Section 3.13

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

OUTLINE

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 studies[1] 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.

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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 5Å 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 5Å molecular

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).

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*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_2O_2, 30 percent							
Isopropanol, 100%* (for Method 6A)							
Drierite							
Ascarite _______ or 5Å 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? ____________________

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*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 $\geq$6 percent H_2O_2* ____________________

3rd: 15 ml of $\geq$6 percent H_2O_2* ____________________

4th: Approx. 25 g of Drierite* ____________________

Approx. 150 g of Ascarite II or 250 g 5Å 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? ____________________

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 $\pm$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 $\pm$0.1 g at room temp?* ____________________

Sample containers sealed and identified?* ____________________

Samples properly stored and locked? ____________________

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*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

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* Most significant items/parameters to be checked.

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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 CO_2 absorber to nearest 0.1 g* ____________

Final weight of CO_2 absorber to nearest 0.1 g* _____________

All data recorded? ___________ Reviewed by _______________

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* Most significant items/parameters to be checked.

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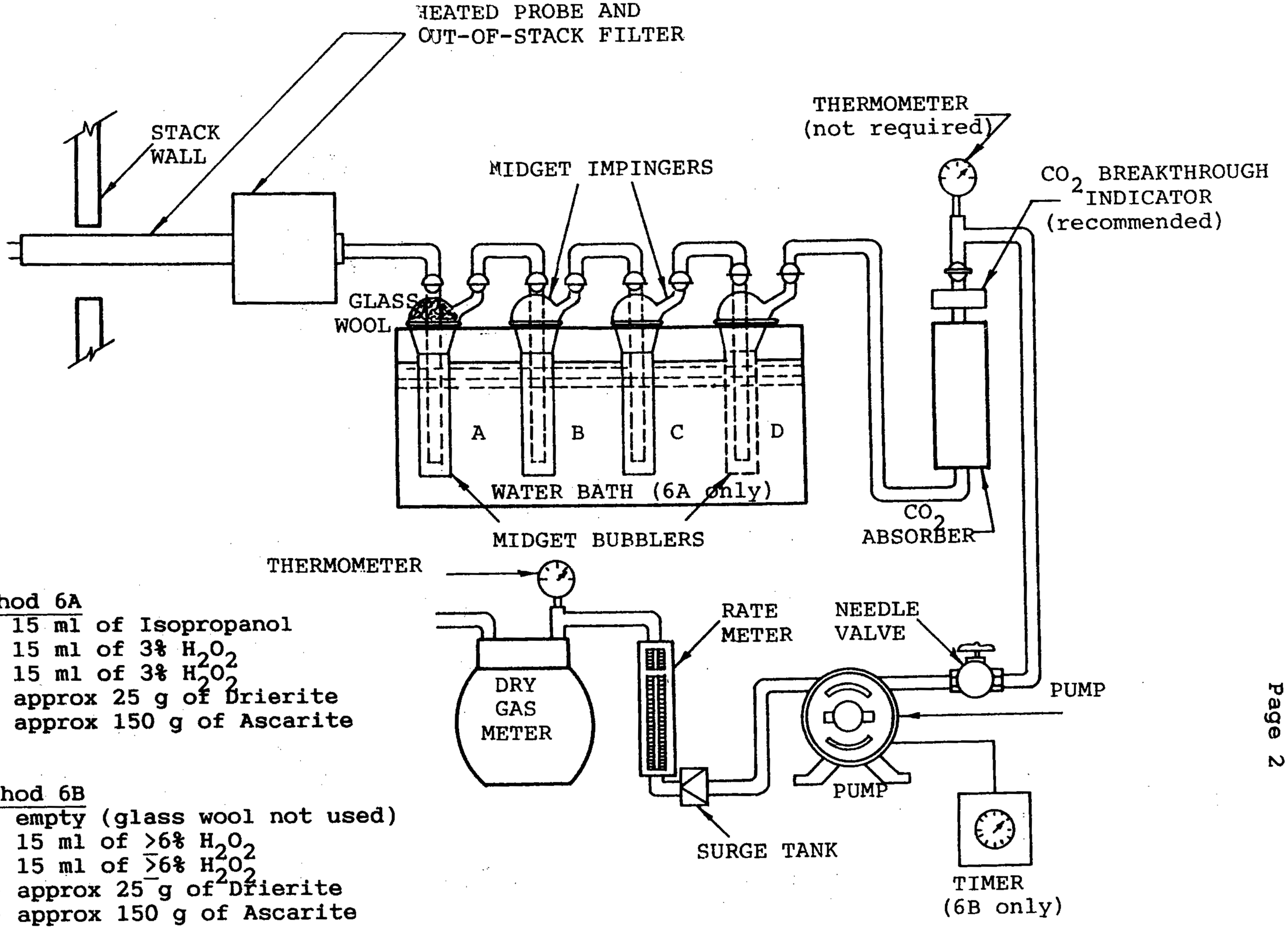
1.0 PROCUREMENT OF APPARATUS AND SUPPLIES

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



Method 6A

A - 15 ml of Isopropanol
B - 15 ml of 3% H_2O_2
C - 15 ml of 3% H_2O_2
D - approx 25 g of Drierite
E - approx 150 g of Ascarite

Method 6B

A - empty (glass wool not used)
B - 15 ml of >6% H_2O_2
C - 15 ml of >6% H_2O_2
D - approx 25 g of Drierite
E - approx 150 g of Ascarite

Figure 1.1. Sampling train.

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Item description	Qty.	Purchase order number	Vendor	Date		Cost	Disposition	Comments
				Ord.	Rec.			
Meter box (Meth 6) w/diaphragm pump	1	77A131	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

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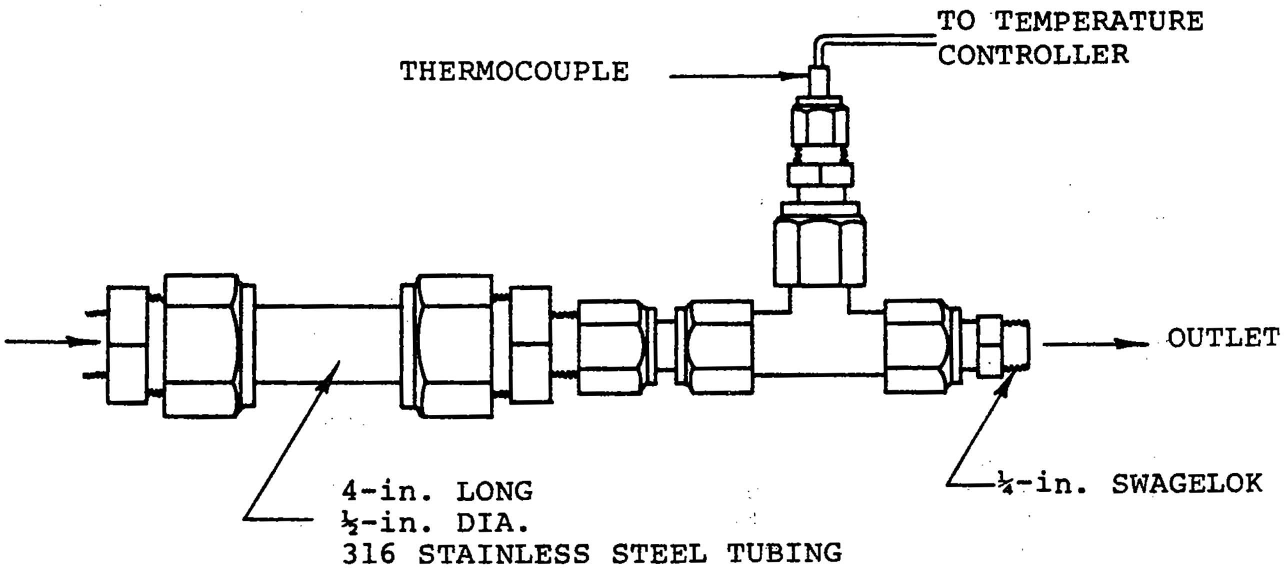
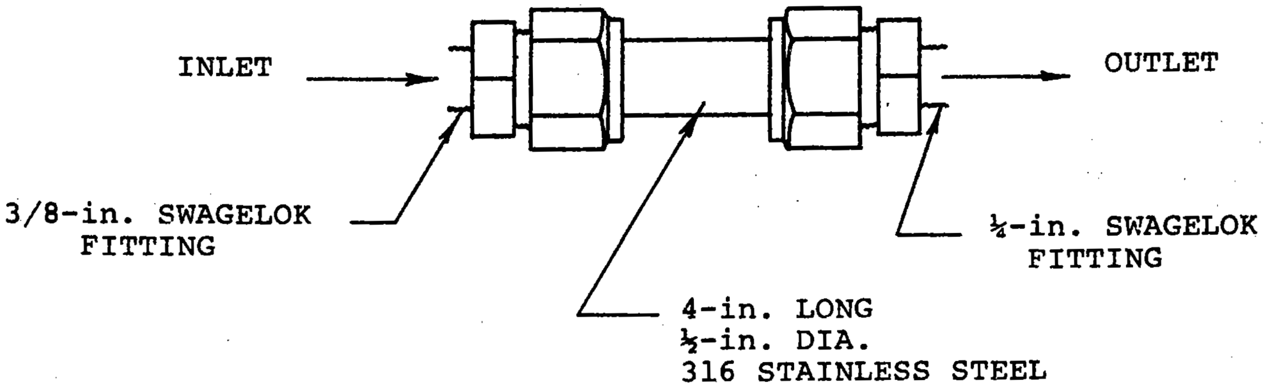


FILTER HOLDER WITH THERMOCOUPLE TO MONITOR EXIT TEMPERATURE.



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 <u>CO_2 Absorber</u> - 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 <u>Vacuum Pump</u> - 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.

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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 CO_2 and SO_2 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 wet test meter must have a capacity of at least 0.003 m^3/min (0.1 ft^3/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.

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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.) H_2O.

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.

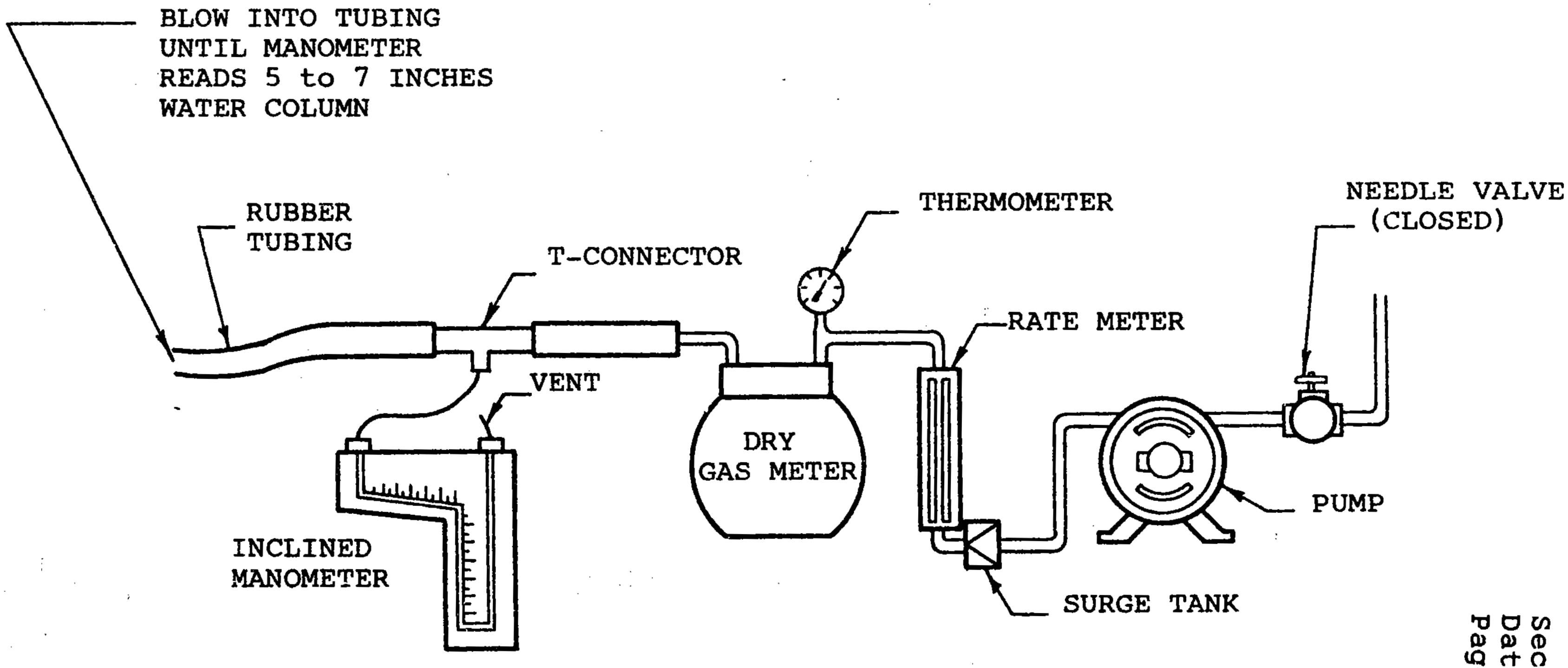

Figure 1.4. Meter box leak check.

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.

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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 CO_2 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 $KMnO_4$ 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 H_2O 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.

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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.

CO_2 Absorber - Ascarite, Ascarite II, or 5Å molecular sieve. Ascarite or Ascarite II is the recommended absorption media to collect the CO_2 for both methods because it is an indicating type of sorbant. The indicating type sorbant will provide a visual check of whether the sorbant was spent prior to the completion of the run. Ascarite may also be used for both methods; the 5A 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 ($Ba(ClO_4)_2 \cdot 3H_2O$) in 200 ml of deionized distilled water and dilute to 1 liter with 100 percent isopropanol. Alternatively, use 1.22 g of ($BaCl_2 \cdot 2H_2O$) 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 ±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
Sampling			
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° 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)

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Table 1.1 (continued)

Apparatus and supplies	Acceptance limits	Frequency and method of measurement	Action if requirements are not met
Balance	Accurate to ±0.05g 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)

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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 ($Ba(ClO_4)_2 \cdot 3H_2O$), reagent grade or certified ACS	As above	As above
Sulfuric acid	Sulfuric acid, 0.0100N ±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

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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.

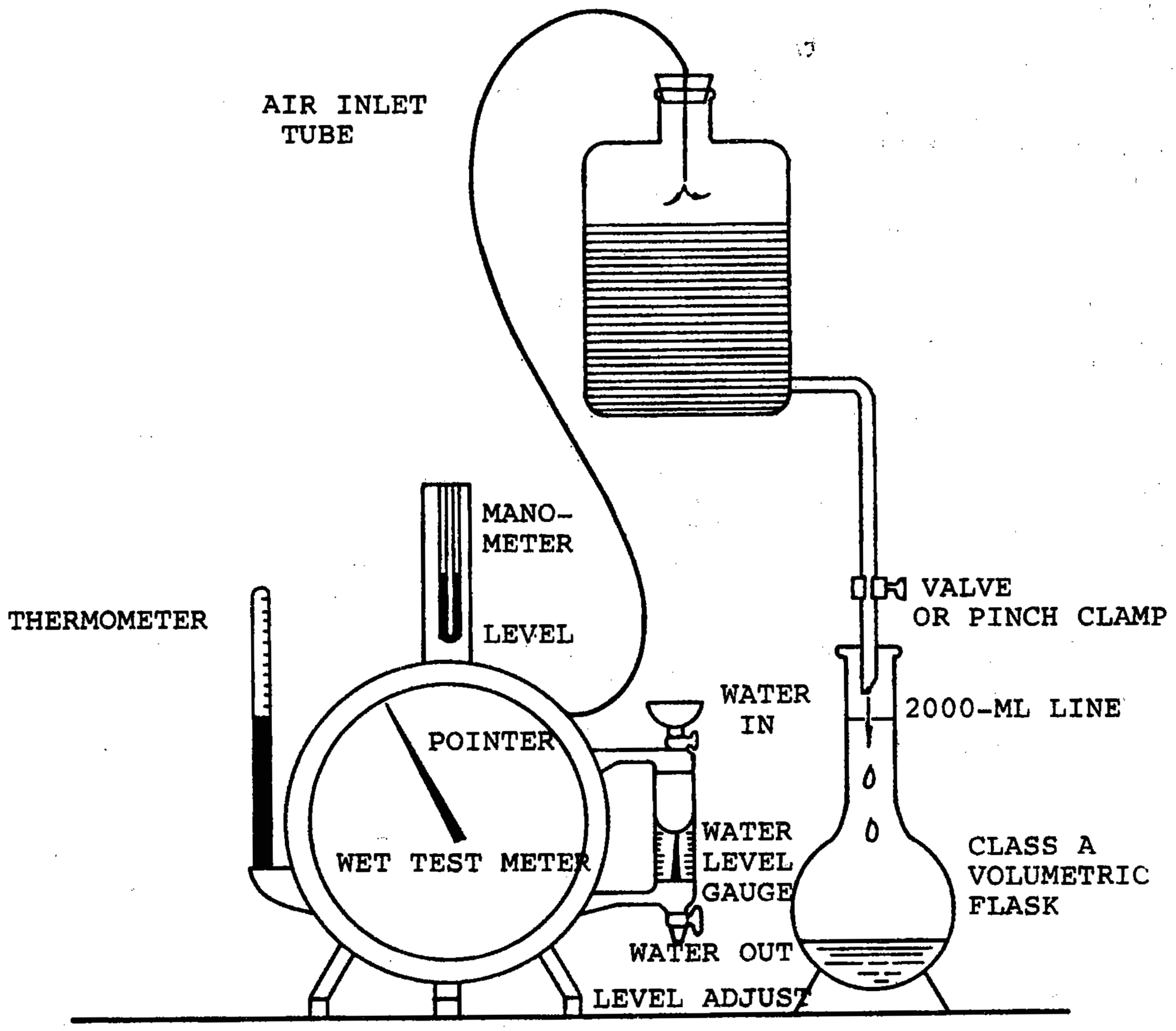

Figure 2.1. Calibration check apparatus for wet test meter.

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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_1) 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_2O	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.) H_2O.

[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 cm^3/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 CO_2 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 CO_2 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).

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

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, m^3 (ft^3),

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

D_m = pressure drop across the wet test meter, mm (in.) H_2O,

t_d = average temperature of dry gas meter, ^oC (^oF),

V_d = volume measured by the dry gas meter, m^3 (ft^3), and

t_w = temperature of wet test meter, ^oC (^oF).

6. Adjust and recalibrate or reject the dry gas meter if one or more values of Y_i fall outside the interval $\bar{Y} \pm 0.02\bar{Y}$, where $\bar{Y}$ is the average for three runs. Otherwise, the $\bar{Y}$ (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

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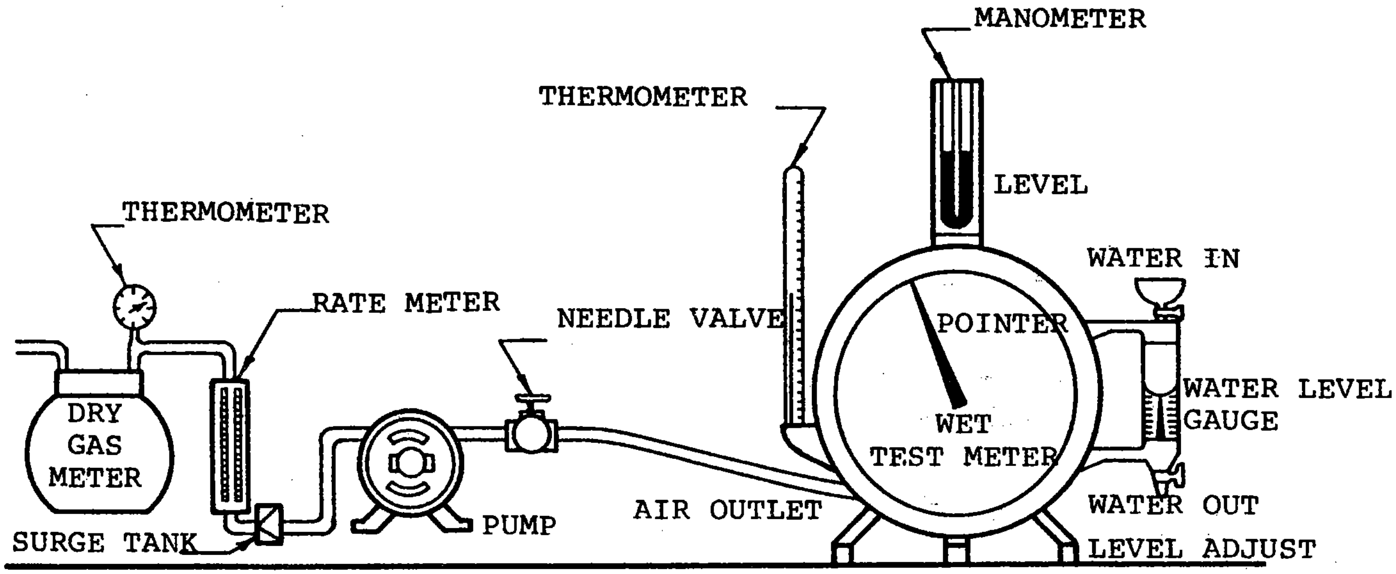

Figure 2.3. Sample metering system calibration setup.

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_2O	Rotameter 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 (θ),[d] min	Average ratio (Y_i),[e]	
0.25	0.035	1.058	725.613	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	1.026
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,

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

[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.

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

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

Date 1-25-85 Calibrated by RRS 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_2O	Rotameter 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,

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

[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.

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

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.

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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 CO_2 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 Calibrated by RKS
Meter box number E-6

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	$Y_i = Y \pm 0.02Y$ at a flow rate of about 1 L/min	Calibrate vs. wet test meter initially and when the posttest check is not within $Y \pm 0.05Y$	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 ± 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 SO_2 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 CO_2 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 Yes	Acceptable No	Quantity required	Ready Yes	Ready No	Loaded and packed Yes	Loaded and packed No
Probe							
Type liner	✓		4	✓		✓	
Glass X							
Stainless steel ____							
Other ____							
Heated properly	✓						
Leak checked on sampling train	✓						
Filter or Filter Assembly							
Glass wool X	✓		4 out-of-stack	✓		✓	
Other ____							
Glassware							
Midget bubbler	✓		8	✓		✓	
Midget impinger	✓		8	✓		✓	
Size N/A							
Type N/A							
Meter System							
With timer ____							
Without timer X							
Leak-free pump*	✓		2	✓		✓	
Rate meter*	✓						
Dry gas meter*	✓						
Reagents							
Distilled water	✓		2 gal	✓		✓	
H_2O_2, 30%	✓		1 qt	✓		✓	
Isopropanol, 100%* (for Method 6A)	✓		1 gal	✓		✓	
Drierite	✓		10#	✓		✓	
Ascarite X	✓		10#	✓		✓	
or 5A molecular sieve* ____							
Other							
Barometer	✓		1	✓		✓	
CO_2 absorber column	✓		4	✓		✓	
Balance	✓		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 CO_2 Absorber and Volumetric Glassware - A rigid container lined with polyethylene foam material protects CO_2 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	1. Clean probe internally by brushing with tap water, then deionized distilled water, then acetone; allow to dry in air before test	1. Retrace cleaning procedure and assembly
	2. Probe leak free at at 250 mm (10 in.) Hg	2. Visual check before test	2. Replace
	3. No moisture condensation	Check out heating system initialy and when moisture appears during testing	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
Reagents			
Sampling	1. Requires all ACS grade reagents	1. Prepare fresh daily and store in sealed containers	1. Prepare new reagent
	2. New CO_2 absorber material	2. Purchase new	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
Package Equipment for Shipment			
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 ~~(ft³)~~	Sample flow rate setting, L/min ~~(ft³/min)~~	Sample volume metered (V_m), L ~~(ft³)~~	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] Percent deviation = $\dfrac{V_m - V_m \text{ avg}}{V_m \text{ avg}}$ x 100 (must be within 10 percent).

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

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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
Inital wt 303.6 g
Net wt 8.5 g of CO_2

Moisture

	1st bubbler	2nd impinger	3rd impinger	4th bubbler
Final wt	73.1 g	89.3 g	88.3 g	96.7 g
Initial wt	73.1 g	87.0 g	88.2 g	95.2 g
Net wt	0.0 g	2.0 g	0.1 g	1.5 g

Total moisture 3.6 g 20 % spent

RECOVERED SAMPLE (If Applicable)

H_2O_2 blank container no. AP-1AB Liquid level marked ✓
Impinger contents container no. AP-1 Liquid level marked ✓
H_2O blank container no. AP-1WB Liquid level marked ✓
Samples stored and locked ✓
Received by Sonya 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 midget bubblers and impingers and CO_2 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 midget 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 H_2O_2 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 midget impingers (100 ml of 30 percent H_2O_2 to 1 liter with water).

3. Pack glass wool into the top of the first midget bubbler to prevent sulfuric acid mist from entering the midget impingers and causing a high bias for SO_2.

(1570

4. Add about 25 g of Drierite to the last midget bubbler.

5. Calibrate the balance by initially placing a CO_2 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 CO_2 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 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 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 CO_2 absorber containing Ascarite or Ascarite II be added in line downstream of the primary CO_2 absorber as a breakthrough indicator. Ascarite II turns white when CO_2 is absorbed. The CO_2 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 $\geq$6 percent hydrogen peroxide to each of the two midget impingers (250 ml of 30 percent H_2O_2 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 CO_2 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	89.9 g	90.8 g	88.4 g	97.6 g
Initial wt	90.2 g	88.2 g	87.9 g	97.1 g
Net wt	−0.3 g	2.6 g	0.5 g	0.5 g

Total moisture 3.3 g 10 % spent

Ascarite column:
Final wt 304.7 g
Initial wt 300.1 g
Net wt 4.6 g of CO_2
30 % spent

Recovered Sample

H_2O_2 blank container no. AP-1AB

Liquid level marked ✓

Impinger contents container no. AP-1

Liquid level marked ✓

H_2O blank container no. AP-1WB

Liquid level marked ✓

Samples stored and locked ✓

Remarks

Received by Sonya Engle Date 12/21/85

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 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 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 CO_2 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 CO_2 results.[1] It is recommended that a second, smaller CO_2 absorber containing Ascarite II be added in line downstream of the primary CO_2 absorber as a breakthrough indicator. Ascarite II turns white when CO_2 is absorbed. The CO_2 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 CO_2 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. H_2O 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

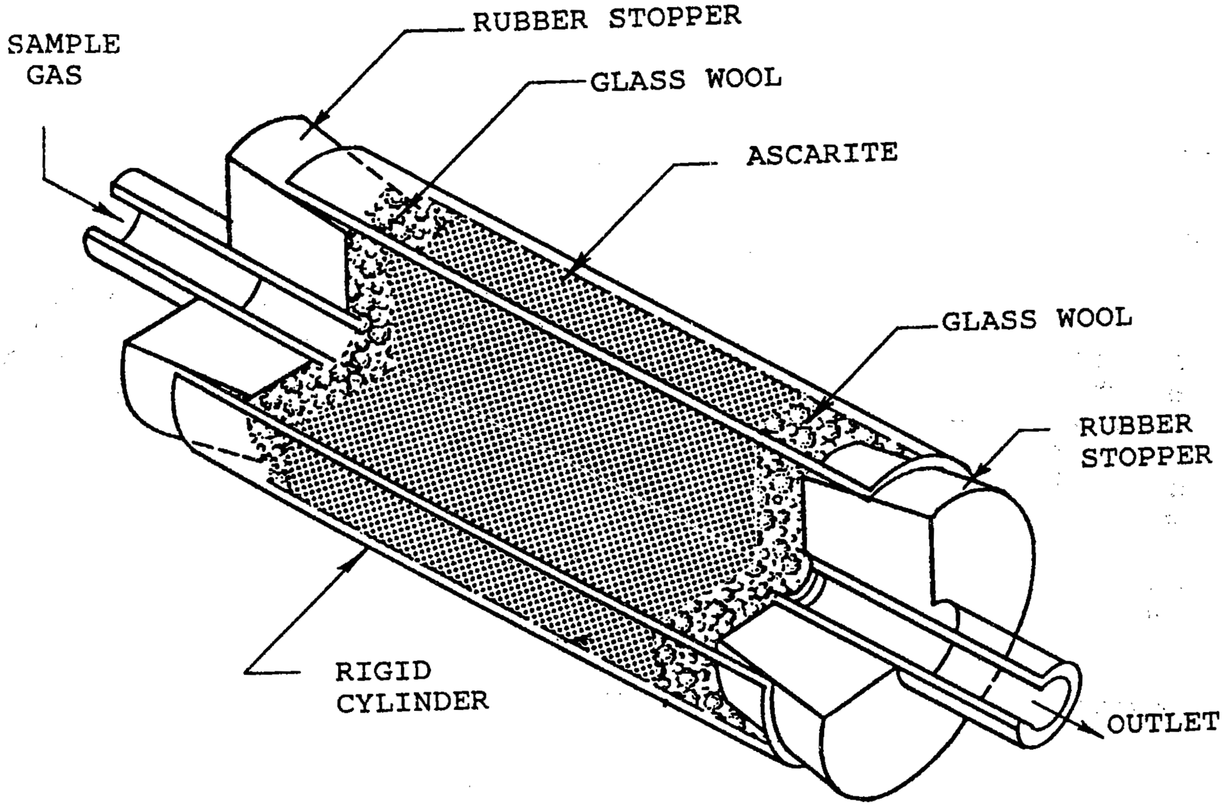


Figure 4.4. CO_2 absorber.

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.

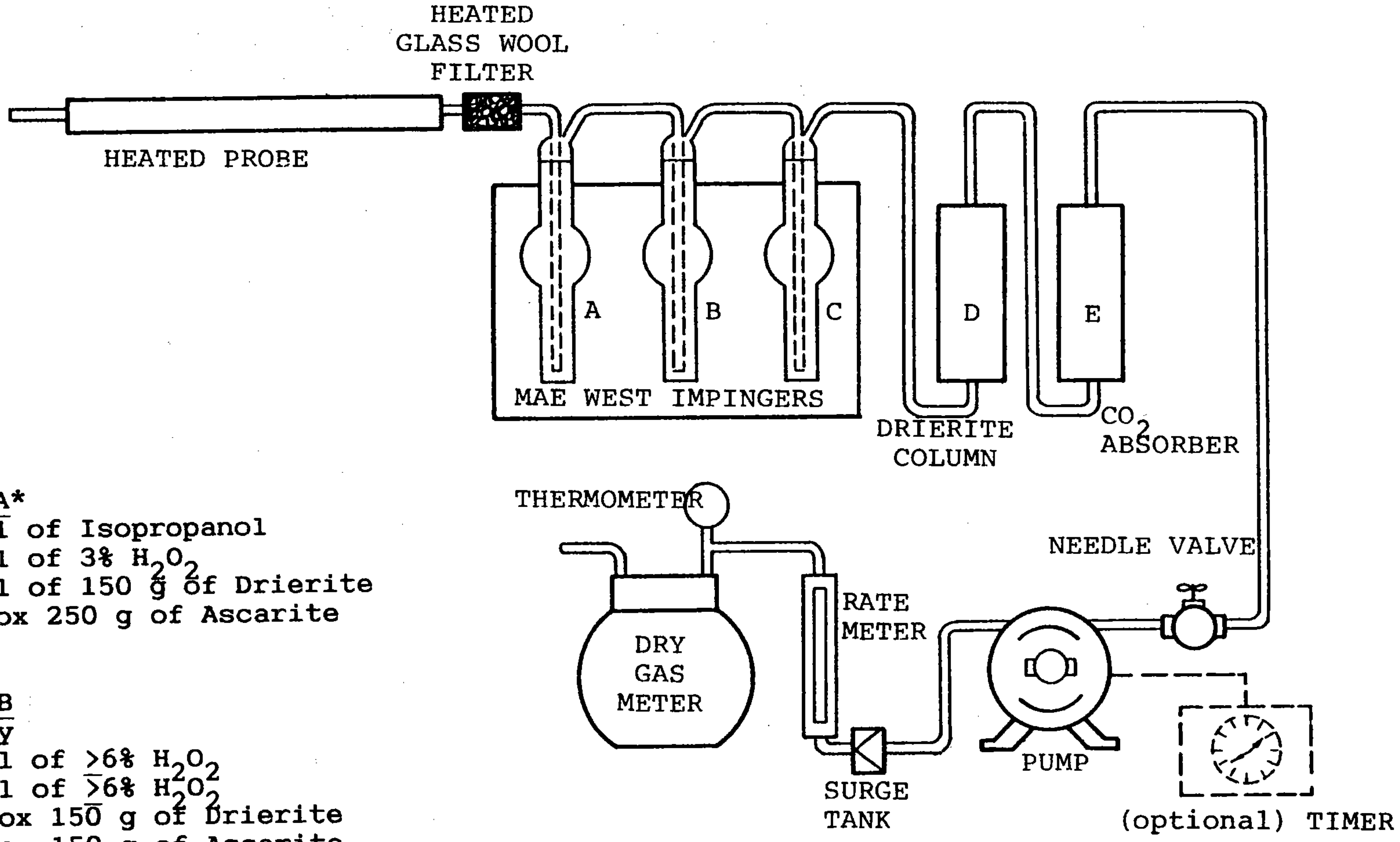
4. Place a loosely packed filter of glass wool in the end of the probe, and connect the probe to the bubbler. Alternately, if the out-of-stack filter is used, it should be packed prior to attaching the probe filter assembly to the bubbler.

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[3] 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 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.

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% H_2O_2
C - 15 ml of 150 g of Drierite
E - approx 250 g of Ascarite

Method 6B

A - Empty
B - 15 ml of $\geq$6% H_2O_2
C - 15 ml of $\geq$6% H_2O_2
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 midget 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 °C (68 °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

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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. H_2O, 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 SO_2. 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.

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2. If the emissions results are to be calculated in terms of ppm SO_2 or lb SO_2/million Btu without using the results of CO_2 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 SO_2 per million Btu using the grams of CO_2 collected in the sampling train, the vacuum gauge may be placed on the inlet to the first impinger of H_2O_2. 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 SO_2/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 stablizes 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 SO_2 in comparison to the CO_2 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 SO_2 corrected to compensate for leakage rate;

M_{SO_2} = mass of SO_2 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 H_2O, 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 SO_2 or lb SO_2/million Btu without using the results of CO_2 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 SO_2/million Btu using the grams of CO_2 collected in the sampling train, the U-tube manometer may be placed on the inlet to the first impinger of H_2O_2. 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 SO_2/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 H_2O 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 H_2O_2. 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 CO_2 absorber to come to room temperature ($\approx 20^\circ C$), 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 CO_2 absorber.

4. Weigh the bubblers, the impingers, and CO_2 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 SO_2.

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.

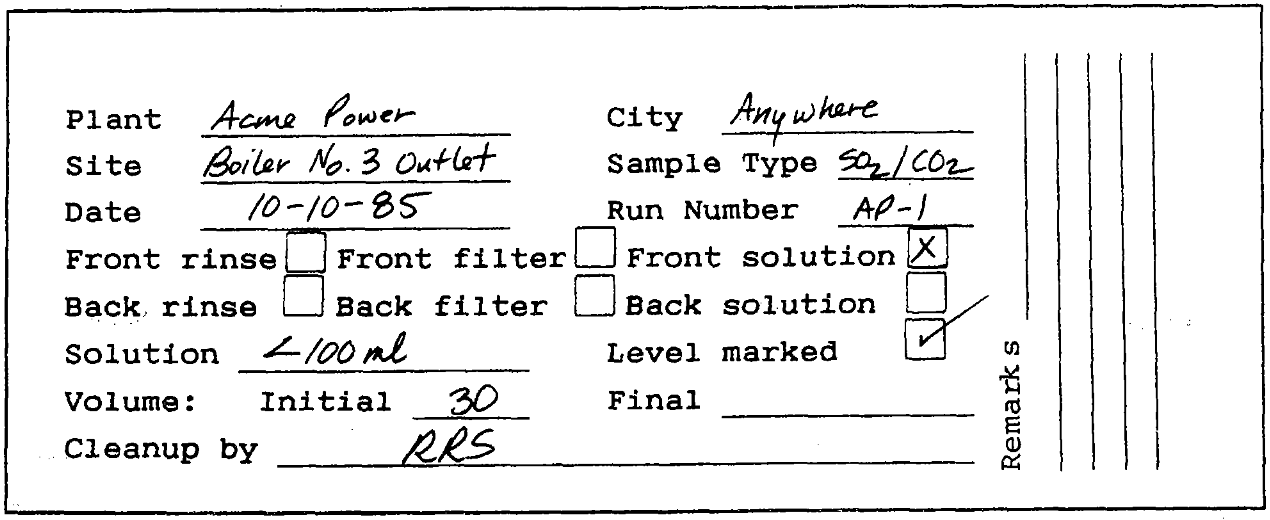
Warning: It has been demonstrated that the contamination of the sample with Ascarite or Drierite will bias the results.

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 Acme Power
City Anywhere
Site Boiler No. 3 Outlet
Sample Type SO_2/CO_2
Date 10-10-85
Run Number AP-1
Front rinse ☐ Front filter ☐ Front solution ☒
Back rinse ☐ Back filter ☐ Back solution ☐
Solution <100 ml
Level marked ☑
Volume: Initial 30
Final
Cleanup by RRS

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 CO_2 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?* ✓

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*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	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	Prepare 3% H_2O_2 fresh daily; use pipette or graduated cylinder to add solutions	Reassemble collection system
	Method 6B. Leave first bubbler empty, add 15 ml of $\geq$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	Prepare $\geq$6% H_2O_2 fresh daily; use pipette or graduated cylinder to add solutions	Reassemble collection system
Assembling the sampling train	1. Assemble to specifications in Fig. 1.1	1. Before each sampling	1. Reassemble
	2. A leakage rate $\leq$2% of the average sampling rate	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 $\geq$250 mm (10 in.) Hg	2. Correct the leak
Sampling (Method 6A constant rate)	1. Method 6A Within 10% of a constant rate	1. Calculate % deviation for each sample using equation in Fig. 4.1	1. Repeat the sampling, or obtain acceptance from a representative of the Administrator

(continued)

Table 4.1. (continued)

Operation	Acceptance limits	Frequency and method of measurement	Action if requirements are not met
	2. Minimum acceptable time is 20 min and volume is 20 liters corrected to STP or as specified by regulation	2. Make a quick calculation prior to completion and an exact calculation after completion	2. As above
	3. Less than 2% leakage rate at 250 mm (10 in.) Hg	3. Leak check after sample run (mandatory); use same procedure as above	3. As above
	4. Purge remaining SO_2 from isopropanol	4. Drain ice, and purge 15 min with clean air at the sample rate	4. As above
Sampling (Method 6B intermittent)	1. At least 12 equally and evenly spaced intermittent sample intervals at about 1.0 L/min	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	1. Repair or recalibrate time and/or rotameter and repeat the sampling or obtain acceptance from a representative of the Administrator
	2. Sample time is 24 hours and the acceptable sample volume is between 25 and 60 liters	2. Make a calculation after each sample run	2. As above
	3. Less than 2% leakage rate at 250 mm (10 in.) Hg	3. Leak check after sample run (mandatory)	3. Void the test, or use an alternative procedure acceptable to a representative of the Administrator

(continued)

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Table 4.1 (continued)

Operation	Acceptance limits	Frequency and method of measurement	Action if requirements are not met
Sampling (Method 6B rate constant)	1. Sample at a constant rate of between 20 and 40 ml/min	1. Calculate sample rate at the completion of run	1. Repair or recalibrate rotameter, and repeat run or obtain acceptance from a representative of the Administrator
	2. Sample time is 24 hours and the acceptable sample volume is between 25 and 60 liters	2. Calculate sample volume at end of sample run	2. As above
	3. Less than 2% leakage at 500 mm (20 in.) H_2O	3. Leak check after sample run (mandatory)	3. Void the test, or use an alternative procedure acceptable to a representative of the Administrator
Sample Recovery	1. Balance accurate to within 0.1 g	1. Calibrate with Class S weights	1. Adjust, repair, or reject
	2. Determine moisture collected in impingers	2. Wipe the outside of the impingers and bubblers clean, and weigh each to the nearest 0.1 g	2. Repeat run, or use alternative moisture determination technique

(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

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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

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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.

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* 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.

$$Ba^{++} + SO_4^{=} + \underset{\text{(yellow)}}{\text{thorin}(x^{++})} \rightarrow BaSO_4 + \underset{\text{(pink)}}{\text{thorin}(Ba^{++})} \qquad \text{Equation 5-1}$$

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 ±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 ±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 ($Ba(ClO_4)_2.3H_2O$) in 200 ml of water, and dilute to 1-liter with isopropanol. Alternatively, 1.22 g of barium chloride dihydrate ($BaCl_2.2H_2O$) 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.)

Equation 5-2

$$N_{NaOH} = \frac{\text{mg KHP}}{(\text{ml Titrant} - \text{ml Blank}) \times (204.23)}$$

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

$$\text{NaOH} + \text{KHP} + \underset{\text{(colorless)}}{\text{phenolphthalein}} \rightarrow \text{KNaP} + \text{HOH} + \underset{\text{(pink)}}{\text{phenolphthalein}}$$

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:

$$N_{H_2SO_4} = \frac{(\text{ml NaOH}_{acid} - \text{ml NaOH}_{blank}) \times N_{NaOH}}{25} \qquad \text{Equation 5-4}$$

where

$N_{H_2SO_4}$ = calculated normality of sulfuric acid,

ml NaOH_{acid} = volume of titrant used for H_2SO_4, ml,

ml NaOH_{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.

$$N_{Ba(ClO_4)_2} = \frac{N_{H_2SO_4} \times 25}{(\text{ml } Ba(ClO_4)_2 - \text{ml Blank})} \qquad \text{Equation 5-5}$$

where

$N_{Ba(ClO_4)_2}$ = calculated normality of barium perchlorate,

$N_{H_2SO_4}$ = normality of standardized sulfuric acid,

ml $Ba(ClO_4)_2$ = 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_{tb} = 0

[a] Volume for the blank must be the same as that of the sample aliquot.

[b] $\frac{\text{1st titration}}{\text{2nd titration}} = 0.99$ to 1.01 or 1st titration - 2nd titration ≤ 0.2 ml.

Signature of analyst Kate N Urquhart

Signature of reviewer or supervisor Sonya 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 <u>Control Samples</u> - 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 ($(NH_4)_2SO_4$) 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. <u>Note</u>: 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
$N_{Ba(ClO_4)_2}$ 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 $Ba(ClO_4)_2$ (must be <0.5 ml)

Control sample number	Time of analysis, 24 h	Titrant volume,[a] ml			
		1st	2nd	3rd	Avg
1	0930	25.0	25.0		25.0

[a] Two titrant volumes must agree within 0.2 ml.

(ml $Ba(ClO_4)_2$ - ml Blank) x $N_{Ba(ClO_4)_2}$ = 25 ml (control sample) x 0.01N (control sample)

(25.0 ml - 0.0 ml) x 0.010 N = 0.250

(must agree within 5%, i.e., 0.238 to 0.262)

Does value agree? ✓ yes ____ no

Katie W Urquhart Signature of analyst
Sonya 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@ 0.100N

Are replicate control samples within 0.2 ml? yes

Is accuracy of control sample analysis ±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 CO_2 absorber to nearest 0.1 g* yes

Final weight of CO_2 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.

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_{soln_i}, correct the sample volume (V_{soln}) by using Equation 5-6,

$$V_{soln}' = V_{soln} \frac{V_{soln_i}}{V_{soln_f}} \qquad \text{Equation 5-6}$$

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 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
Sampling Apparatus			
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 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
Analysis			
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 restandardize
Control sample	Titrants differ by $\leq$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 $\leq$1% or $\leq$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

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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, milliequivalents/ml,

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P_{bar} = barometeric 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, $^{\circ}K$ ($^{\circ}R$),
T_{std} = standard absolute temperature, $293^{\circ}K$ ($528^{\circ}R$),
V_a = volume of sample aliquot titrated, ml,
$V_{CO_2(std)}$ = standard equivalent volume of CO_2 collected, dry basis, m^3,
V_m = dry gas volume measured by dry gas meter, dcm (dcf),
$V_{m(std)}$ = 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_t = 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,
$V_{w(std)}$ = 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 -

$$V_{CO_2(std)} = 5.467 \times 10^{-4} (m_{af} - m_{ai}) \qquad \text{Equation 6-1}$$

6.2.2 Moisture Volume Collected, Corrected to Standard Conditions -

$$V_{w(std)} = 1.336 \times 10^{-3} (m_{wf} - m_{wi}) \qquad \text{Equation 6-2}$$

6.2.3 **SO_2 Concentration** -

$$C_{SO_2} = 32.03 \, \frac{(V_t - V_{tb}) \, N \left(\frac{V_{soln}}{V_a} \right)}{V_{m(std)} + V_{CO_2(std)}} \qquad \text{Equation 6-3}$$

6.2.4 **CO_2 Concentration** -

$$C_{CO_2} = \frac{V_{CO_2(std)}}{V_{m(std)} + V_{CO_2(std)}} \times 100 \qquad \text{Equation 6-4}$$

6.2.5 **Moisture Concentration** -

$$C_w = \frac{V_{H_2O(std)}}{V_{m(std)} + V_{H_2O(std)} + V_{CO_2(std)}} \qquad \text{Equation 6-5}$$

6.3 Emission Rate Calculations

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 Method 6A and the abbreviated procedure are described in Subsection 4.3.

6.3.1 **SO_2 Mass Collected** -

$$m_{SO_2} = 32.03 \, (V_t - V_{tb}) \, N \left(\frac{V_{soln}}{V_a} \right) \qquad \text{Equation 6-6}$$

where

m_{SO_2} = mass of SO_2 collected, mg.

6.3.2 **Sulfur Dioxide Emission Rate** -

$$E_{SO_2} = F_c \, (1.829 \times 10^9) \, \frac{m_{SO_2}}{(m_{af} - m_{ai})} \qquad \text{Equation 6-7}$$

where

E_{SO_2} = emission rate of SO_2, ng/J, and

F_c = carbon F factor for the fuel burned, m^3/J, from Method 19.

METER VOLUME (metric to English)

V_m = 33.68 liter

V = V_m (in liters) x 0.03531 ft^3/liter = 1.1892 ft^3

METER TEMPERATURE (metric to English)

t_m = 22.4 °C

t_m = [t_m (°C) x 1.8] + 32 = 72.3 °F

T_m = t_m (°F) + 460 = 532.3 °R

BAROMETRIC PRESSURE (metric to English)

P_{bar} = 757. mm Hg

P_{bar} = P_{bar} (mm Hg) x 0.03937 in. Hg/mm Hg = 29.80 in. Hg

METER VOLUME (English to metric)

V_m = 1.1892 ft^3

V_m = V_m (ft^3) x 0.02832 m^3/ft^3 = .03368 m^3

METER TEMPERATURE (English to metric)

t_m = 72.3 °F

t_m = [t_m (°F) - 32] x 5/9 = 22.4 °C

T_m = t_m (°C) + 273 = 295.4 °K

BAROMETRIC PRESSURE (English to metric)

P_{bar} = 29.80 in. Hg

P_{bar} = P_{bar} (in. Hg) x 25.4 mm Hg/in. Hg = 757. mm Hg

Figure 6.1. Method 6A and 6B calculation form (conversion factors).

STANDARD METER VOLUME (English units)

V_m = 1.1892 ft^3, Y = 1.071

P_{bar} = 29.80 in. Hg, T_m = 532.3 $^{\circ}$R

$$V_m(\text{std}) = 17.64\ V_m\ Y \left[\frac{P_{bar}}{T_m}\right] = 1.2578 \text{ dscf}$$

CO_2 VOLUME COLLECTED, STANDARD CONDITIONS (English units)

m_{af} = 308.3 g, m_{ai} = 300.1 g

$$V_{CO_2}(\text{std}) = 0.01930\ (m_{af} - m_{ai}) = 0.1583 \text{ dscf}$$

Equation 6-1

CO_2 CONCENTRATION (percent by volume)

$$C_{CO_2} = \frac{V_{CO_2(std)}}{V_m(\text{std}) + V_{CO_2}(\text{std})} \times 100 = 11.17\ \%$$

Equation 6-4

SO_2 CONCENTRATION (English units)

V_t = 11.30 ml, V_{tb} = 0.00 ml, N = 0.0102 (g-eq)/ml
V_{soln} = 100.0 ml, V_a = 20.0 ml

$$C_{SO_2} = \frac{7.061 \times 10^{-5}\ (V_t - V_{tb})N}{V_m(\text{std}) + V_{CO_2}(\text{std})}\left(\frac{V_{soln}}{V_a}\right) = 0.2874 \times 10^{-4} \text{ lb/dscf}$$

Equation 6-3

Figure 6.2A. Method 6A and 6B calculation form (English units).

MOISTURE CONCENTRATION (percent)

m_{wf} = 296.3 g, m_{wi} = 294.1 g

$V_{w(std)} = 0.04707\ (m_{wf} - m_{wi}) =$ .1035 dscf   Equation 6-2

$$C_{H_2O} = \frac{V_{H_2O(std)}}{V_{m(std)} + V_{H_2O(std)} + V_{CO_2(std)}} \times 100 = 6.81\ \%$$

Equation 6-5

EMISSION RATE OF SO_2 (English units)
(using meter volumes)

F_c = 1810 scf of CO_2/million Btu

$$E_{SO_2} = C_{SO_2}\ F_c\ \frac{100}{C_{CO_2}} = 0.465 \text{ lb } SO_2\text{/million Btu}$$

(not using meter sample volume)

F_c = 1810 scf of CO_2/million Btu

$$m_{SO_2} = 32.03\ (V_t - V_{tb})N \left(\frac{V_{soln}}{V_a}\right) = 18.46 \text{ mg of } SO_2 \text{ collected}$$

Equation 6-6

$$E_{SO_2} = F_c\ (1.141 \times 10^{-3})\ \frac{m_{SO_2}}{(m_{af} - m_{ai})} = 0.465 \text{ lb } SO_2\text{/million Btu}$$

Equation 6-7

SO_2 CONCENTRATION (ppm)

$$C_{SO_2}\ (\text{ppm}) = \frac{C_{SO_2}\ (\text{lb/dscf})}{1.663 \times 10^{-7}} = 172.8 \text{ ppm}$$

Figure 6.2A. (continued)

STANDARD METER VOLUME (metric units)
(using meter volumes)

V_m = 33.68 liter x 0.001 = 0.03368 m^3

Y = 1.071, P_{bar} = 757. mm Hg, T_m 295.4 ^oK

$V_m(std) = 0.3858\ V_m Y \frac{P_{bar}}{T_m}$ = .03566 dscm

CO_2 VOLUME COLLECTED, STANDARD CONDITIONS
(metric units)

m_{af} = 308.3 g, m_{ai} = 300.1 g

$V_{CO_2}(std) = 5.467 \times 10^{-4}(m_{af} - m_{ai})$ = .00448 dscm

Equation 6-1

CO_2 CONCENTRATION (percent by volume)

$$C_{CO_2} = \frac{V_{CO_2}(std)}{V_m(std) + V_{CO_2}(std)} \times 100 = 11.17\ \%$$

Equation 6-4

SO_2 CONCENTRATION (metric units)

V_t = 11.03 ml, V_{tb} = 0.00 ml, N = 0.0102 (g - eq)/ml,

V_{soln} = 100.0 ml, V_a = 20.0 ml

$$C_{SO_2} = \frac{32.03\ (V_t - V_{tb})\ N \left(\frac{V_{soln}}{V_a}\right)}{V_{m(std)} + V_{CO_2(std)}} = 448.9 \text{ mg/dscm}$$

Equation 6-3

Figure 6.2B. Method 6A and 6B calculation form (metric units).

MOISTURE CONCENTRATION (percent)

m_{wf} = 296.3 g, m_{wi} = 294.1 g

$V_{m(std)} = 1.336 \times 10^{-3} (m_{wf} - m_{wi})$ = .00294 dscm

Equation 6-2

$$C_{H_2O} = \frac{V_{H_2O}}{V_{m(std)} + V_{H_2O(std)} + V_{CO_2(std)}} \times 100 = 6.82\%$$

Equation 6-5

EMISSION RATE OF SO_2 (metric units)
(using meter volumes)

F_c = 0.486 x 10^{-7} dscm of CO_2/J

$$E_{SO_2} = C_{SO_2} F_c \frac{10^8}{C_{CO_2}} = 195.3 \text{ ng/J}$$

(not using meter volumes)

F_c = 0.486 x 10^{-7} dscm of CO_2/J

$m_{SO_2} = 32.03 (V_t - V_{tb}) N\left(\frac{V_{soln}}{V_a}\right)$ = 18.02 mg of SO_2 collected

Equation 6-6

$$E_{SO_2} = F_c (1.829 \times 10^9) \frac{m_{SO_2}}{(m_{af} - m_{ai})} = 195.3 \text{ ng/J}$$

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 ft^3) 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 maintenance	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 tests[3] 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 SO_2/dsm^3 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 SO_2/dsm^3 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 SO_2 per million Btu which would be about 1300 mg SO_2/dsm^3 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 SO_2 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.

$$RE = \frac{C_d - C_a}{C_a} \times 100 \qquad \text{Equation 8-1}$$

where

C_d = Determined audit sample concentration mg SO_2/dsm^3, and

C_a = Actual audit concentration, mg SO_2/dsm^3.

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 mg SO_2/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 cont
tinous 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 SO_2 and CO_2 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 SO_2 in the range of 200 to 400 ppm and CO_2 in the range of 12 percent to 16 percent, with the balance of the gas as N_2. 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 SO_2 concentration in the cylinder, since a UV fluorescence SO_2 signal is quenched by the presence of CO_2.[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 SO_2 and CO_2 could be expected from commercial gas manufacturers following EPA Protocol No. 1 and to determine if these mixtures were stable. The accuracy for CO_2 was within 1.2 percent for all nine cylinders. The accuracy for SO_2 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 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 SO_2 and 10 percent CO_2 showed the SO_2 to be stable over the entire period of the study (22 months). Finally, in a study conducted by EPA,[11] cylinder gases of nominal 250 ppm SO_2 and 10 percent CO_2 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 SO_2/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 SO_2/ million Btu,

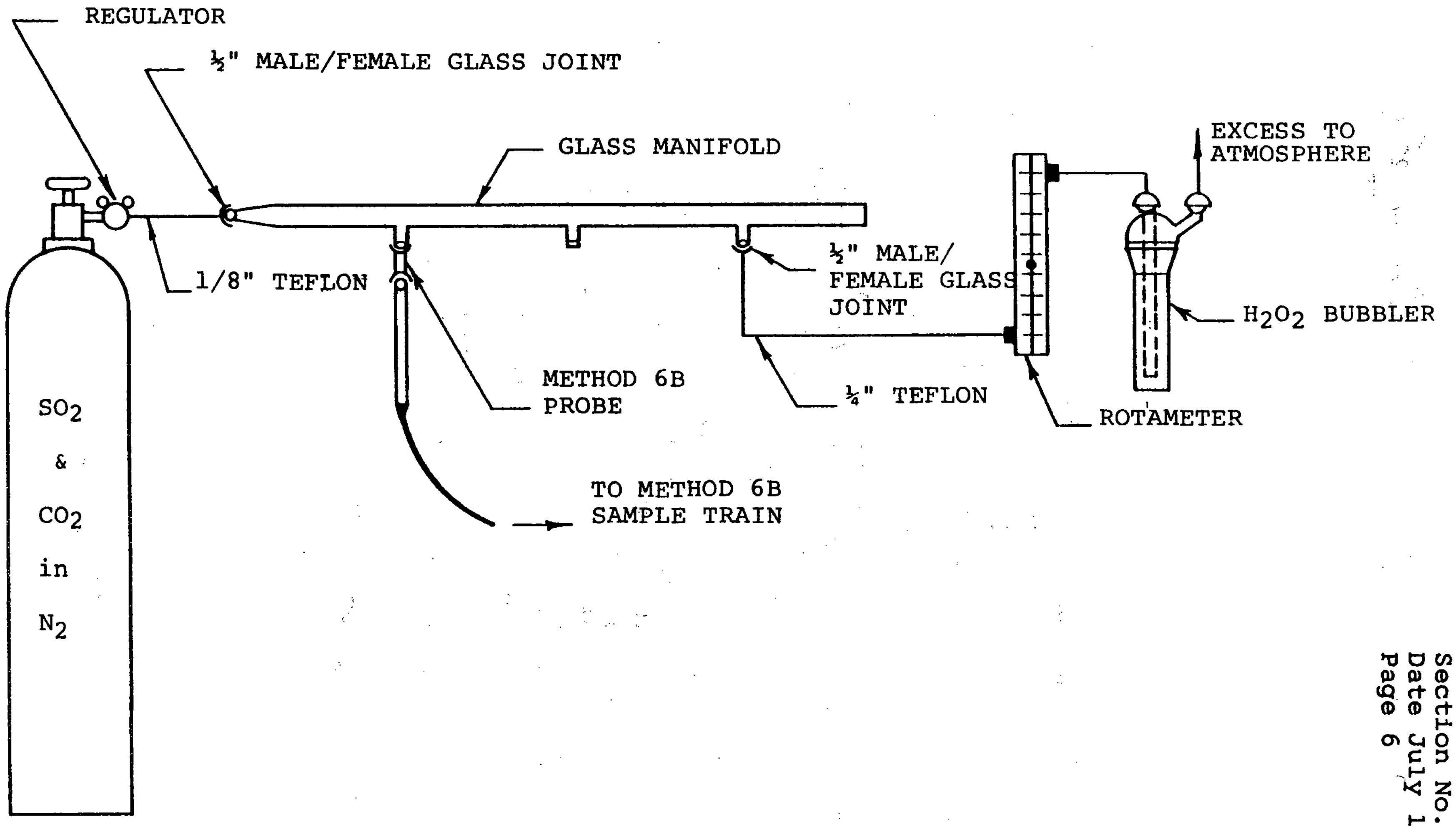

Figure 8.1. Cylinder Gas Audit of Method 6B.

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.

$$C_a = 1.66 \times 10^{-7}\ SO_{2_{ppm}},\ F_c\ \frac{100}{\%\ CO_2} \qquad \text{Equation 8-3}$$

where

C_a = Concentration in audit cylinder, lb SO_2/million Btu,

$SO_{2_{ppm}}$ = 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.

$$RE = \frac{C_{M6B} - C_a}{C_a} \times 100 \qquad \text{Equation 8-4}$$

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.

<u>SO_2 Analysis</u> - 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 <u>Audit of Data Processing</u> - 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.

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Yes	No	Comment	
			Presampling Preparation
✓			1. Knowledge of process conditions
✓			2. Calibration of pertinent equipment, in particular, the dry gas meter, prior to each field test
			On-Site Measurements
✓			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
			Postsampling
✓			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

General Comments

* Analysis of EPA audit samples were successful along with analysis of compliance samples.

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)	<u>Frequency</u>: Once during every enforcement source test <u>Method</u>: 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)	<u>Frequency</u>: Once prior to setting up a new system <u>Method</u>: 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)	<u>Frequency</u>: Within the first 7 days of initial use and every 30 days thereafter during continued use <u>Method</u>: 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)	<u>Frequency</u>: Same as above and on the same day as the cylinder gas audit <u>Method</u>: 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	<u>Frequency</u>: Once during every enforcement source test <u>Method</u>: 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 Handbook	Frequency: Once during every enforcement test until experience gained, then every fourth test Method: 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. Ascarite 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 (≈20° 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

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* 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 CO_2 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 SO_2 absorbing bubbler to the Drierite absorber and to connect the Drierite absorber to the CO_2 absorber. A second, smaller CO_2 absorber containing Ascarite II may be added in line downstream of the primary CO_2 absorber as a breakthrough indicator. Ascarite II turns white when CO_2 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 SO_2 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 CO_2 Absorber. Allow the CO_2 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 SO_2 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.

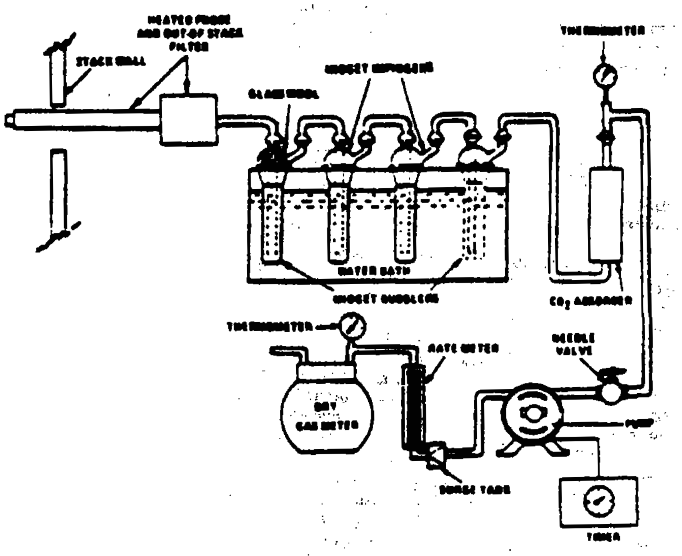

Figure 6A-1. Sampling train.

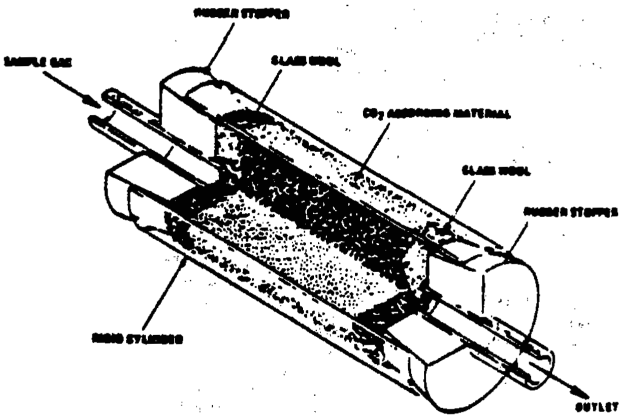

Figure 6A-2. CO_2 absorber.

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_w = 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_{ai} = Initial mass of CO_2 absorber, g.
m_{af} = Final mass of CO_2 absorber, g.
$V_{CO_2(std)}$ = Equivalent volume of CO_2 collected at standard conditions, dsm³.
$V_{w(std)}$ = 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.

$V_{CO_2(std)} = 5.467 \times 10^{-4} (m_{af} - m_{ai})$ (Eq. 6A-1)

6.3 Moisture Volume Collected, Corrected to Standard Conditions.

$V_{w(std)} = 1.336 \times 10^{-3} (m_{wf} - m_{wi})$ (Eq. 6A-2)

6.4 SO_2 Concentration.

$$C_{SO_2} = 32.03 \frac{(V_t - V_{tb}) N \left(\frac{V_{soln}}{V_a}\right)}{V_{m(std)} + V_{CO_2(std)}} \quad \text{(Eq. 6A-3)}$$

6.5 CO_2 Concentration.

$$C_{CO_2} = \frac{V_{CO_2(std)}}{V_{m(std)} + V_{CO_2(std)}} \times 100 \quad \text{(Eq. 6A-4)}$$

6.6 Moisture Concentration.

(Eq. 6A-5)

$$C_w = \frac{V_{w(std)}}{V_{m(std)} + V_{w(std)} + V_{CO_2(std)}}$$

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.

$$m_{SO_2} = 32.03 (V_t - V_{tb}) N \left(\frac{V_{soln}}{V_a}\right) \quad \text{(Eq. 6A-7)}$$

Where:

m_{SO_2} = Mass of SO_2 collected, mg.

7.6.2 Sulfur Dioxide Emission Rate.

$$E_{SO_2} = F_c (1.829 \times 10^9) \frac{m_{SO_2}}{(m_{af} - m_{ai})} \quad \text{(Eq. 6A-8)}$$

Where:

E_{SO_2} = Emission rate of SO_2 (ng/J).
F_c = 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 in 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 ml/min), molecular sieve material may be substituted for Ascarite II as the CO_2 absorbing material. The recommended molecular sieve material is Union Carbide 1/16 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 ml/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 ml/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. Standarize 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_{bar} = Initial barometric pressure for the test period, mm Hg.

T_m = 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_2 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 SO_2 and CO_2. 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.

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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.

Form	Title
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

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_2O	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.) H_2O.

[b] $V_m = V_f - V_i$.

[c] % error = 100 $(V_m - V_s)/V_s$ = ___________ ($\pm$1%).

_____________________________ Signature of calibration person

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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 ________ ^oF

Wet test meter pressure drop (D_m),[a] in. H_2O	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), ^oF	Inlet gas temp (t_{d_i}), ^oF	Dry test meter				(Y_{r_i}),[f]
			Initial	Final			Outlet gas temp (t_{d_o}), ^oF	Average gas temp (t_d),[c] ^oF	Time of run (θ),[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,

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

[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.

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

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_2O	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]	

[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,

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

[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.

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

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

METHOD 6B SAMPLING, SAMPLE RECOVERY, AND SAMPLE INTEGRITY DATA FORM

Plant ______________________
Sample location ______________
Operator ____________________
Run No. _____________________
Sampling period Start: Date ____________ Time ________
Stop: Date ____________ Time ________

Initial leak check ___________
Final leak check _____________
Recovery date ________________
Recovered by _________________

Dry Gas Meter
Final reading ________ L
Initial reading ______ L
Volume metered _______ L
Dry Gas Meter Calibration Factor, Y __________

Rotameter
Initial setting ____ L or cc/min
Final setting _____ L or cc/min

Meter Temperature
____________________ °F
____________________ time

Barometric Pressure
__________________ in. Hg
__________________ time

Probe Temperature
Initial _____ °F
Final _____ °F

Filter Temperature
Initial _____ °F
Final _____ °F

Ascarite Column
Final wt _______ g
Inital 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_2O_2 blank container no. ______________ Liquid level marked ______________
Impinger contents container no. ______________ Liquid level marked ______________
H_2O blank container no. ______________ Liquid level 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 CO_2

____ % spent

Recovered Sample

H_2O_2 blank container no. ____ Liquid level marked ____

Impinger contents container no. ____ Liquid level marked ____

H_2O blank container no. ____ Liquid level marked ____

Samples stored and locked ____

Remarks ____

Received by ____ Date ____

Remarks ____

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SAMPLE LABEL

Plant ____________________ City ________________

Site ____________________ Sample Type _________

Date ____________________ Run Number _________

Front rinse ☐ Front filter ☐ Front solution ☐

Back rinse ☐ Back filter ☐ Back solution ☐

Solution ____________________ Level marked ☐

Volume: Initial _______ Final ________________

Cleanup by ____

Remarks

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] $\frac{\text{1st titration}}{\text{2nd titration}} = 0.99$ to 1.01 or 1st titration - 2nd titration ≤ 0.2 ml.

Signature of analyst ______________________________

Signature of reviewer or supervisor ______________________________

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CONTROL SAMPLE ANALYTICAL DATA FORM

Plant ______________________ Date analyzed ______________

Analyst ______________________ $N_{Ba(ClO_4)_2}$ ______________

Weight of ammonium sulfate is 1.3214 g? __________

Dissolved in 2 L of distilled water? ______________

Titration of blank ______ ml $Ba(ClO_4)_2$ (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.

$$(\text{ml } Ba(ClO_4)_2 - \text{ml Blank}) \times N_{Ba(ClO_4)_2} = \underset{\text{(control sample)}}{25 \text{ ml}} \times \underset{\text{(control sample)}}{0.01N}$$

(_______ 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 = _ _ _ . _ _ liter
V = V_m (in liters) x 0.03531 ft^3/liter = _ . _ _ _ _ ft^3

METER TEMPERATURE (metric to English)

t_m = _ _ . _ ^oC
t_m = [t_m (^oC) x 1.8] + 32 = _ _ _ . _ ^oF
T_m = t_m (^oF) + 460 = _ _ _ . _ ^oR

BAROMETRIC PRESSURE (metric to English)

P_{bar} = _ _ _ . mm Hg
P_{bar} = P_{bar} (mm Hg) x 0.03937 in. Hg/mm Hg = _ _ . _ _ in. Hg

METER VOLUME (English to metric)

V_m = _ . _ _ _ _ _ ft^3
V_m = V_m (ft^3) x 0.02832 m^3/ft^3 = ._ _ _ _ _ m^3

METER TEMPERATURE (English to metric)

t_m = _ _ _ . _ ^oF
t_m = [t_m (^oF) - 32] x 5/9 = _ _ . _ ^oC
T_m = t_m (^oC) + 273 = _ _ _ . _ ^oK

BAROMETRIC PRESSURE (English to metric)

P_{bar} = _ _ . _ _ in. Hg
P_{bar} = P_{bar} (in. Hg) x 25.4 mm Hg/in. Hg = _ _ _ . mm Hg

METHOD 6A AND 6B CALCULATION FORM (ENGLISH UNITS)

STANDARD METER VOLUME (English units)

V_m = _ . _ _ _ _ ft^3, Y = _ . _ _ _

P_{bar} = _ _ . _ _ in. Hg, T_m = _ _ _ . _ ^oR

$$V_m(std) = 17.64\ V_m\ Y \left[\frac{P_{bar}}{T_m}\right] = \_ . \_\ \_\ \_\ \_ \text{ dscf}$$

CO_2 VOLUME COLLECTED, STANDARD CONDITIONS (English units)

m_{af} = _ _ _ . _ g, m_{ai} = _ _ _ . _ g

$$V_{CO_2}(std) = 0.01930\ (m_{af} - m_{ai}) = \_ . \_\ \_\ \_\ \_ \text{ dscf}$$

Equation 6-1

CO_2 CONCENTRATION (percent by volume)

$$C_{CO_2} = \frac{V_{CO_2(std)}}{V_m(std) + V_{CO_2}(std)} \times 100 = \_\ \_ . \_\ \_ \ \%$$

Equation 6-4

SO_2 CONCENTRATION (English units)

V_t = _ _ . _ _ ml, V_{tb} = _ . _ _ ml, N = _ . _ _ _ _ (g-eq)/ml

V_{soln} = _ _ _ . _ ml, V_a = _ _ . _ ml

$$C_{SO_2} = \frac{7.061 \times 10^{-5}\ (V_t - V_{tb})N}{V_m(std) + V_{CO_2}(std)}\left(\frac{V_{soln}}{V_a}\right) = \_ . \_\ \_\ \_\ \_ \times 10^{-4} \text{ lb/dscf}$$

Equation 6-3

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METHOD 6A AND 6B CALCULATION FORM (ENGLISH UNITS)
(continued)

MOISTURE CONCENTRATION (percent)

m_{wf} = _ _ _ . _ g, m_{wi} = _ _ _ . _ g

$V_{w(std)} = 0.04707\,(m_{wf} - m_{wi})$ = . _ _ _ _ dscf Equation 6-2

$$C_{H_2O} = \frac{V_{H_2O(std)}}{V_{m(std)} + V_{H_2O(std)} + V_{CO_2(std)}} \times 100 = \_\ \_\ .\ \_\ \_\ \%$$

Equation 6-5

EMISSION RATE OF SO_2 (English units)
(using meter volumes)

F_c = _ _ _ _ scf of CO_2/million Btu

$$E_{SO_2} = C_{SO_2}\, F_c\, \frac{100}{C_{CO_2}} = \_\ .\ \_\ \_\ \_ \text{ lb } SO_2\text{/million Btu}$$

(not using meter sample volume)

F_c = _ _ _ _ scf of CO_2/million Btu

$$m_{SO_2} = 32.03\,(V_t - V_{tb})N \left(\frac{V_{soln}}{V_a}\right) = \_\ \_\ \_\ .\ \_\ \_ \text{ mg of } SO_2 \text{ collected}$$

Equation 6-6

$$E_{SO_2} = F_c\,(1.141 \times 10^{-3})\, \frac{m_{SO_2}}{(m_{af} - m_{ai})} = \_\ .\ \_\ \_\ \_ \text{ lb } SO_2\text{/million Btu}$$

Equation 6-7

SO_2 CONCENTRATION (ppm)

$$C_{SO_2}\text{ (ppm)} = \frac{C_{SO_2}\text{ (lb/dscf)}}{1.663 \times 10^{-7}} = \_\ \_\ \_\ \_\ .\ \_ \text{ ppm}$$

METHOD 6A AND 6B CALCULATION FORM (METRIC UNITS)

STANDARD METER VOLUME (metric units)
(using meter volumes)

V_m = _ _ _ . _ _ liter x 0.001 = _ . _ _ _ _ _ _ m^3

Y = _ . _ _ _, P_{bar} = _ _ _ . mm Hg, T_m _ _ _ . _ ^oK

$$V_m(std) = 0.3858\ V_m Y \frac{P_{bar}}{T_m} = .\ \_\ \_\ \_\ \_\ \_\ \_ \text{ dscm}$$

CO_2 VOLUME COLLECTED, STANDARD CONDITIONS
(metric units)

m_{af} = _ _ _ . _ g, m_{ai} = _ _ _ . _ g

$$V_{CO_2}(std) = 5.467 \times 10^{-4}(m_{af} - m_{ai}) = .\ \_\ \_\ \_\ \_\ \_\ \_ \text{ dscm}$$

Equation 6-1

CO_2 CONCENTRATION (percent by volume)

$$C_{CO_2} = \frac{V_{CO_2}(std)}{V_m(std) + V_{CO_2}(std)} \times 100 = \_\ \_\ .\ \_\ \_\ \%$$

Equation 6-4

SO_2 CONCENTRATION (metric units)

V_t = _ _ . _ _ ml, V_{tb} = _ . _ _ ml, N = _ . _ _ _ _ _ (g - eq)/ml,

V_{soln} = _ _ _ . _ ml, V_a = _ _ . _ ml

$$C_{SO_2} = \frac{32.03\ (V_t - V_{tb})\ N \left(\frac{V_{soln}}{V_a}\right)}{V_{m(std)} + V_{CO_2(std)}} = \_\ \_\ \_\ \_\ .\ \_ \text{ mg/dscm}$$

Equation 6-3

METHOD 6A AND 6B CALCULATION FORM (METRIC UNITS)
(continued)

MOISTURE CONCENTRATION (percent)

m_{wf} = _ _ _ . _ g, m_{wi} = _ _ _ . _ g

$V_{m(std)} = 1.336 \times 10^{-3} (m_{wf} - m_{wi})$ = . _ _ _ _ _ _ dscm

Equation 6-2

$C_{H_2O} = \dfrac{V_{H_2O}}{V_{m(std)} + V_{H_2O(std)} + V_{CO_2(std)}} \times 100$ = _ _ . _ _ %

Equation 6-5

EMISSION RATE OF SO_2 (metric units)
(using meter volumes)

F_c = _ . _ _ _ x 10^{-7} dscm of CO_2/J

$E_{SO_2} = C_{SO_2} F_c \dfrac{10^8}{C_{CO_2}}$ = _ _ _ . _ ng/J

(not using meter volumes)

F_c = _ . _ _ _ x 10^{-7} dscm of CO_2/J

$m_{SO_2} = 32.03 (V_t - V_{tb}) N\left(\dfrac{V_{soln}}{V_a}\right)$ = _ _ _ . _ _ mg of SO_2 collected

Equation 6-6

$E_{SO_2} = F_c (1.829 \times 10^9) \dfrac{m_{SO_2}}{(m_{af} - m_{ai})}$ = _ _ _ . _ ng/J

Equation 6-7

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METHOD 6A AND 6B CHECKLIST TO BE USED BY AUDITORS

Yes	No	Comment	
			Presampling Preparation
___	___	___	1. Knowledge of process conditions
___	___	___	2. Calibration of pertinent equipment, in particular, the dry gas meter, prior to each field test
			On-Site Measurements
___	___	___	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
			Postsampling
___	___	___	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

General Comments