used to validate this difference.

When a differential pressure gauge other than an inclined manometer is used for velocity pressure measurement, an audit to assess the accuracy of the velocity pressure measurement is recommended. The audit should follow the procedure and frequency as described for Method 2 in Subsection 5.1.

5.3.2.2 Analytical Accuracy - None recommended.

5.3.3 Audit Frequency - When Method 5, 5A or 5D is used for SPNNS purposes, the following audit frequency is recommended for compliance and enforcement tests. An audit for accuracy of the sampling procedures should be conducted prior to the field testing series on all flow totalizing systems (dry gas meters) and on all differential pressure gauges used for velocity pressure determination that do not meet the specifications of Section 2.2 of Method 2. An additional audit should be conducted on the flow totalizing system when (1) a different flow totalizing system is used or (2) repairs are made on the flow totalizing system after auditing. An additional audit should be conducted on the differential pressure gauge when (1) a different differential pressure gauge is used or (2) when repairs are made on the differential pressure gauge after auditing. A lesser frequency may be acceptable when Method 5 is used for applications other than compliance or enforcement.

5.3.4 Availability of Audit Materials - Control agencies responsible for the compliance or enforcement test may obtain certified calibrated orifices (when available) prior to each compliance or enforcement test. By contacting:

U.S. Environmental Protection Agency
Environmental Monitoring Systems Laboratory
Quality Assurance Division (MD-77A)
Research Triangle Park, North Carolina 27711

Attention: Source Test Audit Coordinator

Alternatively, a calibrated orifice can be made as described by Mitchell, et. al. in Reference 5 and sent to the USEPA for certification.

5.3.5 Cost of Audit - The audit of Method 5, 5A or 5D is an audit of the sampling phase. This audit should require less than

two technical hours of effort to complete. This effort should generally represent less than 2 percent of the total effort to conduct, calculate, and report the Method 5 sampling and analysis.

5.4 Method 6, 6A, and 6B (Sulfur Dioxide)

Methods 6, 6A and 6B should be audited using the quality assurance requirements in Method 6. (See Reference 1 for details.)

5.4.1 Method Description - Method 6 is applicable to the determination of sulfur dioxide (SO_2) emissions from stationary sources. A gas sample is extracted at a constant rate from the sampling point in the stack. The SO_2 is separated from the sulfuric acid mist (including sulfur trioxide) and is measured by the barium-thorin titration method. The barium ions react preferentially with sulfate ions in solution to form a highly insoluble barium sulfate precipitate. When the barium has reacted with all sulfate ions, excess barium then reacts with the thorin indicator to form a metal salt of the indicator, resulting in a color change. Section 3.5.10 of this Handbook contains a detailed description of Method 6. Methods 6, 6A and 6B are found in 40 CFR 60, Appendix A.

5.4.2 Audits to Assess Accuracy of Sampling and Analytical Procedures -

5.4.2.1 Sampling Accuracy - No audit is recommended when the midget impingers are used. An audit to assess the accuracy of the flow measuring device (dry gas meter) is recommended when the standard size impingers (i.e., Method 5 or Method 8) are used. The audit of the flow measuring device with the use of a critical orifice is described in Subsection 5.3.2.

5.4.2.2 Analytical Accuracy - According to Method 6, when the Method is used for compliance testing, the analyst must analyze two audit samples along with the field samples. One of these samples should be at a low concentration (500 to 1000 $\text{mg SO}_2/\text{m}^3$ of gas sampled when a EPA specified aliquot of the audit sample is diluted to exactly 100 ml) and one at a high concentration (1500 to 2500 $\text{mg SO}_2/\text{m}^3$ when an EPA specified aliquot of the audit sample is diluted to exactly 100 ml). This is based on an emission standard of 1.2 lb of SO_2 per million Btu which would be about 1300 $\text{mg SO}_2/\text{m}^3$ at 35 percent excess air. The percent relative error (RE) of the audit samples is determined using the following equation. The calculated RE must be included in the emission test report as an assessment of the accuracy of the analytical phase of the Method 6 test.

$$\text{RE} = \frac{C_d - C_a}{C_a} \times 100$$

where:

C_d = Determined audit sample concentration, mg/m^3 , and
 C_a = Actual audit concentration, mg/m^3 .

Method 6 states that the relative error (RE) should be less than 5 percent for both audit samples. When agreement is not met, the audit samples and field samples must be reanalyzed and the initial and reanalysis results included in the test report. Nonagreement on the initial and reanalysis results of the audit samples may void the test.

5.4.2.3 Combined Sampling and Analytical Accuracy - For Method 6B, a cylinder gas (SO_2/CO_2 in N_2) audit that addresses both sampling and analytical accuracy is also available (refer to Section 3.13.8 of this Handbook for details). It is recommended that this audit be conducted in addition to the required liquid sample audit when Method 6B is used for compliance testing.

5.4.3 Audit Frequency - When Method 6 or Method 6A is used for SPNSS purposes, the following audit frequency is recommended for compliance and enforcement tests. An audit for accuracy of the analytical procedures should be conducted simultaneously with the analysis of field samples. The analytical series may contain field samples from more than one stack or test. The audit samples should be analyzed concurrently with the field sample analysis. An additional audit must be conducted when the analyst, analytical reagents and/or analytical system is changed. If acceptable results have been obtained on an audit performed within 30 days of the date of the audit sample analysis and the above conditions are met, the agency may not require an audit. A lesser frequency may be acceptable when Method 6 is used for applications other than compliance and enforcement tests. Note: When Method 6B is used for compliance with 60.47a (f) of 40 CFR Part 60, Subpart Da, the analytical procedures must be audited on a monthly basis (provided the analytical system and analyst do not change). For the cylinder gas audit of Method 6B, audit procedures are shown in Section 3.13.8 of this Handbook.

5.4.4 Availability of Audit Materials - Control agencies responsible for the compliance or enforcement test may obtain SO_2 audit samples prior to each compliance or enforcement test, by contacting the Quality Assurance Coordinator (shown in Table 5.1) in his respective EPA Regional Office. The SO_2 audit samples are prepared by EPA's Environmental Monitoring Systems Laboratory at the Research Triangle Park, North Carolina. For purposes other than compliance and enforcement tests, audit samples may be prepared using primary standard grade ammonium sulfate by the procedure described in this Handbook for control sample preparation. For details, see Method 6, Section 3.5.5, Subsection 5.2.5.

5.4.5 Cost of Audit - The required audit for Methods 6, 6A and 6B is an audit of the analysis phase. The audit should require

less than four technical hours of effort to complete. This effort would generally represent less than 5 percent of the total effort to conduct, calculate, and report the Method 6 sampling and analysis.

5.5 Methods 7, 7A, 7C, and 7D (Oxides of Nitrogen)

Methods 7, 7A, 7C, and 7D should be audited using the quality assurance requirements in Method 7. (See Reference 1 for details.)

5.5.1 Method Description - Methods 7, 7A, 7C, and 7D are applicable to the measurement of nitrogen oxides emitted from stationary sources. The range of the Methods has been determined to be 2 to 400 mg NO_x, expressed as NO₂, per dry standard cubic meter without having to dilute the sample. A gas sample is extracted from the sampling point in the stack. The sample is collected in an evacuated 2-liter round bottom borosilicate flask containing 25 ml of dilute sulfuric acid-hydrogen peroxide absorbing solution (7 and 7A) or in impingers containing alkaline-potassium permanganate solution (7C and 7D). The nitrogen oxides, except nitrous oxide, are measured colorimetrically for Method 7 and 7C, and by ion chromatography for Method 7A and 7D. Section 3.6 of the Handbook contains a detailed description of Method 7. Methods 7, 7A, 7C, and 7D are found in 40 CFR, 60 Appendix A.

5.5.2 Audits to Assess Accuracy of Sampling and Analytical Procedures -

5.5.2.1 Sampling Accuracy - No audit recommended.

5.5.2.2 Analytical Accuracy - According to Method 7, when the Method is used for compliance testing, the analyst must analyze two audit samples along with the field samples. One of the samples should be at a low concentration (250 to 500 mg NO₂/dsm³ of gas sampled when an EPA specified aliquot of the audit sample is diluted to exactly 100 ml), and one at a high concentration (750 to 1500 mg NO₂/dsm³ of gas sampled when an EPA specified aliquot of the audit sample is diluted to exactly 100 ml). This is based on an emission standard of 0.7 lb NO₂ per million Btu which would be about 750 mg/dsm³ at 35 percent excess air.

The audit samples must be analyzed simultaneously with the field samples. The percent relative error (RE) of the audit samples is determined using the equation below. The RE results must be included with the emission test report as an assessment of the accuracy of the analytical phase during the Method 7 test.

$$RE = \frac{C_d - C_a}{C_a} \times 100$$

where:

C_d = Determined audit sample concentration, mg/m³, and

C_a = Audit or given sample concentration, mg/m^3 .

Method 7 states that the relative error (RE) should be less than 10 percent for both audit samples. When the argument is not met, the audit samples and field samples must be reanalyzed and the initial and reanalysis results included in the test report. Nonagreement on the initial analysis and reanalysis of the audit samples may void the test.

5.5.3 Audit Frequency - When Method 7 is used for SPNSS purposes, the following audit frequency is recommended for compliance and enforcement tests. An audit for accuracy should be conducted simultaneously with the analysis of the field samples. The analyses may contain samples from more than one stack or test. An additional audit must be conducted when the analyst, analytical reagents, and/or analytical system is changed. If acceptable results have been obtained on an audit performed within 30 days of the date of the audit sample analysis and the above conditions are not met, the agency may not require an audit. A lesser frequency may be acceptable when Method 7 is used for applications other than compliance and enforcement.

5.5.4 Availability of Audit Materials - Control agencies responsible for the compliance or enforcement test may obtain NO_2 audit samples prior to each compliance or enforcement test by contacting the Quality Assurance Coordinator (shown in Table 5.1) in their respective EPA Regional Office. The NO_2 audit samples are prepared by EPA's Environmental Monitoring Systems Laboratory at the Research Triangle Park, North Carolina. For purposes other than compliance and enforcement tests, audit samples may be prepared using potassium nitrate by the procedure described in this Handbook for control sample preparation. For details, see Method 7, Section 3.6.5, Subsection 5.2.2.

5.5.5 Cost of Audit - The audit for Method 7, 7A, 7C, or 7D is an audit of the analysis phase. This audit should require less than four technical hours of effort to complete. This effort would generally represent less than 5 percent of the total effort to conduct, calculate, and report the Method 7 sampling and analysis.

5.6 Method 8 (Sulfuric Acid and Sulfur Dioxide)

5.6.1 Method Description - This Method is applicable for the determination of sulfuric acid mist (including SO_3) emissions from stationary sources. A gas sample is extracted isokinetically from the stack. The sulfuric acid mist (including SO_3) and the SO_2 are separated; both fractions are then measured separately by the barium-thorin titration method. The barium ions react preferentially with sulfate ions in solution to form a highly insoluble barium sulfate precipitate. When the barium has reacted with all sulfate ions, the excess barium reacts with the thorin indicator to form a metal salt of the indicator and to give a color change. Section 3.7 of this Handbook contains a detailed description of Method 8. The Method can be found in 40 CFR 60, Appendix A.

5.6.2 Audits to Assess Accuracy of Sampling and Analytical Procedures -

5.6.2.1 Sampling Accuracy - The audit for the sampling phase is used to determine the accuracy of the flow totalizing system (dry gas meter) of the Method 8 sampling train and the differential pressure gauge used to measure the velocity when the gauge does not meet the specifications in Section 2.2 of Method 2 (40 CFR 60, Appendix A). The flow totalizing system should be audited using the same procedures and with the same frequency as described in detail for Method 5 in Subsection 5.3.2 of this Section. The differential pressure gauge should be audited using the same procedures and with the same frequency as described in detail for Method 2 in Subsection 5.1.2 of this Section.

5.6.2.2 Analytical Accuracy - The analytical procedures for both the sulfuric acid and sulfur dioxide should be audited using the procedure described for Method 6 in Subsection 5.4.2. An emission standard of 0.15 lb of sulfuric acid per ton of acid produced is about 100 mg/dsm³ at 100 percent excess air,³ and 4.0 lb of SO_2 per ton of acid produced is about 2500 mg/dsm³ at 100 percent excess air. Note: Separate audits are not necessary for both the sulfuric acid and sulfur dioxide. The single audit procedure will provide sufficient accuracy assessment for both pollutants.

5.6.3 Audit Frequency - When Method 8 is used for SPNSS purposes, the following audit frequency is recommended for compliance and enforcement tests. An audit for accuracy of the sampling procedures should be conducted prior to the field testing series on all flow totalizing systems (dry gas meters) and all differential pressure gauges used for velocity pressure determination that do not meet the specifications of Section 2.2 of Method 2. An additional audit should be conducted on the flow totalizing system when (1) a different flow totalizing system is used or (2) repairs are made on the flow totalizing system after

auditing. An additional audit should be conducted on the differential pressure gauge when (1) a different differential pressure gauge is used or (2) repairs are made on the differential pressure gauge after auditing. An audit for accuracy of the analytical procedures should be conducted prior to the analysis of the field samples for every field test series. The analytical series may contain field samples from more than one stack or test. A lesser frequency may be acceptable when Method 8 is used for applications other than compliance and enforcement.

5.6.4 Availability of Audit Materials - Control agencies responsible for the compliance or enforcement test may obtain certified calibrated orifices (when available) prior to each compliance or enforcement source test. Orifices may be obtained by contacting:

U.S. Environmental Protection Agency
Environmental Monitoring Systems Laboratory
Quality Assurance Division (MD-77A)
Research Triangle Park, North Carolina 27711

Attention: Source Test Audit Coordinator

Alternatively, a calibrated orifice can be made as described by Mitchell, et. al. in Reference 1 and sent to the USEPA for certification.

Agencies may obtain SO₂ audit samples prior to each compliance or enforcement test by contacting the Quality Assurance Coordinator (Table 5.1) in his respective EPA Regional Office. The SO₂ audit samples are prepared by EPA's Environmental Monitoring Systems Laboratory at the Research Triangle Park, North Carolina. For purposes other than compliance and enforcement tests, audit samples may be prepared using primary standard grade ammonium sulfate by the procedure described in this Handbook for control sample preparation. For details, see Method 6, Section 3.5.5, Subsection 5.2.5.

5.6.5 Cost of Audit - The audit for Method 8 is an audit of portions of both the sampling and analytical phases. These audits should require less than five technical hours of effort to complete. This effort would generally represent less than 5 percent of the total effort to conduct, calculate, and report the Method 8 sampling and analysis.

5.7 Method 10 (Carbon Monoxide)

5.7.1 Method Description - Method 10 is applicable to the determination of carbon monoxide (CO) from stationary sources. A gas sample is extracted from the stack either at a constant rate using a continuous sampling train (constant rate sampling) or at a rate proportional to the stack gas velocity using an integrated sampling train. The concentration of CO from both sampling methods is determined by a Luft-type nondispersive infrared (NDIR) analyzer. The Method is applicable to stationary sources when specified by a compliance regulation and/or when the CO concentration is >20 parts per million (ppm) for a 0-to-1000-ppm testing range. With this Method, interferences can result from substances with strong infrared absorption energies. Major interferences can be avoided using silica gel and Ascarite traps to remove H₂O and CO₂, respectively. If traps are used, the sample volumes must be adjusted to account for the CO₂ removed. Section 3.8 of this Handbook contains a detailed description of Method 10. The Method can be found in 40 CFR 60, Appendix A. Note: This audit is not applicable to 40 CFR 60, Subpart Z (Ferroalloy Production Facilities).

5.7.2 Audits to Assess Accuracy of Sampling and Analysis Procedures - The accuracy of the sampling and analytical procedure is assessed by conducting a cylinder gas audit. An audit cylinder of CO is needed. Use audit gas that has been certified by comparison with National Bureau of Standards (NBS) gaseous Standard Reference Materials (SRM) or NBS/EPA approved gas manufacturer's Certified Reference Materials (CRM) following EPA Traceability Protocol No. 1 for audit gases (Section 3.0.4 of this Handbook). CRM's may be used directly as audit gases; procedures for preparation of CRM's are described in Reference 6.

The audit sample concentration should be within the range of 40 to 200 percent of the applicable regulation. A typical standard of 0.050 percent would require an audit cylinder of 0.02 to 0.1 percent CO. Note: The audit gas must not be the gas used for normal calibration.

The following recommendations are provided as guidance for conducting a proper audit.

1. The analyzer should be at normal operating conditions. No adjustment must be made during the audit.

2. For a continuous sampling train, attach a manifold or vented bubbler to the probe tip. Be sure that the audit gas flow to the manifold is kept under a slight positive pressure at all times. For integrated sampling trains, fill a sample bag with the audit gas, and attach the bag to the analyzer.

3. Challenge the analyzer prior to the first sample

analysis and again after the last sample analysis.

4. Compute the percent relative error (RE) for the audit,

$$RE = \frac{C_M - C_A}{C_A} \times 100$$

where:

C_M = Concentration measured by NDIR, ppm, and
 C_A = Audit or given concentration of the audit sample, ppm.

5. An acceptable relative error of +15% or +50 ppm (whichever is greater) has been established for this method. These relative errors are based on the SO₂ and NO_x monitor's cylinder gas audits as described in Reference 7, and on the collaborative tests from Method 10 as described in Reference 8.

6. The results of the calculated RE should be included in the emission test report as an assessment of the accuracy of the sampling and analysis phase of Method 10.

5.7.3 Audit Frequency - When Method 10 is used for SPNSS purposes, the following audit frequency is recommended for compliance and enforcement tests. An audit for accuracy should be conducted after the NDIR calibration and prior to and at the conclusion of, the field sample analysis. A lesser frequency may be acceptable when Method 10 is used for applications other than compliance and enforcement.

5.7.4 Availability of Audit Materials - The given concentrations of CO cylinder gases used for audits of Method 10 must be both accurate and stable. Accurate and stable CO cylinder gases are available from several commercial cylinder gas manufacturers. They can be obtained by two methods:

1) Require the gas manufacturer to use Protocol 1 to establish the audit gas concentration. (The gas manufacturer should also be required to guarantee in writing that Protocol 1 was followed to certify the audit gas concentration.)

2) Obtain a CRM gas from a commercial gas manufacturer. A list of commercial gas manufacturers who have CO CRM gases approved for sale by NBS/EPA may be obtained by contacting:

U.S. Environmental Protection Agency
Environmental Monitoring Systems Laboratory
Quality Assurance Division (MD-77A)
Research Triangle Park, North Carolina 27711

Attention: List of CRM Manufacturers

5.7.5 Cost of Audit - The audit of Method 10 is an audit of both the sampling and analysis phases. This audit should require less than four technical hours of effort to complete. This effort will generally represent less than 5 percent of the total effort to conduct, calculate, and report the Method 10 sampling and analysis.

5.8 Method 11 (Hydrogen Sulfide)

5.8.1 Method Description - This Method is applicable for the determination of hydrogen sulfide. The hydrogen sulfide is collected from the source in a series of midget impingers and reacted with acidified cadmium sulfate CdSO_4 to form cadmium sulfide (CdS). The precipitated CdS is then dissolved in hydrochloric acid to regenerate H_2S , which is absorbed in a known volume of iodine solution. The iodine consumed is a measure of the H_2S content of the gas. An impinger containing hydrogen peroxide is included to remove SO_2 as an interfering specie. The sampling and analytical procedures are not described in this Handbook. The promulgated Method is in the Federal Register. Vol. 43, page 1494, January 10, 1978 and 40 CFR, Appendix A.

5.8.2 Audits to Assess Accuracy of Sampling and Analytical Procedures - The accuracy of the sampling and analytical procedure is assessed by conducting a cylinder gas audit. One audit cylinder of H_2S is needed. The audit cylinder will assess both the sampling and analytical procedures. The range of the audit gas should be within about 40 to 200 percent of the applicable standard. An emission standard of 0.016 percent H_2S would require an audit concentration between 64 to 320 percent H_2S . The following items are provided as guidance to conduct a proper audit.

1. The tester should attach a manifold system or vented bubbler to the sample train and keep the audit gas at a slightly positive pressure through the manifold to ensure that the audit sample is not diluted with ambient air. The vented H_2S should be discharged into a well ventilated area for safety reasons.

2. The tester should attach the manifold or bubbler to the sample train and sample the audit gas using the standard sampling procedures. The tester should ensure an undiluted transfer of audit gas to the sample train.

3. The tester should then recover and analyze the audit sample in the same manner and at the same time as the field samples. This requires an additional sample collection run and analysis to be performed.

4. Compute the percent relative error (RE) for the audit,

$$\text{RE} = \frac{C_M - C_A}{C_A} \times 100$$

where:

C_M = Concentration measured by Method 11, ppm H_2S , and
 C_A = Audit or given concentration of the audit sample, ppm H_2S .

5. The results of the calculated RE should be included in the emission test report as an assessment of the accuracy of the sampling and analytical phase of the Method 11 test. An acceptable relative error has been established as +15 percent for this Method. This relative error has been established based on the SO₂ and NO_x monitor's cylinder gas audits, as described in Reference 7, and on the collaborative tests, as described in Reference 9. Due to the cost of auditing and the analytical procedures for this Method, a single audit sample is recommended which is analyzed with the field samples.

5.8.3 Audit Frequency - When Method 11 is used for SPNSS purposes, the following audit frequency is recommended for compliance and enforcement tests. An audit for accuracy should be conducted once during each field testing series and the collected audit sample analysed with the field samples. A lesser frequency may be acceptable when Method 11 is used for other applications, depending on the purpose of the test.

5.8.4 Availability of Audit Materials - Control agencies responsible for compliance and enforcement tests may obtain an audit cylinder of H₂S prior to each compliance or enforcement test by contacting:

U.S. Environmental Protection Agency
Environmental Monitoring Systems Laboratory
Quality Assurance Division (MD-77B)
Research Triangle Park, North Carolina 27711

Attention: Audit Cylinder Gas Coordinator

If an audit cylinder is unavailable, commercial manufacturers should be sought to obtain the desired audit gas.

5.8.5 Cost of Audit - The audit for Method 11 is an audit of both the sampling and analysis phase. This audit should require less than four technical hours of effort to complete. This effort will generally represent less than 5 percent of the total effort to conduct, calculate, and report the Method 11 sampling and analysis.

5.9 Method 12 (Inorganic Lead)

5.9.1 Method Description - This Method applies to the determination of inorganic lead (Pb) emissions. Particulate and gaseous Pb are withdrawn isokinetically from the source and collected on a filter and in dilute nitric acid. The collected samples are digested in acid solution and analyzed by atomic absorption spectrometry using an air acetylene flame. The sampling and analytical procedures are not described in this Handbook. The Method can be found in 40 CFR 60, Appendix A.

5.9.2 Audits to Assess Accuracy of Sampling and Analytical Procedures -

5.9.2.1 Sampling Accuracy - The audit for the sampling phase is to determine the accuracy of the flow totalizing system (dry gas meter) of the Method 12 sampling train and the differential pressure gauge used to measure the velocity when the gauge does not meet the specifications in Section 2.2 of Method 2 (40 CFR 60, Appendix A). The flow totalizing system should be audited using the same procedures and with the same frequency as described in detail for Method 5 in Subsection 5.3.2 of this Section. The differential pressure gauge should be audited using the same procedures and with the same frequency as described in detail for Method 2 in Subsection 5.1.2 of this Section.

5.9.2.2 Analytical Accuracy - The analytical procedures should be audited using two audit samples. The audit samples are glass fiber filters impregnated with lead nitrate. One audit sample should be at a low concentration (between 100 μg and 600 μg total weight of lead per audit sample) and one audit sample at a high concentration (between 900 μg and 2000 μg total weight of lead per audit sample). This requirement is based on emission standards of 0.4 mg/dsm³ and 1.0 mg/dsm³ corresponding to about 400 and 1000 μg of lead per sample. These audit samples should be prepared simultaneously with the field samples using the same procedures, but analyzed prior to the source test filter. The auditor should calculate the relative error (RE) of the audit samples using the equation below. The calculated RE should be included in the emission test report as an assessment of the accuracy of the analytical phase of the Method 12 test.

$$\text{RE} = \frac{C_M - C_A}{C_A} \times 100$$

where:

- C_M = Concentration measured by the lab analyst, total μg lead per audit sample, and
 C_A = Audit or given concentration of the audit sample (glass fiber filter), total μg lead per audit sample.

An acceptable relative error has been established as ± 15 percent for this Method. The relative error was established based on the collaborative tests, as described in Reference 10.

5.9.3 Audit Frequency - When Method 12 is used for SPNSS purposes, the following audit frequency is recommended for compliance and enforcement tests. An audit for accuracy of the sampling procedures should be conducted prior to the field testing series on all flow totalizing systems (dry gas meters) and all differential pressure gauges used for velocity pressure determination that do not meet the specifications of Section 2.2 of Method 2. An additional audit should be conducted on the flow totalizing system when (1) a different flow totalizing system is used or (2) repairs are made on the flow totalizing system after auditing. An additional audit should be conducted on the differential pressure gauge when (1) a different differential pressure gauge is used or (2) repairs are made on the differential pressure gauge after auditing. An audit for accuracy of the analyses of the field sample should be conducted after the preparation of the calibration curve and just prior to the field sample analysis. The analyses may cover samples from more than one stack or test. A lesser frequency may be acceptable when Method 12 is used for applications other than compliance and enforcement.

5.9.4 Availability of Audit Materials - Control agencies responsible for the compliance or enforcement test may obtain lead audit samples (glass fiber filter strips impregnated with lead nitrate) and a certified calibrated orifice prior to each compliance or enforcement test by contacting:

U.S. Environmental Protection Agency
Environmental Monitoring Systems Laboratory
Quality Assurance Division (MD-77A)
Research Triangle Park, North Carolina 27711

Attention: Source Test Audit Coordinator

Alternatively, a calibrated orifice can be made as described by Mitchell, et. al. in Reference 5 and sent to the USEPA for certification.

5.9.5 Cost of Audit - The audit for Method 12 is an audit of portions of both the sampling and the analysis phase. This audit should require less than five technical hours of effort to complete. This effort will generally represent less than 5 percent of the total effort to conduct, calculate, and report the Method 12 sampling and analysis.

5.10 Methods 13A and 13B (Total Fluoride)

5.10.1 Method Description - These Methods are applicable for the determination of fluoride emissions from stationary sources. Fluorocarbons, such as Freons, are not quantitatively collected or measured by these procedures. Both Methods withdraw gaseous and particulate fluorides from the source isokinetically using a sample train with water-filled impingers and filter(s). Method 13A determines the weight of total fluoride by the SPADNS Zirconium Lake colorimetric method. If chloride ion is present, it is recommended that Method 13B be used. Method 13B determines the weight of fluorides by the specific ion electrode method. Section 3.9 and Section 3.10 of this Handbook contain detailed descriptions of Methods 13B and 13A, respectively. The Method can be found in 40 CFR 60, Appendix A.

5.10.2 Audits to Assess Accuracy of Sampling and Analytical Procedures -

5.10.2.1 Sampling Accuracy - The audit for the sampling phase is used to determine the accuracy of the flow totalizing system (dry gas meter) of the Method 13 sampling train and the differential pressure gauge used to measure the velocity when the gauge does not meet the specifications in Section 2.2 of Method 2 (40 CFR 60, Appendix A). The flow totalizing system should be audited using the same procedures and with the same frequency as described in detail for Method 5 in Subsection 5.3.2 of this Section. The differential pressure gauge should be audited using the same procedures and with the same frequency as described in detail for Method 2 in Subsection 5.1.2 of this Section.

5.10.2.2 Analytical Accuracy - The analytical procedures for both Methods 13A and 13B should be audited using the same procedure. The auditor should provide two audit samples to be analyzed along with the field samples, one sample at a low concentration (0.2 to 1.0 mg fluoride/dsm³ of gas sampled or approximately 1 to 5 mg NaF/liter of sample)₃ and one at a high concentration (1 to 5 mg of fluoride/dsm³ of gas sampled or approximately 5 to 25 mg NaF/liter of sample). The above values are typical for fertilizer plants with emission limits of 0.01 lb/ton and 0.02 lb/ton. Actual values can vary since the allowable concentration is dependent on both process design and operation.

The audit samples should be analyzed at the same time as the field samples for Method 13A and after preparation of the calibration curve and just prior to analysis for Method 13B. The percent relative error (RE) of the audit sample is determined using the equation below. The calculated RE should be included in the emission test report as an assessment of the accuracy of the analytical phase of the Method 13A or 13B test.

$$RE = \frac{C_M - C_A}{C_A} \times 100$$

where:

C_M = Concentration measured by the lab analyst, mg/ml, and
 C_A = Audit or given concentration of the audit sample,
mg/ml.

An acceptable relative error has been established as +15 percent for this Method. The relative error has been established based on the collaborative test described in Reference 11.

5.10.3 Audit Frequency - When Method 13A or 13B is used for SPNSS purposes, the following audit frequency is recommended for compliance and enforcement tests. An audit for accuracy of the sampling procedures should be conducted prior to the field testing series on all flow totalizing systems (dry gas meters) and all differential pressure gauges used for velocity pressure determination that do not meet the specifications of Section 2.2 of Method 2. An additional audit should be conducted on the flow totalizing system when (1) a different flow totalizing system is used or (2) repairs are made on the flow totalizing system after auditing. An additional audit should be conducted on the differential pressure gauge when (1) a different differential pressure gauge is used or (2) repairs are made on the differential pressure gauge after auditing.

An audit for accuracy of the analytical procedures should be conducted simultaneously with the analysis of every series of field samples for Method 13A and after the preparation of the calibration curve and prior to field sample analysis for Method 13B. The analytical series may contain field samples from more than one stack or test. A lesser frequency may be acceptable when either Method 13A or 13B is used for other applications, depending on the purpose of the test.

5.10.4 Availability of Audit Materials - Control agencies responsible for the compliance or enforcement test may obtain aqueous sodium fluoride (NaF) audit samples and a certified calibrated orifice by contacting:

U.S. Environmental Protection Agency
Environmental Monitoring Systems Laboratory
Quality Assurance Division (MD-77A)
Research Triangle Park, North Carolina 27711

Attention: Source Test Audit Coordinator

Alternatively, a calibrated orifice can be made as described by Mitchell, et. al. in Reference 5 and sent to the USEPA for

certification.

If audit samples are to be used for other purposes, aqueous NaF audit samples may be prepared by the procedure described in this Handbook for control sample preparation. This procedure is described in Section 3.10.5, Subsection 5.2.6 for Method 13A and Section 3.9.5, Subsection 5.2.6 for Method 13B.

5.10.5 Cost of Audit - The audit for Method 13A or 13B is an audit for portions of both the sampling and analysis phase. These audits should require less than five technical hours of effort to complete. This effort will generally represent less than 5 percent of the total effort to conduct, calculate and report the Method 13 sampling and analysis.

5.11 Method 15 (Hydrogen Sulfide, Carbonyl Sulfide, and Carbon Disulfide)

5.11.1 Method Description - Method 15 is applicable for determination of hydrogen sulfide (H_2S), carbonyl sulfide (COS), and carbon disulfide (CS_2) from tail² gas control units of sulfur recovery plants. A gas sample is extracted from the emission source through a heated probe and diluted with clean dry air. An aliquot of the diluted sample from the sample line is then analyzed for H_2S , COS , and CS_2 by gas chromatographic (GC) separation and flame photometric detection (FPD). The sampling and analytical procedures are not described in this Handbook. The promulgated Method is in the Federal Register, Vol. 43, page 10866, March 15, 1978 and 40 CFR 60 Appendix A.

5.11.2 Audits to Assess Accuracy of Sampling and Analytical Procedures - The accuracy of the sampling and analytical procedure is assessed by conducting a cylinder gas audit. Two audit cylinders [one of hydrogen sulfide (H_2S) and one of carbonyl sulfide (COS)] are needed. The total concentration of the two audit gases should be within about 40 to 200 percent of the applicable standards. For an emissions standard of 0.030 percent by volume reduced sulfur compound and 0.0010 percent by volume hydrogen sulfide, audit gases of 100 to 500 ppm COS and 4 to 20 ppm H_2S would typically be used. The following items are provided as guidance to conduct a proper audit:

1. The standard post-test procedure of determining the sample line loss should be run by the tester.
2. Prior to collection of the field sample, the tester should attach either of the audit cylinders to the opening of the probe. The audit gas should be fed to the probe in sufficient quantity to ensure that the excess sample is vented to the atmosphere. The number of audit sample injections for analysis and the time between sample injections is left to the discretion of the tester.
3. After completion of one audit cylinder, the other audit cylinder should then be attached in the same manner. The tester is responsible for ensuring that the audit gas is introduced into the sample train in an acceptable manner and at an acceptable rate.
4. The results of the audit sample results should be calculated in the same manner used to calculate the field sample results and should be included in the test report.
5. The auditor can then compute the percent relative error (RE) for the audit.

$$RE = \frac{C_M - C_A}{C_A} \times 100$$

where:

C_M = Concentration measured by Method 15, ppm H_2S or ppm COS, and

C_A = Audit or given concentration of the audit sample, ppm H_2S or ppm COS.

6. An acceptable relative error of +20 percent has been established for this Method. This relative error has been established based on the collaborative test described in Reference 12.

7. The calculated RE should be included in the emission test report as an assessment of the accuracy of the sampling and analytical phases of the Method 15 test.

5.11.3 Audit Frequency - When Method 15 is used for SPNSS purposes, the following frequency is recommended for compliance and enforcement tests. An audit for accuracy should be conducted prior to each field test series at the conclusion of the sample line loss determination. A lesser frequency may be acceptable when Method 15 is used for other applications, depending on the purpose of the test.

5.11.4 Availability of Audit Materials - Control agencies responsible for the compliance or enforcement test may obtain audit cylinders of H_2S and COS prior to each compliance or enforcement source test. The H_2S and COS audit cylinders may be obtained by contacting:

U.S. Environmental Protection Agency
Environmental Monitoring Systems Laboratory
Quality Assurance Division (MD-77B)
Research Triangle Park, North Carolina 27711

Attention: Audit Cylinder Gas Coordinator

If the audit cylinders are unavailable, commercial manufacturers should be sought to obtain the desired audit gases.

5.11.5 Cost of Audit - The audit for Method 15 is an audit of both the sampling and analysis phase. This audit should require less than five technical hours of effort to complete. This effort will generally represent less than 5 percent of the total effort to conduct, calculate, and report the Method 15 sampling and analysis.

5.12 Method 16 (Sulfur Emissions)

5.12.1 Method Description - Method 16 is applicable for determination of hydrogen sulfide (H_2S), methyl mercaptan ($MeSH$), dimethyl sulfide (DMS), and dimethyl disulfide ($DMDS$) from recovery furnaces, lime kilns, and smelt dissolving tanks at kraft pulp mills. The four compounds shown above are collectively known as total reduced sulfur (TRS). A gas sample is extracted from the emission source through a heated probe and diluted with clean air. An aliquot of the diluted sample from the sample line is then analyzed for H_2S , $MeSH$, DMS , and $DMDS$ by gas chromatographic (GC) separation² and flame photometric detection (FPD). The sampling and analytical procedures are not described in this Handbook. The promulgated Method can be found in the Federal Register, Vol. 43, page 7568, February 23, 1978 and 40 CFR 60, Appendix A.

5.12.2 Audits to Assess Accuracy of Sampling and Analytical Procedures - The accuracy of the sampling and analytical procedure is assessed by conducting a cylinder gas audit. One audit cylinder of hydrogen sulfide is needed. The hydrogen sulfide (H_2S) concentration should be within 40 to 200 percent of the applicable standard. For an emission standard of 5 ppm by volume of total reduced sulfur, an audit concentration of 2 to 10 ppm of H_2S would typically be used. The following items are provided as guidance to conduct a proper audit.

1. The standard post-test procedure of determining the sample line loss should be run by the tester.

2. Prior to collecting the field samples, the tester should attach the audit cylinder to the opening of the probe. The audit gas should be fed to the probe in sufficient quantity to ensure that an excess of sample is vented to the atmosphere. The gas should be vented into a well-ventilated area for safety reasons. The number of audit sample injections for analysis and the time between sample injections is left to the discretion of the tester.

3. The results of the audit gas sampling should be calculated in the same manner used to calculate the field sample results and should be included in the test report.

4. The auditor can then compute the percent relative error (RE) for the audit.

$$RE = \frac{C_M - C_A}{C_A} \times 100$$

where:

C_M = Concentration measured by Method 16, ppm H_2S , and
 C_A = Audit or given concentration of the audit sample, ppm
 H_2S .

5. An acceptable relative error of +20 percent has been established for this Method. This relative error has been established based on the collaborative test described in Reference 12.

6. The calculated RE should be included in the emission test report as an assessment of the accuracy of the sampling and analytical phase of the Method 16 test.

5.12.3 Audit Frequency - When Method 16 is used for SPNSS purposes, the following frequency is recommended for compliance and enforcement tests. An audit for accuracy should be conducted prior to each field test, at the conclusion of the sample line loss determination. A lesser frequency may be acceptable when Method 16 is used for other applications, depending on the purpose of the test.

5.12.4 Availability of Audit Materials - Control agencies responsible for the compliance or enforcement test may obtain audit cylinders of H_2S prior to each compliance or enforcement source test. The H_2S audit cylinder may be obtained by contacting:

U.S. Environmental Protection Agency
Environmental Monitoring Systems Laboratory
Quality Assurance Division (MD-77B)
Research Triangle Park, North Carolina 27711

Attention: Audit Cylinder Gas Coordinator

If the audit cylinders are unavailable, commercial manufacturers should be sought to obtain the desired audit gases.

5.12.5 Cost of Audit - The audit of Method 16 is an audit of both the sampling and analysis phase. This audit should require less than five technical hours of effort to complete. This effort should generally represent less than 5 percent of the total effort to conduct, calculate, and report the Method 16 sampling and analysis.

5.13 Method 16A (Total Reduced Sulfur Emissions)

Method 16A should be audited using the quality assurance requirements in Method 16A. (See Reference 13 for details.)

5.13.1 Method Description - Method 16A is an alternative method to Method 16 for determining total reduced sulfur (TRS) compounds from recovery furnaces, lime kilns, and smelt dissolving tanks at kraft pulp mills. A gas sample is extracted from the sampling point in the stack. SO_2 is selectively removed from the sample using a citrate buffer solution. The reduced sulfur compounds are then oxidized and analyzed as SO_2 using the barium-thorin titration procedure of Method 6. The sampling and analytical procedures are not described in this Handbook. The promulgated Method can be found in the Federal Register, Vol. 50, page 9578, March 8, 1985 and 40 CFR 60, Appendix A.

5.13.2 Audits to Assess Accuracy of Sampling and Analytical Procedures - The accuracy of the sampling and analytical procedures is assessed by conducting a cylinder gas audit, and the accuracy of the analytical procedures is assessed by analysis of a set of aqueous audit samples.

5.13.2.1 Sampling and Analytical Accuracy - The procedures described in detail in Section 4.2 "System Performance Check" of Method 16A should be used to assess the sampling and analytical accuracy. This audit should be conducted in accordance with the Reference Method and will require a separate sample collection and analysis. The hydrogen sulfide (H_2S) concentration of the audit gas should be between 40 and 200² percent of the applicable standard. For an emission standard of 5 ppm by volume of total reduced sulfur, an audit concentration of 2 to 10 ppm of H_2S would typically be used. The auditor should calculate the percent relative error (RE) for the audit as shown below.

$$\text{RE} = \frac{C_M - C_A}{C_A} \times 100$$

where:

C_M = Concentration measured by Method 16A, ppm H_2S , and
 C_A = Audit or given concentration of the audit sample, ppm H_2S .

An acceptable relative error of + 20% has been established for this Method. The calculated RE should be included in the emission test report as an assessment of the accuracy of the sampling and analytical phase of the Method 16A test.

5.13.2.2 Analytical Accuracy - According to Method 16A, when the Method is used for compliance testing, the analyst must analyze

two aqueous audit samples along with the field samples. The percent relative error (RE) for each of the audit samples is determined using the following equation. The calculated RE's must be included in the emission test report as an assessment of the accuracy of the analytical phase of the Method 16A test.

$$RE = \frac{C_d - C_a}{C_a} \times 100$$

where:

C_d = Determined audit sample concentration, mg/m^3 , and
 C_a = Actual audit concentration, mg/m^3 .

Method 16A states that the relative error shall be less than 5 percent for both audit samples. When this specification is not met, the audit samples and field samples must be reanalyzed and the initial and reanalysis results included in the test report. Failure to meet the 5 percent specification on the initial and reanalysis results of the audit samples may void the test.

5.13.3 Audit Frequency - When Method 16A is used for SPNSS purposes, the following frequency is recommended for compliance and enforcement tests. Audits for both sampling and analytical accuracy and analytical accuracy should be conducted once for each field test in accordance with the Method 16A. A lesser frequency may be acceptable when Method 16A is used for other applications, depending on the purpose of the test.

5.13.4 Availability of Audit Materials - Control agencies responsible for the compliance or enforcement test may obtain aqueous audit samples prior to each compliance or enforcement source test by contacting the respective EPA Regional Office Quality Assurance Coordinator (shown in Table 5.1). Audit cylinders of H_2S may be obtained by contacting:

U.S. Environmental Protection Agency
Environmental Monitoring Systems Laboratory
Quality Assurance Division (MD-77B)
Research Triangle Park, North Carolina 27711

Attention: Audit Cylinder Gas Coordinator

If the audit cylinders are unavailable, commercial manufacturers should be sought to obtain the desired audit gases.

5.13.5 Cost of Audit - The audit of Method 16A is an audit of both the sampling and analysis phase. This audit should require less than five technical hours of effort to complete. This effort should generally represent less than 5 percent of the total effort to conduct, calculate and report the Method 16A sampling and analysis.

5.14 Method 17 (Instack Filterable Particulate)

5.14.1 Method Description - This Method applies to the measurement of particulate matter emissions from stationary sources. This Method is not applicable when stack gases are saturated with water vapor or when the projected cross-sectional area of the probe emission-filter holder assembly covers more than 3 percent of the stack cross-sectional area. For SPNSS, the Method should only be used when (1) specified by the applicable subpart of the standards and only within the temperature limits (if specified) or (2) otherwise approved by the Administrator. Particulate matter is withdrawn isokinetically from a gas stream and collected on a glass filter maintained at stack temperature. The particulate matter mass is determined gravimetrically after removal of uncombined water. Subsection 3.11.10 of this Handbook contains a detailed description of Method 17. The Method can also be found in 40 CFR 60, Appendix A.

5.14.2 Audits to Assess Accuracy of Sampling and Analysis

5.14.2.1 Sampling Accuracy - The audit for the sampling phase is used to determine the accuracy of the flow totalizing system (dry gas meter) of the Method 17 sampling train and the differential pressure gauge used to measure the velocity when the gauge does not meet the specifications in Section 2.2 of Method 2 (40 CFR 60, Appendix A). The flow totalizing system should be audited using the same procedures and with the same frequency as described in detail for Method 5 in Subsection 5.3.2 of this Section. The differential pressure gauge should be audited using the same procedures and with the same frequency as described in detail for Method 2 in Subsection 5.1.2 of this Section.

5.14.2.2 Analytical Accuracy - None recommended.

5.14.3 Audit Frequency - When Method 17 is used for SPNSS purposes, the following audit frequency is recommended for compliance and enforcement tests. An audit for accuracy of the sampling procedures should be conducted prior to the field testing series on all flow totalizing systems (dry gas meters) and on all differential pressure gauges used for velocity pressure determination that do not meet the specifications of Section 2.2 of Method 2. An additional audit should be conducted on the flow totalizing system when (1) a different flow totalizing system is used or (2) repairs are made on the flow totalizing system after auditing. An additional audit should be conducted on the differential pressure gauge when (1) a different differential pressure gauge is used or (2) repairs are made on the differential pressure gauge after auditing. A lesser frequency may be acceptable when Method 17 is used for applications other than compliance and enforcement.

5.14.4 Availability of Audit Materials - Control agencies

responsible for the compliance or enforcement test may obtain certified calibrated orifices (when available) prior to each compliance or enforcement source test. Orifices may be obtained by contacting:

U. S. Environmental Protection Agency
Environmental Monitoring Systems Laboratory
Quality Assurance Division (MD-77A)
Research Triangle Park, North Carolina 27711

Attention: Source Test Audit Coordinator

Alternatively, a calibrated orifice can be made as described by Mitchell, et. al. in Reference 5 and sent to the USEPA for certification.

5.14.5 Cost of Audit - The audit of Method 17 is an audit of the sampling phase. The audit should require less than three technical hours of effort. This effort will generally represent less than 5 percent of the total effort to conduct, calculate and report the Method 17 sampling and analysis.

5.15 Method 18 (Gaseous Organic Compounds)

Method 18 should be audited using the quality assurance requirements in Method 18. (See Reference 2 for details.)

5.15.1 Method Description - Method 18 is applicable to approximately 90 percent of the total gaseous organics emitted from an industrial source. It does not include techniques to identify and measure trace amounts of organic compounds, such as those found in building air and fugitive emission sources. The Method will not determine compounds that (1) are polymeric (high molecular weights), (2) can polymerize before analysis, or (3) have very low vapor pressures at stack or instrument conditions. The Method is based on separating the major components of a gas mixture with a gas chromatograph (GC) and measuring the separated components with a suitable detector. This sampling and analytical technique is not described in this Handbook. The promulgated Method can be found in the Federal Register, Vol. 48, page 48344, November 18, 1983 and 40 CFR 60, Appendix A.

5.15.2 Audits to Assess Accuracy of Sampling and Analytical Procedures - The accuracy of the sampling and analytical procedures is assessed by conducting a cylinder gas audit. Two audit cylinders of an appropriate total gaseous organic are needed. The organic compound should be one of the major organic components being tested and the given concentration of the audit gas should be between 25 to 100 percent of the applicable emission limit for the low concentration, and 100 to 250 percent of the applicable emission limit for the high concentration cylinder. The audit cylinder gas will assess both the sampling and analytical procedures. The audit procedures should follow those described in 40 CFR 61, Appendix C, Procedure 2: "Procedure for Field Auditing GC Analysis" of the Federal Register, Vol. 47, page 39179, September 7, 1982 (Reference 14). The analysis of the audit samples shall be conducted after the preparation of the calibration curve and prior to the final field sample analysis.

The auditor should compute the percent relative error (RE) for each audit.

$$RE = \frac{C_M - C_A}{C_A} \times 100$$

where:

C_M = Concentration measured by Method 18 in ppm of the stated organic, and

C_A = Audit or given concentration of the audit sample in ppm of the stated organic.

Method 18 requires that the calculated relative error be less than +10 percent for both audit sample analyses. The calculated RE should be included in the emission test report as an assessment of the accuracy of the sampling and analytical phase of the Method 18 test.

5.15.3 Audit Frequency - When Method 18 is used for SPNSS purposes, the following audit frequency is recommended for compliance and enforcement tests. An audit for accuracy should be conducted after the preparation of the calibration curve and prior to the field sample final analysis for every field test series. A lesser frequency may be acceptable when Method 18 is used for applications other than compliance and enforcement tests.

5.15.4 Availability of Audit Materials - Control agencies responsible for the compliance or enforcement test may obtain EPA Method 18 audit gas cylinders prior to each compliance or enforcement test. The audit gas cylinders may be obtained by contacting:

U.S. Environmental Protection Agency
Environmental Monitoring Systems Laboratory
Quality Assurance Division (MD-77B)
Research Triangle Park, North Carolina 27711

Attention: Audit Cylinder Gas Coordinator

If an audit gas cylinder is unavailable, commercial manufacturers should be sought to obtain the desired audit gas.

5.15.5 Cost of Audit - The audit of Method 18 is an audit of both the sampling and analysis phase. This audit should require less than six technical hours of effort to complete. This would generally represent less than 10 percent of the total effort to conduct, calculate, and report the Method 18 sampling and analysis.

A complete list of organic compounds for which audit cylinders are available from the U. S. Environmental Protection Agency is shown in Table 5.3. Audit cylinders are generally available at a low concentration level (5 to 20 ppm) and a high concentration level (50 to 700 ppm) for each organic shown in the table. The table also shows those organic compounds which the U. S. Environmental Protection Agency has found to be unsuitable as audit cylinders because of insufficient stability in compressed gas cylinders.

TABLE 5.3. ORGANIC AUDIT CYLINDERS AVAILABLE FROM U. S. EPA

Compound****	Low Concentration Range		High Concentration Range	
	Concentration Range (ppm)	Cylinder Construction***	Concentration Range (ppm)	Cylinder Construction***
Benzene	5-20	S	60-400	A1, S
Ethylene	5-20	A1	300-700	A1
			3000-20,000	A1
Propylene	5-20	A1	300-700	A1
Methane/Ethane	---	--	1000-6000 (M)	A1
			200-700 (E)	
Propane	5-20	A1	300-20,000	A1
Toluene	5-20	S	100-700	S
Hydrogen Sulfide	5-20	A1	100-700	A1
Meta-Xylene	5-20	S	300-700	LS
Methyl Acetate	5-20	S	300-700	S
Chloroform	5-20	S	300-700	S
Carbonyl Sulfide	5-20	S	100-300	S
Methyl Mercaptan	3-10	A1	-----	--
Hexane	20-80	A1	1000-3000	LS
1,2-Dichloroethane	5-20	A1	100-600	A1
Cyclohexane	----	--	80-200	S
Methyl Ethyl Ketone	30-80	S	-----	--
Methanol	30-80	A1	-----	--
1,2-Dichloropropane	5-20	A1	300-700	A1
Trichloroethylene	5-20	A1	100-600	A1
1,1-Dichloroethylene	5-20	A1	100-600	A1
**1,2-Dibromoethylene	5-20	LS	100-600	LS
Perchloroethylene	5-20	S	300-700	LS
Vinyl Chloride	5-30	S	-----	--
1,3-Butadiene	5-30	S	-----	--
Acrylonitrile	5-20	LS, A1	300-700	LS, A1
**Aniline	5-20	A1	-----	--
Methyl Isobutyl Ketone	5-20	A1	-----	--
**Para-dichlorobenzene	5-20	S	-----	--
**Ethylamine	5-20	A1	-----	--
**Formaldehyde	5-20	--	-----	--
Methylene Chloride	1-20	A1	-----	--
Carbon Tetrachloride	5-20	A1	-----	--
Freon 113	5-20	A1	-----	--
Methyl Chloroform	5-20	A1	-----	--
Ethylene Oxide	5-20	A1	-----	--
Propylene Oxide	5-20	A1	75-200	A1

(continued)

TABLE 5.3. ORGANIC AUDIT CYLINDERS AVAILABLE FROM U. S. EPA
(continued)

Compound****	<u>Low Concentration Range</u>		<u>High Concentration Range</u>	
	Concentration Range (ppm)	Cylinder Construc- tion***	Concentration Range (ppm)	Cylinder Construc- tion***
Allyl Chloride	5-20	Al	75-200	S
Acrolein	5-20	Al	-----	--
Chlorobenzene	5-20	Al	-----	--
Carbon Disulfide	--	--	75-200	Al
**Cyclohexanone	5-20	Al	-----	--
*EPA Method 25 Gas	100-200	Al	750-2000	Al
Ethylene Dibromide	5-20	S	100-300	S
Tetrachloroethane	5-20	S	-----	--

* The gas mixture contains an aliphatic, an aromatic and carbon dioxide in nitrogen. Concentrations shown are reported in ppmC.

** Cylinders are no longer available in the repository since the compounds are found to be unstable in the cylinders.

*** Cylinder construction: Al = Aluminum, S = Steel, LS = Low Pressure Steel

****All organic compounds in audit cylinders are in a balance of N₂ gas.

5.16 Method 19 (Sulfur Dioxide Removal Efficiency and Particulate, Sulfur Dioxide and Nitrogen Oxides Emissions)

5.16.1 Methods Description - Method 19 is applicable for determining sulfur dioxide removal efficiencies of fuel pretreatment and sulfur dioxide control devices and the overall reduction of potential sulfur dioxide emissions from electric utility steam generators. This Method is also applicable for the determination of particulate, sulfur dioxide and nitrogen oxides emission rates. Fuel samples from before and after fuel pretreatment systems are collected and analyzed for sulfur and heat content. A sulfur dioxide emission reduction efficiency is calculated from the efficiency of the fuel pretreatment system.

Sulfur dioxide and oxygen or carbon dioxide concentration data obtained from sampling emissions upstream and downstream of sulfur dioxide control devices are used to calculate sulfur dioxide removal efficiencies. As an alternative to sulfur dioxide monitoring upstream of sulfur dioxide control devices, fuel samples may be collected in an as-fired condition and analyzed for sulfur and heat content. An overall sulfur dioxide emission reduction efficiency is calculated from the efficiency of fuel pretreatment systems and the sulfur dioxide control devices.

Particulate, sulfur dioxide, nitrogen oxides, and oxygen or carbon dioxide concentration data from downstream of sulfur dioxide control devices are used along with F factors to calculate particulate, sulfur dioxide, and nitrogen oxides emission rates. The sampling and analytical procedures are not described in this Handbook for the sulfur dioxide removal efficiency. The Method for determination of oxygen, particulate, sulfur dioxide and nitrogen oxides is described in Sections 3.2, 3.4, 3.11, 3.5, and 3.6, respectively. The promulgated Method is in the Federal Register, Vol. 44, page 33580, June 11, 1979 and 40 CFR 60, Appendix A.

5.16.2 Audits to Assess Accuracy of Sampling and Analytical Procedures - When Methods 3, 5, 6, 7, and 17 are used in support of Method 19, the same procedures and audit frequency should be used as described in the individual subsections for each of those Methods. When sulfur dioxide continuous emission monitors (CEM's) are used in support of the determination of sulfur dioxide removal efficiency, the audit procedures and frequency described in Appendix F, Procedure 1, 40 CFR Part 60 are to be used.

When fuel sample analysis is used to determine the sulfur dioxide concentration on a ng/Joule or lb/million Btu basis, an audit of the analytical procedures should be performed. A coal audit sample should be analyzed each quarter with the fuel samples. The coal audit sample should be analyzed at the same time, by the same procedure and analysis as the coal samples from the

pretreatment process and the furnace. The sample must be analyzed until the repeatability of two consecutive analyses of sulfur agree within 0.05% sulfur for coal containing less than 2% sulfur or 0.10% sulfur for coal containing 2% or more of sulfur as described in Reference 15. The auditor can then compute the percent relative error (RE) from the results on a (lb of SO₂)/million Btu or (ng of SO₂)/Joule basis only.

$$RE = C_M - C_A$$

where:

- C_M = Sulfur concentration or the gross calorific value measured by Method 19, % S or Btu/lb, and
 C_A = Audit or known sulfur concentration or the gross calorific value of the audit sample, % S or Btu/lb.

An acceptable relative error for the audit sample, based on reproducibility (between lab) criteria in Reference 15, is 0.10% sulfur for coal containing less than 2% sulfur and 0.20% sulfur for coal containing 2% or more of sulfur. For heating value, an acceptable relative error has been established at 300 Btu/lb based on the EPA coal audit data. The results of the calculated RE from the coal audit plus the audit results from Methods 3, 6, 7 and either 5 or 17, if used in support of Method 19, should be included in the quarterly emissions report as assessments of the accuracy of the sampling and analytical phase during the Method 19 test. The acceptable relative error for Methods 3, 5, 6, 7 and 17 are the same as specified in their respective section.

5.16.3 Audit Frequency - When Method 19 is used for SPNSS purposes, the following audit frequency is recommended for assessing accuracy. Methods 3, 5, 6, 7, and 17 should be audited using the same procedures and frequency as shown in the individual subsection for each Method. The SO₂ CEM should be audited on a quarterly basis using the procedures and frequency described in Appendix F, Procedure 1, 40 CFR Part 60 (see Reference 7 for details). An audit for assessing accuracy of the coal sample analysis should be conducted on a quarterly basis. A lesser frequency may be acceptable when Method 19 is used for applications other than compliance and enforcement.

5.16.4 Availability of Audit Materials - Control agencies responsible for the compliance or enforcement test, may obtain audit materials for Methods 5, 6, 7, and 17 from the locations described in these respective individual subsections. These control agencies may obtain a coal audit sample by contacting:

U.S. Environmental Protection Agency
Environmental Monitoring Systems Laboratory
Quality Assurance Division (MD-77A)
Research Triangle Park, North Carolina 27711

Attention: Source Test Audit Coordinator

The coal audit sample may also be used to assess the accuracy of the moisture and/or ash content analysis. Alternatively, coal audit samples may also be obtained from commercial coal testing laboratories.

5.16.5 Cost of Audit - The audit for Method 19 is an audit of the sampling phase for Method 5 and 17 and an audit of the analytical phase for Methods 6, 7, and coal sampling and analysis. The audit of the initial performance test and performance specification procedures for the continuous emission monitors should require less than 16 technical hours of effort to complete. The effort would generally represent less than 10 percent of the total effort to conduct, calculate and report Method 19 sampling and analysis requirements. Since the allowable combinations of testing analysis procedures for a continuous effort are numerous, no estimate of cost is made. It is unlikely, however, that the effort for the audits with the continuous monitoring would be greater than 10 percent of the total effort.

5.17 Method 20 (Nitrogen Oxide, Sulfur Dioxide and Oxygen Emissions from Stationary Gas Turbines)

5.17.1 Method Description - Method 20 is applicable for the determination of nitrogen oxides (NO_x), sulfur dioxide (SO_2), and oxygen (O_2) emissions from stationary gas turbines. For the NO_x and O_2 determinations, this Method includes: (1) measurement system design criteria; (2) analyzer performance specifications and performance test procedures; and (3) procedures for emission testing. A gas sample is continuously extracted from the exhaust stream of a stationary gas turbine; a portion of the sample stream is then conveyed to instrumental analyzers for determination of NO_x and O_2 content. During each NO_x and O_2 determination, a separate measurement of SO_2 emissions is made by using Method 6, or its equivalent. The O_2 determination is used to adjust the NO_x and SO_2 concentrations to a reference condition. The sampling and analytical procedures are not described in this Handbook. The promulgated Method can be found in the Federal Register, Vol. 44, page 52792, September 10, 1979 and 40 CFR 60, Appendix A.

5.17.2 Audits to Assess Accuracy of Sampling and Analytical Procedures - The accuracy of the sampling and analytical procedure is assessed by conducting a cylinder gas audit. One audit cylinder of NO in N_2 and one cylinder of O_2 in N_2 are needed. These audit gases must be certified by comparison to National Bureau of Standards (NBS) gaseous Standard Reference Materials (SRM) or NBS/EPA approved gas manufacturer's Certified Reference Materials (CRM) following EPA Traceability Protocol 1 for audit gases (Section 3.0.4 of this Handbook). CRM's may be used directly as audit gases; procedures for preparation of CRM's are described in Reference 6.

The NO audit sample concentrations should be within the range of 40 to 200 percent of the applicable emissions limit. An audit gas concentration of 60 to 300 ppm of NO would typically be used for an emission standard of 0.015 percent NO at 15 percent oxygen for stationary gas turbines. Note: The audit gas should not be the same gas used for normal calibration.

The O_2 audit gas cylinder concentration should be between 10 and 15 percent O_2 in N_2 .

The following items are provided as guidance for conducting a proper audit.

1. The monitors should be operating at normal conditions, and no adjustments are permitted during the audit.
2. After the measurement systems calibration and validation, and just prior to the field sampling, the tester should attach the NO audit cylinder to the opening of the probe. The

audit gas should be fed to the probe in sufficient quantity to ensure that an excess of sample is vented to the atmosphere. The tester should record the analyzer readings when a stable value is obtained.

3. The same procedure should be performed with the O₂ audit gas. The tester is responsible for ensuring that the audit gas is introduced into the measurement system in an acceptable manner and at an acceptable rate.

4. The results for the audit gas samples should be calculated in the same manner used to calculate the field test samples.

5. The auditor can then compute the percent relative error (RE) for each audit point.

$$RE = \frac{C_M - C_A}{C_A} \times 100$$

where:

C_M = Concentration measured by Method 20, ppm NO or percent O₂, and

C_A = Audit or given concentration of the audit sample, ppm NO or percent O₂.

6. An acceptable relative error has been established as +15 percent for this Method. This relative error is based on the O₂ and NO_x monitors' cylinder gas audits, as described in Reference 7.

7. The calculated RE should be included in the emission test report as an assessment of the accuracy of the sampling and analytical phase of the Method 20 test.

The Method 6 tests performed in support of Method 20 should be audited using the same procedures as described in the accuracy audit procedures for Method 6 (Section 5.4). The acceptable relative error for Method 6 audits is also shown in Section 5.4.

5.17.3 Audit Frequency - When Method 20 is used for SPNSS purposes, the following audit frequency is recommended for the compliance and enforcement test. An audit for accuracy of the measurement system for NO and O₂ should be conducted before the start of the field testing series. An audit for accuracy of the analytical procedures for Method 6 tests should be conducted simultaneously with the field samples as described in Subsection 5.4.3 of Method 6. A lesser frequency may be acceptable when Method 20 is used for applications other than compliance and enforcement.

5.17.4 Availability of Audit Materials - The given concentrations of O₂ and NO cylinder gases used for audits of Method 20 must be both accurate and stable. Both O₂ and NO are available from several commercial gas manufacturers. ²These cylinder gases may be obtained by two methods:

1. Require the gas manufacturer to use EPA Traceability Protocol 1 to establish the audit gas concentration. (The gas manufacturer should also be required to guarantee in writing that EPA Traceability Protocol 1 was followed to certify the audit gas concentration.)

2. Obtain a CRM gas from a commercial gas manufacturer. A list of commercial gas manufacturers who have no CRM gases approved for sale by NBS/EPA may be obtained by contacting:

U.S. Environmental Protection Agency
Environmental Monitoring Systems Laboratory
Quality Assurance Division (MD-77)
Research Triangle Park, North Carolina 27711

Attention: List of CRM Manufacturers

5.17.5 Cost of Audit - The audit for Method 20 is an audit of both the sampling and analysis phase. This audit should require less than five technical hours of effort to complete. This effort should generally represent less than 5 percent of the total effort to conduct, calculate, and report the Method 20 sampling and analysis.

5.18 Method 25 (Total Gaseous Nonmethane Organic Emissions as Carbon)

5.18.1 Method Description - This Method applies to the measurement of volatile organic compounds (VOC) as total gaseous non-methane organics (TGNMO) analyzed in terms of carbon from source emissions. Organic particulate matter will interfere with the analysis and, therefore in some cases, an in-stack particulate filter is required. An emission sample is withdrawn from the stack at a constant rate through a chilled condensate trap by means of an evacuated sample tank. TGNMO are determined by combining the analytical results obtained from independent analyses of the condensate trap and sample tank fractions. After sampling is completed, the organic contents of the condensate trap are oxidized to carbon dioxide (CO_2). The CO_2 is quantitatively collected in an evacuated vessel, then a portion of the CO_2 is reduced to methane (CH_4) and measured by a FID. The organic content of the sample fraction collected in the sampling tank is measured by injecting a portion into a gas chromatographic (GC) column to separate the nonmethane organics from CO , CO_2 , and CH_4 ; the nonmethane organic (NMO) material is oxidized to CO_2 , reduced to CH_4 and measured by a flame ionization detector (FID). In this manner, the variable response of the FID associated with different types of organics is eliminated. The sampling and analytical procedures are not described in this Handbook. The promulgated Method can be found in the Federal Register, Vol. 45, page 65956, October 3, 1980 and 40 CFR 60, Appendix A.

5.18.2 Audits to Assess Accuracy of Sampling and Analytical Procedures - The accuracy of the sampling and analytical procedures is assessed by conducting a cylinder gas audit. One audit cylinder of EPA Method 25 gas mixture is needed. The audit cylinder will assess both the sampling and analytical procedure. The EPA Method 25 gas mixture includes a combination of aliphatic and aromatic organics plus carbon dioxide in a balance gas of nitrogen. Use of this audit mixture will result in a collection of organics in both the condensate trap and the evacuated sample tank portions of the sampling apparatus. The audit gas should be in the range of about 40 to 200 percent of the concentration of the allowable emission rate.

The following items are provided as guidance to conduct a proper audit.

1. The audit sample analysis should be conducted to coincide with the analysis of source test samples. Normally, it will be conducted after the nonmethane organic analyzer calibration and concurrent with the sample analyses.

2. After a leak check of the sampling apparatus has been completed, attach a manifold to the sample probe. Attach the

audit gas cylinder to the manifold and collect the audit gas with the Method 25 sampling system consistent with normal procedure for the Method.

3. At the end of audit analyses, the auditor requests the calculated concentration from the analyst and then compares the results with the actual audit concentrations. The auditor computes the percent relative error for the audit.

$$RE = \frac{C_M - C_A}{C_A} \times 100$$

where:

C_M = Concentration measured by Method 25, ppm as carbon,
and

C_A = Audit or given concentration of the audit sample,
ppm as carbon.

4. No acceptable relative error has been established for this Method since major revisions to the Method are currently underway. Due to the cost of the audit only a single audit is recommended. The audit sample and field samples should be prepared and analyzed in the same manner and at the same time.

5. The calculated RE should be included in the emission test report as an assessment of the accuracy of the sampling and analytical phase of the Method 25 test.

5.18.3 Audit Frequency - When Method 25 is used for SPNSS purposes, the following frequency is recommended for compliance and enforcement tests. An audit for accuracy should be conducted once for every field test series. A lesser frequency may be acceptable when Method 25 is used for applications other than compliance and enforcement.

5.18.4 Availability of Audit Materials - Control agencies responsible for the compliance or enforcement test may obtain an EPA Method 25 audit gas cylinder prior to each compliance or enforcement source test by contacting:

U.S. Environmental Protection Agency
Environmental Monitoring Systems Laboratory
Quality Assurance Division (MD-77B)
Research Triangle Park, North Carolina 27711

Attention: Audit Cylinder Gas Coordinator

The concentration range of the EPA Method 25 audit gas cylinder available is shown in Table 5.3.

If an audit gas cylinder is unavailable, commercial manufacturers should be sought to obtain the desired audit gas.

5.18.5 Cost of Audit - The audit of Method 25 is an audit of both the sampling and analysis phase. This audit should require less than 10 technical hours of effort to complete. This would generally represent less than 10 percent of the total effort to conduct, calculate and report the Method 25 sampling and analysis.

5.19 Method 25A and 25B (Total Gaseous Organic Concentration)

5.19.1 Method Description - Methods 25A and 25B are applicable to the measurement of total gaseous organic concentration of vapors consisting primarily of alkanes, alkenes, and/or arenes (aromatic hydrocarbons). The concentration is expressed in terms of propane (or other appropriate organic calibration gas) or in terms of carbon. Both Methods extract a gas sample from the stack through a heated sample line and, if necessary, a glass fiber filter. Method 25A uses a flame ionization analyzer (FIA) for analysis and Method 25B uses a nondispersive infrared analyzer (NDIR) for analysis. The sampling and analytical procedures are not described in this Handbook. The promulgated Method 25A and 25B can be found in the Federal Register Vol. 48, pages 37595 and 37597, respectively, August 18, 1983 and in 40 CFR 60, Appendix A.

5.19.2 Audits to Assess Accuracy of Sampling and Analytical Procedures - The accuracy of the sampling and analytical procedures is assessed by conducting a cylinder gas audit. One audit cylinder of an appropriate alkane or alkene is needed. The organic compound in the audit cylinder should be one of the major organic components being tested and the given concentration of the audit gas should be between 40 and 200 percent of the applicable emission limit. The audit cylinder gas will assess both the sampling and analytical procedures. The audit procedures (with the exception that only a single cylinder is recommended) should follow those described in 40 CFR 61, Appendix C, Procedure 2: "Procedure for Field Auditing GC Analysis" or the Federal Register Vol. 47, page 39179, September 7, 1982 (see Reference 14). The analysis of the audit sample should be conducted after the preparation of the calibration curve and prior to the field sample analysis.

The auditor should compute the percent relative error (RE) for the audit:

$$RE = \frac{C_M - C_A}{C_A} \times 100$$

where:

C_M = Concentration measured by Method 25A or 25B in ppm of the stated organic, and
 C_A = Audit or given concentration of the audit sample in ppm of the stated organic.

An acceptable relative error of +10 percent has been established for this Method. This relative error is based on the audits conducted by EPA in Reference 16.

The calculated RE should be included in the emission test report as an assessment of the accuracy of the sampling and analytical phase of Method 25A or 25B test.

5.19.3 Audit Frequency - When Method 25A or 25B is used for SPNSS purposes, the following frequency is recommended for compliance and enforcement tests. An audit for accuracy should be conducted after the preparation of the calibration curve and prior to the field sample analysis for every field test series. A lesser frequency may be acceptable when Method 25A or 25B is used for applications other than compliance and enforcement tests.

5.19.4 Availability of Audit Materials - Control agencies responsible for the compliance or enforcement test may obtain an appropriate alkane or alkene audit gas cylinder prior to each compliance or enforcement source test by contacting:

U.S. Environmental Protection Agency
Environmental Monitoring Systems Laboratory
Quality Assurance Division (MD-77B)
Research Triangle Park, North Carolina 27711

Attention: Audit Cylinder Gas Coordinator

Table 5.3 shows organic compounds available from the U. S. Environmental Protection Agency as audit gas cylinders. An appropriate alkane or alkene audit gas should be selected from this table for a Method 25A or 25B audit.

If an audit gas cylinder is unavailable, commercial manufacturers should be sought to obtain the desired audit gas.

5.19.5 Cost of Audit - The audit of Method 25A or 25B is an audit of both the sampling and analysis phase. This audit should require less than five technical hours of effort to complete. This would generally represent less than 5 percent of the total effort to conduct, calculate and report the Method 25A or 25B sampling and analysis.

5.20 References

1. "Quality Assurance and Quality Control Revisions to Methods 6 and 7," 40 CFR 60, Appendix A or Federal Register Vol. 49, page 26522, June 27, 1984.
2. EPA Method 18 "Measurement of Gaseous Organic Compounds by Gas Chromatography," 40 CFR 60, Appendix A or Federal Register Vol. 48, page 48344, October 18, 1983.
3. "Quality Control Procedures for EPA Method 3," 40 CFR 60, Appendix A or Federal Register Vol. 48, page 49458, October 25, 1983.
4. "Quality Control Procedures for EPA Methods 4 and 5," 40 CFR 60, Appendix A or Federal Register Vol. 48, page 55670, December 14, 1983.
5. Mitchell, W. J., Fuerst, R. G., Margeson, J. H., Streib, E. W., Midgett, M. R., and Hamil, H. F., "New Orifice Opens Way for Fast Calibration," Pollution Engineering, June 1981, pp. 45-57. A correction in this publication was printed in Pollution Engineering, August 1981.
6. "A Procedure for Establishing Traceability of Gas Mixtures to Certain National Bureau of Standards Standard Reference Materials." Joint publication by NBS and EPA. EPA-600/7-81-010. Available from U.S. Environmental Protection Agency, Quality Assurance Division (MD-77A), Research Triangle Park, North Carolina 27711.
7. "Quality Assurance Requirements for Gaseous Continuous Emission Monitoring Systems Used for Compliance Determination," 40 CFR 60, Appendix F, Procedure 1.
8. Constant, P. C., Scheil, G. W., and Sharp, M. C., "Collaborative Study of Method 10 - Reference Method for Determination of Carbon Monoxide Emissions from Stationary Sources - Report of Testing," EPA-650/4-75-001.
9. Scheil, G. W., and Sharp, M. C., "Standardization of Method 11 at a Petroleum Refinery," EPA-600/4-77-008a, January 1977.
10. Mitchell, W. J., and Midgett, M. R., "Evaluation of Stationary Source Particulate Measurement Methods: Volume V, Secondary Lead Smelters," EPA-600/2-79-116, June 1979.
11. Mitchell, W. J., Suggs, J. C., and Bergman, F. J., "Collaborative Study of EPA Method 13A and Method 13B," EPA-600/4-77-050, September 1977.

12. Hamil, H. F., and Swynnerton, N. F., "A Study to Improve EPA Methods 15 and 16 for Reduced Sulfur Compounds," EPA-600/4-80-023, April 1980.
13. Method 16A, Section 4.3 "System Performance Check," and Section 4.4 "Sample Analysis" 40 CFR 60, Appendix A or Federal Register Vol. 50, page 9578, March 8, 1985.
14. "Procedure for Field Auditing GC Analysis," 40 CFR 61, Appendix C, Procedure 2 or Federal Register Vol. 47, page 39179, September 7, 1982.
15. "Total Sulfur in the Analysis of Coal and Coke," ASTM D 3177-84, page 413-417, 1984.
16. Jayanty, R. K. M., Gutknecht, W. F., and Decker, C. E., "Status Report #6 Stability of Organic Audit Materials and Results of Source Test Analysis Audits," report by Research Triangle Institute for U. S. Environmental Protection Agency Environmental Monitoring Systems Laboratory, under Contract No. 68-02-3767, September 1984.

6.0 SPECIFIC PROCEDURES TO ASSESS ACCURACY OF REFERENCE METHODS USED FOR NESHAP

The purpose of this Section is to describe specific procedures to routinely assess and document the accuracy of reference and alternative methods for source test data under NESHAP (National Emission Standards for Hazardous Air Pollutants). Procedures for assessment of precision and completeness are not given, because compliance or enforcement tests are short-term (only a few hours duration), and additional duplicate tests to obtain precision data are costly. Accuracy is determined from results of performance audits (i.e., measurements made by the routine operator or analyst). The routine operator or analyst must not know the concentration or value of the audit standard used, and the results must be submitted to an immediate supervisor or QA coordinator who does know the audit value.

Since a high degree of experience and planning is required for audit sample preparation, and EPA has mandated that quality assurance be an integral part of all agency related measurement programs, the EPA's Environmental Monitoring Systems Laboratory (EMSL) in the Research Triangle Park, North Carolina has been delegated the responsibility for preparation of audit samples and materials for air measurements. Federal, state, and local agency personnel can obtain audit samples and materials for any enforcement and compliance measurement program directly from the Quality Assurance Coordinator at each EPA Regional Office unless otherwise directed in the following Reference Method subsections. The address and telephone number for each EPA Regional Office Quality Assurance Officer is shown in Table 5.1 of Section 3.0.5. When audit materials are unavailable or needed for nonagency use, commercial suppliers should be sought.

Performance audits are recommended here for the assessment of accuracy for the EPA Reference Methods in 40 CFR 61, Appendix B, when used for NESHAP purposes. Several of the methods have no performance audits since there are no reliable and low cost audit procedures available or the time and expense for an audit cannot now be justified. The EPA Reference Methods for which audits are recommended are shown in Table 6.1 with their corresponding subsection number.

The brief description of specific assessment procedures for each promulgated or proposed Reference Method is approximately three pages in length. This brief description includes the following:

1. Method summary (one paragraph).
2. Reference for details on the Method.

TABLE 6.1. EPA REFERENCE METHODS INCLUDED IN SECTION 3.0.6

Method number	Description	Subsection number
101, 101A and 102	Mercury Emissions in Air Streams from Chlor- Alkali Plants, Mercury Emissions from Sewage Sludge Incinerators, and Mercury Emissions in Hydrogen Streams from Chlor- Alkali plants	6.1
104	Beryllium	6.2
105	Mercury in Sewage Sludge	6.3
106	Vinyl Chloride	6.4
108 and 108A	Arsenic	6.5

3. Performance audit program to assess sampling and analytical procedures.

4. Recommended frequency for performance audits of compliance and enforcement tests. A frequency less than that recommended for enforcement could be acceptable when testing for other purposes.

5. Recommended standards and levels for establishing audit values.

6. Procedure to calculate accuracy.

7. Availability of audit materials.

8. Cost of the recommended audits.

The philosophy of these assessments is that relative error calculations will be made of the accuracy (1) to determine errors in the testers'/analysts' techniques and systems; (2) to, where possible, correct errors in these techniques and systems; and (3) for interpretation of the final reported emission test results by the data user. The reported emissions test data are not to be corrected on the basis of these relative error calculations.

The general approach that has been developed for these audits follow those already described in the Reference Method for EPA Methods 6 and 7 (see Reference 1) and/or Method 18 (see Reference 2). These audit procedures require the tester/analyst to provide the auditor with the audit results, either prior to the

field sample analysis or prior to including the field sample results in the report. When large relative errors are identified, the tester/analyst is allowed to correct his system. If possible, this is accomplished prior to the taking of the field samples or performing the final analysis on the field samples; this approach works quite well when the auditor is present for an on-site analysis. However, in the absence of the auditor, the tester/analyst must telephone the auditor with results of the audit sample analysis in order to make necessary corrections prior to analyzing the field samples. If the auditor feels that this is unwarranted or the tester/analyst does not wish to take the possible opportunity to correct an error in the system and/or techniques, the audit sample(s) would then be prepared and analyzed in the same manner and at the same time as the field sample. The approach of notifying the auditor prior to the field sample analysis can provide the source and agency with a greater chance of more accurate data, may require the rejection of less test results, and may improve the techniques and system of the tester and/or analyst.

For compliance determination, the audit sample values should be within the range of the allowable emission limit. The audit sample concentration or value should be within 40 to 200 percent of the value of interest for audits containing a single audit sample. For audits containing two audit samples, the low concentration sample should be between 25 and 100 percent of the value of interest and the high concentration between 100 and 250 percent.

6.1 Method 101 (Mercury Emissions in Air Streams from Chlor-Alkali Plants), Method 101A (Mercury Emissions from Sewage Sludge Incinerators) and Method 102 (Mercury Emissions in Hydrogen Streams from Chlor-Alkali Plants)

6.1.1 Methods Description - Method 101 is applicable for the determination of particulate and gaseous mercury emissions when the carrier gas stream is principally air. Method 101A is applicable for determination of particulate and gaseous mercury emissions from sewage sludge incinerators. Method 102 is applicable for determination of particulate and gaseous mercury emissions when the carrier gas stream is principally hydrogen. These Methods are for use in ducts or stacks at stationary sources. Unless otherwise specified, these Methods are not intended to apply to gas streams other than those emitted directly to the atmosphere without further processing.

Particulate and gaseous mercury emissions are isokinetically sampled from the source and collected in acidic iodine monochloride solution. The mercury collected (in mercuric form) is reduced to elemental mercury. Mercury is aerated from the solution and analyzed using spectrophotometry. The promulgated Methods 101 and 102 are found in the Federal Register, Vol. 38, page 8826, April 6, 1973. Methods 101 and 102 revisions and Method 101A are found in the Federal Register, Vol. 47, page 4703, June 8, 1982. All Methods can also be found in 40 CFR 61, Appendix B.

6.1.2 Audits to Assess Accuracy of Sampling and Analytical Procedures -

6.1.2.1 Sampling Accuracy - The audit for the sampling phase is used to determine the accuracy of the flow totalizing system (dry gas meter) of the Methods 101 and 101A sampling train and the differential pressure gauge used to measure the velocity when the differential pressure gauge does not meet the specifications in Section 2.2 of Method 2 (40 CFR 60, Appendix A). The flow totalizing system should be audited using the same procedures and with the same frequency as described in detail for Method 5 in Subsection 5.3.2 of Section 3.0.5 in this Handbook. The differential pressure gauge should be audited using the same procedures and with the same frequency as described in detail for Method 2 in Subsection 5.1.2 of Section 3.0.5 in this Handbook.

No audit is suggested for Method 102 because of the special equipment or arrangement for sampling a hydrogen stream and the risk of explosion.

6.1.2.2 Analytical Procedures - The analytical procedures should be audited using two audit samples of aqueous mercury chloride. The audit samples should be provided to the tester to be analyzed just prior to the field samples analysis. For Method 101, one

sample should be at a low concentration (1.0 to 5.0 $\mu\text{g/ml}$) and one at a high concentration (5.0 to 10.0 $\mu\text{g/ml}$). For Method 101A, one sample should be at a low concentration (0.1 to 0.5 $\mu\text{g/ml}$) and one at a high concentration (0.5 to 1.0 $\mu\text{g/ml}$). This is based on typical values at sludge dryers for an emission limit of 3200 g/24 hr. This concentration is dependent on both process design and operating conditions. Both concentrations should be obtained by diluting a specified aliquot of the audit sample to exactly 100 ml.

The audit samples should be analyzed after the preparation of the calibration curve and prior to the analysis of the field samples. The percent relative error (RE) of the audit samples is determined using the equation below. The calculated RE should be included with the emission test report as an assessment of the analytical phase of that test.

$$\text{RE} = \frac{C_M - C_A}{C_A} \times 100$$

where:

C_M = Concentration measured by Method 101, 101A, or 102,
 $\mu\text{g/ml}$ Hg, and
 C_A = Audit or given concentration of the audit sample,
 $\mu\text{g/ml}$ Hg.

An acceptable relative error of ± 15 percent has been established for this Method. This relative error is based on collaborative test results for Methods 101 and 101A (References 3 and 4).

6.1.3 Audit Frequency - When Methods 101 or 101A are used for NESHA purposes, the following audit frequency is recommended for compliance and enforcement tests. An audit for accuracy of the sampling procedures should be conducted prior to the field testing series on all flow totalizing systems (dry gas meters), and on all differential pressure gauges used for velocity pressure determination that do not meet the specifications of Section 2.2 of Method 2. An additional audit should be conducted on the flow totalizing system when 1) a different flow totalizing system is used or 2) repairs are made on the flow totalizing system after auditing. An additional audit should be conducted on the differential pressure gauge when 1) a different differential pressure gauge is used or 2) repairs are made on the differential pressure gauge after auditing. An audit for accuracy of the analytical procedures should be conducted after the preparation of the calibration curve and prior to the analyses of the field samples for every field test series. A lesser frequency may be acceptable when Methods 101, 101A, or 102 are used for applications other than compliance and enforcement.

6.1.4 Availability of Audit Materials - Control agencies responsible for the compliance or enforcement test may obtain aqueous mercury chloride audit samples and certified calibrated orifices by contacting:

U.S. Environmental Protection Agency
Environmental Monitoring Systems Laboratory
Quality Assurance Division (MD-77A)
Research Triangle Park, North Carolina 27711

Attention: Source Test Audit Coordinator

Alternatively, a calibrated orifice can be made as described by Mitchell, et. al. in Reference 5 and sent to the USEPA for certification.

6.1.5 Cost of Audit - The audit of Methods 101 and 101A is an audit for portions of both the sampling and analysis phase. The audit of Method 102 is an audit of the analysis phase. Each audit should require less than five technical hours of effort to complete. This effort would generally represent less than 5 percent of the total effort to conduct, calculate and report the Method 101, 101A or 102 sampling and analysis.

6.2 Method 104 (Beryllium)

6.2.1 Methods Description - Method 104 is applicable for the determination of beryllium emissions in ducts or stacks at stationary sources. Unless otherwise specified, this Method is not intended to apply to gas streams other than those emitted directly to the atmosphere without further processing.

Beryllium emissions are isokinetically sampled from the source, and the collected sample is digested in an acid solution and analyzed by atomic absorption spectrophotometry. The promulgated Method can be found in the Federal Register, Vol. 48, page 55268, December 9, 1983 and 40 CFR 61 Appendix B.

6.2.2 Audits to Assess Accuracy of Sampling and Analytical Procedures -

6.2.2.1 Sampling Accuracy - The audit for the sampling phase is to determine the accuracy of the flow totalizing system (dry gas meter) of the Method 104 sampling train and the differential pressure gauge used to measure the velocity when the differential pressure gauge does not meet the specifications in Section 2.2 of Method 2 (40 CFR 60, Appendix A). The flow totalizing system should be audited using the same procedures and with the same frequency as described in detail for Method 5 in Subsection 5.3.2 of Section 3.0.5 of this Handbook. The differential pressure gauge should be audited using the same procedures and with the same frequency as described in detail for Method 2 in Subsection 5.1.2 of Section 3.0.5 of this Handbook.

6.2.2.2 Analytical Accuracy - The analytical procedures should be audited using two audit samples of aqueous beryllium salts. The analyst should analyze the audit samples along with the field samples. One sample should be a low concentration (5 to 20 μg of beryllium per audit sample) and one sample should be a high concentration (50 to 100 μg of beryllium per audit sample). This is based on typical concentration values at beryllium processing facilities that would be equivalent to an emission limit of 10 g/24 h.

The audit samples must be analyzed after the preparation of the calibration curve and prior to the analysis of the field samples. The auditor should calculate the percent relative error (RE) of the audit samples using the equation below. The calculated RE should be included in the emission test report as an assessment of the analytical phase of that test.

$$\text{RE} = \frac{C_M - C_A}{C_A} \times 100$$

where:

C_M = Concentration measured by Method 104, total μg beryllium, and
 C_A = Audit or given concentration of the audit sample, total μg beryllium.

An acceptable relative error of +15 percent has been established for this Method. This relative error is based on the collaborative test results for Method 104 (Reference 6).

6.2.3 Audit Frequency - When Method 104 is used for NESHAP purposes, the following audit frequency is recommended for compliance and enforcement tests. An audit for accuracy of the sampling procedures should be conducted prior to the field testing series on all flow totalizing systems (dry gas meters) and on all differential pressure gauges used for velocity pressure determination that do not meet the specifications of Section 2.2 of Method 2. An additional audit should be conducted on the flow totalizing system when (1) a different flow totalizing system is used or (2) repairs are made on the flow totalizing system after auditing. An additional audit should be conducted on the differential pressure gauge when (1) a different differential pressure gauge is used or (2) repairs are made on the differential pressure gauge after auditing. An audit for accuracy of the analytical procedures should be conducted after the preparation of the calibration curve and prior to the analysis of the field samples for each field test series. A lesser frequency may be acceptable when Method 104 is used for applications other than compliance and enforcement.

6.2.4 Availability of Audit Materials - Control agencies responsible for the compliance or enforcement test may obtain aqueous beryllium salt audit samples and certified calibrated orifices by contacting:

U.S. Environmental Protection Agency
Environmental Monitoring Systems Laboratory
Quality Assurance Division (MD-77A)
Research Triangle Park, North Carolina 27711

Attention: Source Test Audit Coordinator

Alternatively, a calibrated orifice can be made as described by Mitchell, et. al. in Reference 5 and sent to the USEPA for certification.

6.2.5 Cost of Audit - The audit of Method 104 is an audit of portions of both the sampling and analysis phase. This audit should require less than six technical hours of effort to complete. This effort should generally represent less than 10 percent of the total effort to conduct, calculate and report Method 104 sampling and analysis.

6.3 Method 105 (Mercury in Sewage Sludge)

6.3.1 Methods Description - Method 105 is applicable for the determination of total organic and inorganic mercury content in sewage sludges, soils, sediments, and bottom-type materials. The normal range of this Method is 0.2 to 5 µg/g. The range may be extended above or below the normal range by increasing or decreasing sample size and through instrument and recorder control.

A weighted portion of the sewage sludge sample is digested in aqua regia for 3 minutes at 95°C, followed by oxidation with potassium permanganate. Mercury in the digested sample is then measured by the conventional spectrophotometer cold vapor technique. An alternative digestion procedure involves the use of an autoclave and is described in this Method. The promulgated Method can be found in the Federal Register, Vol. 40, page 48299, October 14, 1975 and 40 CFR 60 Appendix B.

6.3.2 Audits to Assess Accuracy of Sampling and Analytical Procedures -

6.3.2.1 Sampling Accuracy - No audit recommended.

6.3.2.2 Analytical Accuracy - The analytical procedures for Method 105 should be audited using the same procedure and frequency as detailed for Methods 101, 101A and 102 in Subsection 6.1.2.2.

6.3.3 Audit Frequency - When Method 105 is used for NESHA purposes, the following audit frequency is recommended for compliance and enforcement tests. An audit for accuracy of the analytical procedures should be conducted after the preparation of the calibration curve and prior to the analysis of the field samples. A lesser frequency may be acceptable when Method 105 is used for applications other than compliance and enforcement.

6.3.4 Availability of Audit Materials - Control agencies responsible for the compliance or enforcement test, may obtain aqueous mercury chloride audit samples by contacting:

U.S. Environmental Protection Agency
Environmental Monitoring Systems Laboratory
Quality Assurance Division (MD-77A)
Research Triangle Park, North Carolina 27711

Attention: Source Test Audit Coordinator

6.3.5 Cost of Audit - The audit of Method 105 is an audit of the analysis phase. This audit should require less than four technical hours of effort to complete. This effort generally represents less than 5 percent of the total effort to conduct, calculate and report Method 105 sampling and analysis.

6.4 Method 106 (Vinyl Chloride)

Method 106 should be audited using the quality assurance requirements in Method 106. (See Reference 7 for details.)

6.4.1 Method Description - Method 106 is applicable to the measurement of vinyl chloride in stack gases from ethylene dichloride, and vinyl chloride and polyvinyl chloride manufacturing processes, except where the vinyl chloride is contained in particulate matter. An integrated bag sample of stack gas containing vinyl chloride (chloroethene) is subjected to chromatographic analysis using a flame ionization detector.

Note: Performance of this Method should not be attempted by persons unfamiliar with the operation of a gas chromatograph, nor by those who are unfamiliar with source sampling, as there are many details that are beyond the scope of the Method 106 description. Care must be exercised to prevent exposure of sampling personnel to vinyl chloride, a carcinogen. The promulgated Method can be found in the Federal Register, Vol. 47, page 39168, September 7, 1982 and 40 CFR 61, Appendix B.

6.4.2 Audits to Assess Accuracy of Sampling and Analytical Procedures - The accuracy of the sampling and analytical procedure is assessed by conducting a cylinder gas audit. Two audit cylinders of vinyl chloride are needed. The audit cylinders are used to assess both the sampling and analytical procedures. The audit cylinders should contain a vinyl chloride concentration between 5 and 20 ppm for the low concentration cylinder and 20 to 50 ppm for the high concentration cylinder. This is based on an emission limit of 10 ppm vinyl chloride. The following recommendations are provided as guidance to conduct a proper audit.

1. The audit should be conducted to coincide with the analysis of source test samples. Normally, it will be conducted immediately after the GC calibration and prior to the sample analyses.

2. After a leak check of the bag has been completed, fill each bag approximately half full with the audit gases. Analyze the bags in the normal manner specified for Method 106.

3. At the end of audit analyses, the auditor requests the calculated concentrations from the analyst and then compares the results with the actual audit concentrations. The auditor computes the percent relative error (RE) for both audit values using the equation below.

$$RE = \frac{C_M - C_A}{C_A} \times 100$$

where:

C_M = Concentration measured by Method 106, ppm, and
 C_A = Audit or given concentration of the audit sample, ppm.

4. Method 106 has an established acceptable relative error of less than +10 percent. If this agreement is not met the tester/analyst should check the system to eliminate problems and repeat the audit prior to field sample collection.

5. The RE should be included in the emission test report as an assessment of the accuracy of the sampling and analytical phases of the Method 106 test.

6.4.3 Audit Frequency - When Method 106 is used for NESHAP purposes, the following audit frequency is recommended for compliance and enforcement tests. An audit for accuracy should be conducted prior to every field test series (but after analyzer calibration). A lesser frequency may be acceptable, when Method 106 is used for applications other than compliance and enforcement.

6.4.4 Availability of Audit Materials - Control agencies responsible for the compliance or enforcement test may obtain an audit cylinder of vinyl chloride prior to each compliance or enforcement source test by contacting:

U.S. Environmental Protection Agency
Environmental Monitoring Systems Laboratory
Quality Assurance Division (MD-77B)
Research Triangle Park, North Carolina 27711

Attention: Audit Cylinder Gas Coordinator

If audit cylinders are unavailable, commercial manufacturers should be sought to obtain the desired audit gases. These commercial gases should meet the specifications described in Section 5.2.3.1 of Method 106.

6.4.5 Cost of Audit - The audit of Method 106 is an audit of both the sampling and analysis phase. This audit should require less than five technical hours of effort to complete. This effort should generally represent less than 5 percent of the total effort to conduct, calculate and report Method 106 sampling and analysis.

6.5 Method 108 and 108A (Arsenic)

6.5.1 Method Description - Methods 108 and 108A are applicable to the determination of organic arsenic (As) emissions from nonferrous smelters and other sources, as specified in the regulations. Particulate and gaseous As emissions are withdrawn isokinetically from the source and collected on a glass mat filter and in water. The collected As is then analyzed by means of atomic absorption spectrophotometry. The sampling and analytical procedures are not included in this Handbook. The promulgated Method can be found in 40 CFR 61, Appendix B.

6.5.2 Audits to Assess Accuracy of Sampling and Analytical Procedures -

6.5.2.1 Sampling Accuracy - The audit for the sampling phase is used to determine the accuracy of the flow totalizing system (dry gas meter) of the Method 108 and 108A sampling train and the differential pressure gauge used to measure the velocity when the differential pressure gauge does not meet the specifications in Section 2.2 of Method 2 (40 CFR 60, Appendix A). The flow totalizing system should be audited using the same procedures and with the same frequency as described in detail for Method 5 in Subsection 5.3.2 of Section 3.0.5 in this Handbook. The differential pressure gauge should be audited using the same procedures and with the same frequency as described in detail for Method 2 in Subsection 5.1.2 of Section 3.0.5 in this Handbook.

6.5.2.2 Analytical Accuracy - The analytical procedures should be audited using duplicate analysis of a single aqueous audit sample. The audit sample should be at a concentration between 40 and 200 percent of the emission limit. The duplicate analysis of the audit sample should be performed after the preparation of the calibration curve and prior to the analysis of the field samples. The auditor should calculate the percent relative error (RE) of the audit samples:

$$RE = \frac{C_M - C_A}{C_A} \times 100$$

where:

C_M = Concentration measured by Method 108 or 108A,
total μg of As, and
 C_A = Audit or given concentration of the audit sample,
total μg of As.

An acceptable relative error of +15% has been established for this Method. The relative error is based on the method evaluation of Method 108 (Reference 8).

The calculated RE should be included in the emission test report as an assessment of the accuracy at the analytical phase of the Method 108 or 108A test.

6.5.3 Audit Frequency - When Method 108 or 108A is used for NESHAP purposes, the following audit frequency is recommended for compliance and enforcement tests. An audit for accuracy of the sampling procedures should be conducted prior to the field testing series on all flow totalizing systems (dry gas meters) and on all differential pressure gauges used for velocity pressure determination that do not meet the specifications of Section 2.2 of Method 2. An additional audit should be conducted on the flow totalizing system when (1) a different flow totalizing system is used or (2) repairs are made on the flow totalizing system after auditing. An additional audit should be conducted on the differential pressure gauge when (1) a different differential pressure gauge is used or (2) repairs are made on the differential pressure gauge after auditing. An audit for accuracy of the analytical procedures should be conducted after the preparation of the calibration curve and prior to the analysis of the field samples for each field test series. A lesser frequency may be acceptable when 108 or 108A is used for applications other than compliance and enforcement.

6.5.4 Availability of Audit Materials - Control agencies responsible for compliance or enforcement test may obtain aqueous audit samples and certified calibrated orifices by contacting:

U.S. Environmental Protection Agency
Environmental Monitoring Systems Laboratory
Quality Assurance Division (MD-77A)
Research Triangle Park, North Carolina 27711

Attention: Source Test Audit Coordinator

Alternatively, a calibrated orifice can be made as described by Mitchell, et. al. in Reference 5 and sent to the USEPA for certification.

6.5.5 Cost of Audit - The audit for Method 108 or 108A is an audit of portions of both the sampling and analysis phase. The audit should require less than eight technical hours of effort to complete. This effort should generally represent less than 10 percent of the total effort to conduct, calculate and report Method 108 or 108A sampling and analysis.

6.6 References

1. "Quality Assurance and Quality Control Revisions to Methods 6 and 7," 40 CFR 60, Appendix A or Federal Register, Vol. 49, page 26522, June 27, 1984.
2. EPA Method 18, "Measurement of Gaseous Organic Compounds by Gas Chromatography," 40 CFR 60, Appendix A or Federal Register, Vol. 48, page 48344, October 18, 1983.
3. Mitchell, W. J. and Midgett, M. R., "Improved Procedure for Determining Mercury Emissions from Mercury Cell Chlor-Alkali Plants." APCA Journal, Vol. 26, No. 7, July 1976.
4. Mitchell, W. J., Midgett, M. R., Suggs, J. C., and Albrinck, D, "Test Methods to Determine the Mercury Emissions from Sludge Incineration Plants." EPA-600/4-79-058, September 1979.
5. Mitchell, W. J., Fuerst, R. G., Margeson, J. H., Streib, E. W., Midgett, M. R., and Hamil, H. F., "New Orifice Opens Way for Fast Calibration." Pollution Engineering, June 1981, pp. 45-57. A correction in this publication was printed in Pollution Engineering, August 1981.
6. Constant, Paul C. and Sharp, Michael C., "Collaborative Study of Method 104 - Reference Method for Determination of Beryllium Emission from Stationary Sources." EPA-650/4-74-023, June 1974.
7. "Preparation of Standard Gas Mixtures, Calibration, and Quality Assurance," EPA Method 106, 40 CFR 61, Appendix B, or Federal Register, Vol. 47, page 39168, September 7, 1982.
8. Ward, T. E., Logan, T. J., Midgett, M. R., Jayanty, R. K. M., and Gutknecht, W. F., "Field Validation of EPA Proposed Method 108 for Measurement of Inorganic Arsenic Emissions from Stationary Sources." APCA Journal, Vol. 35, No. 8, August 1985, pp. 822-827.

8.0 AUDIT MATERIALS AVAILABLE FROM U. S. EPA

In a memo dated May 30, 1979, Douglas M. Costle, the EPA Administrator, presented the Environmental Protection Agency Quality Assurance Policy Statement. He made participation in the quality assurance efforts mandatory for all EPA-supported or required monitoring activities. Furthermore, in a June 14, 1979 memo, Mr. Costle made "quality assurance requirements" mandatory for all environmental measurements conducted under extramural funding. Continued support for the mandatory quality assurance requirements was extended in a memo issued November 2, 1981 by Anne M. Gorsuch, the EPA Administrator. Initially in response to the policy statement and currently in response to the reference method requirements, the Quality Assurance Division of the Environmental Monitoring Systems Laboratory of the U. S. Environmental Protection Agency (EPA) has developed reference materials for performance audits of environmental measurements.

The purpose of the audit materials are two fold: (1) to provide agencies with a means of assessing the relative error of environmental measurements, and (2) to provide EPA with a continuing index of the quality of data reported.

The preparation and distribution of all audit materials are coordinated by the Quality Assurance Division of the Environmental Monitoring System Laboratory, Research Triangle Park, NC. The audit materials are available to all federal, state, and local agencies in support of performance audits for all enforcement testing. The audit materials are generally not available for internal audits by the private sector, except when requested by a federal, state, or local agency. However, the audit materials are available to contractors of government agencies. To request further information about the source audit materials, write to:

Source Test Audit Coordinator
Quality Assurance Division, MD-77A
Environmental Monitoring Systems Laboratory
Research Triangle Park, NC 27709
Commercial: (919) 541-7834
FTS: 629-7834

The available audit materials are shown in the following three tables. Table 8.1 lists available organic gas audit cylinders in the parts per million range. Table 8.2 lists available organic gas audit cylinders in the parts per billion range. Table 8.3 describes the solid samples, aqueous samples, and other audit materials. The audit materials should be requested at least thirty (30) days prior to their actual need.

TABLE 8.1. PARTS PER MILLION LEVEL ORGANIC AUDIT CYLINDERS AVAILABLE
FROM U. S. EPA

Compound***	Low Concentration Range (ppm)	High Concentration Range (ppm)
Benzene	5-20	60-400
Ethylene	5-20	300-700
		3000-20,000
Propylene	5-20	300-700
Methane/Ethane	---	1000-6000(M)
		200-700(E)
Propane	5-20	300-700
Toluene	5-20	300-700
Hydrogen Sulfide	5-40	100-700
Meta-Xylene	5-20	300-700
Methyl Acetate	5-20	300-700
Chloroform	5-20	300-700
Carbonyl Sulfide	5-20	100-400
Methyl Mercaptan	3-10	-----
Hexane	20-80	1000-3000
1,2-Dichloroethane	5-20	100-600
Cyclohexane	----	80-200
Methyl Ethyl Ketone	30-80	-----
Methanol	30-80	-----
1,2-Dichloropropane	5-20	300-700
Trichloroethylene	5-20	100-600
1,1-Dichloroethylene	5-20	100-600
**1,2-Dibromoethylene	5-20	100-600
Perchloroethylene	5-20	300-700
Vinyl Chloride	5-30	-----

(continued)

TABLE 8.1 (continued)

Compound***	Low Concentration Range (ppm)	High Concentration Range (ppm)
1,3-Butadiene	5-50	-----
Acrylonitrile	5-20	300-700
**Aniline	5-20	-----
Methyl Isobutyl Ketone	5-20	75
**Para-dichlorobenzene	5-40	-----
Ethylamine	5-20	-----
**Formaldehyde	--	-----
Methylene Chloride	1-20	-----
Carbon Tetrachloride	5-20	-----
****F-113	5-20	-----
Methyl Chloroform	5-20	-----
Ethylene Oxide	5-20	-----
Propylene Oxide	5-20	75-200
Allyl Chloride	5-20	75-200
Acrolein	5-20	75-200
Chlorobenzene	5-20	-----
Carbon Disulfide	--	75-200
**Cyclohexanone	5-20	-----
*EPA Method 25 Gas	100-200	750-2000
Ethylene Dibromide	5-20	75-400
1,1,2,2-Tetrachloroethane	5-20	-----

* The gas mixture contains an aliphatic, an aromatic and carbon dioxide in nitrogen. Concentrations shown are reported in ppmC.

** Cylinders are no longer available in the repository since the compounds are found to be unstable in the cylinders.

*** All organic compounds in audit cylinders are in a balance of N₂ gas.

****F-113 is the compound 1,1,2-trichloro 1,2,2-trifluoroethane.

TABLE 8.2 PARTS PER BILLION LEVEL ORGANIC AUDIT
CYLINDERS AVAILABLE FROM U. S. EPA

Group	Concentration Range of Each Compound (ppb)
Group I*	7-90 90-430 430-10,000
Group II**	7-90 90-430
Group III***	7-90 90-430
Group IV****	7-90 430-10,000

* Group I Compounds are carbon tetrachloride, chloroform, perchloroethylene, vinyl chloride, and benzene in a balance of N₂ gas.

** Group II Compounds are trichloroethylene, 1,2-dichloroethane, 1,2-dibromoethane, acetonitrile, trichlorofluoromethane (F-11), dichlorodifluoromethane (F-12), bromomethane, methyl ethyl ketone, and 1,1,1-trichloroethane in a balance of N₂ gas.

*** Group III Compounds are vinylidene chloride, 1,1,2-trichloro 1,2,2-trifluoroethane (F-113), 1,2-dichloro 1,1,2,2-tetrafluoroethane (F-114), acetone, 1-4 dioxane, toluene, and chlorobenzene in a balance of N₂ gas.

**** Group IV audit cylinders are under development, and will be available about December 1986. Group IV compounds are acrylonitrile, 1,3-butadiene, ethylene oxide, methylene chloride, propylene oxide and ortho-xylene.

TABLE 8.3. SOLID, LIQUID, AND OTHER AUDIT MATERIALS,
 AVAILABLE FROM THE U. S. EPA

Material	Description
SO ₂ and CO ₂ Gas Samples	SO ₂ and CO ₂ in a balance of N ₂ are contained in gas cylinders in a range of 200 to 400 ppm SO ₂ and 12 to 16% CO ₂ for auditing EPA Method 6B
CO ₂ , O ₂ , and CO Gas Samples	CO ₂ , O ₂ , and CO are contained in a pressurized canister; one canister per set with range of 5 to 8% for CO ₂ , 10 to 15% for O ₂ , and 0.5 to 4% for CO
Calibrated Orifices	Calibrated critical orifices in either of two standard quick connects to check both rate and volume meters at 0.5 to 1.0 cfm for auditing EPA Methods 5, 5A, and 5D
SO ₂ Samples*	Aqueous sulfuric acid solution in glass ampoules; two per set in three ranges with normal values of 750, 1500, and 2500 mg of SO ₂ per dscm for auditing EPA Methods 6, 6A, and 6B
NO _x Samples*	Aqueous potassium nitrate solution in glass ampoules; two per set in three ranges with nominal values of 450, 900, and 1750 mg of NO ₂ per dscm for auditing EPA Methods 7, 7A, 7C, and 7D
Sulfuric Acid Samples*	Same as the SO ₂ samples; use for auditing EPA Method 8
Inorganic Lead Samples	Lead salts impregnated on a glass fiber filter in the range of 100 to 600 µg and 900 to 2000 µg of lead per audit sample for auditing EPA Method 12

(continued)

TABLE 8.3 (continued)

Material	Description
Total Fluoride Samples*	Aqueous sodium fluoride in Nalgene ^R bottle; two per set in the ranges of 0.2 to 1.0 mg of fluoride per dscm and 1 to 5 mg of fluoride per dscm for auditing EPA Methods 13A and 13B
Coal Samples	Coal samples with known quantities of Btu's per pound, %S content, and moisture content; two per set in the range of 11,000 to 14,500 Btu's per pound for heating value, 0.5% to 4% for sulfur content, and 2% to 12% moisture content for auditing EPA Method 19
Mercury Samples*	Aqueous mercury chloride in glass ampoules; two per set in the ranges of 5 to 20 µg of mercury per ml and 50 to 100 µg of mercury per ml of sample for auditing EPA Methods 101, 101A, 102, and 105
Arsenic Samples*	Aqueous arsenic salts in glass ampoules; one per set in the range of 10 to 50 µg/ml or 100 to 500 µg/ml of arsenic for auditing EPA Methods 108 and 108A
Beryllium Samples*	Aqueous beryllium salts in glass ampoules; two per set in the ranges of 5 to 20 µg of beryllium per audit sample and 50 to 100 µg of beryllium per audit sample for auditing EPA Method 104

*Aqueous audit samples can be reduced to known concentration less than the stated range by taking smaller aliquots and/or dilution.

Audit gas cylinder samples can be obtained by contacting:

Audit Cylinder Gas Coordinator
Quality Assurance Division, MD-77B
Environmental Monitoring Systems Laboratory
Research Triangle Park, NC 27711
Commercial: (919) 541-4531
FTS: 629-4531

All other source audit materials can be obtained by contacting the "Source Test Audit Coordinator" listed on Page 1 of this section.

Section 3.13

METHODS 6A AND 6B--DETERMINATIONS OF SULFUR DIOXIDE,
MOISTURE, AND CARBON DIOXIDE EMISSIONS FROM
FOSSIL FUEL COMBUSTION SOURCES

OUTLINE

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SUMMARY

For Method 6A a gas sample is extracted from the stack in the same manner as for Method 6 except that CO_2 is collected in the sampling train in addition to the SO_2 . For Method 6B a gas sample is extracted from the sampling point in the stack intermittently over a 24-hour or other specified time period. Sampling may also be conducted continuously for Method 6B if the apparatus and procedures are appropriately modified. The SO_2 and CO_2 are separated and collected in the sampling train. The SO_2 fraction is measured by the barium-thorin titration method, and CO_2 and moisture are determined gravimetrically.

This method applies to the determination of sulfur dioxide (SO_2) emissions from combustion sources in terms of concentration (mg/m^3) and emission rate (ng/J), and for the determination of carbon dioxide (CO_2) concentration (percent). Method 6A gives results on an hourly basis and Method 6B gives results on a daily (24 hour) basis.

The minimum detectable limit, upper limit, and the interferences for SO_2 measurements are the same as for Method 6. EPA-sponsored collaborative studies¹ 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 evolved from 145 field tests using 9 test teams including comparisons with Methods 3 and 6. For measurements of emission rates from wet, flue gas desulfurization units in (ng/J), the repeatability (within-laboratory precision) is 8.0 percent and the reproducibility (between-laboratory precision) is 11.1 percent at a measured level of about 400 ppm of SO_2 .

The method descriptions given herein are based on the Reference Methods^{2,3} promulgated December 1, 1982, and corrections and additions published on March 14, 1984 (Section 3.13.10), and on collaborative testing.¹ Blank forms for recording data are provided in the Method Highlights and in Section 3.13.12 for the convenience of Handbook users.

METHODS HIGHLIGHTS

Section 3.13 describes specifications for determination of sulfur dioxide, moisture and carbon dioxide emissions from fossil fuel-fired combustion sources. A gas sample is extracted from the stack in the same manner as for Method 6 except that moisture and CO_2 are collected in addition to the SO_2 in the same train. The Method 6A and 6B sampling trains are the same with the exception that the Method 6B train includes an industrial timer-switch for intermittent operation over the 24-hour sampling time. The Method 6B sampling train may be modified to allow for low flow rate continuous sampling.

The sulfuric acid and SO_3 are removed by the filter, probe and midget bubbler with isopropanol with Method 6A. The sulfuric acid is substantially removed by the filter and probe with Method 6B. The SO_2 (and SO_3) are collected in the two midget impingers containing 3 percent and 6 percent hydrogen peroxide for Methods 6A and 6B, respectively. For Method 6B, the SO_3 is collected in the impingers also, and is included in the SO_2 results. The moisture that leaves the last midget impinger containing hydrogen peroxide is then collected by Drierite contained in the final midget bubbler. The dried gases are then passed through a column containing a CO_2 absorber (Ascarite, Ascarite II or 5A molecular sieves) to collect the CO_2 . The analysis of the collected samples includes the barium-thorin titration for SO_2 (same as analysis for Method 6) and a gravimetric determination for moisture and CO_2 . Method 6B, "Determination of SO_2 and CO_2 Daily Average Emissions from Fossil Fuel Combustion Sources," was examined by collaborative testing.¹ There was no difference in the precision estimates produced by the intermittent and continuous modes of Method 6B. Averaged over the two modes of operation and expressed as a percent of the average five day values, the repeatability estimates are: SO_2 , 9.8 percent; CO_2 , 9.9 percent; and Emission Rate (lb per million Btu), 8.0 percent. The reproducibility estimates are: SO_2 , 12.9 percent; CO_2 , 13.2 percent; and Emission Rate, 11.1 percent. The magnitude of both estimates of precision appeared to be independent of the material being measured. In addition to the above precision data, statistical tests indicated that there was no real difference between the continuous, intermittent, and alternative reference methods based on average five-day values. The emission rate calculated by the collaborators for 145, 24-hour runs was within 2.5 percent of the emission rate of 240 Method 6 and 120 Method 3 analyses determined during the entire period of collaborative sampling. Four separate sets of SO_2 data were collected during the collaborative test. They were, for the five-day average, Method 6 (387 ppm), plant monitor (387 ppm), collaborators/Method 6B (393 ppm), and the prime contractor analyst/Method 6B (394 ppm). The experienced analyst ran eight samples each day for the five-day period using 5A molecular

sieves in the low flow rate sampling train instead of Ascarite II (used by collaborators) for CO₂ analysis. This test proved that the molecular sieves absorbed the CO₂ quantitatively when the molecular sieve was properly regenerated² prior to its use. The CO₂ methods and five-day averages were, Method 3 (12 percent), collaborators/Method 6B (12.02 percent), and prime contractor analyst/Method 6B (11.8 percent). Backup Ascarite II cartridges after the molecular sieve cartridges absorbed no CO₂, further showing that molecular sieve absorption of CO₂ was quantitative.

The collaborative test showed that Method 6B is a viable alternative method for continuously monitoring SO₂ emission rates. Quality data capture was achieved by personnel with limited experience. All of the molecular sieves had sufficient absorptive capability for CO₂ when used as prescribed in this procedure. The need for regeneration of a new batch of molecular sieves was noted in a private communication. For this reason, the analyst should recognize the possibility that the molecular sieves may require regeneration. The most frequent cause of error was failure to pass the post run leak test required in the method. Some other reasons were: broken glassware and spilled solution, disconnected sample lines during collection, faulty or uncalibrated dry gas meters, unusually high CO₂ weight gain which the collaborator blamed on weighing errors, and low heat in the flexible connector before the impingers.

The blank data forms at the end of the Highlights section may be removed from the Handbook and used in the pretest, test, and posttest operations. Each form has a subtitle (e.g., Method 6A or 6B, Figure 5.1) to assist the user in finding a similar completed form in the Method Description (e.g., in Section 3.13.5). On the blank and filled-in forms, the item/parameters that can cause the most significant errors are indicated with an asterisk.

The Method Description (Section 3.13.1 to 3.13.9) is based on the detailed specifications in the Reference Method (Section 3.13.10) promulgated by EPA on December 1, 1982 and corrections and additions on March 14, 1984.^{2,3}

1. Procurement of Apparatus and Supplies

Section 3.13.1 gives specifications, criteria, and design features for the required equipment and materials. The sampling apparatus for Methods 6A and 6B has the same design features as that of Method 6, except for the addition of a CO₂ absorption column, an industrial timer-switch (for Method 6B),² and temperature control in the sample probe when required. This section can be used as a guide for procurement and initial checks of equipment and supplies. The activity matrix (Table 1.1) at the end of the section is a summary of the details given in the text and can be used as a quick reference.

2. Pretest Preparations

Section 3.13.2 describes the required calibration procedures for the Method 6A and 6B sampling equipment (same as Method 6). A pretest checklist (Figure 2.5 or a similar form) should be used to summarize the calibration and other pertinent pretest data.

Section 3.13.3 describes the preparation of supplies and equipment needed for the sampling. The pretest preparation form (Figure 3.1 of Section 3.4.3) can be used as an equipment checklist. Suggestions for packing the equipment and supplies for shipping are given to help minimize breakage.

Activity matrices for the calibration of equipment and the presampling operations (Tables 2.1 and 3.1) summarize the activities detailed in the text.

3. On-Site Measurements

Section 3.13.4 describes procedures for sampling and sample recovery. A checklist (Figure 4.7 or 4.8) is an easy reference for field personnel to use in all sampling activities.

4. Posttest Operations

Section 3.13.5 describes the postsampling activities for checking the equipment and the analytical procedures. A form (Figure 5.1) is given for recording data from the posttest equipment calibration checks; a copy of the form should be included in the emission test final report. A control sample of known (SO_2) concentration should be analyzed before analyzing the sample for a quality control check on the analytical procedures. The detailed analytical procedures can be removed for use as an easy reference in the laboratory. An activity matrix (Table 5.1) summarizes the postsampling operations.

Section 3.13.6 describes calculations, nomenclature, and significant digits for the data reduction. A programmed calculator is recommended to reduce calculation errors.

Section 3.13.7 recommends routine and preventive maintenance programs. The programs are not required, but their use should reduce equipment downtime.

5. Auditing Procedures

Section 3.13.8 describes performance and system audits. Performance audits for both the analytical phase and the data processing are described. A checklist (Figure 8.2) outlines a system audit.

Section 3.13.9 lists the primary standards to which the working standards or calibration standards should be traceable.

6. References

Section 3.13.10 contains the promulgated Reference Method; Section 3.13.11 contains the references used throughout this text; and Section 3.13.12 contains copies of data forms recommended for Method 6A and 6B.

PRETEST SAMPLING CHECKS
(Methods 6A and 6B, Figure 2.5)

Date _____ Calibrated by _____

Meter Box Number _____

Rotameter

Pretest calibration factor (Y_r) acceptable? ____yes ____no
(within 10 percent of correct value).

Dry Gas Meter (If applicable)*

Pretest calibration factor (Y) = _____ (within 2 percent of
average factor for each calibration run).

Gas Meter Thermometer (If applicable)

Temperature correction necessary? ____yes ____no
(within 3°C (5.4°F) of reference values for calibration and
within 6°C (10.6°F) of reference values for calibration
check).

If yes, temperature correction _____

Barometer

Field barometer reading correct? ____yes ____no
(within 2.5 mm (0.1 in.) Hg of mercury-in-glass barometer).

Balance

Was the pretest calibration of balance correct? ____yes ____no
(within 0.05 g of true value using Class S weights).

* Most significant items/parameters to be checked.

PRETEST PREPARATIONS
(Methods 6A and 6B, Figure 3.1)

Apparatus check	Acceptable		Quantity required	Ready		Loaded and packed	
	Yes	No		Yes	No	Yes	No
<u>Probe</u>							
Type liner							
Glass _____							
Stainless steel _____							
Other _____							
Heated properly							
Leak checked on sampling train							
<u>Filter or Filter Assembly</u>							
Glass wool _____							
Other _____							
<u>Glassware</u>							
Midget bubbler							
Midget impinger							
Size _____							
Type _____							
<u>Meter System</u>							
With timer _____							
Without timer _____							
Leak-free pump*							
Rate meter*							
Dry gas meter*							
<u>Reagents</u>							
Distilled water							
H ₂ O ₂ , 30 percent							
Isopropanol, 100%* (for Method 6A)							
Drierite							
Ascarite _____ or 5A molecular sieve*							
<u>Other</u>							
Barometer							
CO ₂ absorber column							
Balance							

* Most significant items/parameters to be checked.

ON-SITE MEASUREMENTS
(Method 6A, Figure 4.7)

Sampling

Bubbler and impinger contents properly selected, measured, and placed in proper receptacle?*

Impinger Contents/Parameters

1st: 15 ml of 80 percent isopropanol*

2nd: 15 ml of 3 percent H_2O_2 *

3rd: 15 ml of 3 percent H_2O_2 *

4th: approx. 25 g of Drierite*

150 g of Ascarite in CO_2 absorber?*

Probe heat at proper level?

Crushed ice around impingers?

Pretest leak check at 250 mm (10 in.) Hg?

Leakage rate?

Probe placed at proper sampling point?

Flow rate constant at approximately 1.0 L/min?*

Posttest leak check at 250 mm (10 in.) Hg?*

Leakage rate?

Sample Recovery

Balance calibrated with Class S weights?*

Impingers cleaned and weighed to ± 0.1 g at room temp?

Contents of impingers and rinsings placed in polyethylene bottles?

Fluid level marked?*

CO_2 absorber cleaned and weighed to ± 0.1 g at room temp?

Sample containers sealed and identified?*

Samples properly stored and locked?

*Most significant items/parameters to be checked.

ON-SITE MEASUREMENTS
(Method 6B, Figure 4.8)

Sampling

Impinger contents properly selected, measured, and placed in
impingers?* _____

Impinger Contents/Parameters

1st: Empty* _____
2nd: 15 ml of ≥ 6 percent H_2O_2 * _____
3rd: 15 ml of ≥ 6 percent H_2O_2 * _____
4th: Approx. 25 g of Drierite* _____
Approx. 150 g of Ascarite II or 250 g 5Å molecular sieve (contin-
uous flow rate train only) in CO_2 absorber?* _____
Probe heat at proper level? _____
Crushed ice around impingers? _____
Pretest leak check at 250 mm (10 in.) Hg? _____
Leakage rate? _____
Probe placed at proper sampling point? _____
Flow rate intermittent at approximately 1.0 L/min? _____
Flow rate constant between 20 to 40 ml/min? _____
Posttest leak check at 250 mm (10 in.) Hg? _____
Leakage rate? _____

Sample Recovery

Balance calibrated with Class S weights? _____
Impingers cleaned and weighed to ± 0.1 g at room temp? _____
Contents of impingers and rinsings placed in polyethylene
bottles? _____
Fluid level marked? _____
 CO_2 absorber cleaned and weighed to ± 0.1 g at room temp?* _____
Sample containers sealed and identified?* _____
Samples properly stored and locked? _____

*Most significant items/parameters to be checked.

POSTTEST SAMPLING CHECKS
(Methods 6A and 6B, Figure 5.1)

Meter Box Number _____

Dry Gas Meter (If applicable)

Pretest calibration factor (Y) = _____
Posttest check Y_L = _____ (+5 percent of pretest factor)*

Recalibration required? _____ yes _____ no

If yes, recalibration factor (Y) = _____ (within 2 percent of calibration factor for each calibration run)

Lower calibration factor Y (pretest or posttest) = _____
for calculations

Rotameter

Pretest calibration factor (Y_r) = _____
Posttest check (Y_r) = _____ (within 10 percent of pretest factor)

Recalibration recommended? _____ yes _____ no

If performed, recalibration factor (Y_r) = _____

Was rotameter cleaned? _____ yes _____ no

Dry Gas Meter Thermometer (If applicable)

Was a pretest meter temperature correction used? _____ yes _____ no

If yes, temperature correction _____

Posttest recalibration required? _____ yes _____ no (recalibrate when Y_L recalibrated)

Barometer

Was pretest field barometer reading correct? _____ yes _____ no

Posttest recalibration required? _____ yes _____ no (recalibrate when Y_L recalibrated)

Balance*

Was the balance calibration acceptable? _____ yes _____ no
(+ 0.05 g checked against Class S weights)

If no, the balance should be repaired or replaced prior to weighing field samples

* Most significant items/parameters to be checked.

POSTTEST OPERATIONS
(Methods 6A and 6B, Figure 5.4)

Reagents

Normality of sulfuric acid standard* _____

Date purchased _____ Date standardized _____

Normality of barium perchlorate titrant* _____

Date standardized _____

Normality of control sample* _____

Date prepared _____

Volume of burette _____ Graduations _____

Sample Preparation

Has liquid level noticeably changed?* _____

Original volume _____ Corrected volume _____

Samples diluted to 100 ml?* _____

Analysis

(Sulfur dioxide)

Volume of aliquot analyzed* _____

Do replicate titrant volumes agree within 1 percent or 0.2 ml? _____

Number and normality of control samples analyzed _____

Are replicate control samples within 0.2 ml? _____

Is accuracy of control sample analysis ± 5 percent? _____

Is the relative error of audit sample(s) within acceptable
limits?* _____

(Moisture and carbon dioxide)

Balance calibrated with Class S weights to within 0.05 g?* _____

Initial weight of each impinger to nearest 0.1 g* _____

Final weight of each impinger to nearest 0.1 g* _____

Initial weight of CO₂ absorber to nearest 0.1 g* _____

Final weight of CO₂ absorber to nearest 0.1 g* _____

All data recorded? _____ Reviewed by _____

* Most significant items/parameters to be checked.

1.0 PROCUREMENT OF APPARATUS AND SUPPLIES

A schematic diagram of an assembled Method 6A and 6B sampling train with all components identified is shown in Figure 1.1. An alternative sampling train is shown in Section 3.13.4, page 11. This sampling train uses larger impingers and may be more suitable for many facilities. Specifications, criteria, and design features are given in this section to aid in the selection of equipment and to ensure that the collected data are of good quality. Procedures and, where applicable, limits for acceptance checks are given.

During the procurement of equipment and supplies, it is suggested that a procurement log be used to record the descriptive title of the equipment, the identification number, if applicable, and the results of acceptance checks. An example of a procurement log is shown in Figure 1.2. A blank form is given in Section 3.13.12 for the Handbook user. If calibration is required as part of the acceptance check, the data are recorded in the calibration log book. For facilities that currently have Method 6A or Method 6B sampling trains that are operating in a satisfactory manner, these procedural checks will not be necessary. Table 1.1 at the end of this section summarizes the quality assurance activities for procurement and acceptance of apparatus and supplies.

1.1 Sampling

1.1.1 Sampling Probe - The sampling probe should be either a borosilicate (Pyrex) glass or a type-316 seamless, stainless steel tube of approximately 6-mm inside diameter (ID), encased in a stainless steel sheath and equipped with a heating system capable of preventing water condensation and with a filter (either in-stack or heated out-of-stack) to remove particulate matter, including sulfuric acid mist. Typically, an in-stack filter is used at non-scrubber controlled power plants and a temperature controlled out-of-stack filter is used at scrubber controlled power plants. Stainless steel sampling probes, type-316, are not recommended for use with Method 6B because of potential corrosion and contamination of sample. Glass probes or other types of stainless steel, e.g., Hasteloy or Carpenter 20, are recommended for long-term use. When an in-stack filter is utilized, the probe should have an expanded diameter (38-40 mm) for the first 4 cm on the in-stack end, and this expanded end should be packed with glass wool prior to sampling. The probe's opposite end must have a fitting suitable for attaching it to the midget bubbler. A probe of approximately 1.2 m (4 feet) total length is usually sufficient for sampling. However, the probe tip can be no closer than 1 m (3.28 feet) from the inner wall of stacks >2 m in diameter. When stack gas temperatures exceed 480°C (900°F), a probe fabricated from quartz (Vycon) should be used. The main

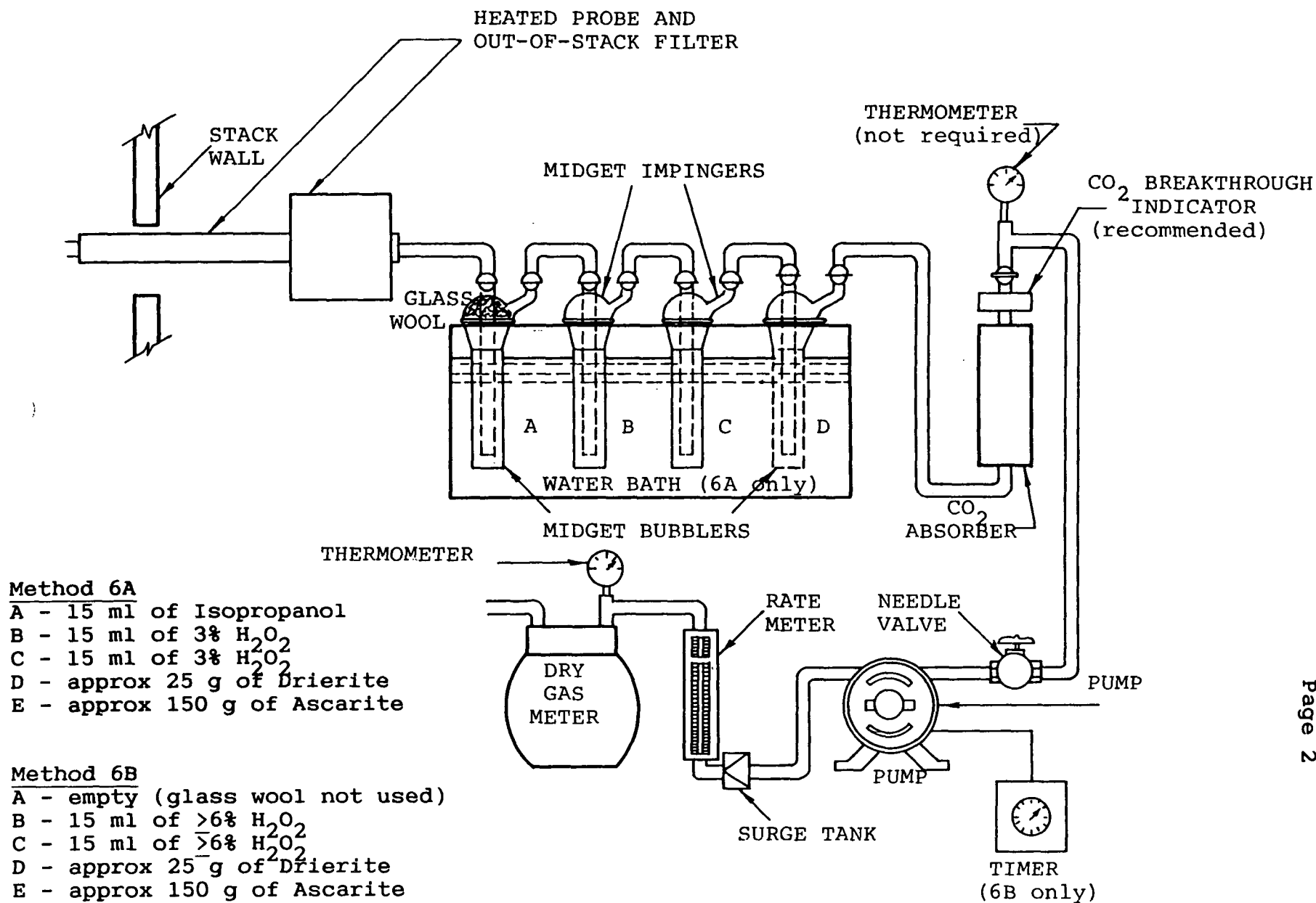


Figure 1.1. Sampling train.

Item description	Qty.	Purchase order number	Vendor	Date		Cost	Disposition	Comments
				Ord.	Rec.			
Meter box (Meth 6) w/diaphragm pump	1	774131	Ace Technologies	1-4-85	1-6-85	\$2500	Calibrated - ready for use	calibrated by SP 1/7/85

Figure 1.2. Example of a procurement log.

criterion in selecting a probe material is that it be nonreactive with the gas constituents so it does not introduce bias into the analysis.

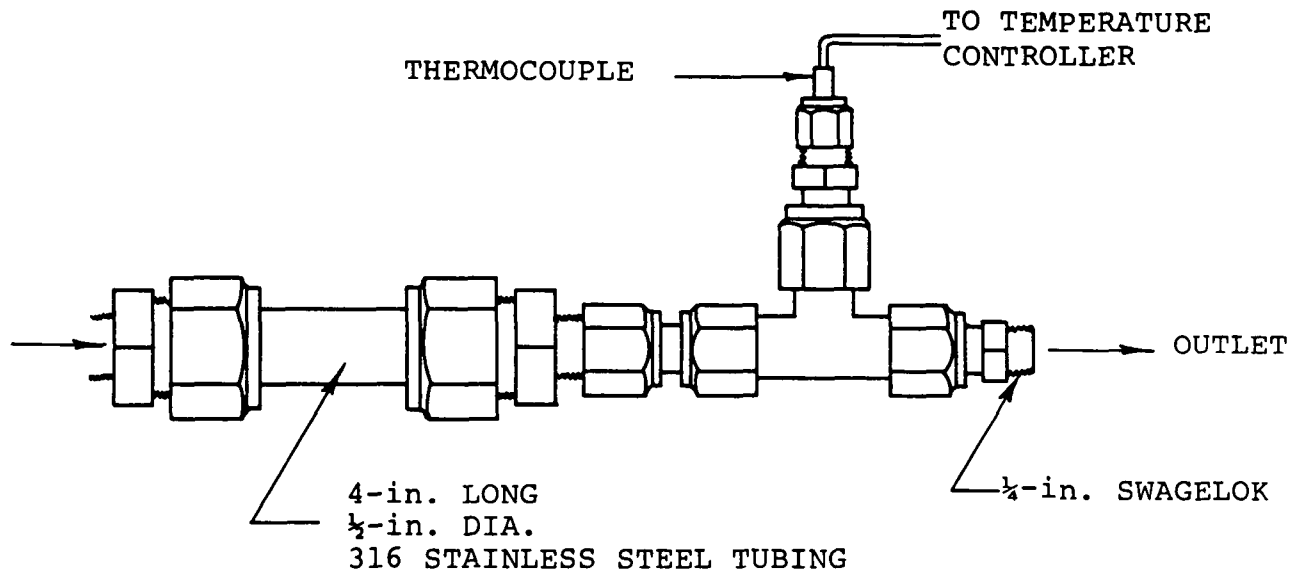
A new probe should be checked for specifications (i.e., the length and composition ordered). It should be checked for cracks and breaks, and then leak checked on a sampling train, as described in Section 3.13.3. The probe heating system should be checked as follows:

1. Connect the probe to the inlet of the pump.
2. Electrically connect and turn on the probe heater for 2 or 3 minutes. If functioning properly, it will become warm to the touch.
3. Start the pump and adjust the needle valve until a flow rate of about 1.0 L/min is achieved.
4. Check the probe. It should remain warm to the touch. The heater must be capable of maintaining the exit air temperature at a minimum of 100°C (212°F) under these conditions. If it cannot, the probe should be rejected. Any probe not satisfying the acceptance check should be repaired, if possible, or returned to the supplier.

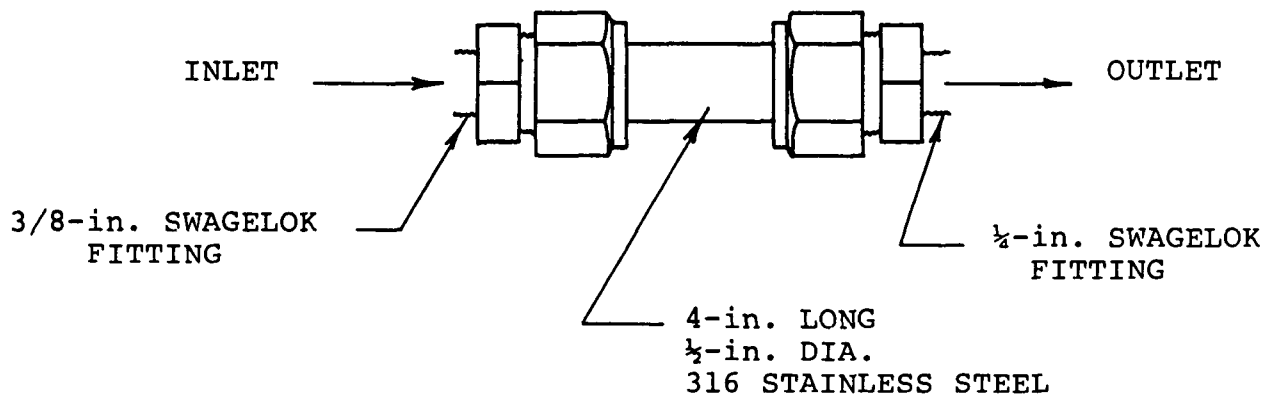
1.1.2 Filter - A heated out-of-stack filter to remove particulate, including sulfuric acid mist. The outlet filter temperature should be monitored and controlled to maintain a temperature sufficient to prevent condensation or to a maximum of 120°C (248°F). A plug of approximately 0.6 grams of borosilicate glass wool with no heavy metals, practically free from fluorine and alumina, low alkali content, and a fiber diameter between 0.005 and 0.008 mm is recommended for the filter media. The filter holder may be constructed as shown in Figure 1.3. The filter heater should be checked by connecting it to the probe and following the procedures described above in Subsection 1.1.1. Caution: Do not pack filter media too tightly, as this will result in a high pressure drop across the filter.

1.1.3 Flexible Connector (optional) - A heated flexible connector may be used between the exit of the heated filter and the inlet of the first impinger. The heated flexible connector should be Teflon (other construction materials may be used) and heated to prevent condensation. The flexible connector can be checked using the same procedure as for the probe with the exception that it should be checked without connecting it to the probe.

1.1.4 Midget Bubbler/Impingers - Each sampling train requires two midget bubblers (30-ml) of medium coarse glass frit, with



FILTER HOLDER WITH THERMOCOUPLE TO MONITOR
EXIT TEMPERATURE.



FILTER HOLDER WITHOUT TEMPERATURE MONITOR.

Figure 1.3. Out-of-stack filters.

glass wool packed in the top of the first to prevent carryover of sulfuric acid mist. A midget impinger may be used in place of either midget bubbler. Larger impingers, such as the Mae West design, may also be used.

Each sampling train requires two midget impingers (30-ml) with glass connections between the midget bubblers and the midget impingers. (Plastic or rubber tubing is not permitted because these materials absorb or desorb gaseous species.) Silicone grease may be used to prevent leakage.

Each bubbler/impinger is checked visually for damage, such as breaks or cracks, and for manufacturing flaws, such as poorly shaped connections.

Other nonspecified collection absorbers and sampling flow rates may be used, subject to the approval of the Administrator, but collection efficiency must be shown to be at least 99 percent for each of three test runs and must be documented in the emission test report. For efficiency testing, an extra absorber must be added and analyzed separately and must not contain more than 1 percent of the total SO_2 .

1.1.5 CO_2 Absorber - A sealable stainless steel or plastic cylinder or glass bottle with an inside diameter between 30 and 90 mm and a length between 125 and 250 mm and with appropriate connections at both ends is required. The cylinder should be checked for flaws or cracks and its ability to hold the required 150 g of Ascarite or 250 g of 5A molecular sieve. The ability to remain leak free can be checked at the same time that the new lot of Ascarite or 5A molecular sieve is checked for acceptability, as later described in Subsection 1.4.1.

It is strongly recommended that a second, smaller CO_2 absorber containing Ascarite be added in-line downstream of the primary CO_2 absorber as a breakthrough indicator. Ascarite turns white when CO_2 is absorbed. Alternatively, a larger container can be used with the primary and secondary absorber separated by glass wool. The thermometer following the CO_2 absorber is not required.

1.1.6 Vacuum Pump - The vacuum pump should be capable of maintaining a flow rate of approximately 1 to 2 L/min for pump inlet vacuums up to 250 mm (10 in.) Hg with the pump outlet near standard pressure, that is 760 mm (29.92 in.) Hg. The pump must be leak free when running and pulling a vacuum (inlet plugged) of 250 mm (10 in.) Hg. Two types of vacuum pumps are commonly used--either a modified sliding fiber vane pump or a diaphragm pump. For safety reasons, the pump should be equipped with a three-wire electrical cord.

To check the pump for leaks, install a vacuum gauge in the pump inlet line. Plug the inlet line, and run the pump until the vacuum gauge reads 250 mm (10 in.) Hg of vacuum, then clamp the pump outlet line, and turn off the pump. The vacuum reading should remain stable for 30 seconds.

1.1.7 Volume Meter - A volume meter is not required or needed for many applications. The tester should check the need prior to purchase. The dry gas meter must be capable of measuring total volume with an accuracy of +2 percent, calibrated at the selected flow rate of 1.0 L/min. and at the gas temperature actually encountered during sampling, and must be equipped with a temperature gauge (dial thermometer, or equivalent) capable of measuring the gas temperature to within 3°C (5.4°F). A volume meter is necessary if CO₂ and SO₂ concentrations are to be measured.

A new dry gas meter may be checked for damage visually and by performing a calibration according to Section 3.13.2. Any dry gas meter that is damaged, behaves erratically, or does not give readings within 2 percent of the selected flow rate for each run is unsatisfactory. Also upon receipt, the meter should be calibrated over a varying flow range to see if there is any effect on the calibration.

Dry gas meters that are equipped with temperature compensation must be calibrated over the entire range of temperature that the meter will encounter under actual field conditions. The calibration must contain at least one data point at each 10°F interval. All temperatures that are to be used in the field must be within 2 percent of the calibrated value.

The wet test meter used to check the dry test meter should be calibrated using the primary displacement technique explained in Section 3.13.2. The wet₃ test meter must have a capacity of at least 0.003 m³/min (0.1 ft³/min) with an accuracy of +1 percent; otherwise at the higher flow rates, the water will not be level and this will possibly result in incorrect readings.

1.1.8 Rotameter - A rotameter, or its equivalent, with a range of 0 to 2 L/min is used to monitor and control the sampling flow rate. The rotameter is checked against the calibrated dry gas meter with which it is to be used or against a wet test meter. The rotameter should be within 5 percent of true value or be able to be set to within 5 percent of true value. The rotameter flow setting of about 1 L/min should be determined.

Changes in pressure, density, and viscosity of the sample gas will affect the calibrated sample rate. However, since sampling at a constant rate is the intent, these changes need not be considered.

1.1.9 Needle Valve - A metering valve with conveniently sized fittings is required in the sampling train to adjust the sample flow rate. It is recommended that the needle valve be placed on the vacuum side of the pump.

1.1.10 Thermometers - A dial thermometer, or its equivalent, is used to measure the temperature of gas leaving the impinger train to within 1° C (2°F). Dial type thermometers are easily damaged, so each new thermometer must be checked visually for damage such as a dented or bent stem. Each thermometer should read within 1° C (2°F) of the true value when checked in an ice water bath and at room temperature against a mercury-in-glass thermometer that conforms to ASTM E-1 No. 63C or 63F. Damaged thermometers that cannot be calibrated must be rejected.

1.1.11 Metering System - For ease of use, the metering system (if required)--which contains the dry gas meter, thermometer(s), vacuum pump, needle valve, and rotameter--can be assembled into one unit (meter box). After a meter box has been either constructed or purchased, then positive and negative pressure leak checks should be performed. The positive pressure leak check, similar to the procedure described in Method 5 (Section 3.4), is performed as follows:

1. Attach rubber tubing and inclined manometer, as shown in Figure 1.4.

2. Shut off the needle valve and blow into the rubber tubing until the inclined manometer or magnehelic gauge reads a positive pressure of 12.5 to 17.5 cm (5 to 7 in.) H₂O.

3. Pinch off the tube, and observe the manometer for 1 minute. A loss of pressure indicates a leak in the apparatus in the meter box.

After the meter box apparatus has passed the positive leak check, then the negative leak check should be performed as follows:

1. Attach the vacuum gauge at the inlet, and pull a 250 mm Hg (10 in.) vacuum.

2. Pinch or clamp the outlet of the flow meter. This can be accomplished by closing the optional shutoff valve, if employed.

3. Turn off the pump. Any deflection noted in the vacuum reading within 30 seconds indicates a leak.

4. Carefully release the vacuum gauge before releasing the flow meter end.

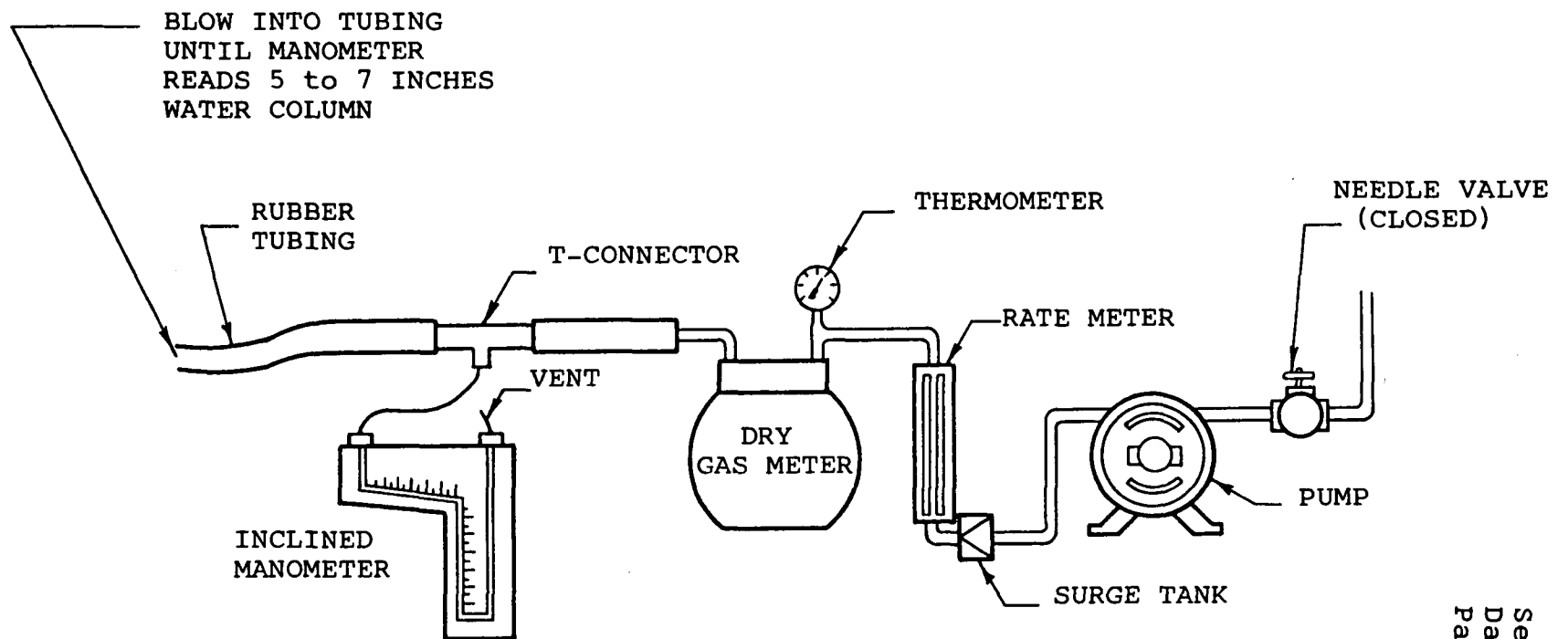


Figure 1.4. Meter box leak check.

If either of these checks detects a leak that cannot be corrected, the meter box must be repaired, rejected, and/or returned to the manufacturer.

The dry gas meter must be equipped with a temperature gauge (dial thermometer or equivalent). Each thermometer is checked visually for damage, such as dented or bent face or stem. Each thermometer should read within 3°C (5.4°F) of the true value when checked at two different ambient temperatures against a mercury-in-glass thermometer that conforms to ASTM E-1 No. 63C or 63F. The two ambient temperatures used to calibrate the thermometer must differ by a minimum of 10°C (18°F). Damaged thermometers that cannot be calibrated are to be rejected.

Note: The metering system may not be required or necessary for many applications of Method 6A or 6B. The tester should determine the necessity of a dry gas meter. Both Method 6A and 6B will determine an emission rate without the use of a metering system. However, if concentration data are desired, a metering system will be necessary.

1.1.12 Barometer - A mercury, aneroid, or other barometer capable of measuring atmospheric pressure to within 2.5 mm (0.1 in.) Hg may be used. However, in many cases, the barometric reading can be obtained from a nearby National Weather Service Station, in which case the station value (which is the absolute barometric pressure) is requested. The tester should be aware that the pressure is normally corrected to sea level. The station value is the uncorrected reading. An adjustment for differences in elevations of the weather station and sampling point is applied at a rate of -2.5 mm Hg/30 m (-0.1 in. Hg/100 ft) of elevation increase, or vice versa for elevation decrease.

Accuracy can be ensured by checking the field barometer against a mercury-in-glass barometer or its equivalent. If the field barometer cannot be adjusted to agree with the mercury-in-glass barometer, it is not acceptable.

1.1.13 Vacuum Gauge - At least one 760-mm (30-in.) Hg gauge is necessary to leak check the sampling train. An acceptable vacuum gauge, when checked in a parallel leakless system with a mercury U-tube manometer at 250-mm (10-in.) Hg vacuum, will agree within 25 mm (1.0 in.) Hg.

1.1.14 Industrial Timer (For Method 6B only) - 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, operation should include at least 12 equal, evenly spaced periods of sampling per 24 hours. Longer sampling durations greatly reduce the significance of sampler timer error.

Initially check the timer as follows:

1. Set the sampling sequence as it will normally be used (i.e., 12 equally spaced, 2-minute samples for a 24-hour period).
2. Turn on the sample console (meter box) without the impinger train.
3. Determine the exact volume that is metered for one of the equally spaced sample times.
4. Operate the sample console for a 24-hour period.
5. The total sample volume collected should be within 10 percent of the number of times of the equal spacing.

If the industrial timer cannot meet these specifications it should be repaired or rejected.

1.1.15 Other Sampling Apparatus - Other sampling equipment, such as Mae West bubblers and rigid cylinders for moisture absorption which require sample or reagent volumes other than those specified in this procedure for full effectiveness, may be used subject to the approval of the Administrator.

1.2 Sample Recovery Apparatus

1.2.1 Wash Bottles - Two 500-ml polyethylene or glass wash bottles are needed for quantitative recovery of collected samples.

1.2.2 Storage Bottles - One 100-ml polyethylene bottle is required to store each collected sample. An additional polyethylene bottle is necessary to retain a blank for each absorbing solution used in testing. Wash and storage bottles should be visually checked for damage. In addition, check each storage bottle seal to prevent sample leakage during transport.

1.3 Analysis Glassware

1.3.1 Pipettes - Several volumetric pipettes (Class A), including 5-, 10-, 20-, and 25-ml sizes, are required for the analysis.

1.3.2 Volumetric Flasks - Volumetric flasks (Class A) are required in 50-, 100-, and 1000-ml sizes.

1.3.3 Burettes - A 50-ml standard burette (Class A) is required for all titrations.

1.3.4 Erlenmeyer Flasks - One 250-ml Erlenmeyer flask is required for each sample, blank, standard, and control sample.

1.3.5 Dropping Bottle - One 125-ml glass dropping bottle is needed to prepare the thorin indicator.

1.3.6 Graduated Cylinder - A 100-ml glass (Class A) graduated cylinder is needed in the preparation of the thorin indicator and the sample.

All glassware must be checked for cracks, breaks, and discernible manufacturing flaws.

1.3.7 Balance - A field balance capable of weighing the midget impingers and the CO₂ absorber column with an accuracy of 0.1 g is needed. The balance may be checked upon initial receipt against Class S weights.

1.4 Reagents

Unless otherwise indicated, it is intended that all reagents conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society (ACS), where such specifications are available; otherwise the best available grade is to be used.

1.4.1 Sampling -

Water - Use deionized distilled water to conform to ASTM specification D 1193-74, Type 3. At the option of the analyst, the KMnO₄ test for oxidizable organic matter may be omitted when high concentrations of organic matter are not expected to be present.

Isopropanol, 80 Percent (Method 6A) - Mix 80 ml of isopropanol (100 percent) with 20 ml of deionized distilled water. Check each lot of isopropanol for peroxide impurities as follows:

1. Shake 10 ml of isopropanol with 10 ml of freshly prepared 10 percent potassium iodide (KI) solution.

2. Prepare a blank by similarly treating 10 ml of water.

3. After 1 minute, read the absorbance of the alcohol sample against the H₂O blank at 352 nm on a spectrophotometer. If absorbance exceeds 0.1, reject the alcohol for use. Peroxides may be removed from isopropanol by redistilling or by passing through a column of activated alumina. After peroxides are removed, check for peroxide impurities using the same method as above. However, reagent grade isopropanol with suitably low peroxide levels may be obtained from commercial sources. Therefore, rejection of contaminated lots may be a more efficient procedure.

Hydrogen Peroxide, 3 Percent (Method 6A) - Dilute 30 percent hydrogen peroxide 1:9 (v/v) with water. Prepare fresh daily. The 30 percent hydrogen peroxide should be stored according to manufacturer's directions.

Hydrogen Peroxide, 6 Percent (Method 6B) - Dilute 30 percent hydrogen peroxide 1:3 (v/v) with water. This mixture results in 7.5 percent H_2O_2 ; it should be acceptable for one week in a closed container. The 30 percent hydrogen peroxide should be stored according to manufacturer's directions.

Potassium Iodide Solution, 10 Percent - Dissolve 10.0 g of potassium iodide in water, and dilute to 100 ml. Prepare when needed. This solution is used to check for peroxide impurities in the isopropanol only.

Drierite - Anhydrous calcium sulfate ($CaSO_4$) desiccant, 8 mesh, indicating type is recommended. Do not use silica gel or similar desiccant in this application. Manufacturer's specifications should be checked upon receipt.

CO₂ Absorber - Ascarite, Ascarite II, or 5Å molecular sieve. Ascarite or Ascarite II is the recommended absorption media to collect the CO₂ for both methods because it is an indicating type of sorbent. The indicating type sorbent will provide a visual check of whether the sorbent was spent prior to the completion of the run. Ascarite may also be used for both methods; the 5Å molecular sieve may only be used with the Method 6B constant rate sampling (low flow rate). Because problems have been detected with molecular sieve lots, it is necessary that new lots of the molecular sieve material be regenerated upon receipt. This can be accomplished by placing the molecular sieve in an oven at 300°C for 4 hours and passing carbon dioxide-free air through the molecular sieve (while it is in the oven) at a flow rate equal to the volume of molecular sieve per minute. The recommended molecular sieve material is Union Carbide 1/16-inch pellets, 5 Å or equivalent. Note: Ascarite may be a skin irritant, and protection should be taken not to breath the Ascarite dust.

1.4.2 Sample Recovery - The following are required for sample recovery:

Water - Use deionized distilled water, as specified in Subsection 1.4.1.

Isopropanol, 80 Percent (Method 6A) - Mix 80 ml of isopropanol with 20 ml of water.

1.4.3 Analysis - The following are required for sample analysis:

Water - Use deionized distilled water, as in Subsection 1.4.1.

Isopropanol, 100 Percent (Method 6A) - As specified above.

Thorin Indicator - Dissolve 0.20 g of 1-(o-arsonophenylazo)-2-naphthol-3, 6-disulfonic acid, disodium salt in 100 ml of water.

Barium Perchlorate Solution, 0.0100N - Dissolve 1.95 g of barium perchlorate trihydrate ($\text{Ba}(\text{ClO}_4)_2 \cdot 3\text{H}_2\text{O}$) in 200 ml of deionized distilled water and dilute to 1 liter with 100 percent isopropanol. Alternatively, use 1.22 g of ($\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$) instead of the perchlorate. Standardize, as in Section 3.13.5.

Sulfuric Acid Standard, 0.0100N - Either purchase the manufacturer's certified or standardize the H_2SO_4 at 0.0100N \pm 0.0002N against 0.0100N NaOH that has been standardized against primary standard grade potassium acid phthalate.

1.5 Analytical Equipment

A spectrophotometer is needed to check the isopropanol for peroxide impurities. The absorbance is read at 352 nm on the spectrophotometer.

Table 1.1 ACTIVITY MATRIX FOR PROCUREMENT OF APPARATUS
AND SUPPLIES

Apparatus and supplies	Acceptance limits	Frequency and method of measurement	Action if requirements are not met
<u>Sampling</u>			
Sampling probe with heating system	Capable of maintaining 100° C (212°F) exit air at flow rate of 1.0 L/min	Visually check and run heating system checkout	Repair or return to supplier
Out-of-stack filter	To remove particulate and to prevent condensation	As above	As above
Flexible connector (optional)	To connect the probe to the midget bubbler and to prevent condensation	As above	As above
Midget bubbler/impinger (large impingers are acceptable)	Standard stock glass	Visually check upon receipt for breaks or leaks	Return to manufacturer
CO ₂ absorber	Minimum capacity of 150 g of Ascarite	Visually check upon receipt for damage and proper size	Return to supplier
Vacuum pump	Capable of maintaining flow rate of 1 to 2 L/min; leak free at 250 mm (10 in.) Hg	Check upon receipt for leaks and capacity	As above
Dry gas meter (if required)	Capable of measuring total volume within 2% at a flow rate of 1.0 L/min	Check for damage upon receipt and calibrate (Sec. 3.13.2) against wet test meter	Reject if damaged, behaves erratically, or cannot be properly adjusted
Wet test meter (if dry gas meter required)	Capable of measuring total volume within 1%	Upon assembly, leak check all connections and check calibration by liquid displacement	As above

(continued)

Table 1.1 (continued)

Apparatus and supplies	Acceptance limits	Frequency and method of measurement	Action if requirements are not met
Rotameter	Within 5% of manufacturer's calibration curve (recommended)	Check upon receipt for damage and calibrate (Sec. 3.13.2) against wet test meter	Recalibrate and construct a new calibration curve
Thermometers	Within 1°C (2°F) of true value in the range of 0°C to 25°C (32°F to 77°F) for impinger and +3°C (5.4°F) for dry gas meter thermometer	Check upon receipt for damage (i.e., dents and bent stem), and calibrate (Sec. 3.13.2) against mercury-in-glass thermometer	Return to supplier if unable to calibrate
Barometer	Capable of measuring atmospheric pressure to within 2.5 mm (0.1 in.) Hg	Check against mercury-in-glass barometer or equivalent (Sec. 3.13.2)	Determine correction factor, or reject if difference is more than ± 2.5
Vacuum gauge	0 to 760 mm (0 to 29.92 in.) Hg range, ± 25 mm (1.0 in.) Hg accuracy at 250 mm (10 in.) Hg	Check against U-tube mercury manometer upon receipt	Adjust or return to supplier
Industrial timer (Method 6B only)	Properly operate pump for specified sampling cycle	Check the sample cycle	Repair or reject
<u>Sample Recovery</u>			
Wash bottles	Polyethylene or glass, 500-ml	Visually check for damage upon receipt	Replace or return to supplier
Storage bottles	Polyethylene, 100-ml	Visually check for damage upon receipt, and be sure that caps seal properly	As above

(continued)

Table 1.1 (continued)

Apparatus and supplies	Acceptance limits	Frequency and method of measurement	Action if requirements are not met
Balance	Accurate to $\pm 0.05\text{g}$ for weighing impingers and CO_2 absorber	Check accuracy with Class S weights	Repair or reject
<u>Analysis Glassware</u> Pipettes, volumetric flasks, burettes, and graduated cylinders	Glass, Class A	Upon receipt, check for stock number, cracks, breaks, and manufacturer flaws	As above
<u>Reagents</u> Distilled water	Must conform to ASTM-D1193-74, Type 3	Check each lot or specify type when ordering	As above
Isopropanol (Method 6A only)	100% isopropanol, reagent grade or certified ACS with no peroxide	Upon receipt, check each lot for peroxide impurities with a spectrophotometer	Redistill or pass through alumina column, or replace
Hydrogen peroxide	30% H_2O_2 , reagent grade or certified ACS	Upon receipt, check label for grade or certification	Replace or return to manufacturer
Potassium iodide solution	Potassium iodide, reagent grade or certified ACS	As above	As above
Drierite	Anhydrous calcium sulfate (CaSO_4) desiccant, 8 mesh, indicating type	Check manufacturer's specification upon receipt	Reject

(continued)

Table 1.1 (continued)

Apparatus and supplies	Acceptance limits	Frequency and method of measurement	Action if requirements are not met
Ascarite or Ascarite II	Capable of collecting CO ₂ for each sample run	Check out each new lot with known amount of CO ₂	Reject
Thorin indicator	1-(o-arsonophenylazo)-2-naphthol-3,6-disulfonic acid, disodium salt, reagent grade or certified ACS	As above	As above
Barium perchlorate solution	Barium perchlorate trihydrate (Ba(ClO ₄) ₂ ·3H ₂ O), reagent grade or certified ACS	As above	As above
Sulfuric acid	Sulfuric acid, 0.0100N \pm 0.0002N	Have certified by manufacturer or standardize against 0.0100N NaOH that has been standardized against potassium acid phthalate (primary standard grade)	As above

2.0 CALIBRATION OF APPARATUS

Calibration of the apparatus is one of the most important functions in maintaining data quality. The detailed calibration procedures included in this section were designed for the equipment specified by Method 6 and described in the previous section. Table 2.1 at the end of this section summarizes the quality assurance functions for calibration. All calibrations should be recorded on standardized forms and retained in a calibration log book.

2.1 Metering System

As previously stated, the metering system may not be required. For Methods 6A and 6B trains that do not use the metering system, no calibration is required.

2.1.1 Wet Test Meter - The wet test meter must be calibrated and have the proper capacity. For Methods 6A and 6B, the wet test meter should have a capacity of at least 2 L/min. No upper limit is placed on the capacity; however, a wet test meter dial should make at least one complete revolution at the specified flow rate for each of the three independent calibrations.

Wet test meters are calibrated by the manufacturer to an accuracy of ± 0.5 percent. Calibration of the wet test meter must be checked initially upon receipt and yearly thereafter.

The following liquid positive displacement technique can be used to verify and adjust, if necessary, the accuracy of the wet test meter to ± 1 percent:

1. Level the wet test meter by adjusting the legs until the bubble on the level located on the top of the meter is centered.
2. Adjust the water volume in the meter so that the pointer in the water level gauge just touches the meniscus.
3. Adjust the water manometer to zero by moving the scale or by adding water to the manometer.
4. Set up the apparatus and calibration system as shown in Figure 2.1.
 - a. Fill the rigid-wall 5-gal jug with water to below the air inlet tube, and allow both to equilibrate to room temperature (about 24 h) before use.
 - b. Start water siphoning through the system, and collect the water in a 1-gal container, located in place of the volumetric flask.

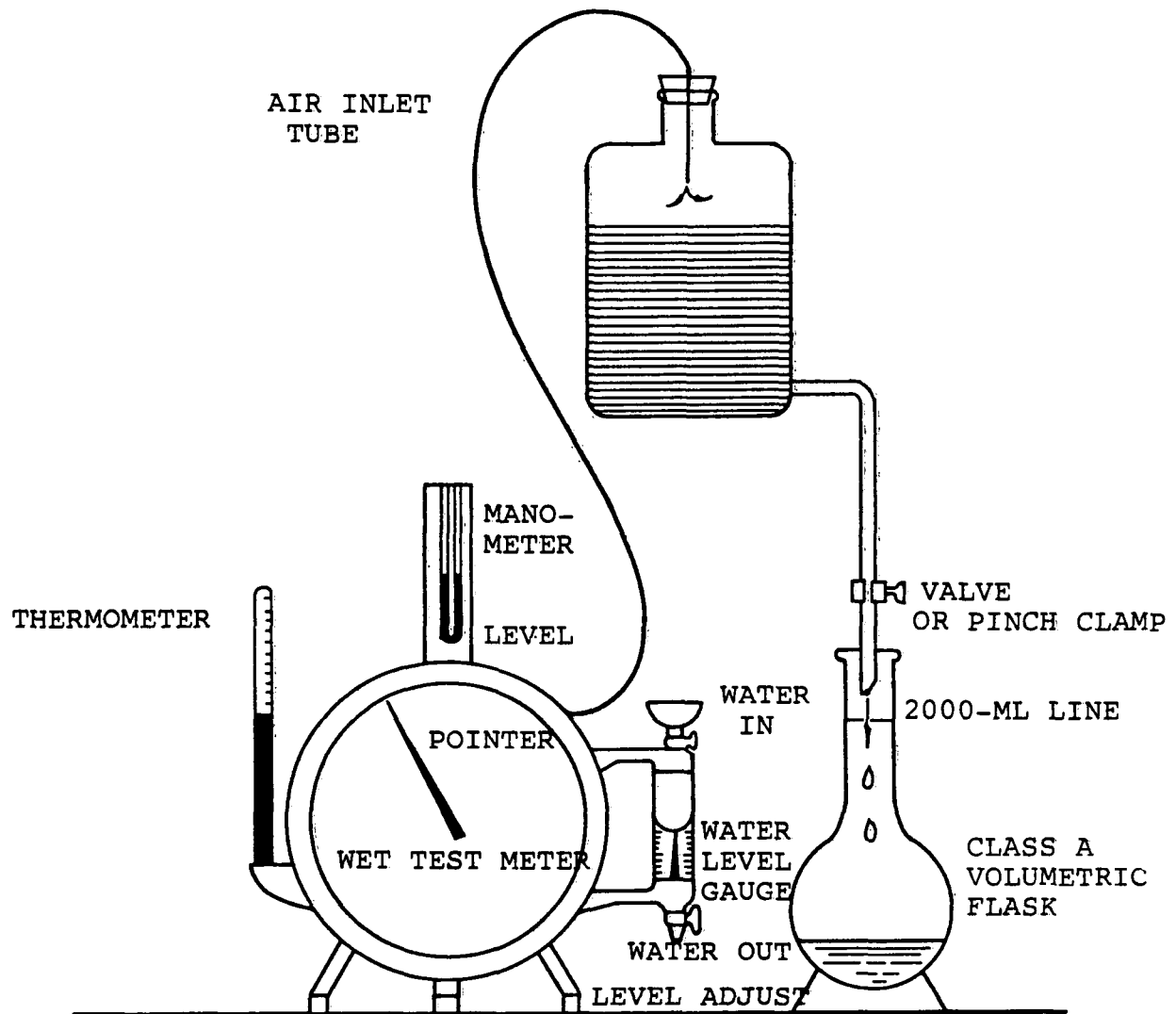


Figure 2.1. Calibration check apparatus for wet test meter.

5. Check operation of the meter as follows:
 - a. If the manometer reading is <10 mm (0.4 in.) H_2O , the meter is in proper working condition. Continue to step 6.
 - b. If the manometer reading is >10 mm (0.4 in.) H_2O , the wet test meter is defective or the saturator has too much pressure drop. If the wet test meter is defective, return to the manufacturer for repair if the defect(s) (e.g., bad connections or joints) cannot be found and corrected.
6. Continue the operation until the 1-gal container is almost full. Plug inlet to the wet test meter. If no leak exists, the flow of liquid to the gallon container should stop. If the flow continues, correct for leaks. Turn the siphon system off by closing the valve, and unplug the inlet to the wet test meter.
7. Read the initial volume (V_i) from the wet test meter dial, and record on the wet test meter calibration log, Figure 2.2.
8. Place a clean, dry volumetric flask (Class A) under the siphon tube, open the pinch clamp, and fill the volumetric flask to the mark. The volumetric flask must be large enough to allow at least one complete revolution of the wet test meter with not more than two fillings of the volumetric flask.
9. Start the flow of water, and record the maximum wet test meter manometer reading during the test after a constant flow of liquid is obtained.
10. Carefully fill the volumetric flask, and shut off the liquid flow at the 2-liter mark. Record the final volume on the wet test meter.
11. Perform steps 7 through 10 three times.

Since the water temperature in the wet test meter and reservoir has been equilibrated to the ambient temperature and since the pressure in the wet test meter will equilibrate with the water reservoir after the water flow is shut off, the air volume can be compared directly with the liquid displacement volume. Any temperature or pressure difference would be less than measurement error and would not affect the final calculations.

The error should not exceed +1 percent; should this error magnitude be exceeded, check all connections within the test apparatus for leaks, and gravimetrically check the volume of the

Wet test meter serial number 43-246

Date 1-27-85

Range of wet test meter flow rate 0-120 L/min

Volume of test flask $V_s =$ 200L

Satisfactory leak check? yes

Ambient temperature of equilibrate liquid in wet test meter and reservoir 74°F

Test number	Manometer reading, ^a mm H ₂ O	Final volume (V_f), L	Initial volume (V_i), L	Total volume (V_m) ^b , L	Flask volume (V_s), L	Percent error, ^c %
1	5	1.99	0	1.99	2.00	0.5
2	5	2.00	0	2.00	2.00	0
3	5	2.00	0	2.00	2.00	0

^a Must be less than 10 mm (0.4 in.) H₂O.

^b $V_m = V_f - V_i$.

^c % error = $100 (V_m - V_s) / V_s =$ _____ (+1%).

S.P.

Signature of calibration person

Figure 2.2. Wet test meter calibration log.

standard flask. Repeat the calibration procedure, and if the tolerance level is not met, adjust the liquid level within the meter (see the manufacturer's manual) until the specifications are met.

2.1.2 Sample Metering System - The sample metering system--consisting of the needle valve, pump, rotameter, and dry gas meter--is initially calibrated by stringent laboratory methods before it is used in the field. The calibration is then rechecked after each field test series for Method 6A and every 30 days of operation for Method 6B. This recheck requires less effort than the initial calibration. When a recheck indicates that the calibration factor has changed, the tester must again perform the complete laboratory procedure to obtain the new calibration factor. After the meter is recalibrated, the metered sample volume is multiplied by the calibration factor (initial or recalibrated) that yields the lower gas volume for each test run. Both sets of calibration results should be reported.

Initial Calibration - The metering system should be calibrated when first purchased and at any time the posttest check yields a calibration factor that does not agree within 5 percent of the pretest calibration factor. A calibrated wet test meter (properly sized, with ± 1 percent accuracy) should be used to calibrate the metering system.

The metering system should be calibrated in the following manner before its initial use in the field.

1. Leak check the metering system (needle valve, pump, rotameter, and dry gas meter) as follows:
 - a. Temporarily attach a suitable rotameter (e.g., 0-40 cm³/min) to the outlet of the dry gas meter (for the 1 L/min sample train), and place a vacuum gauge at the inlet to the sample train. Alternatively, for trains without a dry gas meter, place the rotameter at the discharge of the CO₂ absorber.
 - b. Pull a vacuum of at least 250 mm (10 in.) Hg.
 - c. Note the flow rate as indicated by the rotameter for the 1 L/min sample train or time the movement of the dry gas meter needle for 2 minutes on the low flow train.
 - d. A leak of less than 2 percent of the appropriate sample rate must be recorded or leaks must be eliminated.
 - e. Carefully release the vacuum gauge before turning off pump.

2. Assemble the apparatus, as shown in Figure 2.3, with the wet test meter replacing the CO₂ absorber and impingers; i.e., connect the outlet of the wet test meter to the inlet side of the needle valve.

3. Run the pump for 15 minutes with the flow rate set at 1 L/min to allow the pump to warm up and to permit the interior surface of the wet test meter to become wet.

4. Collect the information required in the forms provided, Figure 2.4A (English units) or 2.4B (metric units), using sample volumes equivalent to at least five revolutions of the dry test meter. Three independent runs must be made.

5. Calculate Y_i for each run of the three runs using Equation 2-1. Record the values on the form (Figure 2.4A or 2.4B).

$$Y_i = \frac{V_w (t_d + 460) [P_m + (D_m/13.6)]}{V_d (t_w + 460) P_m} \quad \text{Equation 2-1}$$

where

Y_i = ratio for each run of volumes measured by the wet test meter and the dry gas meter, dimensionless calibration factor,

V_w = volume measured by wet test meter, m³ (ft³),

P_m = barometric pressure at the meters, mm (in.) Hg,

D_m = pressure drop across the wet test meter, mm (in.) H₂O,

t_d = average temperature of dry gas meter, °C (°F),

V_d = volume measured by the dry gas meter, m³ (ft³), and

t_w = temperature of wet test meter, °C (°F).

6. Adjust and recalibrate or reject the dry gas meter if one or more values of Y_i fall outside the interval $Y \pm 0.02Y$, where Y is the average¹ for three runs. Otherwise, the Y (calibration factor) is acceptable and will be used for future checks and subsequent test runs. The completed form should be forwarded to the supervisor for approval, and then filed in the calibration log book.

An alternative method of calibrating the metering system consists of substituting a dry gas meter, which has been properly

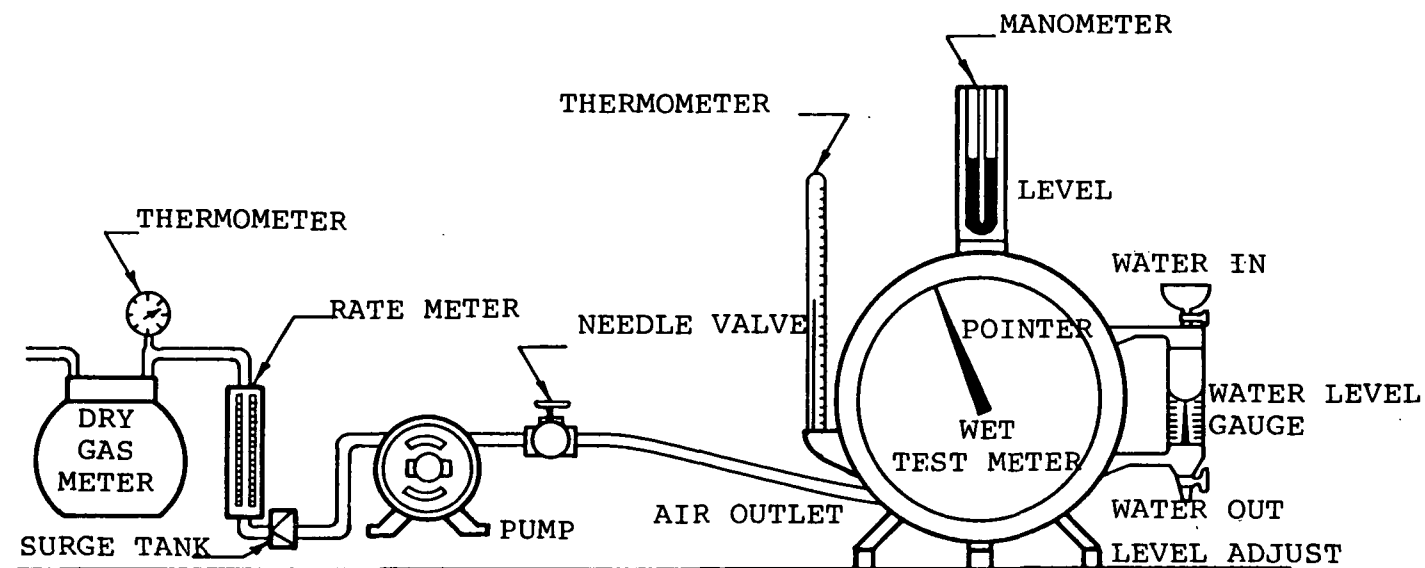


Figure 2.3. Sample metering system calibration setup.

Date 1-25-85 Calibrated by RRS Meter box number E-6 Wet test meter number 101-A
 Barometer pressure, $P_m =$ 29.41 in. Hg Dry gas meter temperature correction factor N/A °F

Wet test meter pressure drop $(D_m)^a$ in. H ₂ O	Rota-meter setting (R_s) , ft ³ /min	Wet test meter gas volume $(V_m)^b$ ft ³	Dry test meter gas volume $(V_d)^b$, ft ³		Wet test meter gas temp (t_w) , °F	Inlet gas temp (t_{d_i}) , °F	Dry test meter				$(Y_{r_i})^f$
			Initial	Final			Outlet gas temp (t_{d_o}) , °F	Average gas temp $(t_d)^c$, °F	Time of run $(\theta)^d$, min	Average ratio $(Y_i)^e$	
0.25	0.035	1.058	725.643	726.672	72	80	78	79	30	1.015	1.022
0.25	0.035	1.059	728.961	730.021	72	82	80	81	30	1.019	1.024
0.25	0.035	1.061	732.098	733.158	72	84	80	82	30	1.018	1.030

^a D_m expressed as negative number.

^b Volume passing through meter. Dry gas volume is minimum for at least five revolutions of the meter.

^c The average of t_{d_i} and t_{d_o} if using two thermometers; the actual reading if using one thermometer.

^d The time it takes to complete the calibration run.

^e With Y defined as the average ratio of volumes for the wet test and the dry test meters, $Y_i = Y \pm 0.02 Y$ for calibration and $Y_i = Y \pm 0.05 Y$ for the posttest checks; thus,

$$Y_i = \frac{V_w (t_d + 460^\circ\text{F}) [P_m + (D_m/13.6)]}{V_d (t_w + 460^\circ\text{F}) (P_m)} \quad (\text{Eq. 1}) \quad \text{and} \quad Y = \frac{Y_1 + Y_2 + Y_3}{3} = \underline{1.017} \quad (\text{Eq. 2})$$

^f With Y_r defined as the average ratio of volumetric measurement by wet test meter to rotameter.

Tolerance $Y_r = 1 \pm 0.05$ for calibration and $Y \pm 0.1$ for posttest checks.

$$Y_{r_i} = \frac{V_w (t_d + 460^\circ\text{F}) [P_m + (D_m/13.6)]}{\theta (t_w + 460^\circ\text{F}) (P_m) (R_s)} \quad (\text{Eq. 3}) \quad \text{and} \quad Y_r = \frac{Y_1 + Y_2 + Y_3}{3} = \underline{1.026} \quad (\text{Eq. 4})$$

Figure 2.4A. Dry gas meter calibration data form (English units).

Date 1-25-85 Calibrated by RLS Meter box number E-6 Wet test meter number 101-A
 Barometer pressure, $P_m =$ 748 in. Hg Dry gas meter temperature correction factor N/A °C

Wet test meter pressure drop (D_m), ^a mm H ₂ O	Rota-meter setting (R_s), cc/min	Wet test meter gas volume (V_m), ^b L	Dry test meter gas volume (V_d), ^b L		Wet test meter gas temp (t_w), °C	Inlet gas temp (t_{d_i}), °C	Dry test meter				(Y_{r_i}) , ^f
			Initial	Final			Outlet gas temp (t_{d_o}), °C	Average gas temp (t_d), ^c °C	Time of run (θ), ^d min	Average ratio (Y_i), ^e	
6.4	1.0	29.958	105.631	135.618	22	27	26	26.5	30	1.015	1.02
6.4	1.0	29.987	140.362	170.377	22	28	27	27.5	30	1.019	1.02
6.4	1.0	30.043	181.619	211.634	22	29	27	28.5	30	1.018	1.03

^a D_m expressed as negative number.

^b Volume passing through meter. Dry gas volume is minimum for at least five revolutions of the meter.

^c The average of t_{d_i} and t_{d_o} if using two thermometers; the actual reading if using one thermometer.

^d The time it takes to complete the calibration run.

^e With Y defined as the average ratio of volumes for the wet test and the dry test meters, $Y_i = Y \pm 0.02 Y$ for calibration and $Y_i = Y \pm 0.05 Y$ for the posttest checks; thus,

$$Y_i = \frac{V_w (t_d + 273^\circ\text{C}) [P_m + (D_m/13.6)]}{V_d (t_w + 273^\circ\text{C}) (P_m)} \quad (\text{Eq. 1}) \quad \text{and} \quad Y = \frac{Y_1 + Y_2 + Y_3}{3} = \underline{1.017} \quad (\text{Eq. 2})$$

^f With Y_r defined as the average ratio of volumetric measurement by wet test meter to rotameter.

Tolerance $Y_r = 1 \pm 0.05$ for calibration and $Y \pm 0.1$ for posttest checks.

$$Y_{r_i} = \frac{V_w (t_d + 273^\circ\text{C}) [P_m + (D_m/13.6)] 1000}{\theta (t_w + 273^\circ\text{C}) (P_m) (R_s)} \quad (\text{Eq. 3}) \quad \text{and} \quad Y_r = \frac{Y_1 + Y_2 + Y_3}{3} = \underline{1.026} \quad (\text{Eq. 4})$$

Figure 2.4B. Dry gas meter calibration data form (metric units).

prepared as a calibration standard, in place of the wet test meter. This procedure should be used only after obtaining approval of the Administrator.

Posttest Calibration Check - After each field test series for Method 6A and after every 30 days of operation for Method 6B, conduct a calibration check as in Subsection 2.1.2 with the following exceptions:

1. The leak check is not conducted because a leak should not be corrected that was present during testing.
2. Three or more revolutions of the dry gas meter may be used.
3. Only two independent runs need be made.
4. If a temperature-compensating dry gas meter was used, the calibration temperature for the dry gas meter must be within 6°C (10.8°F) of the average meter temperature observed during the field test series.

When a lower meter calibration factor is obtained as a result of an uncorrected leak, the tester should correct the leak and then determine the calibration factor for the leakless system. If the new calibration factor changes the compliance status of the facility in comparison to the lower factor, either include this information in the report or consult with the administrator for reporting procedures. If the calibration factor does not deviate by >5 percent from the initial calibration factor Y (determined in Subsection 2.1.2), then the dry gas meter volumes obtained during the test series are acceptable. If the calibration factor does deviate by >5 percent, recalibrate the metering system as in Subsection 2.1.2, and for the calculations, use the calibration factor (initial or recalibration) that yields the lower gas volume for each test run.

2.2 Thermometers

The thermometers used to measure the temperature of gas leaving the CO_2 absorber should be initially compared with a mercury-in-glass thermometer that meets ASTM E-1 No. 63C or 63F specifications:

1. Place both the mercury-in-glass and the dial type or an equivalent thermometer in an ice bath. Compare the readings after the bath stabilizes.
2. Allow both thermometers to come to room temperature. Compare readings after both stabilize.

3. The dial type or equivalent thermometer is acceptable if values agree within 1°C (2°F) at both points. If the difference is greater than 1°C (2°F), either adjust or recalibrate the thermometer until the above criteria are met, or reject it.

4. The thermometer is used as an indicator and accuracy of readings is not important for field use.

The thermometer(s) on the dry gas meter inlet used to measure the metered sample gas temperature should be initially compared with a mercury-in-glass thermometer that meets ASTM E-1 No. 63C or 63F specifications (if the dry gas meter is required, otherwise, no calibration is required):

1. Place the dial type or an equivalent thermometer and the mercury-in-glass thermometer in a hot water bath, 40° to 50°C (104° to 122°F). Compare the readings after the bath stabilizes.

2. Allow both thermometers to come to room temperature. Compare readings after the thermometers stabilize.

3. The dial type or equivalent thermometer is acceptable if values agree within 3°C (5.4°F) at both points (steps 1 and 2 above) or if the temperature differentials at both points are within 3°C (5.4°F) and the temperature differential is taped to the thermometer and recorded on the meter calibration form (Figure 2.4A or 2.4B).

4. Prior to each field trip, compare the temperature reading of the mercury-in-glass thermometer at room temperature with that of the thermometer that is part of the meter system. If the values or the corrected values are not within 6°C (10.8°F) of each other, replace or recalibrate the meter thermometer.

5. The thermometer must be recalibrated only when the volume metering system does not pass the posttest calibration.

2.3 Rotameter

The Reference Method does not require that the tester calibrate the rotameter. The rotameter should be cleaned and maintained according to the manufacturer's instructions. For this reason, it is recommended that the calibration curve and/or rotameter markings be checked upon receipt and then routinely checked with the posttest meter system check or at the required frequency for the posttest meter check when a dry gas meter is not used. The rotameter may be calibrated as follows:

1. Ensure that the rotameter has been cleaned as specified by the manufacturer, and is not damaged.

2. Use the manufacturer's calibration curve and/or markings on the rotameter for the initial calibration. Calibrate the rotameter as described in the meter system calibration of Subsection 2.1.2, and record the data on the calibration form (Figure 2.4A or 2.4B).

3. Use the rotameter for testing if the pretest calculated calibration is within the range 1.0 ± 0.05 L/min. If, however, the calibration point is not within 5 percent, determine a new flow rate setting, and recalibrate the system until the proper setting is determined.

4. Check the rotameter calibration with each posttest meter system check. If the rotameter check is within 10 percent of the 1-L/min setting, the rotameter can be acceptable with proper maintenance. If, however, the check is not within 10 percent of the flow setting, disassemble and clean the rotameter and perform a full recalibration.

2.4 Barometer

The field barometer should be adjusted initially and before each test series to agree within 2.5 mm (0.1 in.) Hg with a mercury-in-glass barometer or with the pressure value reported from a nearby National Weather Service Station and corrected for elevation. The tester should be aware that the pressure readings are normally corrected to sea level. The uncorrected readings should be obtained. The correction for the elevation difference between the weather station and the sampling point should be applied at a rate of -2.5 mm Hg/30m (-0.1 in. Hg/100 ft) elevation increase, or vice versa for elevation decrease.

The calibration checks should be recorded on the pretest sampling form (Figure 2.5).

2.5 Balance

The balance must be checked prior to each series of weighings, but not more than once a day. Place the CO₂ absorber or a midget impinger on the balance. Record the weight. Place a 5 g Class S weight on the balance and record the weight. The difference must be 5.0 ± 0.1 g or the balance must be adjusted, repaired, or rejected.

Date 10/23/85
Meter box number E-6

Calibrated by RKS

Rotameter

Pretest calibration factor (Y_r) acceptable? ☒ yes ☐ no
(within 10 percent of correct value).

Dry Gas Meter (If applicable)*

Pretest calibration factor (Y) = 1.021 (within 2 percent of
average factor for each calibration run).

Gas Meter Thermometer (If applicable)

Temperature correction necessary? ☐ yes ☒ no
(within 3°C (5.4°F) of reference values for calibration and
within 6°C (10.8°F) of reference values for calibration
check).

If yes, temperature correction _____

Barometer

Field barometer reading correct? ☒ yes ☐ no
(within 2.5 mm (0.1 in) Hg of mercury-in-glass barometer).

Balance

Was the pretest calibration of the balance correct? ☒ yes ☐ no
(within 0.05 g of true value using Class S weights).

* Most significant items/parameters to be checked.

Figure 2.5. Pretest sampling checks.

Table 2.1. ACTIVITY MATRIX FOR CALIBRATION OF EQUIPMENT

Apparatus	Acceptance limits	Frequency and method of measurement	Action if requirements are not met
Wet test meter	Capacity of at least 2 L/min and an accuracy within 1.0%	Calibrate initially and then yearly by liquid displacement	Adjust until specifications are met, or return to manufacturer
Dry gas meter	$Y_1 = Y + 0.02Y$ at a flow rate of about 1 L/min	Calibrate vs. wet test meter initially and when the posttest check is not within $Y + 0.05Y$	Repair and then recalibrate or replace
CO ₂ absorber thermometer	Within 1°C (2°F) of true value	Calibrate each initially as a separate component against a mercury-in-glass thermometer	Adjust, determine a constant correction factor, or reject
Dry gas meter thermometer	Within 3°C (5.4°F) of true value	Calibrate initially and recalibrate when the meter system does not pass the posttest check	As above
Rotameter	Clean and maintain according to manufacturer's instructions (required); calibrate to $\pm 5\%$ (recommended)	Initially and after each field trip for Method 6A and every 30 days of operation for Method 6B	Adjust and recalibrate, or reject
Barometer	± 2.5 mm (0.1 in.) Hg of mercury-in-glass barometer or of weather station value	Calibrate initially using a mercury-in-glass barometer; check before and after each field test	Adjust to agree with certified barometer
Balance	Weigh impinger and CO ₂ absorber to ± 0.1 g	Check prior to each series of weighings	Adjust to agree, repair, or reject

3.0 PRESAMPLING OPERATIONS

The quality assurance activities for presampling preparation are summarized in Table 3.1 at the end of this section. See Section 3.0 of this Handbook for details on preliminary site visits.

3.1 Apparatus Check and Calibration

Figure 3.1 or a similar form is recommended to aid the tester in preparing an equipment checklist, status report form, and packing list.

3.1.1 Sampling Train - The schematic of the SO₂ train is given in Figure 1.1. Commercial models of this system are available. Each individual or fabricated train must be in compliance with the specifications in the Method, Section 3.5.10.

3.1.2 Probe - The probe should be cleaned internally by brushing first with tap water, then with deionized distilled water, and finally with acetone. Allow probe to dry in the air. In extreme cases, the glass or stainless steel liner can be cleaned with stronger reagents; the objective is to leave the liner free from contaminants. The probe's heating system should be checked to see that it is operating properly. The probe must be leak free when sealed at the inlet or tip and checked for leaks at a vacuum of 250 mm (10 in.) Hg with the meter box. Any leaks should be corrected. The liner should be sealed inside the metal sheath to prevent diluent air from entering the source since most stacks are under negative pressure.

3.1.3 Midget Bubblers, Midget Impingers, and Glass Connectors - All glassware should be cleaned with detergent and tap water, and then with deionized distilled water. Any items that do not pass a visual inspection for cracks or breakage must be repaired or discarded.

3.1.4 CO₂ Absorber - The cylinders or bottles may be packed with the Ascarite, numbered, weighed, and sealed in the laboratory prior to the field trip. If molecular sieve material is used, ensure that it has been regenerated as described in Subsection 1.4.1.

3.1.5 Valve and Rotameter - Prior to each field trip or at any sign of erratic behavior, the flow control valve and rotameter should be cleaned according to the maintenance procedure recommended by the manufacturer.

3.1.6 Pump - The vacuum pump and oiler should be serviced as recommended by the manufacturer, every 3 months, or upon erratic behavior (nonuniform or insufficient pumping action).

Apparatus check	Acceptable		Quantity required	Ready		Loaded and packed	
	Yes	No		Yes	No	Yes	No
<u>Probe</u> Type liner Glass <u>X</u> Stainless steel _____ Other _____ Heated properly ✓ Leak checked on sampling train ✓	✓		4	✓		✓	
<u>Filter or Filter Assembly</u> Glass wool <u>X</u> Other _____	✓		4 out-of-stock	✓		✓	
<u>Glassware</u> Midget bubbler ✓ Midget impinger ✓ Size <u>N/A</u> Type <u>N/A</u>	✓		8 8	✓ ✓		✓ ✓	
<u>Meter System</u> With timer _____ Without timer <u>X</u> Leak-free pump* ✓ Rate meter* ✓ Dry gas meter* ✓	✓ ✓ ✓		2	✓		✓	
<u>Reagents</u> Distilled water ✓ H ₂ O ₂ , 30% ✓ Isopropanol, 100%* ✓ (for Method 6A) Drierite ✓ Ascarite <u>X</u> ✓ or 5A molecular sieve* _____	✓ ✓ ✓ ✓ ✓		2 gal 1 qt 1 gal 10# 10#	✓ ✓ ✓ ✓ ✓		✓ ✓ ✓ ✓ ✓	
<u>Other</u> Barometer ✓ CO ₂ absorber ✓ column ✓ Balance ✓	✓ ✓ ✓		1 4 1	✓ ✓ ✓		✓ ✓ ✓	

*Most significant items/parameters to be checked.

Figure 3.1. Pretest preparations.

3.1.7 Dry Gas Meter - A dry gas meter calibration check should be made in accordance with the procedure in Section 3.13.2. An acceptable posttest check from the previous test is sufficient.

3.1.8 Thermometers - The thermometers should be compared with the mercury-in-glass thermometer at room temperature prior to each field trip.

3.1.9 Barometer - The field barometer should be compared with either the mercury-in-glass barometer or a National Weather Service Station prior to each field trip.

3.1.10 Balance - Check balance with Class S weights using procedures from Subsection 2.5 and pack in rigid foam container.

3.1.11 Other Sampling Apparatus - Other sampling equipment, such as Mae West bubblers and rigid cylinders for moisture absorption, which require sample or reagent volumes other than those specified in this procedure for full effectiveness, may be used subject to the approval of the Administrator.

3.2 Reagents and Equipment

3.2.1 Sampling - The midget bubbler solution (for Method 6A) is prepared by mixing 80 ml of isopropanol (100 percent) with 20 ml of water. The midget impinger absorbing reagent is prepared by diluting 100 ml of 30 percent hydrogen peroxide to 1 liter with water for Method 6A or 250 ml of 30 percent hydrogen peroxide to 1 liter with water for Method 6B. All reagents must be prepared fresh for each test series, using ACS reagent grade chemicals. Solutions containing isopropanol must be kept in sealed containers to prevent evaporation. Twenty five (25) g of Drierite is needed for each sample collection. Sufficient quantity should be brought in a sealed container.

3.2.2 Sample Recovery - Deionized distilled water is required on site for quantitative transfer of impinger solutions to storage containers. This water and isopropanol are used to clean the midget bubbler after testing and prior to taking another sample.

3.3 Packaging Equipment for Shipment

Equipment should be packed in rigid containers to protect it against rough handling during shipping and field operations (not mandatory).

3.3.1 Probe - The inlet and outlet of the probe must be sealed and protected from breakage. A suggested container is a wooden case lined with polyethylene foam or other suitable packing material; the case should have separate compartments for individual devices. The case should be equipped with handles or eye

hooks that can withstand hoisting, and should be rigid to prevent bending or twisting during shipping and handling.

3.3.2 Midget Bubblers, Impingers, Connectors, and Assorted Glassware - All bubblers, impingers, and glassware should be packed in a rigid container and protected by polyethylene foam or other suitable packing material. Individual compartments for glassware help to organize and protect each item. The impinger train may be charged and assembled in the laboratory if sampling is to be performed within 24 hours.

3.3.3 CO₂ Absorber and Volumetric Glassware - A rigid container lined with polyethylene foam material protects CO₂ absorber and assorted volumetric glassware.

3.3.4 Meter Box - The meter box (if required)--which contains the valve, rotameter, vacuum pump, dry gas meter, and thermometers--should be packed in a rigid shipping container unless its housing is strong enough to protect components during travel. Additional pump oil should be packed if oil is required for operation. It is advisable to ship a spare meter box in case of equipment failure.

3.3.5 Wash Bottles and Storage Containers - Storage containers and miscellaneous glassware may be safely transported, if packed in a rigid foam-lined container. Samples being transported in the containers should be protected from extremely high ambient temperatures (>50°C or about 120°F).

Table 3.1. ACTIVITY MATRIX FOR PRESAMPLING OPERATIONS

Operation	Acceptance limits	Frequency and method of measurement	Action if requirements are not met
<u>Apparatus</u>			
Probe	1. Probe liner free of contaminants 2. Probe leak free at at 250 mm (10 in.) Hg 3. No moisture condensation	1. Clean probe internally by brushing with tap water, then deionized distilled water, then acetone; allow to dry in air before test 2. Visual check before test Check out heating system initially and when moisture appears during testing	1. Retrace cleaning procedure and assembly 2. Replace 3. Repair or replace
Midget bubbler, midget impinger, CO ₂ absorber, and glass connectors	Clean and free of breaks, cracks, etc.	Clean with detergent, tap water, and then with deionized distilled water	Repair or discard
Flow control valve and rotameter	Clean and without sign of erratic behavior (such as ball not moving freely)	Clean prior to each field trip or upon erratic behavior	Repair or return to manufacturer
Vacuum pump	Maintain sampling rate of about 1 L/min up to 250 mm (10 in.) Hg	Service every 3 mo or upon erratic behavior; check oiler jars every 10th test	As above
Dry gas meter (if required)	Clean and within 2% of calibration factor	Calibrate according to Sec. 3.13.2; check for excess oil if oiler is used	As above
Balance	Accurate to within 0.1 g	Check with Class S weights	As above

(continued)

Table 3.1. (continued)

Operation	Acceptance limits	Frequency and method of measurement	Action if requirements are not met
<u>Reagents</u>			
Sampling	1. Requires all ACS grade reagents 2. New CO ₂ absorber material	1. Prepare fresh daily and store in sealed containers 2. Purchase new	1. Prepare new reagent 2. Reorder
Sample recovery	Requires deionized distilled water on site	Use water and reagent grade isopropanol to clean midget bubbler after test and before sampling	Prepare new reagent
<u>Package Equipment for Shipment</u>			
Probe	Protect with polyethylene foam	Prior to each shipment	Repack
Midget bubbler, impingers, connectors, and assorted glassware	Pack in rigid containers with polyethylene foam	As above	As above
CO ₂ absorber, volumetric glassware	Sturdy container lined with foam	As above	As above
Meter box	Meter box case and/or container to protect components; pack spare meter box and oil	As above	As above
Wash bottles and storage containers	Pack in rigid foam-lined container	As above	As above
Balance	Pack in rigid foam-lined container	As above	As above

4.0 ON-SITE MEASUREMENTS

On-site activities may include transporting the equipment to the test site, unpacking and assembling, sampling for sulfur dioxide and carbon dioxide analyses, and recording the data. In general for Method 6B, the equipment would be maintained at or near the test site and testing would be on a more routine basis. Since Method 6B is used to determine a daily average, facilities should consider running duplicate Method 6B sampling trains. One Method 6B sampling train would be designated as the primary and the other would be the backup train. This would prevent the loss of data, provide a check of sampling problems, provide sampling precision data, and provide a complete backup sample system for when the primary train is inoperable. The additional manpower requirements should not be significant when compared to the possible gain in emissions data recovery. The on-site quality assurance activities are summarized in Table 4.1 at the end of this section.

4.1 Transport of Equipment to the Sampling Site

The most efficient means of transporting the equipment from ground level to the sampling site (often above ground level) should be decided during the preliminary site visit or by prior correspondence. Care should be taken to prevent damage to the equipment or injury to test personnel during the moving. A laboratory type area should be designated for preparation of the absorbing reagents, for charging of the bubblers and impingers, and for sample recovery and analyses.

4.2 Preliminary Measurements and Setup

The Reference Method outlines the procedure used to determine the concentration of sulfur dioxide in the gas stream in terms of pounds of sulfur dioxide per million Btu's. The accuracy of the equipment after transport to the sampling site and possible rough handling can be determined by making a one-point check of the rotameter reading against the dry gas meter reading at the test site. Use Equation 3 in Figure 2.4A or 2.4B and substitute dry gas meter readings in place of wet test meter readings (i.e., $V_d = V_w$). The value Y_{ri} should be between 0.9 and 1.1; if not, the meter box has lost its rate or volume calibration. The tester can still use the meter box, but the data should not be released for decision making until a posttest recalibration has been made. If the dry gas meter calibration factor did change, the dry gas meter volumes may have to be corrected. Record the test identification number on the appropriate sampling form, Figure 4.1 (for Method 6A) or Figure 4.2 (for Method 6B).

Plant name Acme Power Plant
 Sample location Boiler No. 3
 Operator RRS
 Barometric pressure, mm (in.) Hg 758
 Probe material glass
 Meter box number E-6
 Ambient temperature, °C (°F) 25°
 Initial leak check 0.004 L/min @ 250 mm Hg
 Final leak check 0.006 L/min @ 250 mm Hg

City Anywhere USA
 Date 8/10/85
 Sample number AP-1
 Probe length m (ft) 1.5
 Probe heater setting 250°F
 Meter calibration factor (Y) 1.01
 Sampling point location 1.35m in from Port A
 Sample purge time, min 15
 Remarks maximum deviation <10%

Sampling time, min	Clock time, 24 h	Sample volume, L (ft ³)	Sample flow rate setting, L/min (ft ³ /min)	Sample volume metered (V _m), L (ft ³)	Percent deviation, ^a %	Dry gas meter temp, °C (°F)	Impinger temp, °C (°F)
0	1100	120.20	—	—	—	—	—
5	1105	125.30	1.0	5.1	2	27	19
10	1110	130.10	1.0	4.8	4	29	20
15	1115	135.20	1.0	5.1	2	30	20
20	1120	140.20	1.0	5.0	0	30	20
25	1125	145.20	1.0	5.0	0	30	20
Total 25		Total 25.00		V _m avg 5.0	Avg dev 1.6	Avg 29	Max temp 20

$$^a \text{ Percent deviation} = \frac{V_m - V_m \text{ avg}}{V_m \text{ avg}} \times 100 \text{ (must be within 10 percent).}$$

Figure 4.1. Field sampling data form for Method 6A.

Plant Acme Power Plant
Sample location Boiler No. 3
Operator RRS
Run No. AP-1
Sampling period Start: Date 10/12/85 Time 9:33 am
Stop: Date 10/13/85 Time 9:33 am
Initial leak check 6 ml/min
Final leak check 2 ml/min
Recovery date 10/13/85
Recovered by RRS

Dry Gas Meter
Final reading 744.14 L
Initial reading 716.32 L
Volume metered 27.82 L
Dry Gas Meter Calibration Factor, Y 1.017
Rotameter
Initial setting 1.0 L or cc/min
Final setting 1.0 L or cc/min

Meter Temperature 73 °F
10:30 am time
Barometric Pressure 29.73 in. Hg
10:45 am time

Probe Temperature Initial 100 °F
Final 100 °F
Filter Temperature Initial 120 °F
Final 120 °F
Ascarite Column
Final wt 312.1 g
Initial wt 303.6 g
Net wt 8.5 g of CO₂

Moisture

	1st bubbler	2nd impinger	3rd impinger	4th bubbler
Final wt	<u>73.1</u> g	<u>89.3</u> g	<u>88.3</u> g	<u>96.7</u> g
Initial wt	<u>73.1</u> g	<u>87.0</u> g	<u>88.2</u> g	<u>95.2</u> g
Net wt	<u>0.0</u> g	<u>2.0</u> g	<u>0.1</u> g	<u>1.5</u> g
Total moisture	<u>3.6</u> g			<u>20</u> % spent

RECOVERED SAMPLE (If Applicable)

H₂O₂ blank
container no. AP-1AB
Impinger contents
container no. AP-1
H₂O blank
container no. AP-1WB
Samples stored and locked ☒
Received by Donna Engle Date 10/14/85
Remarks _____

Figure 4.2. Method 6B sampling, sample recovery, and sample integrity data form.

4.3 Sampling

The on-site sampling includes the following steps:

1. Preparation and/or addition of the absorbing reagents to the midjet bubblers and impingers and CO₂ absorber.
2. Setup of the sampling train.
3. Connection to the electrical service.
4. Preparation of the probe (leak check of entire sampling train and addition of particulate filter).
5. Insertion of the probe into the stack.
6. Sealing the port.
7. Checking the temperature of the probe.
8. Sampling.
9. Recording the data in Figure 4.1.

A final leak check of the train is always performed after sampling.

4.3.1 Preparation and/or Addition of Absorbing Reagents to Collection System - Absorbing reagents can be prepared on site, if necessary, according to the directions in Section 3.13.3.

For Method 6A

1. Use a pipette or a graduated cylinder to introduce 15 ml of 80 percent isopropanol (IPA) into the midjet bubbler or into a graduated impinger bottle. Do not use the pipette or graduated cylinder that was used to add the hydrogen peroxide solution without cleaning. Pipettes or graduated cylinders should be marked for use of H₂O₂ or IPA to minimize any possibility of introducing hydrogen peroxide into the isopropanol. The accuracy of a pipette is not required but may be used for convenience.

2. Add 15 ml of 3 percent hydrogen peroxide to each of the two midjet impingers (100 ml of 30 percent H₂O₂ to 1 liter with water).

3. Pack glass wool into the top of the first midjet bubbler to prevent sulfuric acid mist from entering the midjet impingers and causing a high bias for SO₂.

4. Add about 25 g of Drierite to the last midget bubbler.
5. Calibrate the balance by initially placing a CO₂ absorber or midget impinger on the balance and recording the weight. Then add a 5 g or 10 g Class S weight. The difference must be accurate to within 0.05 g. (Calibrate only once a day.)
6. Weigh each impinger and bubbler, including contents, to the nearest 0.1 g, and record the data on the sample recovery and integrity form (Figure 4.3).
7. With one end of the CO₂ absorber sealed, place glass wool in the cylinder to a depth of about 1 cm. Place about 150 g of Ascarite II in the cylinder on top of the glass wool, and fill the remaining space in the cylinder with glass wool. Assemble the cylinder as shown in Figure 4.4. With the cylinder in a horizontal position, rotate it around the horizontal axis. The CO₂ absorbing material should remain in position during the rotation, and no open spaces or channels should be formed. If necessary, pack more glass wool into the cylinder to make the CO₂ absorbing material stable. Clean the outside of the cylinder of loose dirt and moisture, and weigh at room temperature to the nearest 0.1 g. Record this initial mass on the data form (Figure 4.3). It is strongly recommended that a second, smaller CO₂ absorber containing Ascarite or Ascarite II be added in line downstream of the primary CO₂ absorber as a breakthrough indicator. Ascarite II turns white when CO₂ is absorbed. The CO₂ absorber may be pre-packed.

For Method 6B

1. The first midget bubbler remains empty or dry. It is also advisable to break off the stem to prevent the solutions from backing up into the probe.
2. Add 15 ml of >6 percent hydrogen peroxide to each of the two midget impingers (250 ml of 30 percent H₂O₂ to 1 liter with distilled water).
3. Add about 25 g of Drierite to the last bubbler or more to a cylinder.
4. Weigh each impinger or bubbler including contents, to the nearest 0.1 g and record the data on the sample data form (Figure 4.2). Note: If large impingers are used more solution should be added and more Drierite used.
5. With one end of the CO₂ absorber sealed, place glass wool in the cylinder to a depth of about 1 cm. Place about 150 g of Ascarite II in the cylinder on top of the glass wool, and fill the remaining space in the cylinder with glass wool. Assemble

	1st bubbler	2nd impinger	3rd impinger	4th bubbler
Final wt	<u>89.9</u> g	<u>90.8</u> g	<u>88.4</u> g	<u>97.6</u> g
Initial wt	<u>90.2</u> g	<u>88.2</u> g	<u>87.9</u> g	<u>97.1</u> g
Net wt	<u>-0.3</u> g	<u>2.6</u> g	<u>0.5</u> g	<u>0.5</u> g
Total moisture	<u>3.3</u> g		<u>10</u>	% spent

Ascarite column: Final wt 304.7 g
Initial wt 300.1 g
Net wt 4.6 g of CO₂
30 % spent

Recovered Sample

H ₂ O ₂ blank container no. <u>AP-1AB</u>	Liquid level marked <u>✓</u>
Impinger contents container no. <u>AP-1</u>	Liquid level marked <u>✓</u>
H ₂ O blank container no. <u>AP-1WB</u>	Liquid level marked <u>✓</u>
Samples stored and locked <u>✓</u>	
Remarks _____	
Received by <u>Souza Engle</u>	Date <u>12/21/85</u>
Remarks _____	

Figure 4.3. Method 6A sample recovery and integrity data form.

the cylinder as shown in Figure 4.4. With the cylinder in a horizontal position, rotate it around the horizontal axis. The CO₂ absorbing material should remain in position during the rotation, and no open spaces or channels should be formed. If necessary, pack more glass wool into the cylinder to make the CO₂ absorbing material stable. Clean the outside of the cylinder of loose dirt and moisture, and weigh at room temperature to the nearest 0.1 g. Record this initial mass on the data form (Figure 4.2). If Method 6B is to be operated in a low sample flow condition (less than 100 ml/min), molecular sieve material may be substituted for Ascarite II as the CO₂ absorbing material; however, 250 g of sieve material should be used and it must have been regenerated prior to use. The recommended molecular sieve material is Union Carbide 1/16 inch pellets, 5Å, or equivalent. Molecular sieve material need not be discarded following the sampling run provided it is regenerated. Use of molecular sieve material at flow rates higher than 100 ml/min may cause erroneous CO₂ results. It is recommended that a second, smaller CO₂ absorber containing Ascarite II be added in line downstream of the primary CO₂ absorber as a breakthrough indicator. Ascarite II turns white when CO₂ is absorbed. The CO₂ absorber may be pre-packed, however molecular sieve must be weighed the day of testing.

4.3.2 Assembling the Sampling Train - After assembling the sampling train as shown in Figure 1.1, perform the following:

1. Ensure that the CO₂ absorber is mounted in a vertical position with the entrance at the bottom to prevent channeling of gases.

2. Adjust probe heater to operating temperature. Place crushed ice and water around the impingers and bubblers.

3. Leak check the sampling train just prior to use at the sampling site (not mandatory) by temporarily attaching a rotameter (capacity of 0 to 40 ml/min) to the outlet of the dry gas meter and placing a vacuum gauge at or near the probe inlet. Plug the probe inlet, pull a vacuum of at least 250 mm (10 in.) Hg, and note the flow rate indicated by the rotameter. A leakage rate <2 percent of the average sampling rate is acceptable. The Method 6B constant rate low flow sampling train (20 to 40 ml/min) will be checked by placing a U-tube water manometer at or near the probe inlet. A vacuum of at least 20 in. H₂O should be pulled; the sample valve should be shut and then the pump should be turned off. The system must not lose more than 0.25 in. vacuum in 2 minutes. Note: Carefully release the probe inlet plug before turning off the pump. Observe the impingers during the leak check to ensure that none of the solution is transferred to another impinger and that the glass wool (if applicable) is not wetted. If this occurs, the impinger section of the train

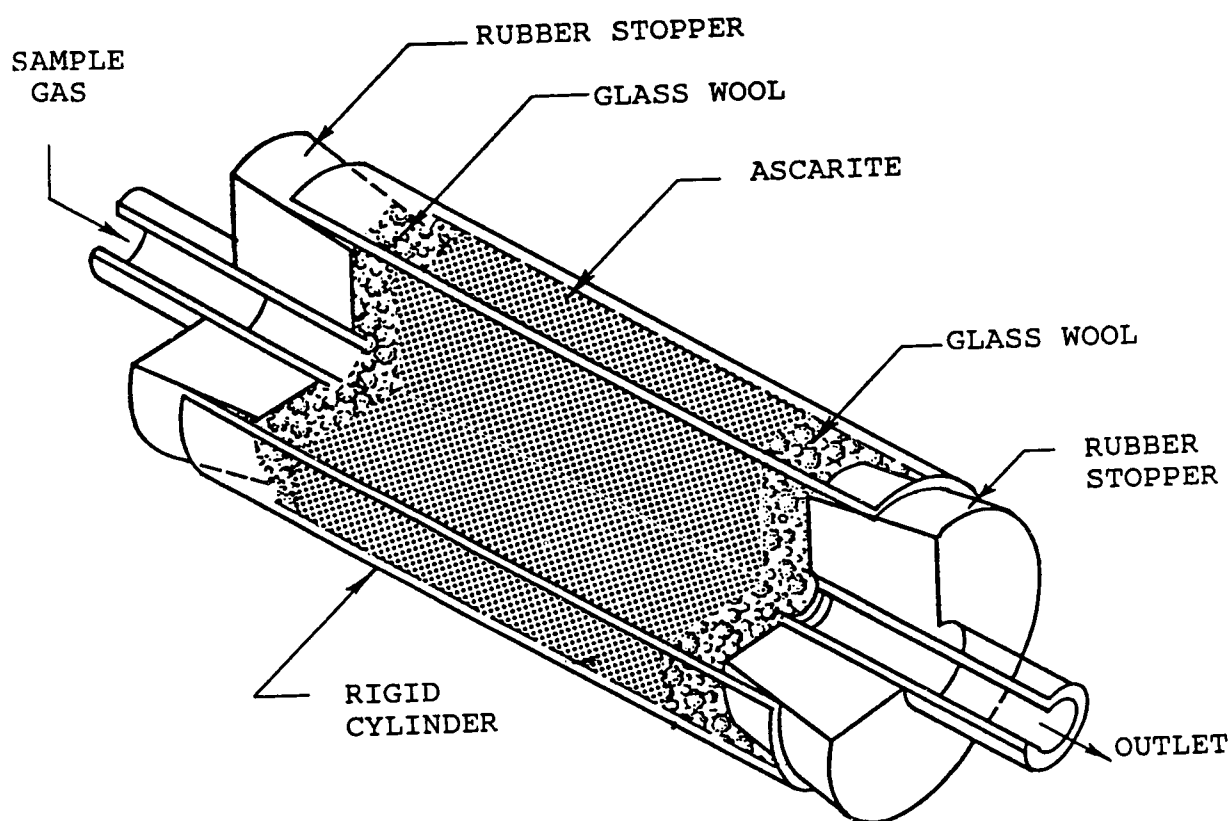


Figure 4.4. CO₂ absorber.

must be prepared again. It is suggested (but not mandatory) that the pump be leak checked separately, either prior to or after the sampling run. If prior to the run, the pump leak check shall follow the train leak check. To leak check the pump, proceed as follows. Place a vacuum gauge at the inlet to the pump. Pull a vacuum of 250 mm (10 in.) Hg. Plug or pinch off the outlet of the flow meter, and then turn off the pump. The vacuum should remain stable for at least 30 seconds.

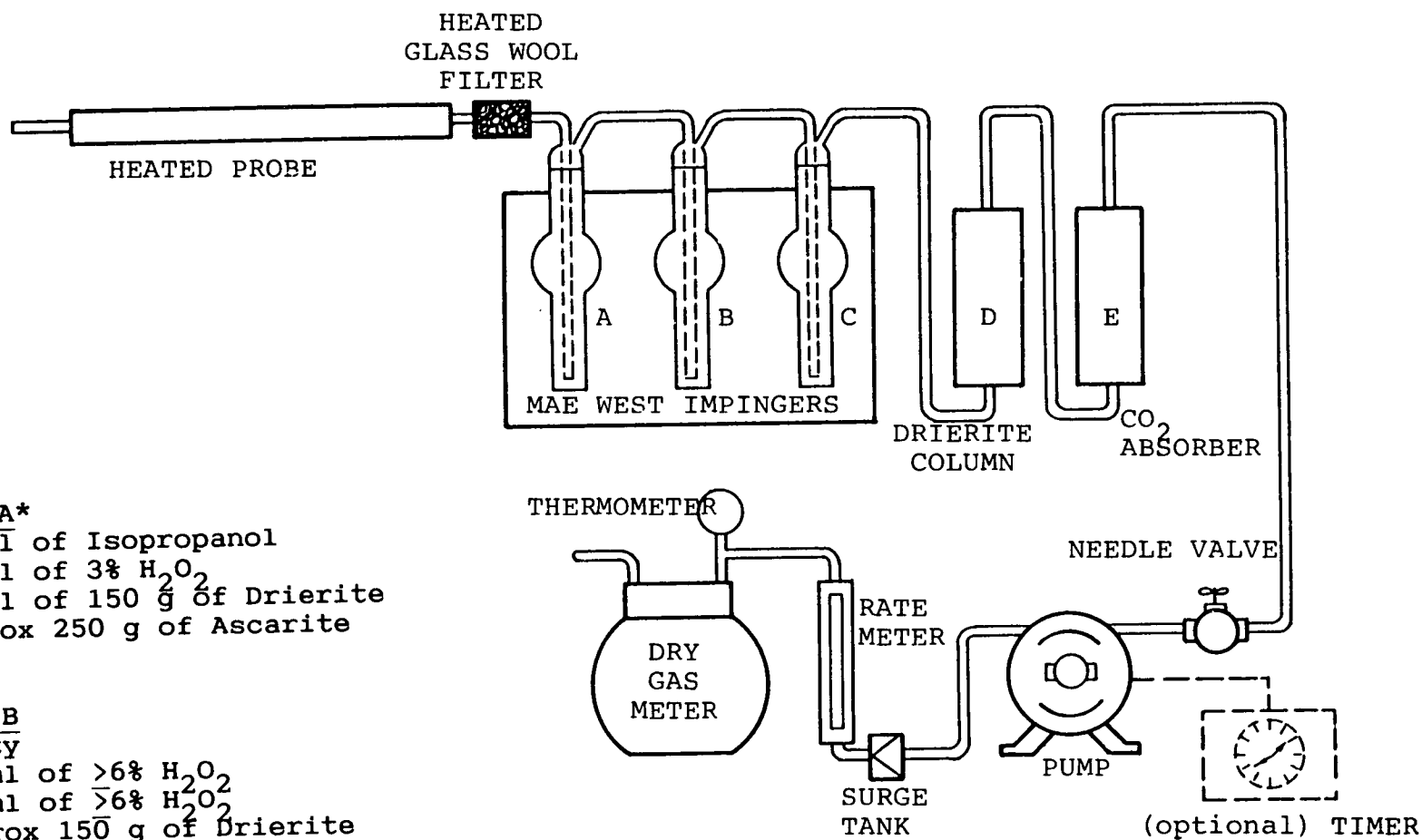
4. Place a loosely packed filter of glass wool in the end of the probe, and connect the probe to the bubbler. Alternately, if the out-of-stack filter is used, it should be packed prior to attaching the probe filter assembly to the bubbler.

5. Other sampling equipment, such as Mae West bubblers and rigid cylinders for moisture absorption, which requires sample or reagent volumes other than those specified in this procedure for full effectiveness, may be used subject to the approval of the Administrator. An example of an alternative sampling train used successfully in the collaborative testing program is shown in Figure 4.5.

4.3.3 Sampling - For Method 6A, the sampling shall be conducted at a constant rate of approximately 1.0 L/min. For Method 6B, the sampling shall be conducted either (1) intermittently with at least 12 equal flows (approximately 1.0 L/min), evenly spaced sampling collections of between 2 to 4 minutes over a 24-hour period, or (2) continuously at a rate of between 20 to 40 ml/min for the 24-hour period. The intermittent Method 6B sampling method is the recommended system for Method 6B testing because it uses Method 6 sampling components. The detailed procedures for each method are described below.

Note: For applications downstream of wet scrubbers, a heated out-of-stack filter (either borosilicate glass wool or glass fiber mat) is necessary. The filter may be a separate heated unit or may be within the heated portion of the probe. If the filter is within the sampling probe, the filter should not be within 15 cm of the probe inlet or any unheated section of the probe, such as the connection to the first SO₂ absorber. The probe and filter should be heated to at least 20° C above the source temperature, but not greater than 120° C. The filter temperature (i.e., the sample gas temperature) should be monitored to assure the desired temperature is maintained. A heated Teflon connector may be used to connect the filter holder or probe to the first impinger.

Constant Rate Sampling for Method 6A - Sampling is performed at a constant rate of approximately 1.0 L/min as indicated by the rotameter during the entire sampling run. The procedure is as follows:



Method 6A*

- A - 15 ml of Isopropanol
- B - 15 ml of 3% H₂O₂
- C - 15 ml of 150 g of Drierite
- E - approx 250 g of Ascarite

Method 6B

- A - Empty
- B - 15 ml of >6% H₂O₂
- C - 15 ml of >6% H₂O₂
- D - approx 150 g of Drierite
- E - approx 150 g of Ascarite

* This Method 6A train was not used during collaborative testing.

Figure 4.5. Alternative sampling train.

1. Place crushed ice and water around the impingers.
2. Record the initial dry gas meter readings, barometer reading, and other data as indicated in Figure 4.1. Double check the dry gas meter reading and check the midjet bubbler to be sure that no hydrogen peroxide has been allowed to siphon back and wet the glass wool.
3. Position the tip of the probe at the sampling point, connect the probe to the bubbler, and start the pump. Warning: If the stack is under a negative pressure of >50 mm (2 in.) H_2O vacuum, the probe should be positioned at the sampling point, the sample pump started prior to probe connection, and then the probe immediately connected to the impinger to prevent the impinger solutions from being siphoned backwards and contaminating the isopropanol and glass wool. Alternatively, the first impinger stem may be broken off and/or a check valve placed in the system.
4. Adjust the sample flow to a constant rate of approximately 1.0 L/min as indicated by the rotameter.
5. Maintain this constant rate within 10 percent during the entire sampling run, and take readings (dry gas meter; rate meter; and temperatures at the dry gas meter and the CO_2 absorber outlet) at least every 5 minutes. Add more ice during the run to keep the temperature of the gases leaving the last impinger at $20^{\circ}C$ ($68^{\circ}F$) or less. Salt may be added to the ice bath to further reduce the temperature.
6. Refer to emission standards for minimum sampling time and/or volume. (For example, the Federal standard for fossil fuel-fired steam generators specifies a minimum sampling time of 20 minutes and a minimum sampling volume of 20 liters corrected to standard conditions.) The total sample volume at meter conditions should be approximately 28 liters (1 ft^3). Make a quick calculation near the end of the run to guarantee that sufficient sample volume has been drawn; if the volume is insufficient, sample for an additional 5 minutes.
7. Turn off the pump at the conclusion of each run, remove probe from the stack, and record the final readings. Warning: Again, if the stack is under a negative pressure, disconnect the probe first, and turn off the pump immediately thereafter or have the first impinger modified and a check valve added.
8. Conduct a leak check, as described in Subsection 4.3.2 (mandatory).
9. If the train passes the leak check, drain the ice bath and purge the remainder of the train by drawing clean ambient air through the system for 15 minutes at the sampling rate. To

provide clean ambient air, pass air through a charcoal filter or through an extra midget impinger containing 15 ml of 3 percent H_2O_2 . The tester may opt to use ambient air without purification or to use only a filter. Note: It is important to drain or remove the ice and water to allow the isopropanol to warm.

10. If the train fails the leak check, either void the run or use an alternative procedure acceptable to the Administrator to adjust the sample volume for leakage. An alternative procedure that may be acceptable to the Administrator is described at the end of this subsection.

11. Calculate the sampling rate during the purging of the sample. The sample volume (V_m) for each point should be within 10 percent of the average sample volume for all points. If the average of all points is within the specified limit, the sample rate is acceptable. Noncompliance with the ± 10 percent of constant rate for a single sample should not have a significant effect on the final results of the test for noncyclic processes. However, the Administrator should be consulted as to the acceptability of the sample collection run results.

12. Change the particulate filter (glass-wool plug) at the end of each test since particulate buildup on the probe filter may result in a loss of SO_2 due to reactions with particulate matter.

Intermittent Sampling for Method 6B - Sampling is performed at a rate of approximately 1.0 L/min as indicated by the rotameter. It is conducted for 12 equally spaced intervals; the sample collection periods are 2 to 4 minutes in length. The Method 6B sample train has the same sample train components as the Method 6A sample train with the exception of an addition of an industrial timer switch, designed 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. At a minimum, the sample operation should include at least 12 equal, evenly spaced periods of sampling per 24 hours and, for the amount of sampling reagents prescribed in this Method, the total sample volume collected should be between 25 and 60 liters. The sample procedure is as follows:

1. Add cold water to the container holding the impingers until the impingers and bubblers are covered on at least two-thirds of their length. The impingers, bubbler, and their container 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.

2. Record the initial dry gas meter readings, probe/filter temperatures, and other data as indicated in Figure 4.2. Double check the dry gas meter reading and ensure the impinger and bubbler container has the proper amount of cold water and is protected from extreme heat or cold.

3. Position the tip of the probe at the sampling point, connect the probe to the bubbler, and turn on the time and start the pump. Warning: If the stack is under a negative pressure of >50 mm (2 in.) H_2O , the probe should be positioned at the sampling point, the sample pump turned on, and then the probe immediately connected to the impinger to prevent the impinger solutions from being siphoned backwards and contaminating the system. The first impinger must be modified by breaking off the stem and adding a check valve.

4. Adjust the sample flow to a constant rate of approximately 1.0 L/min as indicated by the rotameter.

5. Observe the sample train operations until the conclusion of the first 2- to 4-minute sample collection period. Determine the volume of sample collected and make a quick calculation to ensure that the volume from the given number of equal, evenly spaced sample collection periods will be within the specified sample volume (i.e., 25 to 60 liters).

6. During the 24-hour sampling period, record the dry gas meter temperature and barometric pressure one time between 9:00 a.m. and 11:00 a.m.

7. At the conclusion of the 24-hour period, turn off the timer and the sample pump, remove the probe from the stack, and record the final gas meter volume reading, the probe/filter temperature and rotameter setting.

8. Conduct a leak check as described in Subsection 4.3.2. If a leak is found, void the test run or use procedures acceptable to the Administrator to adjust the sample volume for leakage. An alternative procedure that may be acceptable to the Administrator is included at the end of this Subsection.

9. Check the final probe temperature, filter temperature, and total sample volume to ensure that all systems are still working properly.

10. For scrubbed units change the filter material prior to the next sample run to ensure that the collected materials do not scrub the SO_2 . For unscrubbed units change the filter weekly.

11. To conduct the next sample run repeat all the above steps.

Note: Method 6B does not require a purge at the completion of the sample run since the train does not include isopropanol.

Constant Rate Sampling for Method 6B - Sampling is performed at a constant rate of between 20 to 40 ml/min as indicated by the rotameter during the entire sampling run. Lower flow rates and longer sampling intervals have been more successful for some applications. The procedure is as follows:

1. Add cold water to the container holding the impingers until the impingers and bubblers are covered on at least two-thirds of their length. The impingers and bubbler, and their container, 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.

2. Record the initial dry gas meter readings, probe/filter temperature, and other data as indicated in Figure 4.2. Double check the dry gas meter reading and ensure the impinger and bubbler container has the proper amount of cold water and is protected from extreme heat or cold.

3. Position the tip of the probe at the sampling point, connect the probe to the bubbler, and start the pump. Warning: If the stack is under a negative pressure of >50 mm (2 in.) H_2O , the probe should be positioned at the sampling point, the sample pump turned on, and then the probe immediately connected to the impinger to prevent the impinger solutions from being siphoned backwards and contaminating the system. The system may be modified as mentioned above.

4. Adjust the sample flow to a constant rate of between 20 and 40 ml/min as indicated by the rotameter. Maintain this constant rate during the entire test.

5. During the 24-hour sampling period, record the dry gas meter temperature and the barometric pressure one time between 9:00 a.m. and 11:00 a.m.

6. At the conclusion of the 24-hour period, record the rotameter setting, turn off the pump, remove the probe from the stack and record the final gas meter volume reading and the probe/filter temperatures. Warning: Again, if the stack is under a negative pressure, disconnect the probe first, and turn off the pump immediately thereafter.

7. Conduct a leak check in the following manner. Attach a U-tube water manometer to the inlet to the probe. Turn on the pump and pull a vacuum of 20 in. H_2O . After the vacuum has stabilized, shut off the main sample valve and then the pump. The leakage rate must be less than 0.25 in. over a 2-minute

period. If the leakage rate is in excess of 0.25 in. H₂O, void the test run or use procedures acceptable to the Administrator to adjust the sample volume. An alternative procedure that may be acceptable to the Administrator is included at the end of this Subsection.

8. Check the final probe temperature, filter temperature and total sample volume to ensure that all systems were functioning properly.

9. For scrubbed units change the filter material prior to the next sample run to ensure that the collected material does not scrub the SO₂. For nonscrubbed units change the filter weekly.

10. To conduct the next sample run repeat all the above steps.

Note: Method 6B does not require a sample purge at the completion of the sample run since the train does not include isopropanol.

Alternative Leak Check Procedure for Unacceptable Leak Rates-
The leak check procedure for Method 6A and intermittent Method 6B require that a vacuum gauge be placed at the probe inlet, a 10 in. Hg vacuum be pulled on the system (as read on the vacuum gauge), and that the leak rate be checked with a more sensitive rotameter (0 - 40 ml/min). This system provides a quick indication when the leak rate is over 4 percent (the rotameter ball will be pegged). It provides the actual value when the leak rate is under 4 percent. Thus, these procedures and equipment as specified do not quantify the leakage rate greater than 4 percent.

In an effort to retain and make useful the maximum amount of emissions data possible, the following alternative may be acceptable to the Administrator when an unacceptable leak rate is detected for the Method 6A and intermittent Method 6B trains. This alternative procedure should be approved by the Administrator prior to its use.

When an unacceptable post test leak check is detected the following procedure may be used to compensate for the leak rate (for Method 6A and intermittent Method 6B). This procedure assumes that the leak occurred for the duration of the test run and may bias the results high.

1. After the sample train leakage rate is found to be unacceptable at 10 in. Hg, release the vacuum in the proper manner and shut-off the sampling train.

2. If the emissions results are to be calculated in terms of ppm SO₂ or lb SO₂/million Btu without using the results of CO₂ collected by the sampling train, the vacuum gauge must be left on the inlet to the probe. However, if the emissions results are to be calculated in terms of lb SO₂ per million Btu using the grams of CO₂ collected in the sampling train, the vacuum gauge may be placed on the inlet to the first impinger of H₂O₂. Alternatively, the gauge may be left at the probe inlet; however, the leakage correction may then compensate for leakage rates that do not affect the results in terms of lb SO₂/million Btu.

3. Turn on the pump, and pull a vacuum of 2 in. Hg as shown by the vacuum gauge.

4. After the vacuum stabilizes determine the leak rate by measuring the volume on the dry gas meter for at least 2 minutes.

5. The leak rate will be used to compensate only for the mass of SO₂ in comparison to the CO₂ as shown in the equation below.

Equation 4-1

$$M_{SO_2(\text{corrected})} = M_{(SO_2)} \frac{\text{Sampling Rate}}{\text{Sampling Rate} - \text{Leak Rate}}$$

where

$M_{SO_2(\text{corrected})}$ = mass of SO₂ corrected to compensate for leakage rate;

M_{SO_2} = mass of SO₂ determined for sample analysis;

Sampling Rate = Sample volume divided by the sample time (continuous sample methods), for the intermittent method use 1.0 L/min; and

Leak Rate = leak rate determined by this alternative procedure (metered leak volume divided by the time checked).

When an unacceptable posttest leak check is detected for the constant rate Method 6B train, the following procedure may be used to compensate for the leak rate:

1. After the sampling train leakage rate is found to be unacceptable at 10 in. of H₂O, release the vacuum in the proper manner and shut off the sampling train.

2. If the emission results are to be calculated in terms of ppm SO₂ or lb SO₂/million Btu without using the results of CO₂ collected by the sampling train, the U-tube manometer must be left on the inlet to the probe. However, if the emission results are to be calculated in terms of lb SO₂/million Btu using the grams of CO₂ collected in the sampling train, the U-tube manometer may be placed on the inlet to the first impinger of H₂O₂. Alternatively, the manometer may be left at the probe inlet; however, the leakage correction may then compensate for leakage rates that do not affect the results in terms of lb SO₂/million Btu.

3. Attach a 10-ml graduated pipette with a "T" and a bulb with soap solution to the outlet of the dry gas meter.

4. Turn on the pump and pull a vacuum of 20 in. of H₂O as shown by the manometer.

5. After the vacuum stabilizes, start a bubble up the pipette.

6. Time the movement of the bubble over at least 1.0 ml of the pipette with a stop watch. Use the integer markings of the pipette.

7. The leakage rate will be determined by dividing the volume by the time.

8. Use Equation 4-1 to determine the correction for the determined leakage rate.

4.4 Sample Recovery

The Reference Method requires the weighing and transfer of the impinger contents and the connector washings to a polyethylene storage container. This weighing and transfer should be done in the "laboratory" area to prevent contamination of the test sample.

After completing the leak check (for Method 6B) or the purge (for Method 6A), disconnect the impingers and transport them to the cleanup area. The contents of the midget bubbler (contains isopropanol for Method 6A only) may be discarded after the weight is determined. However, it is usually advisable to retain this fraction until analysis is performed on the H₂O₂. Analysis of the isopropanol may be useful in detecting cleanup or sampling errors. Cap off the midget impinger section with the use of polyethylene or equivalent caps before transport to the cleanup area.

The sample should be recovered as follows:

1. Allow the impingers and CO₂ absorber to come to room temperature ($\approx 20^{\circ}\text{C}$), which should take approximately 10 minutes.

2. If the balance has not been calibrated or has been moved within the past 24 hours, calibrate it as described in Subsection 4.3.1 prior to the weighing of the samples.

3. Wipe the outside of the bubblers, impingers, and CO₂ absorber.

4. Weigh the bubblers, the impingers, and CO₂ absorber separately, and record their weights to the nearest 0.1 g on the proper data sheet (Figure 4.3 for Method 6A and Figure 4.2 for Method 6B).

5. Method 6A - Transfer the contents of the two impingers containing solution to a labeled, leak-free, polyethylene sample bottle. Wash the impingers and connection glassware with three 15 ml portions of water. Place the rinsings in the sample bottle. The contents of the midget bubbler may be discarded or saved for analysis if problems are detected in the subsequent analysis of SO₂.

Method 6B - Recover the sample contents from the midget bubbler and the two midget impingers containing solution. Rinse the bubbler, impingers, and connecting glassware with three 15 ml portions of water. The impinger contents and rinsings should be transferred to a labeled, leak-free polyethylene sample bottle.

Note: The total rinse and sample volume should be less than 100 ml; a 100-ml mark can be placed on the outside of the polyethylene sample bottle as a guide. Alternatively, if the sample recovery is conducted in the laboratory, the sample recovery may be conducted directly into a 100 ml volumetric flask.

Warning: It has been demonstrated that the contamination of the sample with Ascarite or Drierite will bias the results.

6. Place 100 ml of the absorbing reagent in a polyethylene bottle, and label it for use as a blank during sample analysis. An example sample label is shown in Figure 4.6.

7. Mark the liquid level on the outside of all sample bottles, and ensure that the caps are on tightly providing a leak-free container.

8. Discard the Ascarite and Drierite material.

4.5 Sample Logistics (Data) and Packing Equipment - The sampling and sample recovery procedures are followed until the required

Plant	<u>Acme Power</u>	City	<u>Any where</u>
Site	<u>Boiler No. 3 Outlet</u>	Sample Type	<u>SO₂/CO₂</u>
Date	<u>10-10-85</u>	Run Number	<u>AP-1</u>
Front rinse	<input type="checkbox"/>	Front filter	<input type="checkbox"/>
Front solution	<input checked="" type="checkbox"/>		
Back rinse	<input type="checkbox"/>	Back filter	<input type="checkbox"/>
Back solution	<input type="checkbox"/>		
Solution	<u><100 ml</u>	Level marked	<input checked="" type="checkbox"/>
Volume: Initial	<u>30</u>	Final	
Cleanup by	<u>RRS</u>		

Remarks

Figure 4.6. Example of a sample label.

number of runs are completed. Log all data on the Sample and Sample Recovery Data Form, Figure 4.3 (Method 6A) and Figure 4.2 (Method 6B). If the bubbler, impingers, and connectors are to be used in the next test, they should be rinsed with distilled water, and the bubbler should be rerinsed with isopropanol (for Method 6A only). A new or recharged CO₂ absorber column should be inserted into the sampling train. At the completion of the test:

1. Check all sample containers for proper labeling (time, date, location, number of test, and any pertinent documentation). Be sure that a blank has been taken.
2. If data is to be removed from the source area, record all data collected during the field test in duplicate by using data forms and a field laboratory notebook. One set of data should be mailed to the base laboratory, and one given to another team member or to the Agency. Hand carrying the other set (not mandatory) can prevent a very costly and embarrassing mistake.
3. Examine all sample containers and sampling equipment for damage, and pack them for shipment to the base laboratory, being careful to label all shipping containers to prevent loss of samples or equipment.
4. Make a check of the sampling and sample recovery procedures using the data form, Figure 4.7 (Method 6A) or Figure 4.8 (Method 6B).

Sampling

Bubbler and impinger contents properly selected, measured, and placed in proper receptacle?* ✓

Impinger Contents/Parameters

1st: 15 ml of 80 percent isopropanol ✓
2nd: 15 ml of 3 percent H_2O_2 * ✓
3rd: 15 ml of 3 percent H_2O_2 * ✓
4th: approx. 25 g of Drierite* ✓
150 g of Ascarite in CO_2 absorber?* ✓
Probe heat at proper level? ✓
Crushed ice around impingers? ✓
Pretest leak check at 250 mm (10 in.) Hg? ✓
Leakage rate? 0.0 cc/min
Probe placed at proper sampling point? ✓
Flow rate constant at approximately 1.0 L/min?* ✓
Posttest leak check at 250 mm (10 in.) Hg?* ✓
Leakage rate? 15 cc/min

Sample Recovery

Balance calibrated with Class S weights?* ✓
Impingers cleaned and weighed to ± 0.1 g at room temp? ✓
Contents of impingers and rinsings placed in polyethylene bottles? ✓
Fluid level marked?* ✓
 CO_2 absorber cleaned and weighed to ± 0.1 g at room temp?* ✓
Sample containers sealed and identified? ✓
Samples properly stored and locked? ✓

*Most significant items/parameters to be checked.

Figure 4.7. On-Site measurements for Method 6A.

Sampling

Impinger contents properly selected, measured, and placed in
impingers? _____ ✓

Impinger Contents/Parameters

1st: Empty* _____ ✓
2nd: 15 ml of ≥ 6 percent H_2O_2 * _____ ✓
3rd: 15 ml of ≥ 6 percent H_2O_2 * _____ ✓
4th: Approx. 25 g of Drierite* _____ ✓
Approx. 150 g of Ascarite II or 250 g 5A molecular sieve
(continuous flow rate train only) in CO_2 absorber?* _____ ✓
Probe heat at proper level? _____ ✓
Crushed ice around impingers? _____ ✓
Pretest leak check at 250 mm (10 in.) Hg? _____ ✓
Leakage rate? _____ 0.0 cc/min
Probe placed at proper sampling point? _____ ✓
Flow rate intermittent at approximately 1.0 L/min?* _____ ✓
Flow rate constant between 20 to 40 ml/min? _____ N/A
Posttest leak check at 250 mm (10 in.) Hg?* _____ ✓
Leakage rate? _____ 0.0 cc/min

Sample Recovery

Balance calibrated with Class S weights?* _____ ✓
Impingers cleaned and weighed to ± 0.1 g at room temp? _____ ✓
Contents of impingers and rinsings placed in polyethylene
bottles? _____ ✓
Fluid level marked?* _____ ✓
 CO_2 absorber cleaned and weighed to ± 0.1 g at room temp?* _____ ✓
Sample containers sealed and identified?* _____ ✓
Samples properly stored and locked?* _____ ✓

*Most significant items/parameters to be checked.

Figure 4.8. On-Site measurements for Method 6B.

Table 4.1. ACTIVITY MATRIX FOR ON-SITE MEASUREMENT CHECKS

Operation	Acceptance limits	Frequency and method of measurement	Action if requirements are not met
Preparation and/or addition of absorbing reagents	<p>Method 6A. Add 15 ml 80% isopropanol to first midget bubbler, 15 ml of 3% H_2O_2 to two midget impingers, approx 25 g of Drierite to the last bubbler, and 150 g of Ascarite to column</p> <p>Method 6B. Leave first bubbler empty, add 15 ml of >6% H_2O_2 to the two midget impingers, approximately 25 g of Drierite to the last midget bubbler, and 150 g of Ascarite to column</p>	<p>Prepare 3% H_2O_2 fresh daily; use pipette or graduated cylinder to add solutions</p> <p>Prepare >6% H_2O_2 fresh daily; use pipette or graduated cylinder to add solutions</p>	<p>Reassemble collection system</p> <p>Reassemble collection system</p>
Assembling the sampling train	<p>1. Assemble to specifications in Fig. 1.1</p> <p>2. A leakage rate <2% of the average sampling rate</p>	<p>1. Before each sampling</p> <p>2. Leak check before sampling (recommended) by attaching a rotameter to dry gas meter outlet, placing a vacuum gauge at or near probe inlet, and pulling a vacuum of >250 mm (10 in.) Hg</p>	<p>1. Reassemble</p> <p>2. Correct the leak</p>
Sampling (Method 6A constant rate)	<p>1. Method 6A Within 10% of a constant rate</p>	<p>1. Calculate % deviation for each sample using equation in Fig. 4.1</p>	<p>1. Repeat the sampling, or obtain acceptance from a representative of the Administrator</p>

(continued)

Table 4.1. (continued)

Operation	Acceptance limits	Frequency and method of measurement	Action if requirements are not met
	<p>2. Minimum acceptable time is 20 min and volume is 20 liters corrected to STP or as specified by regulation</p> <p>3. Less than 2% leakage rate at 250 mm (10 in.) Hg</p> <p>4. Purge remaining SO₂ from isopropanol</p>	<p>2. Make a quick calculation prior to completion and an exact calculation after completion</p> <p>3. Leak check after sample run (mandatory); use same procedure as above</p> <p>4. Drain ice, and purge 15 min with clean air at the sample rate</p>	<p>2. As above</p> <p>3. As above</p> <p>4. As above</p>
Sampling (Method 6B intermittent)	<p>1. At least 12 equally and evenly spaced intermittent sample intervals at about 1.0 L/min</p> <p>2. Sample time is 24 hours and the acceptable sample volume is between 25 and 60 liters</p> <p>3. Less than 2% leakage rate at 250 mm (10 in.) Hg</p>	<p>1. Check the volume of the first sample interval and the total volume should be within 10% of first sample volume times the number of intervals</p> <p>2. Make a calculation after each sample run</p> <p>3. Leak check after sample run (mandatory)</p>	<p>1. Repair or recalibrate time and/or rotameter and repeat the sampling or obtain acceptance from a representative of the Administrator</p> <p>2. As above</p> <p>3. Void the test, or use an alternative procedure acceptable to a representative of the Administrator</p>

(continued)

Table 4.1 (continued)

Operation	Acceptance limits	Frequency and method of measurement	Action if requirements are not met
Sampling (Method 6B rate constant)	<p>1. Sample at a constant rate of between 20 and 40 ml/min</p> <p>2. Sample time is 24 hours and the acceptable sample volume is between 25 and 60 liters</p> <p>3. Less than 2% leakage at 500 mm (20 in.) H₂O</p>	<p>1. Calculate sample rate at the completion of run</p> <p>2. Calculate sample volume at end of sample run</p> <p>3. Leak check after sample run (mandatory)</p>	<p>1. Repair or recalibrate rotameter, and repeat run or obtain acceptance from a representative of the Administrator</p> <p>2. As above</p> <p>3. Void the test, or use an alternative procedure acceptable to a representative of the Administrator</p>
Sample Recovery	<p>1. Balance accurate to within 0.1 g</p> <p>2. Determine moisture collected in impingers</p>	<p>1. Calibrate with Class S weights</p> <p>2. Wipe the outside of the impingers and bubblers clean, and weigh each to the nearest 0.1 g</p>	<p>1. Adjust, repair, or reject</p> <p>2. Repeat run, or use alternative moisture determination technique</p>

(continued)

Table 4.1. (continued)

Operation	Acceptance limits	Frequency and method of measurement	Action if requirements are not met
	3. Recover SO ₂ sample	3. Place contents of the two midget impingers and the rinsings in a marked polyethylene bottle (Method 6A); place contents of the two midget impingers, the first midget bubbler, and the rinsings in a marked polyethylene bottle (Method 6B)	3. Repeat run, or place contents and rinsings directly into the volumetric flask
	4. Determine CO ₂ absorber weight	4. Wipe clean the outside of the CO ₂ absorber, and weigh to the nearest 0.1 g	4. Repeat run, or weigh absorber again
Sample logistics (data) and packing	1. All data are recorded correctly	1. Visually check upon completion of each run and before packing	1. Complete the data form
	2. All equipment examined for damage and labeled for shipment	2. As above	2. Redo test if damage occurred during testing
	3. All sample containers properly labeled and packaged	3. Visually check upon completion of test	3. Correct when possible

5.0 POSTSAMPLING OPERATIONS

Table 5.1 at the end of this section summarizes the quality assurance activities for postsampling operations.

5.1 Apparatus Check

A posttest check--including a calibration check, the cleaning, and/or the performance of routine maintenance--should be made on most of the sampling apparatus. Cleaning and maintenance of the sampling apparatus are discussed in Section 3.13.7. Figure 5.1 should be used to record the posttest checks.

5.1.1 Metering System - The metering system has three components that must be checked: dry gas meter thermometer(s), dry gas meter, and rotameter.

The dry gas meter thermometer should be checked by comparison with the ASTM mercury-in-glass thermometer at room temperature. If the readings agree within 6°C (10.8°F), they are acceptable. When the readings are outside this limit, the thermometer must be recalibrated according to Section 3.13.2 after the posttest check of the dry gas meter. For calculations, the dry gas meter thermometer reading (field or recalibration) that would give the higher temperature is used. That is, if the field reading is higher, no correction of the data is necessary; if the recalibration value is higher, the difference in the two readings is added to the average dry gas meter temperature reading.

The posttest checks of the dry gas meter and rotameter are similar to the initial calibration, as described in Section 3.13.2, but they include the following exceptions:

1. The metering system should not have had any leaks corrected prior to the posttest check.
2. Three or more revolutions of the dry gas meter are sufficient.
3. Only two independent runs need be made. If the posttest dry gas meter calibration factor (Y) does not deviate by >5 percent from the initial calibration factor, the dry gas meter volumes obtained during the test series are acceptable. If it deviates by >5 percent, recalibrate the metering system as in Section 3.13.2 using the calibration factor (initial and recalibration) that yields the lower gas volume for each test run. The lesser calibration factor will give the lower gas volume.

The rotameter calibration factor (Y_r) can also be determined during the calibration of the dry gas meter. If Y_r does not

Meter Box Number E-6

Dry Gas Meter (If applicable)

Pretest calibration factor (Y) = 1.021
Posttest check (Y) = 1.033 (+5 percent of pretest factor)*
Recalibration required? yes ☒ no
If yes, recalibration factor (Y) = _____ (within 2 percent of calibration factor for each calibration run)
Lower calibration factor Y (pretest or posttest) = _____ for calculations

Rotameter

Pretest calibration factor (Y_r) = 1.1
Posttest check (Y_r) = 1.1 (within 10 percent of pretest factor)
Recalibration recommended? yes ☒ no
If performed, recalibration factor (Y_r) = _____
Was rotameter cleaned? yes ☐ no

Dry Gas Meter Thermometer (If applicable)

Was a pretest meter temperature correction used? yes ☒ no
If yes, temperature correction _____
Posttest recalibration required? yes ☒ no (recalibrated when Y_L recalibrated)

Barometer

Was pretest field barometer reading correct? ☒ yes ☐ no
Posttest recalibration required? yes ☒ no (recalibrated when Y_L recalibrated)

Balance*

Was the balance calibration acceptable? ☒ yes ☐ no
(+ 0.05 g checked against Class S weights)
If no, the balance should be repaired or replaced prior to weighing field samples.

* Most significant items/parameters to be checked.

Figure 5.1. Posttest sampling checks.

deviate by >10 percent from the initial calibration factor, the rotameter operation is acceptable. If Y_r changes by >10 percent, the rotameter should be cleaned and recalibrated. No corrections need be made for any calculations.

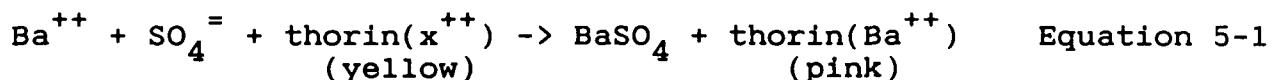
5.1.2 Barometer - The field barometer readings are acceptable if they agree within 5 mm (0.2 in.) Hg when compared with those of the mercury-in-glass barometer. When the comparison is not within this range, the lesser calibration value should be used for the calculations. If the field barometer reads lower than the mercury-in-glass barometer, the field data are acceptable; but if the mercury-in-glass barometer gives the lower reading, the barometric value adjusted for the difference in the two readings should be used in the calculation.

5.1.3 Balance - The balance should have been calibrated as described in Subsection 4.3.1.

5.2 Analysis (Laboratory)

The purpose of Method 6B is to provide an average daily emission rate for each 24-hour sample. These emission rates are used for decision making and determining rolling average compliance status. As a result, the values must be determined in a timely manner. It is therefore assumed that the Method 6B analyses are performed either on-site or within a reasonably short distance from the site. Both the analytical equipment and techniques lend themselves, when performed in a clean area by skilled technicians, to providing the necessary accuracy. A base laboratory is not required.

Calibrations and standardizations are of the utmost importance to a precise and accurate analysis. The analysis is based on the insolubility of barium sulfate (BaSO_4) and on the formation of the colored complex between excess barium ions and the thorin indicator, 1-(o-arsonophenylazo)-2-naphthol-3, 6-disulfonic acid, disodium salt. Aliquots from the impinger solution are analyzed by titration with barium perchlorate to the pink endpoint. The barium ions react preferentially with sulfate ions in solution to form a highly insoluble barium sulfate precipitate. When the barium has reacted with all of the sulfate ions, the excess barium then reacts with the thorin indicator to form a metallic salt of the indicator and to give a color change as shown in Equation 5-1.



Upon completion of each step of the standardization or of each sample analysis, the data should be entered on the proper

data form. At the conclusion of the sample analysis, the data form should be reviewed and signed by the laboratory person with direct responsibility for the sample.

5.2.1 Reagents (Standardization and Analysis) - The following reagents are required for the analysis of the samples:

Water - Deionized distilled water that conforms to ASTM specification D1193-74, Type 3 is required. At the option of the analyst, the KMnO_4 test for oxidizable organic matter may be omitted when high concentrations of organic matter are not expected. Note: The water must meet the ASTM specifications since sulfate ions and many other anions present in distilled water are not identified in the normal standardization of the acid by NaOH titration, which measures the hydrogen ion concentration rather than the sulfate ion concentration. This added sulfate concentration will result in an erroneous standardization of the barium perchlorate titration, which directly measures sulfate ion concentration and not hydrogen ion concentration. A check on the acceptability of the water is detailed in Subsection 5.13.4.

Isopropanol - 100 percent, ACS reagent grade is needed. Check for peroxide impurities as described in Section 3.13.1 (Method 6A).

Thorin indicator - Dissolve 0.20 \pm 0.002 g of 1-(o-arsonophenylazo)-2-naphthol-3,6-disulfonic acid, disodium salt, or the equivalent, in 100 ml of water. Measure the distilled water in the 100-ml graduated cylinder (Class A).

Sulfuric acid standard, 0.0100N - Either purchase manufacturer-guaranteed or standardize the H_2SO_4 to \pm 0.002N against 0.0100N NaOH that has been standardized against potassium acid phthalate (primary standard grade) as described in Subsection 5.13.3. The 0.01N H_2SO_4 may be prepared in the following manner:

- a. Prepare 0.5N H_2SO_4 by adding approximately 1500 ml of water to a 2-liter volumetric flask.
- b. Cautiously add 28 ml of concentrated sulfuric acid and mix.
- c. Cool if necessary.
- d. Dilute to 2-liters with water.
- e. Prepare 0.01N H_2SO_4 by first adding approximately 800 ml of distilled water to a 1-liter volumetric flask and then adding 20.0 ml of the 0.5N H_2SO_4 .
- f. Dilute to 1-liter with water and mix thoroughly.

Barium perchlorate solution 0.0100N - Dissolve 1.95 g of barium perchlorate trihydrate ($\text{Ba}(\text{ClO}_4)_2 \cdot 3\text{H}_2\text{O}$) in 200 ml of water, and dilute to 1-liter with isopropanol. Alternatively, 1.22 g of barium chloride dihydrate ($\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$) may be used instead of the perchlorate. Standardize, as in Subsection 5.13.4, with 0.0100N H_2SO_4 . Note: Protect the 0.0100N barium perchlorate solution from evaporation at all times by keeping the bottle capped between uses.

Note: It is recommended that 0.1N sulfuric acid be purchased. Pipette 10.0 ml of sulfuric acid (0.1N) into a 100-ml volumetric flask and dilute to volume with water that has been determined to be acceptable as detailed in Subsection 5.13.4. When the 0.0100N sulfuric acid is prepared in this manner, procedures in Subsections 5.13.2. and 5.13.3 may be omitted since the standardization of barium perchlorate will be validated with the control sample.

5.2.2 Standardization of Sodium Hydroxide - To standardize NaOH, proceed as follows:

1. Purchase a 50 percent w/w NaOH solution. Dilute 10 ml to 1-liter with water. Dilute 52.4 ml of the diluted solution to 1-liter with water.

2. Dry the primary standard grade potassium acid phthalate for 1 to 2 hours at 110°C (230°F), and cool in desiccator.

3. Weigh to the nearest 0.1 mg, three 40-mg portions of the phthalate. Dissolve each portion in 100 ml of freshly boiled water in a 250-ml Erlenmeyer flask.

4. Add two drops of phenolphthalein indicator, and titrate the phthalate solutions with the NaOH solution. Observe titrations against a white background to facilitate detection of the pink endpoint. The endpoint is the first faint pink color that persists for at least 30 seconds.

5. Compare the endpoint colors of the other two titrations against the first.

6. Titrate a blank of 100 ml of freshly boiled distilled water using the same technique as in step 4. (The normality is the average of the three values calculated using the following equation.)

$$N_{\text{NaOH}} = \frac{\text{mg KHP}}{(\text{ml Titrant} - \text{ml Blank}) \times (204.23)}$$

Equation 5-2

where

N_{NaOH} = calculated normality of sodium hydroxide,

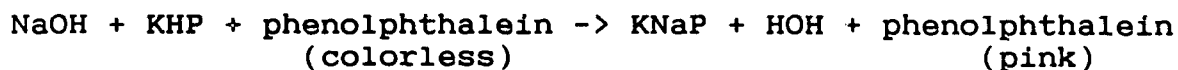
mg KHP = weight of the phthalate, mg,

ml Titrant = volume of sodium hydroxide titrant, and

ml Blank = volume of sodium hydroxide titrant for blank (ml).

The chemical reaction for this standardization is shown in Equation 5-3. The sodium hydroxide is added to the potassium hydrogen phthalate and colorless phenolphthalein solution until there is an excess of diluted hydroxyl ions which causes the phenolphthalein solution to change to a pink color.

Equation 5-3



5.2.3 Standardization of Sulfuric Acid - To standardize sulfuric acid, proceed as follows:

1. Pipette 25 ml of the H_2SO_4 into each of three 250-ml Erlenmeyer flasks.

2. Add 25 ml of water to each.

3. Add two drops of phenolphthalein indicator, and titrate with the standardized NaOH solution to a persistent pink endpoint, using a white background.

4. Titrate a blank of 25 ml of water, using the same technique as step 3. The normality will be the average of the three independent values calculated using the following equation:

$$N_{\text{H}_2\text{SO}_4} = \frac{(\text{ml NaOH}_{\text{acid}} - \text{ml NaOH}_{\text{blank}}) \times N_{\text{NaOH}}}{25} \quad \text{Equation 5-4}$$

where

$N_{\text{H}_2\text{SO}_4}$ = calculated normality of sulfuric acid,

ml $\text{NaOH}_{\text{acid}}$ = volume of titrant used for H_2SO_4 , ml,

ml $\text{NaOH}_{\text{blank}}$ = volume of titrant used for blank, ml, and

N_{NaOH} = normality of sodium hydroxide.

5.2.4 Standardization of Barium Perchlorate (0.01N) - To standardize barium perchlorate, proceed as follows:

1. Pipette 25 ml of sulfuric acid standard (0.0100N) into each of three 250-ml Erlenmeyer flasks.

2. Add 100 ml of reagent grade isopropanol and two to four drops of thorin indicator, and titrate to a pink endpoint using 0.0100 N barium perchlorate. Perform all thorin titrations against a white background to facilitate the detection of the pink endpoint color.

3. Prepare a blank by adding 100 ml of isopropanol to 25 ml of water. If a blank requires >0.5 ml of titrant, the analyst should determine the source of contamination. If the distilled water contains high concentrations of sulfate of other polyvalent anions, then all reagents made with the water will have to be remade using distilled water that is acceptable.

4. Use the endpoint of the blank or the endpoint of the first titration as a visual comparator for the succeeding titrations.

5. Record data on analytical data form, Figure 5.2. The normality of the barium perchlorate will be the average of the three independent values calculated using Equation 5-5.

$$N_{\text{Ba}(\text{ClO}_4)_2} = \frac{N_{\text{H}_2\text{SO}_4} \times 25}{(\text{ml Ba}(\text{ClO}_4)_2 - \text{ml Blank})} \quad \text{Equation 5-5}$$

where

$N_{\text{Ba}(\text{ClO}_4)_2}$ = calculated normality of barium perchlorate,

$N_{\text{H}_2\text{SO}_4}$ = normality of standardized sulfuric acid,

ml $\text{Ba}(\text{ClO}_4)_2$ = volume of barium perchlorate titrant, ml, and

ml Blank = volume of barium perchlorate titrant for blank, ml.

The chemical reaction for this standardization was shown in Equation 5-1. The standardized barium perchlorate should be protected from evaporation of the isopropanol at all times.

Note: It is suggested that the analyst unfamiliar with this titration carry out titrations on aliquots at low, medium, and high concentrations in the following manner:

1. Pipette 2.0-, 10.0-, and 20.0-ml aliquots of 0.0100N H_2SO_4 into three 250-ml Erlenmeyer flasks.

2. Dilute to 25 ml with distilled water.

Plant Acme Power Plant Date 8/12/85
Sample location Boiler No. 3 Analyst Kate Urquhart
Volume and normality of barium perchlorate 1 24.52 ml 0.01019 N
2 24.50 ml 0.01020 N
Standardization blank 0.0 ml (< 0.5 ml) 3 24.50 ml 0.01020 N
0.0102 N, avg

Sample number	Sample identification number	Total sample volume (V_{soln}), ml	Sample aliquot volume (V_a) ^a , ml	Volume of titrant (V_t) ^b , ml		
				1st titration	2nd titration	Average
1	AP-1	100	20	11.31	11.29	11.30
2						
3						
4						
5						
6						
Field Blank		N/A		0	0	$V_{\text{tb}} = 0$

^a Volume for the blank must be the same as that of the sample aliquot.

^b 1st titration = 0.99 to 1.01 or 1st titration - 2nd titration < 0.2 ml.
2nd titration

Signature of analyst Kate Urquhart

Signature of reviewer or supervisor Donna Eagle

Figure 5.2. Sulfur dioxide analytical data form.

3. Add a 100-ml volume of 100 percent isopropanol and two to four drops of thorin indicator to each.

4. Titrate with barium perchlorate to become familiar with the endpoint.

5.2.5 Control Samples - The accuracy and precision of the sample analysis should be checked. The accuracy of the analytical technique is determined by control samples. The precision is checked by duplicate analyses of both the control and the field samples. Acceptable accuracy and precision should be demonstrated on the analysis of the control sample prior to the analysis of the field samples.

The control sample should be prepared and analyzed in the following manner:

1. Dry the primary standard grade ammonium sulfate ($(\text{NH}_4)_2\text{SO}_4$) for 1 to 2 hours at 110°C (230°F), and cool in a desiccator.

2. Weigh to the nearest 0.5 mg, 1.3214 g of primary standard grade ammonium sulfate.

3. Dissolve the reagent in about 1800 ml of distilled water in a 2-liter volumetric flask.

4. Dilute to the 2-liter mark with distilled water. The resulting solution is 0.0100N ammonium sulfate.

5. Enter all data on the form shown in Figure 5.3.

6. Pipette 25 ml of the control sample into each of three 250-ml Erlenmeyer flasks, and pipette a 25-ml blank of distilled water into a fourth 250-ml Erlenmeyer flask. Note: Each control sample will contain 16.5 mg of ammonium sulfate.

7. Add 100 ml of reagent grade isopropanol to each flask and then two to four drops of thorin indicator.

8. Initially, titrate the blank to a faint pink endpoint using the standardized barium perchlorate. The blank must contain < 0.5 ml of titrant, or the water is unacceptable for use in this method.

9. Titrate two of the control samples with the standardized barium perchlorate to a faint pink endpoint using the blank endpoint as a guide. The endpoint is the first faint pink endpoint that persists for at least 30 seconds. All titrations should be done against a white background.

Plant Acme Power Plant Date analyzed 9/22/85
Analyst Kate Urquhart $N_{\text{Ba}(\text{ClO}_4)_2}$ 0.010N

Weight of ammonium sulfate is 1.3214 g? yes
Dissolved in 2 L of distilled water? yes
Titration of blank 0.0 ml $\text{Ba}(\text{ClO}_4)_2$ (must be <0.5 ml)

Control sample number	Time of analysis, 24 h	Titrant volume, ^a ml			
		1st	2nd	3rd	Avg
<u>1</u>	<u>0930</u>	<u>25.0</u>	<u>25.0</u>		<u>25.0</u>

^a Two titrant volumes must agree within 0.2 ml.

$$(\text{ml } \text{Ba}(\text{ClO}_4)_2 - \text{ml Blank}) \times N_{\text{Ba}(\text{ClO}_4)_2} = 25 \text{ ml} \times 0.01N$$

(control) (control)
sample) sample)

$$(\underline{25.0} \text{ ml} - \underline{0.0} \text{ ml}) \times \underline{0.010} N = \underline{0.250}$$

(must agree within 5%, i.e., 0.238 to 0.262)

Does value agree? ☒ yes ☐ no

Kate Urquhart

Signature of analyst

Donna Engle

Signature of reviewer

Figure 5.3. Control sample analytical data form.

10. If the titrant volumes from the first two control samples agree within 0.2 ml, the average of the two values can be used to complete the calculations shown in Figure 5.3. If not within 0.2 ml, titrate the third control sample. If the titration volume agrees within 0.2 ml of either of the first two samples, use the two titrant volumes that are consistent for the remaining calculations. If this criterion cannot be met with the first set of control samples, follow the same procedure on a second set of two control samples.

11. If the criterion cannot be met for the second set of control samples, the analyst should have the analytical techniques observed by a person knowledgeable in chemical analysis, or should have all reagents checked.

12. After consistent titrant volumes are obtained, calculate the analytical accuracy as shown in Figure 5.3. If the measured value is within 5 percent of the stated value, the technique and standard reactions are acceptable, and the field samples may be analyzed. When the 5 percent accuracy cannot be met, the barium perchlorate must be restandardized or the control sample must be checked until the accuracy criterion of the control sample analysis can be obtained.

13. The recommended frequency for analysis of control samples is the following:

- a. Analyze two control samples each analysis day immediately prior to analysis of the actual collected source samples.
- b. Analyze two control samples after the last collected source sample is analyzed each analysis day.

14. Enter results from the control sample analyses on Figure 5.3, and submit Figure 5.3 with the source test report as documentation of the quality of the source test analysis.

5.2.6 Sample Analysis - Check the level of liquid in the container to determine whether any sample was lost during shipment, and note this on the data form, Figure 4.3. Figure 5.4 can be used to check analytical procedures. If a noticeable amount of leakage has occurred, follow the alternative method described below. Approval should have been requested prior to testing in case of subsequent leakage. The alternative method is as follows:

1. Mark the new level of the sample.
2. Transfer the sample to a 100-ml volumetric (V_{soln}) flask, and dilute to exactly 100 ml with deionized distilled water.

Reagents

Normality of sulfuric acid standard* 0.0100 N
Date purchased 10/10/85 Date standardized 10/16/85
Normality of barium perchlorate titrant* 0.009614 N
Date standardized 9/16/85
Normality of control sample* 0.0100 N
Date prepared 10/16/85
Volume of burette 50 ml Graduations 0.1 ml

Sample Preparation

Has liquid level noticeably changed?* no
Original volume _____ Corrected volume _____
Samples diluted to 100 ml?* yes

Analysis

(Sulfur dioxide)

Volume of aliquot analyzed* 20 ml
Do replicate titrant volumes agree within 1% or 0.2 ml? yes
Number and normality of control samples analyzed 2 @ 0.100 N
Are replicate control samples within 0.2 ml? yes
Is accuracy of control sample analysis $\pm 5\%$?* yes
Is the relative error of audit sample(s) within acceptable limits?* yes

(Moisture and carbon dioxide)

Balance calibrated with Class S weights to within 0.05 g?*

yes
Initial weight of each impinger to nearest 0.1 g* yes
Final weight of each impinger to nearest 0.1 g* yes
Initial weight of CO₂ absorber to nearest 0.1 g* yes
Final weight of CO₂ absorber to nearest 0.1 g* yes

All data recorded? ✓ Reviewed by PM

*Most significant items/parameters to be checked.

Figure 5.4. Posttest operations.

6.0 CALCULATIONS

Calculation errors due to procedural or mathematical mistakes can be a part of total system error. Therefore, it is recommended that each set of calculations be repeated or spotchecked, preferably by a team member other than the one who performed the original calculations. If a difference greater than typical round-off error is detected, the calculations should be checked step-by-step until the source of error is found and corrected. A computer program is advantageous in reducing calculation errors. If a standardized computer program is used, the original data entry should be included in the printout to be checked; if differences are observed, a new computer run should be made. Table 6.1 at the end of this section summarizes the quality assurance activities for calculations.

Calculations should be carried out to at least one extra decimal figure beyond that of the acquired data and should be rounded off after final calculation to two significant digits for each run or sample. All rounding off of numbers should be performed in accordance with the ASTM 380-76 procedures. All calculations should then be recorded on a calculation form such as the ones in Figures 6.2A and 6.2B, at the end of this section.

6.1 Nomenclature

The following nomenclature is used in the calculations:

- C_{CO_2} = concentration of CO_2 , dry basis, percent,
- C_{SO_2} = concentration of sulfur dioxide, dry basis
corrected to standard conditions, mg/dscm (lb/dscf),
- C_w = concentration of moisture, percent,
- E_{SO_2} = emission rate of SO_2 , lb SO_2 /million Btu (ng/J),
- F_c = volume of CO_2 liberated per million Btu of
heat release, dscm (dscf),
- m_{wi} = initial mass of impingers, bubblers, and moisture
absorber, g,
- m_{wf} = final mass of impingers, bubblers, and moisture
absorber, g,
- m_{ai} = initial mass of CO_2 absorber, g,
- m_{af} = final mass of CO_2 absorber, g,
- m_{SO_2} = mass of SO_2 collected, mg,
- N = normality of barium perchlorate titrant, milliequi-
valents/ml,

P_{bar} = barometric pressure at the exit orifice of the dry gas meter, mm Hg (in. Hg),
 P_{std} = standard absolute pressure, 760 mm Hg (29.92 in. Hg),
 T_{m} = average dry gas meter absolute temperature, $^{\circ}\text{K}$ ($^{\circ}\text{R}$),
 T_{std} = standard absolute temperature, 293°K (528°R),
 V_{a} = volume of sample aliquot titrated, ml,
 $V_{\text{CO}_2(\text{std})}$ = standard equivalent volume of CO_2 collected, dry basis, m^3 ,
 V_{m} = dry gas volume measured by dry gas meter, dcm (dcf),
 $V_{\text{m}(\text{std})}$ = dry gas volume measured by dry gas meter, corrected to standard conditions, dscm (dscf),
 V_{soln} = total volume of solution in which the sulfur dioxide sample is contained, 100 ml,
 V_{i} = volume of barium perchlorate titrant used for the sample (average of replicate titrations), ml,
 V_{tb} = volume of barium perchlorate titrant used for the blank, ml,
 $V_{\text{w}(\text{std})}$ = volume of water at standard conditions, dscm (dscf),
 Y = dry gas meter calibration factor, and
32.03 = equivalent weight of sulfur dioxide.

6.2 Calculations for Concentration

The following formulas for calculating the concentration of sulfur dioxide, using metric units, are to be used along with the example calculation forms shown in Figures 6.1, 6.2A, and 6.2B.

6.2.1 CO_2 Volume Collected, Corrected to Standard Conditions -

$$V_{\text{CO}_2(\text{std})} = 5.467 \times 10^{-4} (m_{\text{af}} - m_{\text{ai}}) \quad \text{Equation 6-1}$$

6.2.2 Moisture Volume Collected, Corrected to Standard Conditions -

$$V_{\text{w}(\text{std})} = 1.336 \times 10^{-3} (m_{\text{wf}} - m_{\text{wi}}) \quad \text{Equation 6-2}$$

3. Put water in the sample storage container to the initial sample mark, and measure the initial sample volume (V_{soln_i}).

4. Put water in the sample storage container to the mark of the transferred sample, and measure the final volume (V_{soln_f}).

5. If V_{soln_f} is $< V_{\text{soln}_i}$, correct the sample volume (V_{soln}) by using Equation 5-6,

$$V_{\text{soln}}' = V_{\text{soln}} \frac{V_{\text{soln}_i}}{V_{\text{soln}_f}} \quad \text{Equation 5-6}$$

where

V_{soln}' = sample volume to be used for the calculations, ml,

V_{soln} = total volume of solution in which the sulfur dioxide is contained, ml,

V_{soln_i} = initial sample volume placed in storage container, ml, and

V_{soln_f} = final sample volume removed from storage container, ml.

6. Both the corrected and uncorrected values should be submitted in the test report to the Agency.

Proceed with the analysis as follows:

1. Transfer the contents of the sample bottle to a 100-ml volumetric flask (V_{soln}), and dilute to the mark with deionized distilled water.

2. Pipette a 20-ml aliquot (V_a) of this solution into a 250-ml Erlenmeyer flask, and add 80^a ml of 100 percent isopropanol.

3. Add two to four drops of thorin indicator, and titrate to an orange-pink endpoint using standardized 0.0100N barium perchlorate. Record the volume of barium perchlorate used in titrating the sample (V_t). If more than 100 ml of titrant is required, then a smaller sample aliquot should be used (i.e., 1.0 ml). If less than 5 ml of titrant is required, the analyst may prepare the titrant with a normality of 0.0010 when a greater precision is desired.

4. Repeat the above analysis on a new aliquot from the same sample. Replicate titrant volumes must be within 1 percent or 0.2 ml, whichever is greater. If the titrant volumes do not meet this criterion, repeat analyses on new aliquots of the sample until two consecutive titrations agree within 1 percent or 0.2 ml, whichever is greater, or until sample is spent.

5. Record all data on the data form, Figure 5.2. Average the consistent titrant volumes, and use them as V_t in subsequent calculations. All analytical data must then be reviewed by a person familiar with procedures, and this review should be noted on the data form, Figure 5.2. Note: Protect the 0.0010N barium perchlorate solution from evaporation at all times.

Warning: Contamination of the sample with Ascarite or Drierite will cause bias. The analyst should take precautions when handling Ascarite or Drierite and the field sample or absorbing solution so as not to introduce these materials into the sample or absorbing solution.

Note: References 2 and 3 contain additional information on improved temperature stability and application of Method 6 to high sulfur dioxide concentration.

Table 5.1. ACTIVITY MATRIX FOR POSTSAMPLING OPERATIONS

Activity	Acceptance limits	Frequency and method of measurement	Action if requirements are not met
<u>Sampling Apparatus</u>			
Dry gas meter	Within 5% of pretest calibration factor	Make two independent runs after each field test	Recalibrate and use calibration factor that gives lower sample volume
Rate meter	Within 10% of desired flow rate (recommended)	Make two independent runs during the check of the rate meter	Clean and recalibrate
Meter thermometer	Within 6°C (10.8°F) at ambient temperature	Compare with ASTM mercury-in-glass thermometer after each field test	Recalibrate and use higher temperature value for calculations
Barometer	Within 5.0 mm (0.2 in.) Hg at ambient pressure	Compare with mercury-in-glass barometer after each field test	Recalibrate and use lower barometric value for calculations
Balance	Within 0.05 g	Compare against Class S weights	Adjust, repair, or replace
<u>Analysis</u>			
Reagents	Prepare according to requirements detailed in Subsection 5.2	Prepare and/or standardize within 24 h of sample analysis	Prepare new solutions and/or re-standardize
Control sample	Titriments differ by <0.2 ml; analytical results within 5% of stated value	Before and after analysis of field samples	Prepare new solutions and/or restandardize
Sample analysis	Titrant volumes differ by <1% or <0.2 ml, whichever is greater	Titrate until two or more consecutive aliquots agree within 1% or 0.2 ml, whichever is greater, review all analytical data	Void sample if a set of two titrations do not meet criterion

6.2.3 SO₂ Concentration -

$$C_{SO_2} = 32.03 \frac{(V_t - V_{tb}) N \left(\frac{V_{soln}}{V_a} \right)}{V_{m(std)} + V_{CO_2(std)}} \quad \text{Equation 6-3}$$

6.2.4 CO₂ Concentration -

$$C_{CO_2} = \frac{V_{CO_2(std)}}{V_{m(std)} + V_{CO_2(std)}} \times 100 \quad \text{Equation 6-4}$$

6.2.5 Moisture Concentration -

$$C_w = \frac{V_{H_2O(std)}}{V_{m(std)} + V_{H_2O(std)} + V_{CO_2(std)}} \quad \text{Equation 6-5}$$

6.3 Emission Rate Calculations

If the only emission measurement desired is in terms of emission rate of SO₂ (ng/J), an abbreviated procedure may be used. The differences between Method 6A and the abbreviated procedure are described in Subsection 4.3.

6.3.1 SO₂ Mass Collected -

$$m_{SO_2} = 32.03 (V_t - V_{tb}) N \left(\frac{V_{soln}}{V_a} \right) \quad \text{Equation 6-6}$$

where

m_{SO_2} = mass of SO₂ collected, mg.

6.3.2 Sulfur Dioxide Emission Rate -

Equation 6-7

$$E_{SO_2} = F_c (1.829 \times 10^9) \frac{m_{SO_2}}{(m_{af} - m_{ai})}$$

where

E_{SO_2} = emission rate of SO₂, ng/J, and

F_c = carbon F factor for the fuel burned, m³/J, from Method 19.

METER VOLUME (metric to English)

$$V_m = \underline{33.68} \text{ liter}$$

$$V = V_m (\text{in liters}) \times 0.03531 \text{ ft}^3/\text{liter} = \underline{1.1892} \text{ ft}^3$$

METER TEMPERATURE (metric to English)

$$t_m = \underline{22.4} ^\circ\text{C}$$

$$t_m = [t_m (^{\circ}\text{C}) \times 1.8] + 32 = \underline{72.3} ^\circ\text{F}$$

$$T_m = t_m (^{\circ}\text{F}) + 460 = \underline{532.3} ^\circ\text{R}$$

BAROMETRIC PRESSURE (metric to English)

$$P_{\text{bar}} = \underline{757} \text{ mm Hg}$$

$$P_{\text{bar}} = P_{\text{bar}} (\text{mm Hg}) \times 0.03937 \text{ in. Hg/mm Hg} = \underline{29.80} \text{ in. Hg}$$

METER VOLUME (English to metric)

$$V_m = \underline{1.1892} \text{ ft}^3$$

$$V_m = V_m (\text{ft}^3) \times 0.02832 \text{ m}^3/\text{ft}^3 = \underline{0.03368} \text{ m}^3$$

METER TEMPERATURE (English to metric)

$$t_m = \underline{72.3} ^\circ\text{F}$$

$$t_m = [t_m (^{\circ}\text{F}) - 32] \times 5/9 = \underline{22.4} ^\circ\text{C}$$

$$T_m = t_m (^{\circ}\text{C}) + 273 = \underline{295.4} ^\circ\text{K}$$

BAROMETRIC PRESSURE (English to metric)

$$P_{\text{bar}} = \underline{29.80} \text{ in. Hg}$$

$$P_{\text{bar}} = P_{\text{bar}} (\text{in. Hg}) \times 25.4 \text{ mm Hg/in. Hg} = \underline{757} \text{ mm Hg}$$

Figure 6.1. Method 6A and 6B calculation form (conversion factors).

STANDARD METER VOLUME (English units)

$$V_m = 1.1892 \text{ ft}^3, Y = 1.071$$

$$P_{\text{bar}} = 29.80 \text{ in. Hg}, T_m = 532.3^\circ \text{R}$$

$$V_m(\text{std}) = 17.64 V_m Y \left[\frac{P_{\text{bar}}}{T_m} \right] = 1.2578 \text{ dscf}$$

CO₂ VOLUME COLLECTED, STANDARD CONDITIONS
 (English units)

$$m_{\text{af}} = 308.3 \text{ g}, m_{\text{ai}} = 300.1 \text{ g}$$

$$V_{\text{CO}_2}(\text{std}) = 0.01930 (m_{\text{af}} - m_{\text{ai}}) = 0.1583 \text{ dscf}$$

Equation 6-1

CO₂ CONCENTRATION (percent by volume)

$$C_{\text{CO}_2} = \frac{V_{\text{CO}_2}(\text{std})}{V_m(\text{std}) + V_{\text{CO}_2}(\text{std})} \times 100 = 11.17 \%$$

Equation 6-4

SO₂ CONCENTRATION (English units)

$$V_t = 11.30 \text{ ml}, V_{\text{tb}} = 0.00 \text{ ml}, N = 0.0102 \text{ (g-eq)/ml}$$

$$V_{\text{soln}} = 100.0 \text{ ml}, V_a = 20.0 \text{ ml}$$

$$C_{\text{SO}_2} = \frac{7.061 \times 10^{-5} (V_t - V_{\text{tb}}) N \left(\frac{V_{\text{soln}}}{V_a} \right)}{V_m(\text{std}) + V_{\text{CO}_2}(\text{std})} = 0.2814 \times 10^{-4} \text{ lb/dscf}$$

Equation 6-3

Figure 6.2A. Method 6A and 6B calculation form (English units).

MOISTURE CONCENTRATION (percent)

$$m_{wf} = 296.3 \text{ g}, m_{wi} = 294.1 \text{ g}$$

$$V_{w(std)} = 0.04707 (m_{wf} - m_{wi}) = .1035 \text{ dscf} \quad \text{Equation 6-2}$$

$$C_{H_2O} = \frac{V_{H_2O(std)}}{V_{m(std)} + V_{H_2O(std)} + V_{CO_2(std)}} \times 100 = \underline{6.81} \% \quad \text{Equation 6-5}$$

EMISSION RATE OF SO_2 (English units)
(using meter volumes)

$$F_C = \underline{1810} \text{ scf of } CO_2/\text{million Btu}$$

$$E_{SO_2} = C_{SO_2} F_C \frac{100}{C_{CO_2}} = \underline{0.465} \text{ lb } SO_2/\text{million Btu}$$

(not using meter sample volume)

$$F_C = \underline{1810} \text{ scf of } CO_2/\text{million Btu}$$

$$m_{SO_2} = 32.03 (V_t - V_{tb})^N \left(\frac{V_{soln}}{V_a} \right) = \underline{18.46} \text{ mg of } SO_2 \text{ collected}$$

Equation 6-6

$$E_{SO_2} = F_C (1.141 \times 10^{-3}) \frac{m_{SO_2}}{(m_{af} - m_{ai})} = \underline{0.465} \text{ lb } SO_2/\text{million Btu}$$

Equation 6-7

SO_2 CONCENTRATION (ppm)

$$C_{SO_2} \text{ (ppm)} = \frac{C_{SO_2} \text{ (lb/dscf)}}{1.663 \times 10^{-7}} = \underline{172.8} \text{ ppm}$$

Figure 6.2A. (continued)

STANDARD METER VOLUME (metric units)
(using meter volumes)

$$V_m = \underline{33.68} \text{ liter} \times 0.001 = \underline{0.03368} \text{ m}^3$$

$$Y = \underline{1.071}, P_{\text{bar}} = \underline{757} \text{ mm Hg}, T_m \underline{295.4} \text{ }^\circ\text{K}$$

$$V_m(\text{std}) = 0.3858 V_m Y \frac{P_{\text{bar}}}{T_m} = \underline{.03566} \text{ dscm}$$

CO₂ VOLUME COLLECTED, STANDARD CONDITIONS
(metric units)

$$m_{\text{af}} = \underline{308.3} \text{ g}, m_{\text{ai}} = \underline{300.1} \text{ g}$$

$$V_{\text{CO}_2}(\text{std}) = 5.467 \times 10^{-4} (m_{\text{af}} - m_{\text{ai}}) = \underline{.00448} \text{ dscm}$$

Equation 6-1

CO₂ CONCENTRATION (percent by volume)

$$C_{\text{CO}_2} = \frac{V_{\text{CO}_2}(\text{std})}{V_m(\text{std}) + V_{\text{CO}_2}(\text{std})} \times 100 = \underline{11.17} \%$$

Equation 6-4

SO₂ CONCENTRATION (metric units)

$$V_t = \underline{11.03} \text{ ml}, V_{\text{tb}} = \underline{0.00} \text{ ml}, N = \underline{0.0102} \text{ (g - eq)/ml},$$

$$V_{\text{soln}} = \underline{100.0} \text{ ml}, V_a = \underline{20.0} \text{ ml}$$

$$C_{\text{SO}_2} = \frac{32.03 (V_t - V_{\text{tb}}) N \left(\frac{V_{\text{soln}}}{V_a} \right)}{V_m(\text{std}) + V_{\text{CO}_2}(\text{std})} = \underline{448.9} \text{ mg/dscm}$$

Equation 6-3

Figure 6.2B. Method 6A and 6B calculation form (metric units).

MOISTURE CONCENTRATION (percent)

$$m_{wf} = \underline{296} . \underline{3} \text{ g}, m_{wi} = \underline{294} . \underline{1} \text{ g}$$

$$V_{m(\text{std})} = 1.336 \times 10^{-3} (m_{wf} - m_{wi}) = . \underline{00294} \text{ dscm}$$

Equation 6-2

$$C_{H_2O} = \frac{V_{H_2O}}{V_{m(\text{std})} + V_{H_2O(\text{std})} + V_{CO_2(\text{std})}} \times 100 = \underline{6.82} \%$$

Equation 6-5

EMISSION RATE OF SO_2 (metric units)
(using meter volumes)

$$F_c = \underline{0.486} \times 10^{-7} \text{ dscm of } CO_2/J$$

$$E_{SO_2} = C_{SO_2} F_c \frac{10^8}{C_{CO_2}} = \underline{195.3} \text{ ng/J}$$

(not using meter volumes)

$$F_c = \underline{0.486} \times 10^{-7} \text{ dscm of } CO_2/J$$

$$m_{SO_2} = 32.03 (V_t - V_{tb}) N \left(\frac{V_{soln}}{V_a} \right) = \underline{18.02} \text{ mg of } SO_2 \text{ collected}$$

Equation 6-6

$$E_{SO_2} = F_c (1.829 \times 10^9) \frac{m_{SO_2}}{(m_{af} - m_{ai})} = \underline{195.3} \text{ ng/J}$$

Equation 6-7

Figure 6.2B. (continued)

Table 6.1. ACTIVITY MATRIX FOR CALCULATION CHECKS

Characteristics	Acceptance limits	Frequency and method of measurement	Action if requirements are not met
Analysis data form	All data and calculations are shown	Visually check	Complete the missing data values
Calculations	Difference between check and original calculations should not exceed round-off error	Repeat all calculations starting with raw data for hand calculations; check all raw data input for computer calculations; hand calculate one sample per test	Indicate errors on sulfur dioxide calculation form, Fig. 6.1A or 6.1B

7.0 MAINTENANCE

The normal use of emission-testing equipment subjects it to corrosive gases, extremes in temperature, vibration, and shock. Keeping the equipment in good operating order over an extended period of time requires knowledge of the equipment and a program of routine maintenance which is performed quarterly or after 2830 liters (100 ft³) of operation, whichever comes first. In addition to the quarterly maintenance, a yearly cleaning of the entire meter box is recommended. Maintenance procedures for the various components are summarized in Table 7.1 at the end of the section. The following procedures are not required, but are recommended to increase the reliability of the equipment.

7.1 Pump

In the present commercial sampling train, several types of pumps are used; the most common are the fiber vane pump with in-line oiler and the diaphragm pump. The fiber vane pump requires a periodic check of the oiler jar. Its contents should be translucent; the oil should be changed if it is not translucent. Use the oil specified by the manufacturer. If none is specified, use SAE-10 nondetergent oil. Whenever the fiber vane pump starts to run erratically or during the yearly disassembly, the head should be removed and the fiber vanes changed. Erratic operation of the diaphragm pump is normally due to either a bad diaphragm (causing leakage) or to malfunctions of the valves, which should be cleaned annually by complete disassembly.

7.2 Dry Gas Meter

The dry gas meter should be checked for excess oil or corrosion of the components by removing the top plate every 3 months. The meter should be disassembled and all components cleaned and checked whenever the rotation of the dials is erratic, whenever the meter will not calibrate properly over the required flow rate range, and during the yearly maintenance.

7.3 Rotameter

The rotameter should be disassembled and cleaned according to the manufacturer's instructions using only recommended cleaning fluids every 3 months or upon erratic operation.

7.4 Sampling Train

All remaining sample train components should be visually checked every 3 months and completely disassembled and cleaned or replaced yearly. Many items, such as quick disconnects, should be replaced whenever damaged rather than checked periodically. Normally, the best procedure for maintenance in the field is to

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use another entire unit such as a meter box, sample box, or umbilical cord (the hose that connects the sample box and meter box) rather than replacing individual components.

Table 7.1. ACTIVITY MATRIX FOR EQUIPMENT MAINTENANCE CHECKS

Apparatus	Acceptance limits	Frequency and method of measurement	Action if requirements are not met
Routine main-tenance	No erratic behavior	Routine maintenance performed quarterly or after 2830 liters (100 ft ³) of operation; disassemble and clean yearly	Replace parts as needed
Fiber vane pump	In-line oiler free of leaks	Periodically check oiler jar; remove head and change fiber vanes	Replace as needed
Diaphragm pump	Leak-free valves functioning properly	Clean valves during yearly disassembly	Replace when leaking or malfunctioning
Dry gas meter	No excess oil, corrosion, or erratic rotation of the dial	Check every 3 mo. for excess oil or corrosion by removing the top plate; check valves and diaphragm yearly and whenever meter dial runs erratically or whenever meter will not calibrate	Replace parts as as needed or replace meter
Rotameter	Clean and no erratic behavior	Clean every 3 mo. or whenever ball does not move freely	Replace
Sampling train	No damage	Visually check every 3 mo; completely disassemble and clean or replace yearly	If failure noted, use another entire meter box, sample box, or umbilical cord

8.0 AUDITING PROCEDURE

An audit is an independent assessment of data quality. Independence is achieved if the individual(s) performing the audit and their standards and equipment are different from the regular field crew and their standards and equipment. Routine quality assurance checks by a field team are necessary in generation of good quality data, but they are not part of the auditing procedure. Table 8.1 at the end of this section summarizes the quality assurance functions for auditing.

Based on the results of performance audits^{6,7} and collaborative tests³ of Method 6, two specific performance audits are recommended:

1. Audit of the analytical phase of Method 6A, or an audit of the sampling and analytical phase for Method 6B.

2. Audit of data processing for both Methods.

It is suggested that a systems audit be conducted as specified by the quality assurance coordinator, in addition to these performance audits. The two performance audits and the systems audit are described in detail in Subsections 8.1 and 8.2, respectively.

8.1 Performance Audits

Performance audits are made to evaluate quantitatively the quality of data produced by the total measurement system (sample collection, sample analysis, and data processing). It is recommended that these audits be performed by the responsible control agency once during every enforcement source test. A source test for enforcement comprises a series of runs at one source. The performance audit of the analytical phase is subdivided into two steps: (1) a pretest audit which is optional, and (2) an audit during the field sampling and/or analysis phase which is required.

8.1.1 Pretest Audit of Analytical Phase Using Aqueous Ammonium Sulfate (Optional) - The pretest audit described in this section can be used to determine the proficiency of the analyst and the standardization of solutions in the Method 6A or 6B analysis and should be performed at the discretion of the agency auditor. The analytical phase of Method 6A or 6B can be audited with the use of aqueous ammonium sulfate samples provided to the testing laboratory before the enforcement source test. Aqueous ammonium sulfate samples may be prepared by the procedure described in Subsection 3.13.5 on control sample preparation.

The pretest audit provides the opportunity for the testing laboratory to check the accuracy of its analytical procedure. This audit is especially recommended for a laboratory with little

or no experience with the Method 6A or 6B analysis procedure described in this Handbook.

The testing laboratory should provide the agency/organization requesting the performance test with a notification of the intent to test 30 days prior to the enforcement source test. The testing laboratory should also request that the agency/organization provide the following performance audit samples: two samples at a low concentration (500 to 1000 mg SO₂/dsm³ of gas sampled or approximately 10 to 20 mg of ammonium sulfate per sample) and two samples at a high concentration (1500 to 2500 mg SO₂/dsm³ of gas sampled or about 30 to 50 mg of ammonium sulfate per sample). This is based on an emission standard of 1.2 lb of SO₂ per million Btu which would be about 1300 mg SO₂/dsm³ at 35 percent excess air. At least 10 days prior to the enforcement source test, the agency/organization should provide the four audit samples. The concentration of the two low and the two high audit samples should not be identical.

The testing laboratory will analyze one sample at the low concentration and one at the high concentration, and submit their results to the agency/organization prior to the enforcement source test. (Note: The analyst performing this optional audit must be the same analyst audited during the field sample analysis described in Subsection 8.1.2).

The agency/organization determines the relative error (RE) between the measured SO₂ concentration and the audit or known values of concentration. The RE is a measure of the bias of the analytical phase of Method 6A or 6B. Calculate RE using Equation 8-1.

$$RE = \frac{C_d - C_a}{C_a} \times 100 \quad \text{Equation 8-1}$$

where

C_d = Determined audit sample concentration mg SO₂/dsm³, and

C_a = Actual audit concentration, mg SO₂/dsm³.

The recommended control limit for the pretest audit is +5 percent for both audit samples.

If the results of the pretest audit exceed 5 percent, the agency/organization should have the tester/analyst check the analytical system and repeat the audit sample analysis using a second aliquot of the same audit sample. After taking any necessary corrective action, the testing laboratory should then analyze the same audit samples and report the results immediately to the agency/organization before the enforcement source test analysis.

8.1.2 Audit of Analytical Phase Using Aqueous Ammonium Sulfate for Method 6A - The audit described here is exactly the same audit promulgated as part of Method 6 in the Federal Register, Vol. 49, June 27, 1984. The agency responsible for the enforcement source test should obtain the audit samples from the EPA Quality Assurance Coordinator in the respective EPA Regional Office.

The agency should provide the tester with two audit samples to be analyzed at the same time as the field samples from the enforcement source test. The purpose of this audit is to assess the data quality at the time of the analysis. The relative error (RE) for the audit samples results are determined using Equation 8-1. The results of the calculated RE should be included in the enforcement source test report as an assessment of accuracy of the analytical phase of Method 6A during the actual enforcement source test.

The two audit samples should be analyzed concurrently with and in the same manner as the set of compliance samples to evaluate the technique of the analyst and the preparation of the standards. The same analyst, analytical reagents, and analytical system must be used for both the compliance samples and the EPA audit samples; if this condition is met, auditing of subsequent compliance analyses within 30 days for the same enforcement agency may not be required. An audit sample set may not be used to validate different sets of compliance samples under the jurisdiction of different enforcement agencies unless prior arrangements are made with both enforcement agencies.

Calculate the concentrations in mg/dsm^3 using the specified sample volume in the audit instructions. (Note: Indication of acceptable results may be obtained immediately by reporting by telephone to the responsible enforcement agency the audit results in mg/dsm^3 and compliance results in total $\text{mg SO}_2/\text{sample}$.) Include the results of both audit samples, their identification numbers, and the analyst's name with the results of the compliance determination samples in appropriate reports to the EPA Regional Office or the appropriate enforcement agency. Include this information with subsequent compliance analyses for the same enforcement agency during the 30-day period.

The concentration of the audit samples obtained by the analyst shall agree within 5 percent of the actual concentrations. If the 5 percent specification is not met, reanalyze the compliance samples and audit samples, and include initial and reanalysis values in the test report.

Failure to meet the 5 percent specification may result in retests until the audit problems are resolved. However, if the audit results do not affect the compliance or noncompliance status of the affected facility, the Administrator may waive the

reanalysis requirement, further audits, or retests and accept the results of the compliance test. While steps are being taken to resolve audit analysis problems, the Administrator may also choose to use the data to determine the compliance or noncompliance status of the affected facility.

Note: It is recommended that known quality control samples be analyzed prior to the compliance and audit sample analysis to optimize the system accuracy and precision. One source of these samples is:

U. S. Environmental Protection Agency
Environmental Monitoring and Systems Laboratory
Quality Assurance Division (MD-77A)
Research Triangle Park, North Carolina 27711

Attention: Source Test Audit Coordinator

8.1.3 Audit of Sampling and Analytical Phase for Method 6B - When Method 6B is used to demonstrate compliance with a 30-day rolling average standard (e.g., 40 CFR 60, Subpart Da), the following audits should be conducted:

Cylinder Gas Audit (CGA) - During the first 7 days of continuous use of Method 6B at the same source, a CGA should be conducted. Thereafter, a CGA should be conducted once every calendar quarter that Method 6B is used at the same source. The purpose of the CGA is to measure the RE for the SO₂ and CO₂ sampling and analyses. The RE should be within 15 percent. The testers must obtain an audit gas in an aluminum cylinder that meets the requirements of EPA Protocol No. 1 (Section 3.0.4 of this Handbook) and contains SO₂ in the range of 200 to 400 ppm and CO₂ in the range of 12 percent to 16 percent, with the balance² of the gas as N₂. In addition, the tester must specify that the gas manufacturer (1) blends moisture-free carbon dioxide with the sulfur dioxide and (2) does not use a UV fluorescent analyzer to determine the SO₂ concentration in the cylinder, since a UV fluorescence SO₂ signal is quenched by the presence of CO₂.⁸

In a study conducted by EPA,⁹ audit cylinders containing sulfur dioxide (200 to 400 ppm) and carbon dioxide (12 to 16 percent) were purchased from nine different commercial gas manufacturers. All nine cylinders ordered were to be prepared according to EPA Protocol No. 1. The purpose of this study was to determine whether accurate mixtures of SO₂ and CO₂ could be expected from commercial gas manufacturers following EPA Protocol No. 1 and to determine if these mixtures were stable. The accuracy for CO₂ was within 1.2 percent for all nine cylinders. The accuracy for SO₂ was within 5.2 percent for seven cylinders and within 9.8 percent for the remaining two cylinders. The sulfur dioxide and carbon dioxide concentrations were found to be stable over the entire period of the study (473 days). In another study conducted by EPA,¹⁰ three cylinders containing a

nominal 250 ppm SO₂ and 10 percent CO₂ showed the SO₂ to be stable over the entire period of the study (22 months).² Finally, in a study conducted by EPA,¹¹ cylinder gases of nominal 250 ppm SO₂ and 10 percent CO₂ were used to audit three contractors using Method 6B. These audits demonstrated that cylinder gases are an effective means to assess the accuracy of Method 6B.

To conduct the CGA using the Protocol No. 1 gases, the following procedures should be followed:

1. Attach the audit gas cylinder as shown in Figure 8.1.
2. Open the audit cylinder until 2 times the sample flow rate is obtained on the discharge rotameter. This would be approximately 2.0 L/min for the intermittent sampling train, and approximately 60 ml/min for the continuous sampling train. Allow the audit gas to flow through the manifold for 5 minutes to condition the manifold.
3. Start the Method 6B sampling train, and adjust to desired rate. The audit sample will be collected at a continuous sampling rate for both the continuous and intermittent sampling train. This is done in an effort to minimize the use of the audit gas. The intermittent sampling train should be operated for 30 minutes. The continuous train should be operated for 24 hours.
4. The sampling train should be set at the proper sampling rate for the train; the audit gas flow rate should then be adjusted so that the discharge rotameter is reading at about equal to the sampling rate. This will ensure that the audit gas is collected properly from the glass manifold.
5. At the completion of the run, shut off the sampling train, then shut off the audit gas flow.
6. The audit sample should be recovered and analyzed in the same manner as the field samples.
7. Calculate lb SO₂/million Btu for the Method 6B sampling train (C_{M6B}) using Equation 8.2.

$$C_{M6B} = 1.141 \times 10^{-3} F_c \frac{M_{SO_2}}{M_{CO_2}} = \text{lb SO}_2/\text{million Btu}$$

Equation 8-2

where

C_{M6B} = Concentration measured by Method 6B, lb SO₂/million Btu,

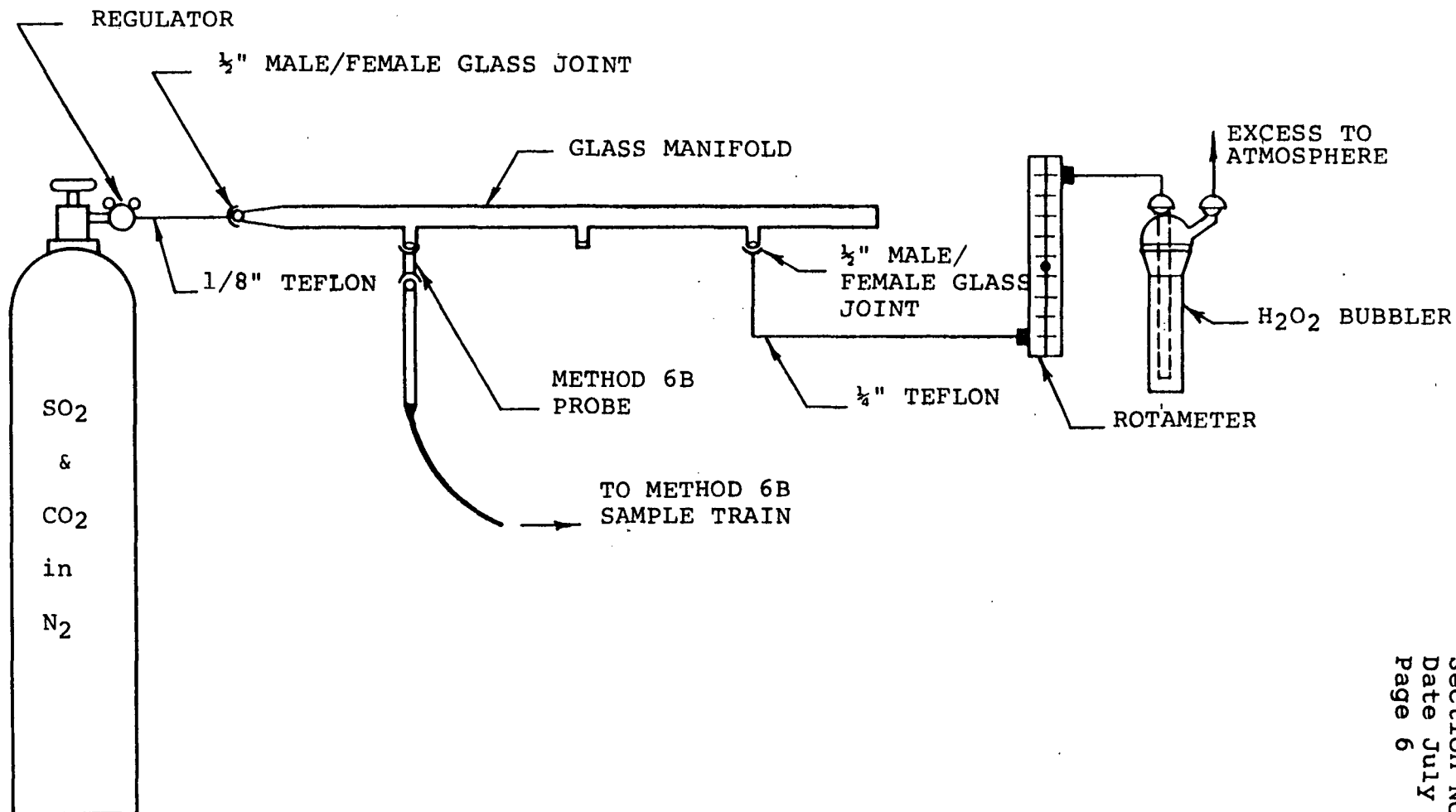


Figure 8.1. Cylinder Gas Audit of Method 6B.

F_C = F factor (use the actual F factor or assume F_C of 1800 for both calculations), scf of CO_2 /million Btu,

M_{SO_2} = Mass of SO_2 per total sample analyzed, mg of SO_2 , and

M_{CO_2} = Mass of CO_2 per total sample analyzed, g of CO_2 .

8. Calculate lb SO_2 /million Btu for the audit gas (C_a) using Equation 8-3.

$$C_a = 1.66 \times 10^{-7} SO_{2\text{ppm}} F_C \frac{100}{\% CO_2} \quad \text{Equation 8-3}$$

where

C_a = Concentration in audit cylinder, lb SO_2 /million Btu,

$SO_{2\text{ppm}}$ = Concentration of SO_2 in audit cylinder, ppm,

$\% CO_2$ = Concentration of CO_2 in audit cylinder, %, and

F_C = F factor (same as above), scf of CO_2 /million Btu.

9. The auditor should then calculate the RE using Equation 8-4.

$$RE = \frac{C_{M6B} - C_a}{C_a} \times 100 \quad \text{Equation 8-4}$$

10. The RE should be within 15 percent. The results of the audit should be included in the report as an audit of the accuracy of the sampling and analysis phase of Method 6B.

SO_2 Analysis - During the first 7 days of continuous use of Method 6B at the same source, an SO_2 analysis audit should be performed. Thereafter, an SO_2 analysis audit should be conducted once every 30 days that Method 6B is used at the same source. The purpose of this audit is to measure the RE for SO_2 analysis. The RE should be within 5 percent. The audit samples described in Section 8.1.3 should be used. The CGA and the SO_2 analysis should be conducted on the same day.

8.1.4 Audit of Data Processing - Data processing errors can be determined by auditing the data recorded on the field and laboratory forms. The original and audit (check) calculation should agree within roundoff error; if not, all of the remaining data should be checked. The data processing may also be audited by

providing the testing laboratory with specific data sets (exactly as would appear in the field), and by requesting that the data calculation be completed and that the results be returned to the agency/organization. This audit is useful in checking both computer programs and manual methods of data processing.

8.2 Systems Audit

A systems audit is an on-site qualitative inspection and review of the total measurement system (sample collection, sample analysis, data processing, etc.). Initially, a systems audit is recommended for each enforcement source test, defined here as a series of three runs at one source. After the test team gains experience with the method, the frequency of auditing may be reduced--once for every four tests.

The auditor should have extensive background experience in source sampling, specifically with the measurement system being audited. The functions of the auditor are summarized below:

1. Inform the testing team of the results of pretest audits, specifying any area(s) that need special attention or improvement.
2. Observe procedures and techniques of the field team during sample collection.
3. Check/verify records of apparatus calibration checks and quality control used in the laboratory analysis of control samples from previous source tests, where applicable.
4. Record the results of the audit, and forward them with comments to the test team management so that appropriate corrective action may be initiated.

While on site, the auditor observes the source test team's overall performance, including the following specific operations:

1. Setting up and leak testing the sampling train.
2. Preparing and adding the absorbing solution to the impingers.
3. Checking for constant rate sampling (for Method 6A only).
4. Purging the sampling train (for Method 6A only).

Figure 8.2 is a suggested checklist for the auditor.

Yes	No	Comment	
			<u>Presampling Preparation</u>
<input checked="" type="checkbox"/>	<input type="checkbox"/>		1. Knowledge of process conditions
<input checked="" type="checkbox"/>	<input type="checkbox"/>		2. Calibration of pertinent equipment, in particular, the dry gas meter, prior to each field test
			<u>On-Site Measurements</u>
<input checked="" type="checkbox"/>	<input type="checkbox"/>		3. Leak testing of sampling train after sample run
<input checked="" type="checkbox"/>	<input type="checkbox"/>		4. Preparation and addition of absorbing solutions to impingers
<input checked="" type="checkbox"/>	<input type="checkbox"/>		5. Constant rate sampling (for Method 6A only)
<input checked="" type="checkbox"/>	<input type="checkbox"/>		6. Purging of the sampling train and rinsing of the impingers and connecting tubes to recover the sample (for Method 6A only)
<input checked="" type="checkbox"/>	<input type="checkbox"/>		7. Recording of pertinent process conditions during sample collection
<input checked="" type="checkbox"/>	<input type="checkbox"/>		8. Maintaining the probe at a given temperature
			<u>Postsampling</u>
<input checked="" type="checkbox"/>	<input type="checkbox"/>		9. Control sample analysis--accuracy and precision
<input checked="" type="checkbox"/>	<input type="checkbox"/>		10. Sample aliquoting techniques
<input checked="" type="checkbox"/>	<input type="checkbox"/>		11. Titration technique, particularly endpoint precision
<input checked="" type="checkbox"/>	<input type="checkbox"/>		12. Use of detection blanks in correcting field sample results
<input checked="" type="checkbox"/>	<input type="checkbox"/>		13. Weighing of the CO ₂ absorbant
<input checked="" type="checkbox"/>	<input type="checkbox"/>		14. Calculation procedure/check
<input checked="" type="checkbox"/>	<input type="checkbox"/>		15. Calibration checks
<input checked="" type="checkbox"/>	<input type="checkbox"/>		16. Standardized barium perchlorate solution
<input checked="" type="checkbox"/>	<input type="checkbox"/>	*	17. Result of the audit sample
<u>General Comments</u> <i>* Analysis of EPA audit samples were successful along with analysis of compliance samples.</i>			

Figure 8.2. Method 6A and 6B checklist to be used by auditors.

Table 8.1. ACTIVITY MATRIX FOR AUDITING PROCEDURE

Audit	Acceptance limits	Frequency and method of measurement	Action if requirements are not met
Analytical phase using aqueous ammonium sulfate (Method 6A)	Measured RE of the pretest audit sample should be less than +5% of given value (optional); RE for audit during test +5% (mandatory)	Frequency: Once during every enforcement source test Method: Analyze audit samples and compare with given values	Review operating technique and repeat audit and field sample analysis
Analytical phase using aqueous ammonium sulfate (Method 6B)	Measured RE of the pretest audit sample should be less than +5% of given value (optional)	Frequency: Once prior to setting up a new system Method: Measure audit samples and compare with given value	Review operating technique and repeat audit sample analysis
Sampling and analytical phase using cylinder gas audit and aqueous ammonium sulfate (continuous use of Method 6B)	Measured RE of the cylinder gas audit should be less than +15% (mandatory)	Frequency: Within the first 7 days of initial use and every 30 days thereafter during continued use Method: Perform cylinder gas audit and compare with given value	Review operating technique and repeat audit
	Measured RE of the aqueous audit samples should be less than +5% (mandatory)	Frequency: Same as above and on the same day as the cylinder gas audit Method: Perform audit sample analysis and compare with given value	Same as above CGA
Data processing errors	The original and check calculations within round-off error	Frequency: Once during every enforcement source test Method: Independent calculations, starting with recorded data	Check and correct all data for the source test

(continued)

Table 8.1 (continued)

Audit	Acceptance limits	Frequency and method of measurement	Action if requirements are not met
System audit	Operation technique described in this section of the Hand- book	<u>Frequency:</u> Once during every enforcement test until experience gained, then every fourth test <u>Method:</u> Observation of techniques, assisted by audit checklist, Fig. 8.2	Explain to team the deviations from recommended techniques; note on Fig. 8.2

9.0 RECOMMENDED STANDARDS FOR ESTABLISHING TRACEABILITY

To achieve data of desired quality, two considerations are essential: the measurement process must be in a state of statistical control at the time of the measurement, and the systematic errors, when combined with the random variation (errors of measurement), must result in an acceptable uncertainty. To ensure good quality data, it is necessary to perform quality control checks and independent audits of the measurement process; to document these data by means of a quality control chart as appropriate; and to use materials, instruments, and measurement procedures that can be traced to an appropriate standard of reference.

Data must be routinely obtained by replicate measurements of control standard samples and working standards. The working calibration standards should be traceable to standards that are considered primary, such as those listed below.

1. Dry gas meter must be calibrated against a wet test meter that has been verified by an independent liquid displacement method (Section 3.13.2) or by use of a spirometer.

2. The barium perchlorate is standardized against sulfuric acid. The sulfuric acid should have been standardized with primary standard grade potassium acid phthalate. The standardized barium perchlorate should then be validated with an aqueous solution of primary standard grade ammonium sulfate. This makes the titrant solution traceable to two primary standard grade reagents.

3. The audit of Method 6B is conducted with a cylinder gas that is traceable to an NBS gas Standard Reference Material (SRM) or an NBS/EPA approved gas Certified Reference Material (CRM) with the use of EPA Protocol No. 1.

10.0 REFERENCE METHODS*

METHOD 6A—DETERMINATION OF SULFUR DIOXIDE, MOISTURE, AND CARBON DIOXIDE EMISSIONS FROM FOSSIL FUEL COMBUSTION SOURCES

1. Applicability and Principle

1.1 Applicability. This method applies to the determination of sulfur dioxide (SO_2) emissions from fossil fuel combustion sources in terms of concentration (mg/m^3) and in terms of emission rate (ng/J) and to the determination of carbon dioxide (CO_2) concentration (percent). Moisture, if desired, may also be determined by this method.

The minimum detectable limit, the upper limit, and the interferences of the method for the measurement of SO_2 are the same as for Method 6. For a 20-liter sample, the method has a precision of 0.5 percent CO_2 for concentrations between 2.5 and 25 percent CO_2 and 1.0 percent moisture for moisture concentrations greater than 5 percent.

1.2 Principle. The principle of sample collection is the same as for Method 6 except that moisture and CO_2 are collected in addition to SO_2 in the same sampling train. Moisture and CO_2 fractions are determined gravimetrically.

2. Apparatus

2.1 Sampling. The sampling train is shown in Figure 6A-1; the equipment required is the same as for Method 6, Section 2.1, except as specified below:

2.1.1 SO_2 Absorbers. Two 30-ml midget impingers with a 1-mm restricted tip and two 30-ml midget bubblers with an unrestricted tip. Other types of impingers and bubblers, such as Mae West for SO_2 collection and rigid cylinders for moisture absorbers containing Drierite, may be used with proper attention to reagent volumes and levels, subject to the Administrator's approval.

2.1.2 CO_2 Absorber. A sealable rigid cylinder or bottle with an inside diameter between 30 and 90 mm and a length between 125 and 250 mm and with appropriate connections at both ends.

NOTE: For applications downstream of wet scrubbers, a heated out-of-stack filter (either borosilicate glass wool or glass fiber mat) is necessary. The filter may be a separate heated unit or may be within the heated portion of the probe. If the filter is within the sampling probe, the filter should not be within 15 cm of the probe inlet or any unheated section of the probe, such as the connection to the first SO_2 absorber. The probe and filter should be heated to at least 20°C above the source temperature, but not greater than 120°C . The filter temperature (i.e., the sample gas temperature) should be monitored to assure the desired temperature is maintained. A heated Teflon connector may be used to connect the filter holder or probe to the first impinger.

NOTE: Mention of a brand name does not constitute endorsement by the Environmental Protection Agency.

2.2 Sample Recovery and Analysis. The equipment needed for sample recovery and analysis is the same as required for Method 6. In addition, a balance to measure within 0.05 g is needed for analysis.

3. Reagents

Unless otherwise indicated, all reagents must conform to the specifications established by the committee on analytical reagents of the American Chemical Society. Where such specifications are not available, use the best available grade.

3.1 Sampling. The reagents required for sampling are the same as specified in Method 6. In addition, the following reagents are required:

3.1.1 Drierite. Anhydrous calcium sulfate (CaSO_4) desiccant, 8 mesh, indicating type is recommended. (Do not use silica gel or similar desiccant in the application.)

3.1.2 CO_2 Absorbing Material. Ascariite II. Sodium hydroxide coated silica, 8 to 20 mesh.

3.2 Sample Recovery and Analysis. The reagents needed for sample recovery and analysis are the same as for Method 6, Sections 3.2 and 3.3, respectively.

4. Procedure

4.1 Sampling.

4.1.1 Preparation of Collection Train. Measure 15 ml of 80 percent isopropanol into the first midget bubbler and 15 ml of 3 percent hydrogen peroxide into each of the first two midget impingers as described in Method 6. Insert the glass wool into the top of the isopropanol bubbler as shown in Figure 6A-1. Into the fourth vessel in the train, the second midget bubbler, place about 25 g of Drierite. Clean the outsides of the bubblers and impingers, and weigh at room temperature ($\approx 20^\circ\text{C}$) to the nearest 0.1 g. Weigh the four vessels simultaneously, and record this initial mass.

With one end of the CO_2 absorber sealed, place glass wool in the cylinder to a depth of about 1 cm. Place about 150 g of CO_2 absorbing material in the cylinder on top of the glass wool, and fill the remaining space in the cylinder with glass wool. Assemble the cylinder as shown in Figure 6A-2. With the cylinder in a horizontal position, rotate it around the horizontal axis. The CO_2 absorbing material should remain in position during the rotation, and no open spaces or channels should be formed. If necessary, pack more glass wool into the cylinder to make the CO_2 absorbing material stable. Clean the outside of the cylinder of loose

* Federal Register, Volume 47, No. 231, December 1, 1982 and Volume 49, No. 51, March 14, 1984.

dirt and moisture and weigh at room temperature to the nearest 0.1 g. Record this initial mass.

Assemble the train as shown in Figure 6A-1. Adjust the probe heater to a temperature sufficient to prevent condensation (see Note in paragraph 2.1.1). Place crushed ice and water around the impingers and bubblers. Mount the CO₂ absorber outside the water bath in a vertical flow position with the sample gas inlet at the bottom. Flexible tubing, e.g., Tygon, may be used to connect the last SO₂ absorbing bubbler to the Drierite absorber and to connect the Drierite absorber to the CO₂ absorber. A second, smaller CO₂ absorber containing Ascarite II may be added in line downstream of the primary CO₂ absorber as a breakthrough indicator. Ascarite II turns white when CO₂ is absorbed.

4.1.2 Leak-Check Procedure and Sample Collection. The leak-check procedure and sample collection procedure are the same as specified in Method 6, Sections 4.1.2 and 4.1.3, respectively.

4.2. Sample Recovery.

4.2.1 Moisture Measurement. Disconnect the isopropanol bubbler, the SO₂ impingers, and the moisture absorber from the sample train. Allow about 10 minutes for them to reach room temperature, clean the outsides of loose dirt and moisture, and weigh them simultaneously in the same manner as in Section 4.1.1. Record this final mass.

4.2.2 Peroxide Solution. Discard the contents of the isopropanol bubbler and pour the contents of the midget impingers into a leak-free polyethylene bottle for shipping. Rinse the two midget impingers and connecting tubes with deionized distilled water, and add the washings to the same storage container.

4.2.3 CO₂ Absorber. Allow the CO₂ absorber to warm to room temperature (about 10 minutes), clean the outside of loose dirt and moisture, and weigh to the nearest 0.1 g in the same manner as in Section 4.1.1. Record this final mass. Discard used Ascarite II material.

4.3 Sample Analysis. The sample analysis procedure for SO₂ is the same as specified in Method 6, Section 4.3.

5. Calibration

The calibrations and checks are the same as required in Method 6, Section 5.

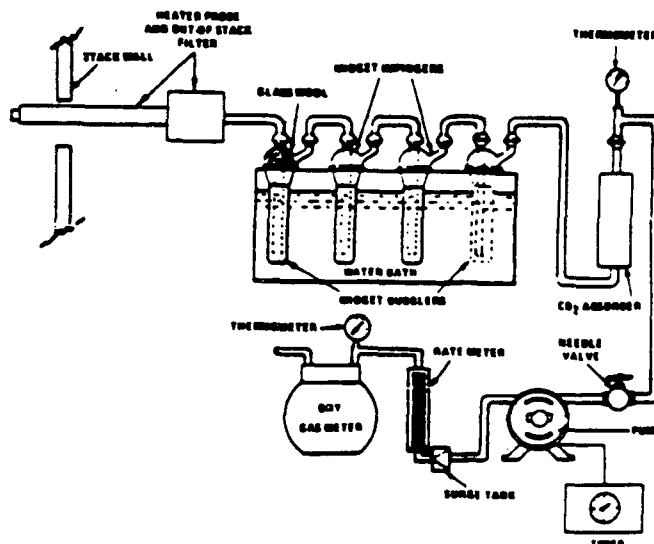


Figure 6A-1. Sampling train.

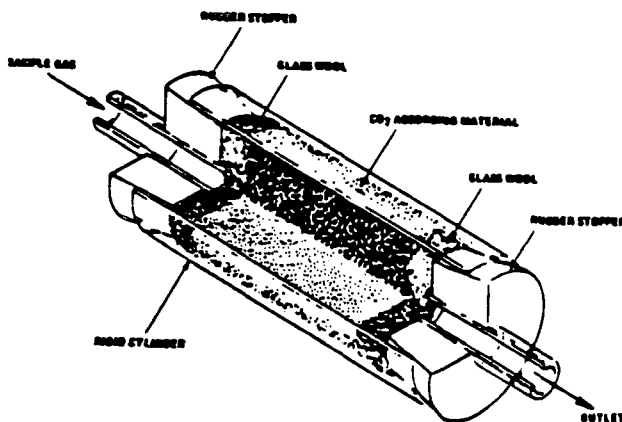


Figure 6A-2. CO₂ absorber.

6. Calculations

Carry out calculations, retaining at least one extra decimal figure beyond that of the acquired data. Round off figures after final calculations. The calculations, nomenclature, and procedures are the same as specified in Method 6 with the addition of the following:

6.1 Nomenclature.

C_m = Concentration of moisture, percent.
 C_{CO_2} = Concentration of CO_2 , dry basis, percent.
 M_{wi} = Initial mass of impingers, bubblers, and moisture absorber, g.
 m_{wf} = Final mass of impingers, bubblers, and moisture absorber, g.
 m_{wi} = Initial mass of CO_2 absorber, g.
 m_{wf} = Final mass of CO_2 absorber, g.
 $V_{CO_2(Std)}$ = Equivalent volume of CO_2 collected at standard conditions, dm³.
 $V_{moist(Std)}$ = Equivalent volume of moisture collected at standard conditions, sm³.
 5.467×10^{-4} = Equivalent volume of gaseous CO_2 at standard conditions per gram, sm³/g.
 1.336×10^{-3} = Equivalent volume of water vapor at standard conditions per gram, sm³/g.

6.2 CO_2 Volume Collected, Corrected to Standard Conditions.

$$V_{CO_2(Std)} = 5.467 \times 10^{-4} (m_{wf} - m_{wi}) \quad (\text{Eq. 6A-1})$$

6.3 Moisture Volume Collected, Corrected to Standard Conditions.

$$V_{moist(Std)} = 1.336 \times 10^{-3} (m_{wf} - m_{wi}) \quad (\text{Eq. 6A-2})$$

6.4 SO_2 Concentration.

$$C_{SO_2} = 32.03 \frac{(V_i - V_{wi})N\left(\frac{V}{V_s}\right)}{V_{moist} + V_{CO_2(Std)}} \quad (\text{Eq. 6A-3})$$

6.5 CO_2 Concentration.

$$C_{CO_2} = \frac{V_{CO_2(Std)}}{V_{moist(Std)} + V_{CO_2(Std)}} \times 100 \quad (\text{Eq. 6A-4})$$

6.6 Moisture Concentration. (Eq. 6A-5)

$$C_m = \frac{V_{moist(Std)}}{V_{moist(Std)} + V_{moist(Std)} + V_{CO_2(Std)}}$$

7. Emission Rate Procedure.

If the only emission measurement desired is in terms of emission rate of SO_2 (ng/J), an abbreviated procedure may be used. The differences between the above procedure and the abbreviated procedure are described below.

7.1 Sample Train. The sample train is the same as shown in Figure 6A-1 and as described in Section 4, except that the dry gas meter is not needed.

7.2 Preparation of the Collection Train. Follow the same procedure as in Section 4.1.1, except do not weigh the isopropanol bubbler, the SO_2 absorbing impingers or the moisture absorber.

7.3 Sampling. Operate the train as described in Section 4.1.3, except that dry gas meter readings, barometric pressure, and dry gas meter temperatures need not be recorded.

7.4 Sample Recovery. Follow the procedure in Section 4.2, except do not weigh the isopropanol bubbler, the SO_2 absorbing impingers, or the moisture absorber.

7.5 Sample Analysis. Analysis of the peroxide solution is the same as described in Section 4.3.

7.6 Calculations.

7.6.1 SO_2 Mass Collected.

$$m_{SO_2} = 32.03 (V_i - V_{wi})N\left(\frac{V}{V_s}\right) \quad (\text{Eq. 6A-7})$$

Where:

m_{SO_2} = Mass of SO_2 collected, mg.

7.6.2 Sulfur Dioxide Emission Rate.

$$E_{SO_2} = F_f (1.829 \times 10^9) \frac{m_{SO_2}}{(m_{wf} - m_{wi})} \quad (\text{Eq. 6A-8})$$

Where:

E_{SO_2} = Emission rate of SO_2 (ng/J).

F_f = Carbon F Factor for the fuel burned, m³/J, from Method 19.

8. Bibliography

8.1 Same as for Method 6, citations 1 through 8, with the addition of the following:

8.2 Stanley, Jon and P.R. Westlin. An Alternate Method for Stack Gas Moisture Determination. Source Evaluation Society Newsletter, Vol. 3, No. 4, November 1978.

8.3 Whittle, Richard N. and P.R. Westlin. Air Pollution Test Report: Development and Evaluation of an Intermittent Integrated SO_2/CO_2 Emission Sampling Procedure. Environmental Protection Agency, Emission Standard and Engineering Division, Emission Measurement Branch, Research Triangle Park, North Carolina, December 1979. 14 pages.

METHOD 6B—DETERMINATION OF SULFUR DIOXIDE AND CARBON DIOXIDE DAILY AVERAGE EMISSIONS FROM FOSSIL FUEL COMBUSTION SOURCES

1. Applicability and Principle

1.1 **Applicability.** This method applies to the determination of sulfur dioxide (SO_2) emissions from combustion sources in terms of concentration (ng/m^3) and emission rate (ng/J), and for the determination of carbon dioxide (CO_2) concentration (percent) on a daily (24 hours) basis.

The minimum detectable limits, upper limit, and the interferences for SO_2 measurements are the same as for Method 6. 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 (within laboratory precision) is 8.0 percent and the reproducibility (between laboratory precision) is 11.1 percent.

1.2 **Principle.** A gas sample is extracted from the sampling point in the stack intermittently over a 24-hour or other specified time period. Sampling may also be conducted continuously if the apparatus and procedures are appropriately modified (see Note in Section 4.1.1). The SO_2 and CO_2 are separated and collected in the sampling train. The SO_2 fraction is measured by the barium-thorin titration method, and CO_2 is determined gravimetrically.

2. Apparatus.

The equipment required for this method is the same as specified for Method 6A, Section 2, except the isopropanol bubbler is not used. An empty bubbler for the collection of liquid droplets and does not allow direct contact between the collected liquid and the gas sample may be included in the train. 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.

For applications downstream of wet scrubbers, a heated out-of-stack filter (either borosilicate glass wool or glass fiber mat) is necessary. The probe and filter should be heated continuously to at least 20°C above the sourced temperature, but not greater than 120°C . The filter (i.e., sample gas) temperature should be monitored to assure the desired temperature is maintained.

Stainless steel sampling probes, type 316, are not recommended for use with Method 6B because of potential corrosion and contamination of sample. Glass probes or other types of stainless steel, e.g., Hasteloy or Carpenter 20 are recommended for long-term use.

Other sampling equipment, such as Mae West bubblers and rigid cylinders for moisture absorption, which requires sample or reagent volumes other than those specified in this procedure for full effectiveness may be used, subject to the approval of the Administrator.

3. Reagents.

All reagents for sampling and analysis are the same as described in Method 6A, Section 3, except isopropanol is not used for sampling. The hydrogen peroxide absorbing solution shall be diluted to no less than 6 percent by volume, instead of 3 percent as specified in Method 6. If Method 6B is to be operated in a low sample flow condition (less than $100\text{ ml}/\text{min}$), molecular sieve material may be substituted for Ascarite II as the CO_2 absorbing material. The recommended molecular sieve material is Union Carbide $\frac{1}{8}$ inch pellets, 5A, or equivalent. Molecular sieve material need not be discarded following the sampling run provided it is regenerated as per the manufacturer's instruction. Use of molecular sieve material at flow rates higher than $100\text{ ml}/\text{min}$ may cause erroneous CO_2 results.

4. Procedure

4.1 Sampling.

4.1.1 **Preparation of Collection Train.** Preparation of the sample train is the same as described in Method 6A, Section 4.1.4, with the addition of the following:

The sampling train is assembled as shown in Figure 6A-1, except the isopropanol bubbler is not included. The probe must be heated to a temperature sufficient to prevent water condensation and must include a filter (either in-stack, out-of-stack, or both) to prevent particulate entrainment in the peroxide impingers. The electric supply for the probe heat should be continuous and separate from the timed operation of the sample pump.

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 for the amounts of sampling reagents prescribed in this method.

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 $40\text{ ml}/\text{min}$ for the reagent volumes described in this method) is used. Then 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 for the amounts of sampling reagents prescribed in this method.

4.1.2 **Leak-Check Procedure.** The leak-check procedure is the same as described in Method 6, Section 4.1.2.

4.1.3 Sample Collection. 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 as indicated by the rotameter. Assure that the timer is operating as intended, i.e., in the "on" position for the desired period and the cycle repeats as required.

During the 24-hour sampling period, record the dry gas meter temperature one time between 9:00 a.m. and 11:00 a.m., and the barometric pressure.

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 4.1.2. 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 this section (4.1.3) for successive runs.

4.2 Sample Recovery. The procedures for sample recovery (moisture measurement, peroxide solution, and ascarite bubbler) are the same as in Method 6A, Section 4.2.

4.3 Sample Analysis. Analysis of the peroxide impinger solutions is the same as in Method 6, Section 4.3.

5. Calibration

5.1 Metering System.

5.1.1 Initial Calibration. The initial calibration for the volume metering system is the same as for Method 6, Section 5.1.1.

5.1.2 Periodic Calibration Check. After 30 days of operation of the test train, conduct a calibration check as in Section 5.1.1 above, except for the following variations: (1) The leak check is not to be conducted, (2) three or more revolutions of the dry gas meter must be used, and (3) only two independent runs need be made. If the calibration factor does not deviate by more than 5 percent from the initial calibration factor determined in Section 5.1.1, then the dry gas meter volumes obtained during the test series are acceptable and use of the train can continue. If the calibration factor deviates by more than 5 percent, recalibrate the metering system as in Section 5.1.1; and for the calculations for the preceding 30 days of data, use the calibration factor (initial or recalibration) that yields the lower gas volume for each test run. Use the latest calibration factor for succeeding tests.

5.2 Thermometers. Calibrate against mercury-in-glass thermometers initially and at 30-day intervals.

5.3 Rotameter. The rotameter need not be calibrated, but should be cleaned and maintained according to the manufacturer's instruction.

5.4 Barometer. Calibrate against a mercury barometer initially and at 30-day intervals.

5.5 Barium Perchlorate Solution. Standardize the barium perchlorate solution against 25 ml of standard sulfuric acid to which 100 ml of 100 percent isopropanol has been added.

6. Calculations

The nomenclature and calculation procedures are the same as in Method 6A with the following exceptions:

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

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

7. Emission Rate Procedure

The emission rate procedure is the same as described in Method 6A, section 7, except that the timer is needed and is operated as described in this method.

8. Bibliography

8.1 Same as for Method 6, citations 1 through 8, with the addition of the following:

8.2 Stanley, Jon and P.R. Westlin. An Alternate Method for Stack Gas Moisture Determination. Source Evaluation Society Newsletter, Vol. 3, No. 4, November 1978.

8.3 Whittle, Richard N. and P.R. Westlin. Air Pollution Test Report: Development and Evaluation of an Intermittent Integrated SO_2/CO_2 Emission Sampling Procedure. Environmental Protection Agency, Emission Standard and Engineering Division, Emission Measurement Branch, Research Triangle Park, North Carolina, December 1979, 14 pages.

8.4 Butler, Frank E; J.E. Knoll, J.C. Suggs, M.R. Midgett, and W. Mason. The Collaborative Test of Method 6B: Twenty-Four-Hour Analysis of SO_2 and CO . JAPCA, Vol. 33, No. 10, October 1983.

11.0 REFERENCES

1. Butler, Frank E., Joseph E. Knoll, Jack C. Suggs, M. Rodney Midgett, and Wade Mason. The Collaborative Test of Method 6B: Twenty-Four-Hour Analysis of SO₂ and CO₂. JAPCA, Volume 33, No. 10, October 1983, pp. 968-973.
2. Federal Register, Volume 47, No. 231, December 1, 1982. Method 6A - Determination of Sulfur Dioxide, Moisture, and Carbon Dioxide Emissions From Fossil Fuel Combustion Sources and Method 6B - Determination of Sulfur Dioxide and Carbon Dioxide Daily Average Emissions From Fossil Fuel Combustion Sources.
3. Federal Register, Volume 49, No. 51, March 14, 1984. Additions and Corrections to Methods 6A and 6B.
4. Fuerst, Robert G. Improved Temperature Stability of Sulfur Dioxide Samples Collected by the Federal Reference Method. EPA-600/4-78-018, April 1978.
5. Knoll, Joseph E. and M. Rodney Midgett. The Application of EPA Method 6 to High Sulfur Dioxide Concentrations. EPA-600/4-76-038, July 1976.
6. Fuerst, R. G., R. L. Denny, and M. R. Midgett. A Summary of Interlaboratory Source Performance Surveys for EPA Reference Methods 6 and 7 - 1977. Available from U. S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory (MD-77), Research Triangle Park, N.C. 27711.
7. Fuerst, R. G. and M. R. Midgett. A Summary of Interlaboratory Source Performance Surveys for EPA Reference Methods 6 and 7 - 1978. Report in preparation by U. S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory (MD-77), Research Triangle Park, N.C. 27711.
8. Zolner, W. J. Quenching in a Fluorescent Instrument. Thermo Electron Corporation, 85 First Avenue, Waltham, Mass. 17 pages.
9. Wright, R. J. and C. E. Decker. Analysis of EPA Protocol No. 1 Gases for Use as EPA Method 6B Audit Materials. Project Report under EPA Contract No. 68-02-4125, June 1986.

10. Hines, A., EPA, Environmental Monitoring Systems Laboratory, Research Triangle Park, NC 27711. Unpublished research.
11. Jayanty, R. K. M., J. A. Sokash, R. G. Fuerst, T. J. Logan, and M. R. Midgett. Validation of an Audit Material for Method 6B. Proceedings of APCA International Specialty Conference on Continuous Emission Monitoring -- Advances and Issues, October 1985.

12.0 DATA FORMS

Blank data forms are provided on the following pages for the convenience of the Handbook user. Each blank form has the customary descriptive title centered at the top of the page. However, the section-page documentation in the top right-hand corner of each page of other sections has been replaced with a number in the lower right-hand corner that will enable the user to identify and refer to a similar filled-in form in a text section. For example, Form M6A&B-1.2 indicates that the form is Figure 1.2 in Section 3.13.1 (Methods 6A and B) of the Handbook. Future revisions of these forms, if any, can be documented as 1.2A, 1.2B, etc. Fifteen of the blank forms listed below are included in this section. Five are in the Method Highlights subsection as shown by the MH following the form number.

<u>Form</u>	<u>Title</u>
1.2	Procurement Log
2.2	Wet Test Meter Calibration Log
2.4 A&B	Dry Gas Meter Calibration Data Form (English and metric units)
2.5 (MH)	Pretest Sampling Checks
3.1 (MH)	Pretest Preparations
4.1	Field Sampling Data Form for Method 6A
4.2	Method 6B Sampling, Sample Recovery, and Sample Integrity Data Form
4.3	Method 6A Sample Recovery and Integrity Data Form
4.6	Sample Label
4.7 (MH)	On-Site Measurements for Method 6A
4.8 (MH)	On-Site Measurements for Method 6B
5.1 (MH)	Posttest Sampling Checks
5.2	Sulfur Dioxide Analytical Data Form
5.3	Control Sample Analytical Data Form

5.4 (MH)	Posttest Operations
6.1	Method 6A and 6B Calculation Form (Conversion Factors)
6.2A & 6.2B	Method 6A and 6B Sulfur Dioxide Calculation Form (English and metric units)
8.2	Method 6A and 6B Checklist to Be Used by Auditors

PROCUREMENT LOG

Item description	Qty.	Purchase order number	Vendor	Date		Cost	Disposition	Comments
				Ord.	Rec.			

WET TEST METER CALIBRATION LOG

Wet test meter serial number _____ Date _____

Range of wet test meter flow rate _____

Volume of test flask $V_s =$ _____

Satisfactory leak check? _____

Ambient temperature of equilibrate liquid in wet test meter and reservoir _____

Test number	Manometer reading, ^a mm H ₂ O	Final volume (V_f), L	Initial volume (V_i), L	Total volume (V_m) ^b , L	Flask volume (V_s), L	Percent error, ^c %
1						
2						
3						

^a Must be less than 10 mm (0.4 in.) H₂O.

^b $V_m = V_f - V_i$.

^c % error = $100 (V_m - V_s) / V_s =$ _____ (+1%).

Signature of calibration person

DRY GAS METER CALIBRATION DATA FORM (ENGLISH UNITS)

Date _____ Calibrated by _____ Meter box number _____ Wet test meter number _____

Barometer pressure, $P_m =$ _____ in. Hg Dry gas meter temperature correction factor _____ °F

Wet test meter pressure drop (D_m), ^a	Rota-meter setting (R_s),	Wet test meter gas volume (V_m), ^b	Dry test meter gas volume (V_d), ^b ft ³		Wet test meter gas temp (t_w),	Inlet gas temp (t_{d_i}),	Dry test meter				(Y_{r_i}) , ^f
							Outlet gas temp (t_{d_o}),	Average gas temp (t_d), ^c	Time of run (θ), ^d	Average ratio (Y_i), ^e	
in. H ₂ O	ft ³ /min	ft ³	Initial	Final	°F	°F	°F	°F	min		

^a D_m expressed as negative number.

^b Volume passing through meter. Dry gas volume is minimum for at least five revolutions of the meter.

^c The average of t_{d_i} and t_{d_o} if using two thermometers; the actual reading if using one thermometer.

^d The time it takes to complete the calibration run.

^e With Y defined as the average ratio of volumes for the wet test and the dry test meters, $Y_i = Y \pm 0.02 Y$ for calibration and $Y_i = Y \pm 0.05 Y$ for the posttest checks; thus,

$$Y_i = \frac{V_w (t_d + 460^\circ\text{F}) [P_m + (D_m/13.6)]}{V_d (t_w + 460^\circ\text{F}) (P_m)} \quad (\text{Eq. 1}) \quad \text{and} \quad Y = \frac{Y_1 + Y_2 + Y_3}{3} = \underline{\hspace{2cm}}. \quad (\text{Eq. 2})$$

^f With Y_r defined as the average ratio of volumetric measurement by wet test meter to rotameter.

Tolerance $Y_r = 1 \pm 0.05$ for calibration and $Y \pm 0.1$ for posttest checks.

$$Y_{r_i} = \frac{V_w (t_d + 460^\circ\text{F}) [P_m + (D_m/13.6)]}{\theta (t_w + 460^\circ\text{F}) (P_m) (R_s)} \quad (\text{Eq. 3}) \quad \text{and} \quad Y_r = \frac{Y_1 + Y_2 + Y_3}{3} = \underline{\hspace{2cm}}. \quad (\text{Eq. 4})$$

DRY GAS METER CALIBRATION DATA FORM (METRIC UNITS)

Date _____ Calibrated by _____ Meter box number _____ Wet test meter number _____
 Barometer pressure, $P_m =$ _____ in. Hg Dry gas meter temperature correction factor _____ °C

Wet test meter pressure drop, $(D_m)^a$ mm H ₂ O	Rota-meter setting (R_s) , cc/min	Wet test meter gas volume $(V_m)^b$ L	Dry test meter gas volume $(V_d)^b$ L		Wet test meter gas temp (t_w) , °C	Inlet gas temp (t_{d_i}) , °C	Dry test meter				$(Y_{r_i})^f$
			Initial	Final			Outlet gas temp (t_{d_o}) , °C	Average gas temp $(t_d)^c$, °C	Time of run $(\theta)^d$, min	Average ratio $(Y_i)^e$	

^a D_m expressed as negative number.

^b Volume passing through meter. Dry gas volume is minimum for at least five revolutions of the meter.

^c The average of t_{d_i} and t_{d_o} if using two thermometers; the actual reading if using one thermometer.

^d The time it takes to complete the calibration run.

^e With Y defined as the average ratio of volumes for the wet test and the dry test meters, $Y_i = Y \pm 0.02 Y$ for calibration and $Y_i = Y \pm 0.05 Y$ for the posttest checks; thus,

$$Y_i = \frac{V_w (t_d + 273^\circ\text{C}) [P_m + (D_m/13.6)]}{V_d (t_w + 273^\circ\text{C}) (P_m)} \quad (\text{Eq. 1}) \quad \text{and} \quad Y = \frac{Y_1 + Y_2 + Y_3}{3} = \underline{\hspace{2cm}}. \quad (\text{Eq. 2})$$

^f With Y_r defined as the average ratio of volumetric measurement by wet test meter to rotameter.

Tolerance $Y_r = 1 \pm 0.05$ for calibration and $Y \pm 0.1$ for posttest checks.

$$Y_{r_i} = \frac{V_w (t_d + 273^\circ\text{C}) [P_m + (D_m/13.6) 1000]}{\theta (t_w + 273^\circ\text{C}) (P_m) (R_s)} \quad (\text{Eq. 3}) \quad \text{and} \quad Y_r = \frac{Y_1 + Y_2 + Y_3}{3} = \underline{\hspace{2cm}}. \quad (\text{Eq. 4})$$

FIELD SAMPLING DATA FORM FOR METHOD 6A

Plant name _____ City _____
 Sample location _____ Date _____
 Operator _____ Sample number _____
 Barometric pressure, mm (in.) Hg _____ Probe length m (ft) _____
 Probe material _____ Probe heater setting _____
 Meter box number _____ Meter calibration factor (Y) _____
 Ambient temperature, °C (°F) _____ Sampling point location _____
 Initial leak check _____ Sample purge time, min _____
 Final leak check _____ Remarks _____

Sampling time, min	Clock time, 24 h	Sample volume, L (ft ³)	Sample flow rate setting, L/min (ft ³ /min)	Sample volume metered (V _m), L (ft ³)	Percent deviation, ^a %	Dry gas meter temp, °C (°F)	Impinger temp, °C (°F)
Total		Total		V _m avg	Avg dev	Avg	Max temp

$$^a \text{ Percent deviation} = \frac{V_m - V_m \text{ avg}}{V_m \text{ avg}} \times 100 \text{ (must be within 10 percent).}$$

METHOD 6B SAMPLING, SAMPLE RECOVERY, AND
SAMPLE INTEGRITY DATA FORM

Plant _____ Initial leak check _____
 Sample location _____ Final leak check _____
 Operator _____ Recovery date _____
 Run No. _____ Recovered by _____
 Sampling period Start: Date Time _____
 Stop: Date Time _____

Dry Gas Meter Rotameter
 Final reading _____ L Initial setting _____ L or cc/min
 Initial reading _____ L Final setting _____ L or cc/min
 Volume metered _____ L
 Dry Gas Meter Calibration Factor, Y _____

Meter Temperature _____ °F Barometric Pressure _____ in. Hg
 time _____ time

Probe Temperature	Filter Temperature	Ascarite Column
Initial _____ °F	Initial _____ °F	Final wt _____ g
Final _____ °F	Final _____ °F	Initial wt _____ g
		Net wt _____ g of CO ₂

Moisture

	1st bubbler	2nd impinger	3rd impinger	4th bubbler
Final wt	_____ g	_____ g	_____ g	_____ g
Initial wt	_____ g	_____ g	_____ g	_____ g
Net wt	_____ g	_____ g	_____ g	_____ g
	Total moisture _____ g			% spent

RECOVERED SAMPLE (If Applicable)

H ₂ O ₂ blank	Liquid level
container no. _____	marked _____
Impinger contents	Liquid level
container no. _____	marked _____
H ₂ O blank	Liquid level
container no. _____	marked _____
Samples stored and locked _____	
Received by _____	Date _____
Remarks _____	

METHOD 6A SAMPLE RECOVERY AND INTEGRITY DATA FORM

	1st bubbler	2nd impinger	3rd impinger	4th bubbler
Final wt	_____g	_____g	_____g	_____g
Initial wt	_____g	_____g	_____g	_____g
Net wt	_____g	_____g	_____g	_____g
Total moisture	_____g			_____ % spent

Ascarite column: Final wt _____g
 Initial wt _____g
 Net wt _____g of CO₂
 _____ % spent

Recovered Sample

H ₂ O ₂ blank container no. _____	Liquid level marked _____
Impinger contents container no. _____	Liquid level marked _____
H ₂ O blank container no. _____	Liquid level marked _____

Samples stored and locked _____

Remarks _____

Received by _____ Date _____

Remarks _____

SAMPLE LABEL

Plant	_____	City	_____	Remarks _____ _____ _____ _____		
Site	_____	Sample Type	_____			
Date	_____	Run Number	_____			
Front rinse	<input type="checkbox"/>	Front filter	<input type="checkbox"/>		Front solution	<input type="checkbox"/>
Back rinse	<input type="checkbox"/>	Back filter	<input type="checkbox"/>		Back solution	<input type="checkbox"/>
Solution	_____	Level marked	<input type="checkbox"/>			
Volume:	Initial	_____	Final		_____	
Cleanup by	_____					

SULFUR DIOXIDE ANALYTICAL DATA FORM

Plant _____ Date _____

Sample location _____ Analyst _____

Volume and normality of barium perchlorate 1 _____ ml _____ N

2 _____ ml _____ N

Standardization blank _____ ml (< 0.5 ml) 3 _____ ml _____ N

_____ N, avg

Sample number	Sample identification number	Total sample volume (V_{soln}), ml	Sample aliquot volume (V_a) ^a , ml	Volume of titrant (V_t) ^b , ml		
				1st titration	2nd titration	Average
1						
2						
3						
4						
5						
6						
Field Blank		N/A				$V_{tb} =$

^a Volume for the blank must be the same as that of the sample aliquot.

^b 1st titration = 0.99 to 1.01 or 1st titration - 2nd titration ≤ 0.2 ml.
2nd titration

Signature of analyst _____

Signature of reviewer or supervisor _____

CONTROL SAMPLE ANALYTICAL DATA FORM

Plant _____ Date analyzed _____

Analyst _____ $N_{\text{Ba}(\text{ClO}_4)_2}$ _____

Weight of ammonium sulfate is 1.3214 g? _____

Dissolved in 2 L of distilled water? _____

Titration of blank _____ ml $\text{Ba}(\text{ClO}_4)_2$ (must be <0.5 ml)

Control sample number	Time of analysis, 24 h	Titrant volume, ^a ml			
		1st	2nd	3rd	Avg

^a Two titrant volumes must agree within 0.2 ml.

$$(\text{ml } \text{Ba}(\text{ClO}_4)_2 - \text{ml Blank}) \times N_{\text{Ba}(\text{ClO}_4)_2} = 25 \text{ ml} \times 0.01N$$

(control) (control)
sample) sample)

(_____ ml - _____ ml) x _____ N = _____

(must agree within 5%, i.e., 0.238 to 0.262)

Does value agree? ____yes ____no

Signature of analyst

Signature of reviewer

METHOD 6A AND 6B CALCULATION FORM (CONVERSION FACTORS)

METER VOLUME (metric to English)

$$V_m = \text{---} \cdot \text{---} \text{ liter}$$

$$V = V_m (\text{in liters}) \times 0.03531 \text{ ft}^3/\text{liter} = \text{---} \cdot \text{---} \text{ ft}^3$$

METER TEMPERATURE (metric to English)

$$t_m = \text{---} \cdot \text{---} ^\circ\text{C}$$

$$t_m = [t_m (^\circ\text{C}) \times 1.8] + 32 = \text{---} \cdot \text{---} ^\circ\text{F}$$

$$T_m = t_m (^\circ\text{F}) + 460 = \text{---} \cdot \text{---} ^\circ\text{R}$$

BAROMETRIC PRESSURE (metric to English)

$$P_{\text{bar}} = \text{---} \cdot \text{---} \text{ mm Hg}$$

$$P_{\text{bar}} = P_{\text{bar}} (\text{mm Hg}) \times 0.03937 \text{ in. Hg/mm Hg} = \text{---} \cdot \text{---} \text{ in. Hg}$$

METER VOLUME (English to metric)

$$V_m = \text{---} \cdot \text{---} \text{ ft}^3$$

$$V_m = V_m (\text{ft}^3) \times 0.02832 \text{ m}^3/\text{ft}^3 = \text{---} \cdot \text{---} \text{ m}^3$$

METER TEMPERATURE (English to metric)

$$t_m = \text{---} \cdot \text{---} ^\circ\text{F}$$

$$t_m = [t_m (^\circ\text{F}) - 32] \times 5/9 = \text{---} \cdot \text{---} ^\circ\text{C}$$

$$T_m = t_m (^\circ\text{C}) + 273 = \text{---} \cdot \text{---} ^\circ\text{K}$$

BAROMETRIC PRESSURE (English to metric)

$$P_{\text{bar}} = \text{---} \cdot \text{---} \text{ in. Hg}$$

$$P_{\text{bar}} = P_{\text{bar}} (\text{in. Hg}) \times 25.4 \text{ mm Hg/in. Hg} = \text{---} \cdot \text{---} \text{ mm Hg}$$

METHOD 6A AND 6B CALCULATION FORM (ENGLISH UNITS)

STANDARD METER VOLUME (English units)

$$V_m = _ \cdot _ _ _ \text{ ft}^3, Y = _ \cdot _ _ _$$

$$P_{\text{bar}} = _ \cdot _ _ \text{ in. Hg}, T_m = _ _ _ \cdot _ \text{ } ^\circ\text{R}$$

$$V_m(\text{std}) = 17.64 V_m Y \left[\frac{P_{\text{bar}}}{T_m} \right] = _ \cdot _ _ _ \text{ dscf}$$

CO₂ VOLUME COLLECTED, STANDARD CONDITIONS (English units)

$$V_{\text{CO}_2}(\text{std}) = 0.01930 (m_{\text{af}} - m_{\text{ai}}) = _ \cdot _ _ _ \text{ dscf}$$

Equation 6-1

CO₂ CONCENTRATION (percent by volume)

$$C_{\text{CO}_2} = \frac{V_{\text{CO}_2}(\text{std})}{V_m(\text{std}) + V_{\text{CO}_2}(\text{std})} \times 100 = _ \cdot _ _ _ \%$$

Equation 6-4

SO₂ CONCENTRATION (English units)

$$V_t = _ \cdot _ _ \text{ ml}, V_{\text{tb}} = _ \cdot _ _ \text{ ml}, N = _ \cdot _ _ _ \text{ (g-eq)/ml}$$

$$V_{\text{soln}} = _ \cdot _ _ \text{ ml}, V_a = _ \cdot _ _ \text{ ml}$$

$$C_{\text{SO}_2} = \frac{7.061 \times 10^{-5} (V_t - V_{\text{tb}}) N \left(\frac{V_{\text{soln}}}{V_a} \right)}{V_m(\text{std}) + V_{\text{CO}_2}(\text{std})} = _ \cdot _ _ _ \times 10^{-4} \text{ lb/dscf}$$

Equation 6-3

METHOD 6A AND 6B CALCULATION FORM (ENGLISH UNITS)

(continued)

MOISTURE CONCENTRATION (percent)

$$\begin{aligned} m_{wf} &= \text{---} \cdot \text{---} \text{ g, } m_{wi} = \text{---} \cdot \text{---} \text{ g} \\ V_{w(\text{std})} &= 0.04707 (m_{wf} - m_{wi}) = \text{---} \text{ dscf} \end{aligned} \quad \text{Equation 6-2}$$

$$C_{H_2O} = \frac{V_{H_2O(\text{std})}}{V_{m(\text{std})} + V_{H_2O(\text{std})} + V_{CO_2(\text{std})}} \times 100 = \text{---} \cdot \text{---} \% \quad \text{Equation 6-5}$$

EMISSION RATE OF SO₂ (English units) (using meter volumes)

$$\begin{aligned} F_c &= \text{---} \text{ scf of CO}_2/\text{million Btu} \\ E_{SO_2} &= C_{SO_2} F_c \frac{100}{C_{CO_2}} = \text{---} \cdot \text{---} \text{ lb SO}_2/\text{million Btu} \end{aligned}$$

(not using meter sample volume)

$$F_c = \text{---} \text{ scf of CO}_2/\text{million Btu}$$

$$m_{SO_2} = 32.03 (V_t - V_{tb})^N \left(\frac{V_{\text{soln}}}{V_a} \right) = \text{---} \cdot \text{---} \text{ mg of SO}_2 \text{ collected} \quad \text{Equation 6-6}$$

$$E_{SO_2} = F_c (1.141 \times 10^{-3}) \frac{m_{SO_2}}{(m_{af} - m_{ai})} = \text{---} \cdot \text{---} \text{ lb SO}_2/\text{million Btu} \quad \text{Equation 6-7}$$

SO₂ CONCENTRATION (ppm)

$$C_{SO_2} (\text{ppm}) = \frac{C_{SO_2} (\text{lb/dscf})}{1.663 \times 10^{-7}} = \text{---} \cdot \text{---} \text{ ppm}$$

METHOD 6A AND 6B CALCULATION FORM (METRIC UNITS)

STANDARD METER VOLUME (metric units) (using meter volumes)

$$V_m = \text{---} \cdot \text{---} \text{ liter} \times 0.001 = \text{---} \cdot \text{---} \text{ m}^3$$

$$Y = \text{---} \cdot \text{---}, P_{\text{bar}} = \text{---} \cdot \text{---} \text{ mm Hg}, T_m = \text{---} \cdot \text{---} \text{ } ^\circ\text{K}$$

$$V_m(\text{std}) = 0.3858 V_m Y \frac{P_{\text{bar}}}{T_m} = \text{---} \cdot \text{---} \text{ dscm}$$

CO₂ VOLUME COLLECTED, STANDARD CONDITIONS (metric units)

$$m_{\text{af}} = \text{---} \cdot \text{---} \text{ g}, m_{\text{ai}} = \text{---} \cdot \text{---} \text{ g}$$

$$V_{\text{CO}_2}(\text{std}) = 5.467 \times 10^{-4} (m_{\text{af}} - m_{\text{ai}}) = \text{---} \cdot \text{---} \text{ dscm}$$

Equation 6-1

CO₂ CONCENTRATION (percent by volume)

$$C_{\text{CO}_2} = \frac{V_{\text{CO}_2}(\text{std})}{V_m(\text{std}) + V_{\text{CO}_2}(\text{std})} \times 100 = \text{---} \cdot \text{---} \%$$

Equation 6-4

SO₂ CONCENTRATION (metric units)

$$V_t = \text{---} \cdot \text{---} \text{ ml}, V_{\text{tb}} = \text{---} \cdot \text{---} \text{ ml}, N = \text{---} \cdot \text{---} \text{ (g - eq)/ml},$$

$$V_{\text{soln}} = \text{---} \cdot \text{---} \text{ ml}, V_a = \text{---} \cdot \text{---} \text{ ml}$$

$$C_{\text{SO}_2} = \frac{32.03 (V_t - V_{\text{tb}}) N \left(\frac{V_{\text{soln}}}{V_a} \right)}{V_m(\text{std}) + V_{\text{CO}_2}(\text{std})} = \text{---} \cdot \text{---} \text{ mg/dscm}$$

Equation 6-3

METHOD 6A AND 6B CALCULATION FORM (METRIC UNITS)
(continued)

MOISTURE CONCENTRATION (percent)

$$m_{wf} = \text{---} \cdot \text{---} \text{ g}, m_{wi} = \text{---} \cdot \text{---} \text{ g}$$

$$V_{m(std)} = 1.336 \times 10^{-3} (m_{wf} - m_{wi}) = \text{---} \text{ dscm}$$

Equation 6-2

$$C_{H_2O} = \frac{V_{H_2O}}{V_{m(std)} + V_{H_2O(std)} + V_{CO_2(std)}} \times 100 = \text{---} \cdot \text{---} \%$$

Equation 6-5

EMISSION RATE OF SO₂ (metric units)
(using meter volumes)

$$F_C = \text{---} \cdot \text{---} \times 10^{-7} \text{ dscm of CO}_2/\text{J}$$

$$E_{SO_2} = C_{SO_2} F_C \frac{10^8}{C_{CO_2}} = \text{---} \cdot \text{---} \text{ ng/J}$$

(not using meter volumes)

$$F_C = \text{---} \cdot \text{---} \times 10^{-7} \text{ dscm of CO}_2/\text{J}$$

$$m_{SO_2} = 32.03 (V_t - V_{tb}) N \left(\frac{V_{soln}}{V_a} \right) = \text{---} \cdot \text{---} \text{ mg of SO}_2 \text{ collected}$$

Equation 6-6

$$E_{SO_2} = F_C (1.829 \times 10^9) \frac{m_{SO_2}}{(m_{af} - m_{ai})} = \text{---} \cdot \text{---} \text{ ng/J}$$

Equation 6-7

METHOD 6A AND 6B CHECKLIST TO BE USED BY AUDITORS

Yes	No	Comment	
			<u>Presampling Preparation</u>
—	—	—	1. Knowledge of process conditions
—	—	—	2. Calibration of pertinent equipment, in particular, the dry gas meter, prior to each field test
			<u>On-Site Measurements</u>
—	—	—	3. Leak testing of sampling train after sample run
—	—	—	4. Preparation and addition of absorbing solutions to impingers
—	—	—	5. Constant rate sampling (for Method 6A only)
—	—	—	6. Purging of the sampling train and rinsing of the impingers and connecting tubes to recover the sample (for Method 6A only)
—	—	—	7. Recording of pertinent process conditions during sample collection
—	—	—	8. Maintaining the probe at a given temperature
			<u>Postsampling</u>
—	—	—	9. Control sample analysis--accuracy and precision
—	—	—	10. Sample aliquoting techniques
—	—	—	11. Titration technique, particularly endpoint precision
—	—	—	12. Use of detection blanks in correcting field sample results
—	—	—	13. Weighing of the CO ₂ absorbant
—	—	—	14. Calculation procedure/check
—	—	—	15. Calibration checks
—	—	—	16. Standardized barium perchlorate solution
—	—	—	17. Result of the audit sample
<u>General Comments</u>			