

Section 3.5

METHOD 6--DETERMINATION OF SULFUR DIOXIDE  
EMISSIONS FROM STATIONARY SOURCES

OUTLINE

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#### SUMMARY

This Method 6 test procedure is applicable to the determination of sulfur dioxide emissions from stationary sources. A gas sample is extracted from the sampling point in the stack. The sulfur dioxide is separated from the sulfuric acid mist (including sulfur trioxide) and is measured by the barium-thorin titration method. The barium ions react preferentially with sulfate ions in solution to form a highly insoluble barium sulfate precipitate. When the barium has reacted with all sulfate ions, excess barium then reacts with the thorin indicator to form a metal salt of the indicator, resulting in a color change.

The minimum detectable limit of the method has been determined to be  $3.4 \text{ mg SO}_2/\text{m}^3$  ( $2.12 \times 10^{-7} \text{ lb SO}_2/\text{ft}^3$ ). Although no upper limit has been established, tests have shown that concentrations as high as  $80,000 \text{ mg SO}_2/\text{m}^3$  can be collected efficiently in two midjet impingers, each containing 15 ml of 3% hydrogen peroxide and the sampling rate is 1.0  $\ell/\text{min}$  for 20 min. Based on theoretical calculations, the upper concentration limit in a 20- $\ell$  sample is about  $93,300 \text{ mg SO}_2/\text{m}^3$  if two such impingers are used. The limits may be extended by increasing the number of impingers or by increasing the peroxide concentration.

Interferences include free ammonia, water-soluble cations, and fluorides. The cations and fluorides are removed by glass-wool filters and an initial isopropanol bubbler, and hence do not affect the  $\text{SO}_2$  analysis. When samples are being taken from a gas stream with high concentrations of very fine metallic fumes (such as from inlets to control devices), a high-efficiency glass-fiber filter must be used in place of the glass-wool plug in the probe to remove the cation interferences. Free ammonia interferes by reacting with  $\text{SO}_2$  to form particulate sulfite and thus preventing it from reaching the peroxide impingers, and by reacting with the indicator. If free ammonia is present (as indicated by white

particulate matter in the probe and the isopropanol bubbler), an alternative method, subject to the approval of the administrator of the U.S. Environmental Protection Agency, is required.

The tester has the option of substituting sampling equipment described in Method 8 for the midget impinger equipment of Method 6. However, the Method 8 train must be modified to include a heated filter between the probe and the isopropanol impinger and must be operated at the flow rates defined in Method 8. The heated filter will help to eliminate the possibility of the SO<sub>2</sub> reacting with the particulate matter.

The tester also has the option of determining the emissions of SO<sub>2</sub> simultaneously with particulate matter and moisture determinations by (1) replacing the water in a Method 5 impinger system with 3% peroxide solution or (2) replacing the Method 5 water impinger system with a Method 8 isopropanol-filter-peroxide system. The analysis for SO<sub>2</sub> and the calibration of the metering system must be consistent with the procedure in Method 8.

The method description that follows is based on the Reference Method that was promulgated on August 18, 1977, and amended March 23, 1978.

Section 3.5.10 contains a complete copy of the Reference Method, and Section 3.5.12 provides blank data forms for the convenience of the Handbook user. References are in Section 3.5.11. Reference 1 was used in preparing the method description. References 2, 3, and 4 are collaborative test studies of this and other related methods. Data from these test studies were used in establishing quality control limits using the techniques of Reference 5. References 6 through 12 are included because of their potential value to the user.

The accuracy of Method 6 was checked using three standard gas mixtures containing 224, 1121, and 2082 mg SO<sub>2</sub>/m<sup>3</sup> (14, 70, and 130 × 10<sup>-6</sup> lb SO<sub>2</sub>/scf), respectively. The individual measurements by the participating laboratories were all within 24% of the true concentration.

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The accuracy of the analytical phase of Method 6 was checked using standard sulfuric acid solutions of three concentrations that were equivalent to sampled concentrations of 281.9, 563.8, and 845.7 mg SO<sub>2</sub>/m<sup>3</sup> (17.6, 35.2, and 52.8 × 10<sup>-6</sup> lb SO<sub>2</sub>/scf), and a blank solution. The individual measurements by all of the participating laboratories were within 6% of the true concentration.

The estimated within-laboratory precision (relative standard deviation) was 4.0%. The between-laboratory precision was 5.8%. The relative standard deviation is the ratio of the standard deviation of the measurement to the mean measured value, expressed as a percentage of this mean value.

#### METHOD HIGHLIGHTS

Specifications described in this Method 6 (Section 3.5) are only for the uses of midget impingers and midget bubblers with sample rates of about 1 liter per minute (ℓ/min). If the tester opts to use the standard-sized impingers, the Method 8 description (Section 3.7) should be used as the reference for equipment calibration, sample setup, leak check, operation, and sample recovery. The only exceptions are that glass wool may be put in the U-tube between the isopropanol and peroxide impinger as an option to the filter; the sampling is to be conducted at a constant rate of about 0.02 scm/min (0.75 scfm) ( $\Delta H@$ , orifice pressure differential that gives 0.75 scfm of air at 70°F at 29.92 in. Hg; and the isopropanol need not be analyzed.

The five blank data forms at the end of this section may be removed from the Handbook and used in the pretest, test, and the posttest operations. Each form has a subtitle (e. g., Method 6, Figure 3.1) for helping the user find a similar filled-in form in the method description (Section 3.5.3). On the blank and the filled-in forms, the items/parameters that can cause the most significant errors are starred.

#### 1. Procurement of Equipment

Section 3.5.1 (Procurement of Apparatus and Supplies) gives the specifications, criteria, and design features of the equipment and material required to perform Method 6 tests with the midget impinger train. This section is designed to provide the tester with a guide for the procurement and initial check of equipment and supplies. The activity matrix (Table 1.1) at the end of Section 3.5.1 can be used as a quick reference, and is a summary of the corresponding written descriptions.

#### 2. Pretest Preparations

Section 3.5.2 (Calibration of Apparatus) provides a step-by-step description of the recommended calibration procedures. The accuracy and precision for the equipment calibrations are the

same as those for Methods 5 and 8, with the exception that there is no calibration requirement for the rotameter. The lower sampling rate required for the midget impinger train allows the use of a wet test meter with a capacity of 3 l/min or greater. The calibration section can be removed along with the corresponding sections for the other methods and used as a separate quality assurance reference manual by the calibration personnel. The calibration data are summarized on the pretest sampling checks form (Figure 2.5, Section 3.5.2).

Section 3.5.3 (Presampling Operations) provides the tester with a preparation guide for equipment and supplies for the field test. The pretest sampling checks and pretest preparation forms (Figure 3.1, Section 3.5.3) or appropriate substitutes should be used as equipment checkout and packing lists. The sample impingers may be charged in the base laboratory if the testing is to be performed within 24 h of charging. The recommended method described for packing the containers should help protect the equipment.

### 3. On-Site Measurements

Section 3.5.4 (On-Site Measurements) contains step-by-step procedures to perform the sampling and sample recovery. A checklist (Figure 4.4, Section 3.5.4) is provided to assist the tester with a quick method of checking that the procedures have been completed satisfactorily. Section 3.5.4 may be taken to the field for reference but it would not normally be needed by an experienced crew. The most common problem with the midget impinger train is that the hydrogen peroxide ( $H_2O_2$ ) solution can easily be backed up into the isopropanol solution. This causes the  $SO_2$  to be removed in the first impinger or in the glass wool. For this reason, it is important to take precautions in preventing this occurrence, and it is suggested that the isopropanol and glass-wool plug be saved. The isopropanol can then be analyzed if any of the  $SO_2$  data indicate questionable results.

#### 4. Posttest Operations

Section 3.5.5 (Postsampling Operations) gives the posttest equipment check procedures and a step-by-step analytical procedure for determination of SO<sub>2</sub> concentration. The two posttest data forms (Figure 5.1, Section 3.5.5) and Figure 5.4, Section 3.5.5) or similar forms should be used and the posttest sampling checks form should be included in the emission test report to document the calibration checks. The step-by-step analytical procedure can be removed and made into a separate quality assurance analytical reference manual for the laboratory personnel. Analysis of a control sample is required prior to the analysis of the field samples. This analysis of an independently prepared known standard will provide the laboratory with quality control checks on the accuracy and precision of the analytical techniques.

Section 3.5.6 (Calculations) provides the tester with the required equations, nomenclature, and significant digits. It is suggested that a programmed calculator be used, if available, to reduce the chance of calculation error.

Section 3.5.7 (Maintenance) provides the tester with a guide for maintenance procedures; these are not required, but should reduce equipment malfunctions.

#### 5. Auditing Procedure

Section 3.5.8 (Auditing Procedure) provides a description of activities necessary for conducting performance and system audits. The performance audit of the analytical phase can be performed using aqueous ammonium sulfate solution. Performance audits for the analytical phase and the data processing are described in Section 3.5.8. A checklist for a systems audit is also included in this section.

Section 3.5.9 (Recommended Standards for Establishing Traceability) recommends the primary standards for establishing the traceability of the working standards. The volume measures are compared to a primary liquid displacement method, and the analysis of the SO<sub>2</sub> is traceable to primary standard grade potassium acid pthalate.

6. Reference Material

Section 3.5.10 (Reference Method) is the reference method and thus the basis for the quality assurance method description.

Section 3.5.11 (References) is a listing of the references that were used in this method description.

PRETEST SAMPLING CHECKS  
(Method 6, Figure 2.5)

Date \_\_\_\_\_ Calibrated by \_\_\_\_\_

Meter box number \_\_\_\_\_  $\Delta H@$  \_\_\_\_\_

Dry Gas Meter\*

Pretest calibration factor = \_\_\_\_\_ (within  $\pm 2\%$  of average factor for each calibration run).

Impinger Thermometer

Was a pretest temperature correction used? \_\_\_yes \_\_\_no

If yes, temperature correction \_\_\_\_\_ (within  $\pm 1^\circ\text{C}$  ( $2^\circ\text{F}$ ) of reference values for calibration and within  $\pm 2^\circ\text{C}$  ( $4^\circ\text{F}$ ) of reference values for calibration check).

Dry Gas Meter Thermometer

Was a pretest temperature correction made? \_\_\_yes \_\_\_no

If yes, temperature correction \_\_\_\_\_ (within  $\pm 3^\circ\text{C}$  ( $5.4^\circ\text{F}$ ) of reference values for calibration and within  $\pm 6^\circ\text{C}$  ( $10.8^\circ\text{F}$ ) of reference values for calibration check).

Barometer

Was the pretest field barometer reading correct? \_\_\_yes \_\_\_no  
(within  $\pm 2.5$  mm (0.1 in) Hg of mercury-in-glass barometer).

\* Most significant items/parameters to be checked.

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PRETEST PREPARATIONS  
 (Method 6, 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</u>							
Glass wool							
Other _____							
<u>Glassware</u>							
Midget bubbler							
Midget impinger							
Size _____							
Type _____							
<u>Meter System</u>							
Leak-free pumps*							
Rate meter*							
Dry gas meter*							
<u>Reagents</u>							
Distilled water							
H <sub>2</sub> O <sub>2</sub> , 30%							
Isopropanol, 100%*							
Silica gel							
<u>Other</u>							
Barometer							
Drying tube							

\* Most significant items/parameters to be checked.

ON-SITE MEASUREMENTS  
(Method 6, Figure 4.4)

Sampling

Bubbler and impinger contents properly selected, measured, and placed in impinger? \* \_\_\_\_\_

Impinger Contents/Parameters\*

1st: 15 ml of 80% isopropanol \_\_\_\_\_

2nd: 15 ml of 3% H<sub>2</sub>O<sub>2</sub> \_\_\_\_\_

3rd: 15 ml of 3% H<sub>2</sub>O<sub>2</sub> \_\_\_\_\_

Final impinger dry? \_\_\_\_\_

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

System purged at least 15 min at test sampling rate? \* \_\_\_\_\_

Contents of impingers placed in polyethylene bottles? \_\_\_\_\_

Fluid level marked? \* \_\_\_\_\_

Sample containers sealed and identified? \* \_\_\_\_\_

\* Most significant items/parameters to be checked. \_\_\_\_\_

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POSTTEST SAMPLING CHECKS  
(Method 6, Figure 5.1)

Meter Box Number \_\_\_\_\_

Dry Gas Meter

Pretest calibration factor  $Y =$  \_\_\_\_\_  
Posttest check  $Y_1 =$  \_\_\_\_\_  $Y_2 =$  \_\_\_\_\_ (+5% of pretest factor)\*  
Recalibration required? \_\_\_\_\_ yes \_\_\_\_\_ no  
If yes, recalibration factor  $Y =$  \_\_\_\_\_ (within +2% of calibration factor for each calibration run)  
Lower calibration factor,  $Y =$  \_\_\_\_\_ for pretest or posttest calculations

Rotameter

Pretest calibration factor  $Y_r =$  \_\_\_\_\_  
Posttest check  $Y_r =$  \_\_\_\_\_ (within  $\pm 10\%$  of pretest factor)  
Recalibration recommended? \_\_\_\_\_ yes \_\_\_\_\_ no  
If performed, recalibration factor  $Y_r =$  \_\_\_\_\_  
Was rotameter cleaned? \_\_\_\_\_ yes \_\_\_\_\_ no

Dry Gas Meter Thermometer

Was a pretest meter temperature correction used? \_\_\_\_\_ yes \_\_\_\_\_ no  
If yes, temperature correction \_\_\_\_\_  
Posttest comparison with mercury-in-glass thermometer  
\_\_\_\_\_ within  $+6^\circ\text{C}$  ( $10.8^\circ\text{F}$ ) of reference values  
Recalibration required? \_\_\_\_\_ yes \_\_\_\_\_ no  
Recalibration temperature correction if used \_\_\_\_\_ within  
 $+3^\circ\text{C}$  ( $5.4^\circ\text{F}$ ) of reference values  
If meter thermometer temperature is higher no correction needed  
If recalibration temperature is higher, add correction to  
average meter temperature for calculations

Barometer

Was pretest field barometer reading correct? \_\_\_\_\_ yes \_\_\_\_\_ no  
Posttest comparison \_\_\_\_\_ mm (in.) Hg within  $\pm 5.0$  mm  
(0.2 in.) Hg) of mercury-in-glass barometer  
Was recalibration required? \_\_\_\_\_ yes \_\_\_\_\_ no  
If field barometer reading is lower, no correction is needed  
If mercury-in-glass reading is lower, subtract difference from  
field data readings for calculations

\*Most significant items/parameters to be checked.

POSTTEST OPERATIONS  
(Method 6, 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

Volume of aliquot analyzed\* \_\_\_\_\_  
Do replicate titrant volumes agree within 1% 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  $\pm 5\%$ ?\* \_\_\_\_\_  
All data recorded? \_\_\_\_\_ Reviewed by \_\_\_\_\_

\* Most significant items/parameters to be checked.

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## 1.0 PROCUREMENT OF APPARATUS AND SUPPLIES

A schematic diagram of an assembled sulfur dioxide sampling train with all components identified is shown in Figure 1.1. 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 3.5.12 for the Handbook user. If calibration is required as part of the acceptance check, the data are recorded in the calibration log book. 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-stack) to remove particulate matter, including sulfuric acid mist. 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 ft) total length is usually sufficient for sampling. However, the probe tip can be no closer

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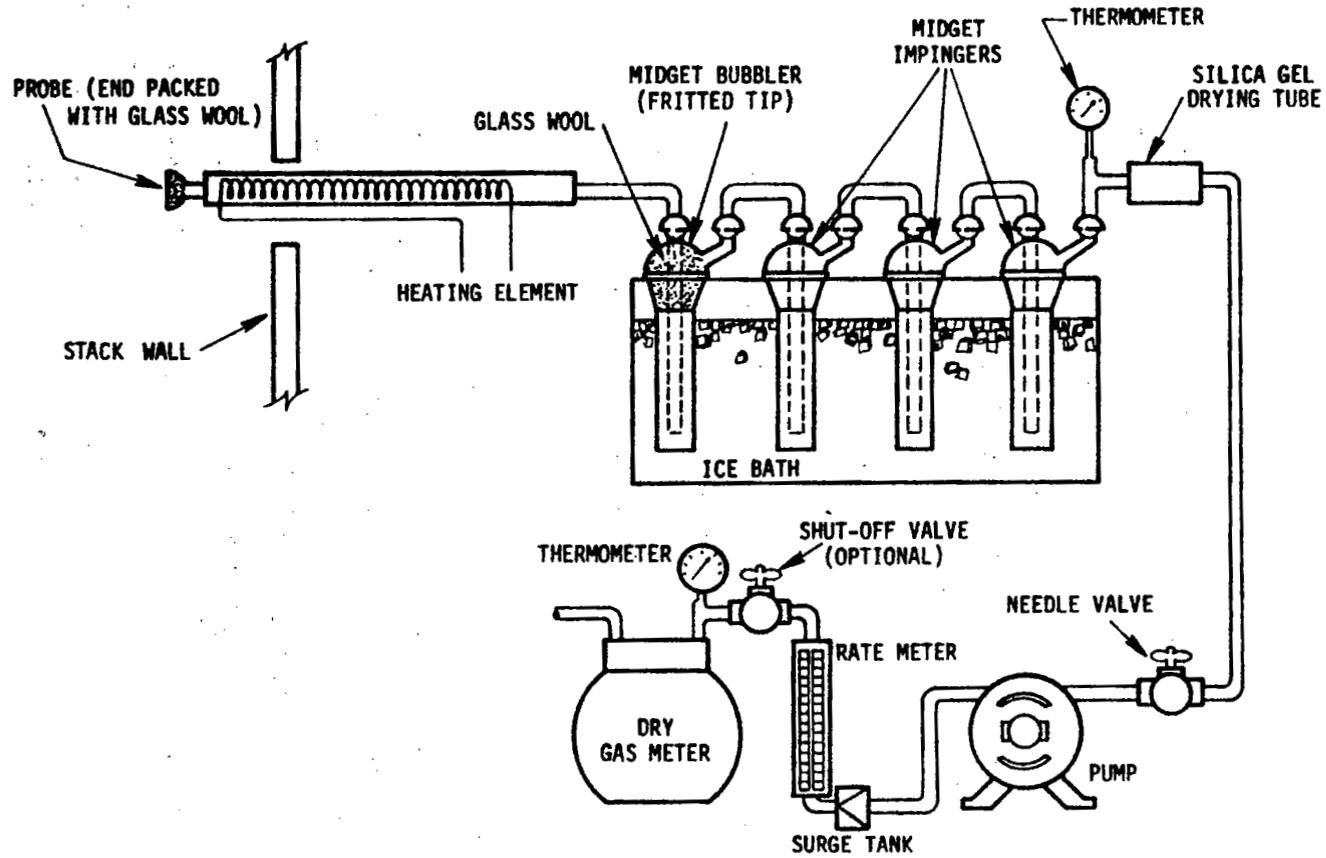


Figure 1.1. SO<sub>2</sub> sampling train.

Item description	Qty.	Purchase order number	Vendor	Date		Cost	Disposition	Comments
				Ord.	Rec.			
Meter Box (Method 6) w/ diaphragm pump	1	77A131	ARC Technology	4/77	6/77	\$1700	Calibrated Ready for use	Calibrated by J.B. 7/77

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Figure 1.2. Example of a procurement log.

than 1 m (3.28 ft) 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 criterion in selecting a probe material is that it be nonreactive with the gas constituents and therefore not introduce bias into the analysis.

A new probe should be visually 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 3.5.3. The probe heating system should be checked as follows:

1. Connect the probe (without filter) to the inlet of the pump.
2. Electrically connect and turn on the probe heater for 2 or 3 min. 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 Midget Bubbler/Impingers - Each sampling train requires one midget bubbler (30 ml) of medium coarse glass frit, with glass wool packed in the top to prevent carryover of sulfuric acid mist. A midget impinger may be used in place of the midget bubbler.

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

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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% 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% of the total SO<sub>2</sub>.

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

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

1.1.4 Volume Meter - The dry gas meter must be capable of measuring total volume with an accuracy of  $\pm 2\%$ , 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 new dry gas meter may be checked for damage visually and by performing a calibration according to Section 3.5.2. Any dry gas meter that is damaged, behaves erratically, or does not give readings within  $\pm 2\%$  of the selected flow rate for each run is

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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 encounters 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% 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 3.5.2. The wet test meter must have a capacity of at least 0.003 m<sup>3</sup>/min (0.1 ft<sup>3</sup>/min) with an accuracy of ±1%; otherwise at the higher flow rates, the water will not be level and possibly will result in an incorrect reading.

1.1.5 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 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 is performed at a constant rate, which need not be isokinetic, these changes do not affect the sample volume measured by the dry gas meter.

1.1.6 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.

1.1.7 Drying Tube - The drying tube should be packed with 6- to 16-mesh indicating-type silica gel, or equivalent, to dry the sample gas and protect the meter and pump. A drying tube can be made by filling a 10-mm polyethylene tube with silica gel and packing glass wool in each end to hold the silica gel and

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protect the sampling system. Plastic tubing can be utilized in any connections past the collection system without affecting the sampling results. The drying tube should have a minimum capacity of 30 to 50 g of silica gel and should be visually checked for proper size and for damage.

If the silica gel has been used previously, it must be dried at 175°C (350°F) for 2 h. New silica gel may be used, subject to approval of the administrator.

1.1.8 Thermometers - A dial thermometer, or its equivalent, is used to measure the temperature of gas leaving the impinger train to within  $\pm 1^\circ\text{C}$  ( $2^\circ\text{F}$ ). 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  $\pm 1^\circ\text{C}$  ( $2^\circ\text{F}$ ) 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.

1.1.9 Meter System - For ease of use, the metering system--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 1.3.

2. Shut off the needle valve and insert positive pressure in the system by blowing into the rubber tubing until the inclined manometer or magnehelic gauge reads from 12.5 to 17.5 cm (5 to 7 in.)  $\text{H}_2\text{O}$ .

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

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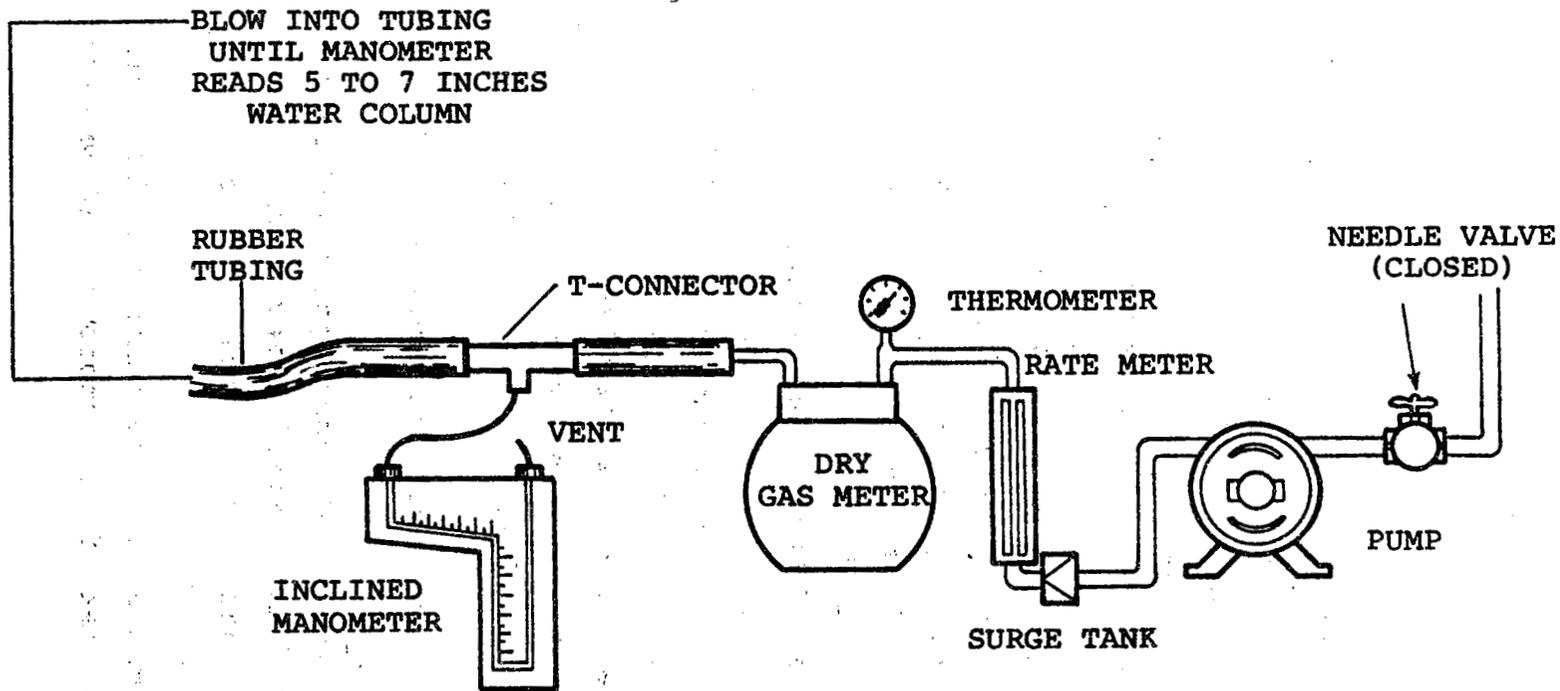


Figure 1.3. Meter box leak check.

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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 to the drying tube, 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 s indicates a leak.
4. Carefully release the vacuum gauge before releasing the flow meter end.

If either of these checks detects a leak that cannot be corrected, the meter box must be 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  $\pm 3^{\circ}\text{C}$  ( $5.4^{\circ}\text{F}$ ) 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  $10^{\circ}\text{C}$  ( $18^{\circ}\text{F}$ ). Damaged thermometers that cannot be calibrated are to be rejected.

1.1.10 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.

1.1.11 Vacuum Gauge - At least one 760-mm (29.92-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  $\pm 25$  mm (1.0 in.) Hg.

## 1.2 Sample Recovery Apparatus

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

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

## 1.3 Analysis Glassware

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

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

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

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

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

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

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

#### 1.4 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 D1193-74, Type 3. At the option of the analyst, the  $\text{KMnO}_4$  test for oxidizable organic matter may be omitted when high concentrations of organic matter are not expected to be present.

Isopropanol, 80% - Mix 80 ml of reagent grade or certified ACS isopropanol (100%) 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% potassium iodide (KI) solution.
2. Prepare a blank by similarly treating 10 ml of deionized distilled water.
3. After 1 min, read the absorbance of the alcohol sample against the  $\text{H}_2\text{O}$  blank at 352 nm on a spectrophotometer. If absorbance exceeds 0.1, reject the alcohol for use. Peroxides may be removed from isopropanol by redistilling or by passing through a column of activated alumina. After peroxides are removed, check for peroxide impurities using the same method as above. However, reagent grade isopropanol with suitably low peroxide levels may be obtained from commercial sources. Therefore, rejection of contaminated lots may be a more efficient procedure.

Hydrogen Peroxide, 3% - Dilute 30% reagent grade or certified ACS hydrogen peroxide 1:9 (v/v) with deionized distilled water. Prepare fresh daily. The 30% hydrogen peroxide should be stored according to manufacturer's directions.

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Potassium Iodide Solution, 10% - Dissolve 10.0 g of reagent grade or certified ACS potassium iodide in deionized distilled water and dilute to 100 ml. Prepare when needed. This solution is used to check for peroxide impurities in the isopropanol only.

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

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

Isopropanol, 80% - Mix 80 ml of reagent grade or certified ACS isopropanol with 20 ml of deionized distilled 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% - Use reagent grade or certified ACS isopropanol.

Thorin Indicator - Use reagent grade or certified ACS 1-(o-arsonophenylazo)-2-naphthol-3, 6-disulfonic acid, disodium salt. Dissolve 0.20 g in 100 ml of deionized distilled water.

Barium Perchlorate Solution, 0.0100N - Dissolve 1.95 g of reagent grade or certified ACS barium perchlorate trihydrate ( $\text{Ba}(\text{ClO}_4)_2 \cdot 3\text{H}_2\text{O}$ ) in 200 ml of distilled water and dilute to 1 l with 100% isopropanol. Alternatively, use 1.22 g of ( $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ ) instead of the perchlorate. Standardize, as in Section 3.5.5.

Sulfuric Acid Standard, 0.0100N - Either purchase the manufacturer's certified or standardize the  $\text{H}_2\text{SO}_4$  at 0.0100N  $\pm 0.0002\text{N}$  against 0.0100N reagent grade or certified ACS 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.

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Table 1.1 ACTIVITY MATRIX FOR PROCUREMENT OF APPARATUS AND SUPPLIES

Apparatus and supplies	Acceptance limits	Frequency and method of measurement	Action if requirements are not met
<u>Sampling</u>			
Sampling probe with heating system	Capable of maintaining 100°C (212°F) exit air at flow rate of 1.0 l/min	Visually check and run heating system checkout	Repair or return to supplier
Midget bubbler/impinger	Standard stock glass	Visually check upon receipt for breaks or leaks	Return to manufacturer
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	Capable of measuring total volume within +2% at a flow rate of 1 l/min	Check for damage upon receipt and calibrate (Sec. 3.5.2) against wet test meter	Reject if damaged, behaves erratically, or cannot be properly adjusted
Wet test meter	Capable of measuring total volume within +1% at a flow rate of 1 l/min	Upon assembly, leak check all connections and check calibration by liquid displacement	As above
Rotameter	Within +5% of manufacturer's calibration curve (recommended)	Check upon receipt for damage and calibrate (Sec. 3.5.2) against wet test meter	Recalibrate and construct a new calibration curve
Drying tube	Minimum capacity of 30 to 50 g of silica gel	Visually check upon receipt for damage and proper size	Return to supplier
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. 3.5.2) against mercury-in-glass thermometer	Return to supplier if unable to calibrate

(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
<u>Sampling</u> (cont'd) Barometer	Capable of measuring atmospheric pressure to within +2.5 mm (0.1 in.) Hg calibrate	Check against mercury-in-glass barometer or equivalent (Sec. 3.5.2)	Determine correction factor, or reject if difference is more than $\pm 2.5$
Vacuum gauge	0 to 760 mm (0 to 29.92 in.) Hg range, $\pm 2.5$ mm (0.1 in.) Hg accuracy at 250 mm (10 in.) Hg	Check against U-tube mercury manometer upon receipt	Adjust or return to supplier
<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
<u>Analysis Glassware</u>			
Pipettes, volumetric flasks, burettes, and graduated cylinder	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	100% isopropanol, reagent grade or certified ACS with no peroxide impurities	Upon receipt, check each lot for peroxide impurities with a spectrophotometer	Redistill or pass through alumina column, or replace

(continued)

Table 1.1 (continued)

Apparatus and supplies	Acceptance limits	Frequency and method of measurement	Action if requirements are not met
Hydrogen peroxide	30% H <sub>2</sub> O <sub>2</sub> , 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
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 <sub>4</sub> ) <sub>2</sub> · 3H <sub>2</sub> O), reagent grade or certified ACS	As above	As above
Sulfuric acid solution	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. If the tester opts to use Method 5 or Method 8 sampling apparatus, then the calibration procedures governing that equipment will apply and must be used. 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

2.1.1 Wet Test Meter - The wet test meter must be calibrated and have the proper capacity. For Method 6, the wet test meter should have a capacity of at least 3 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  $\pm 0.5\%$ . 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  $\pm 1\%$ :

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.

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4. Set up the apparatus and calibration system as shown in Figure 2.1.

- a. Fill the rigid-wall 5-gal jug with distilled water to below the air inlet tube. Put water in the impinger or saturator 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.

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 the inlet to the saturator. 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 saturator.

7. Read the initial volume ( $V_i$ ) from the wet test meter dial, and record on the wet test meter calibration log, Figure 2.2.

8. Place a clean, dry volumetric flask (Class A) under the siphon tube, open the pinch clamp, and fill the volumetric flask to the mark. The volumetric flask must be large enough to allow at least one complete revolution of the wet test meter with not more than two fillings of the volumetric flask.

9. Start the flow of water and record the maximum wet test meter manometer reading during the test after a constant flow of liquid is obtained.

10. Carefully fill the volumetric flask, and shut off the liquid flow at the 2- $\ell$  mark. Record the final volume on the wet test meter.

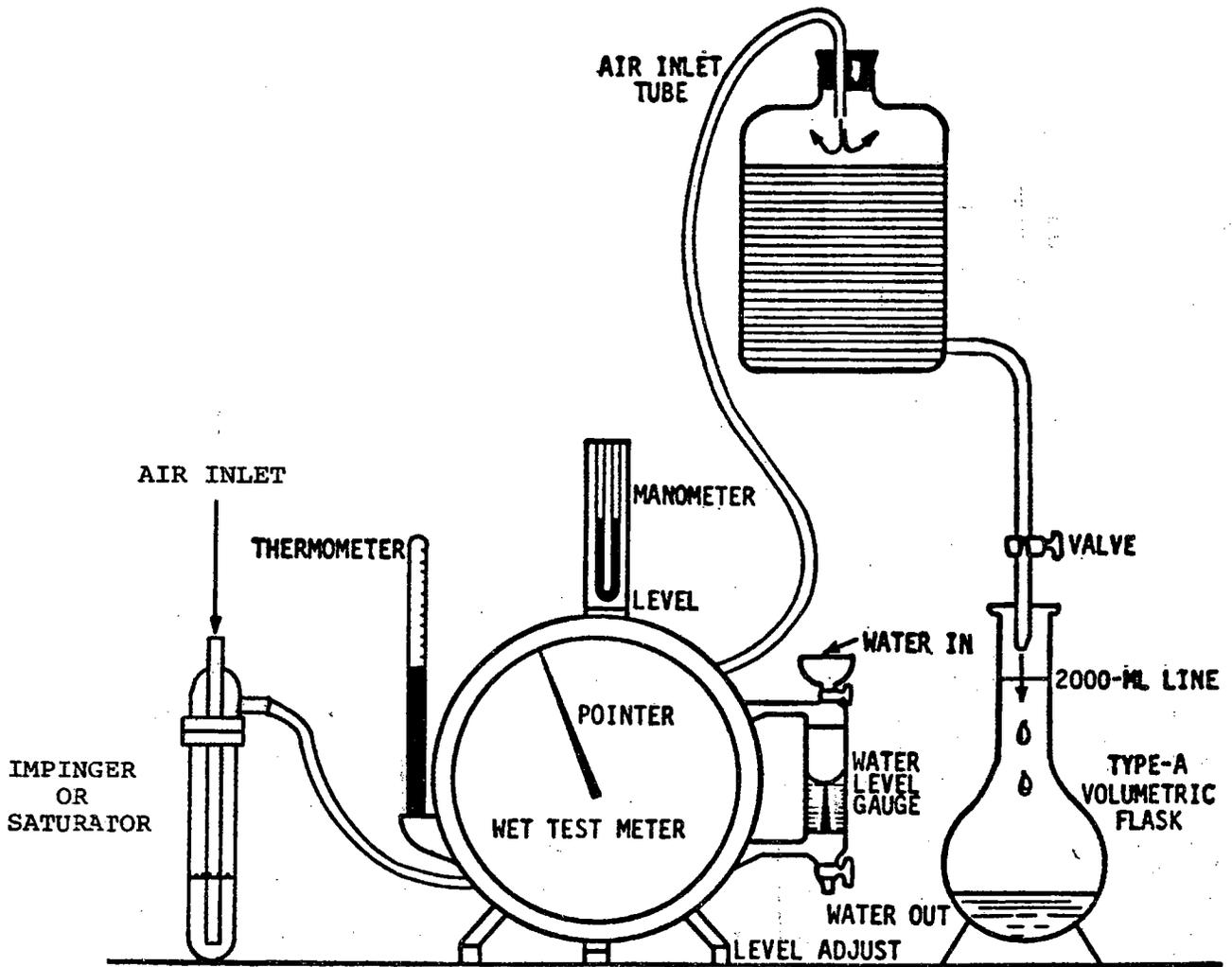


Figure 2.1. Calibration check apparatus for wet test meter.

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Wet test meter serial number 43-246

Date 1/27/77

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

Volume of test flask  $V_s =$  2.00 l

Satisfactory leak check? yes

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

Test number	Manometer reading, <sup>a</sup> mm H <sub>2</sub> O	Final volume ( $V_f$ ), l	Initial volume ( $V_i$ ), l	Total volume ( $V_m$ ) <sup>b</sup> , l	Flask volume ( $V_s$ ), l	Percent error, <sup>c</sup> %
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

<sup>a</sup> Must be less than 10 mm (0.4 in.) H<sub>2</sub>O.

Calculations:

<sup>b</sup>  $v_m = v_f - v_i$ .

<sup>c</sup> % error =  $100 (V_m - V_s) / V_s =$  \_\_\_\_\_ (+1%).

Johnny Bench Signature of calibration person

Figure 2.2. Wet test meter calibration log.

11. Steps 7 through 10 must be performed 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  $\pm 1\%$ ; should this error magnitude be exceeded, check all connections within the test apparatus for leaks, and gravimetrically check the volume of the 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 Meter System - The sample meter system--consisting of the drying tube, 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. 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.

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% of the pretest calibration factor. A calibrated wet test meter (properly sized, with  $\pm 1\%$  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.

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1. Leak check the metering system (drying tube, needle valve, pump, rotameter, and dry gas meter) as follows:
  - a. Temporarily attach a suitable rotameter (e.g., 0-40 cm<sup>3</sup>/min) to the outlet of the dry gas meter, and place a vacuum gauge at the inlet to the drying tube.
  - b. Plug the drying tube inlet. Pull a vacuum of at least 250 mm (10 in.) Hg.
  - c. Note the flow rate as indicated by the rotameter.
  - d. A leak of <0.02 l/min 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 drying tube and impingers; that is, connect the outlet of the wet test meter to the inlet side of the needle valve and the inlet side of the wet test meter to a saturator which is open to the atmosphere. Note: Do not use a drying tube.

3. Run the pump for 15 min 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 of the three runs using Equation 2-1. Record the values in the form (Figure 2.4A or 2.4B).

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

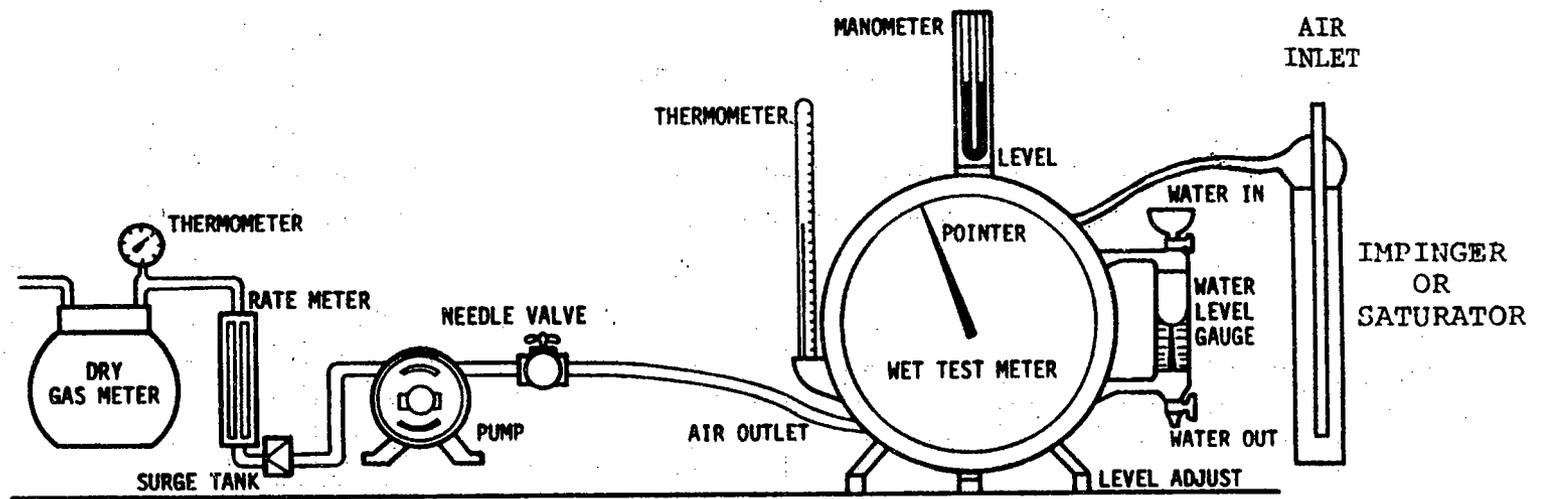


Figure 2.3. Sample meter system calibration setup.

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Date 1/25/78 Calibrated by S. J. Jones Meter box number 33-1  
 Barometer pressure,  $P_m =$  29.41 in. Hg Wet test meter number 101-A  
 Meter temperature correction factor N/A °F

Wet test meter pressure drop ( $D_m$ ), <sup>a</sup> in. H <sub>2</sub> O	Rota-meter setting ( $R_s$ ), ft <sup>3</sup> /min	Wet test meter gas volume ( $V_w$ ), <sup>b</sup> ft <sup>3</sup>	Dry test meter gas volume ( $V_d$ ), <sup>b</sup> ft <sup>3</sup>		Wet test meter gas temp ( $t_w$ ), °F	Inlet gas temp ( $t_{d1}$ ), °F	Dry test meter				$(Y_{r_i})$ , <sup>f</sup>
			Initial	Final			Outlet gas temp ( $t_{d0}$ ), °F	Average gas temp ( $t_d$ ), <sup>c</sup> °F	Time of run ( $\theta$ ), <sup>d</sup> min	Average ratio ( $Y_1$ ), <sup>e</sup>	
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

<sup>a</sup>  $D_m$  expressed as negative number.

<sup>b</sup> Volume passing through meter. Dry gas volume is minimum for at least five revolutions of the meter.

<sup>c</sup> The average of  $t_{d1}$  and  $t_{d0}$  if using two thermometers; the actual reading if using one thermometer.

<sup>d</sup> The time it takes to complete the calibration run.

<sup>e</sup> With  $Y$  defined as the average ratio of volumes for the wet test and the dry test meters,  $Y_1 = Y \pm 0.02 Y$  for calibration and  $Y_1 = Y \pm 0.05 Y$  for the posttest checks, thus,

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

<sup>f</sup> With  $Y_r$  defined as the average ratio of volumetric measurements by wet test meter to rotameter, tolerance  $Y_r = 1 \pm 0.05$  for calibration and  $Y \pm 0.1$  for posttest checks.

$$Y_{r_i} = \frac{V_w (t_d + 460^\circ\text{F}) [P_m + (D_m/13.6) 60]}{\theta (t_w + 460^\circ\text{F}) P_m 0.035} \quad (\text{Eq. 3}) \quad \text{and} \quad Y_r = \frac{Y_1 + Y_2 + Y_3}{3} = \underline{1.026} \quad (\text{Eq. 4})$$

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

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 Revision No. 0  
 Date May 1, 1979  
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Date 1/25/78 Calibrated by J. J. Jones Meter box number 55-1  
 Barometer pressure,  $P_m =$  748 mm Hg Wet test meter number 101-A  
 Meter temperature correction factor N/A °C

Wet test meter pressure drop ( $D_m$ ), <sup>a</sup> mm H <sub>2</sub> O	Rota-meter setting ( $R_s$ ), l/min	Wet test meter gas volume ( $V_w$ ), <sup>b</sup> l	Dry test meter gas volume ( $V_d$ ), <sup>b</sup> l		Wet test meter gas temp ( $t_w$ ), °C	Inlet gas temp ( $t_{d_1}$ ), °C	Dry test meter				$(Y_{r_1})$ , <sup>f</sup>
			Initial	Final			Outlet gas temp ( $t_{d_0}$ ), °C	Average gas temp ( $t_d$ ), <sup>c</sup> °C	Time of run ( $\theta$ ), <sup>d</sup> min	Average ratio ( $Y_1$ ), <sup>e</sup>	
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	27	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

<sup>a</sup>  $D_m$  expressed as negative number.

<sup>b</sup> Volume passing through meter. Dry gas volume is minimum for at least five revolutions of the meter.

<sup>c</sup> The average of  $t_{d_1}$  and  $t_{d_0}$  if using two thermometers; the actual reading if using one thermometer.

<sup>d</sup> The time it takes to complete the calibration run.

<sup>e</sup> With  $Y$  defined as the average ratio of volumes for the wet test and the dry test meters,  $Y_1 = Y \pm 0.02 Y$  for calibration and  $Y_1 = Y \pm 0.05 Y$  for the posttest checks, thus,

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

<sup>f</sup> With  $Y_r$  defined as the average ratio of volumetric measurements by wet test meter to rotameter, tolerance  $Y_r = 1 \pm 0.05$  for calibration and  $Y_r \pm 0.1$  for posttest checks.

$$Y_{r_1} = \frac{V_w (t_d + 273^\circ\text{F}) \left[ P_m + (D_m/13.6) 60 \right]}{\theta (t_w + 273^\circ\text{F}) P_m (0.035)} \quad (\text{Eq. 3}) \quad \text{and} \quad Y_r = \frac{Y_1 + Y_2 + Y_3}{3} = \underline{1.026} \quad (\text{Eq. 4})$$

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

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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,  $^{\circ}C$  ( $^{\circ}F$ ),

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

$t_w$  = temperature of wet test meter,  $^{\circ}C$  ( $^{\circ}F$ ),

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

An alternative method of calibrating the metering system consists of substituting a dry gas meter, which has been properly 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, conduct a calibration check as in Subsection 2.1.2 with the following exceptions:

1. The leak check is not conducted because a leak may have been 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  $\pm 6^{\circ}C$  ( $10.8^{\circ}F$ ) 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  $>5\%$  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  $>5\%$ , 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 impinger train should be initially compared with a mercury-in-glass thermometer that meets ASTM E-1 No. 63C or 63F specifications:

1. Place both the mercury-in-glass and the dial type or an equivalent thermometer in an ice bath. Compare the readings after the bath stabilizes.

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

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

4. Prior to each field trip, compare the temperature reading of the mercury-in-glass thermometer with that of the meter thermometer at room temperature. If the values are not within  $\pm 2^{\circ}\text{C}$  ( $4^{\circ}\text{F}$ ) of each other, replace or recalibrate the meter thermometer.

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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:

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  $\pm 3^\circ\text{C}$  (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  $\pm 6^\circ\text{C}$  (10.8°F) of each other, replace or recalibrate the meter thermometer.

### 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. 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

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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  $1.0 \pm 0.05$  l/min. If, however, the calibration point is not within  $\pm 5\%$ , 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  $\pm 10\%$  of the 1-l/min setting, the rotameter can be acceptable with proper maintenance. If, however, the check is not within  $\pm 10\%$  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  $\pm 2.5$  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).

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Date 9/15/78 Calibrated by WGD  
Meter box number FM-1 ΔH@ 1.41

Dry Gas Meter\*

Pretest calibration factor = 0.986 (within ±2% of average factor for each calibration run).

Impinger Thermometer

Was a pretest temperature correction used?  yes  no

If yes, temperature correction \_\_\_\_\_ (within ±1°C (2°F) of reference values for calibration and within ±2°C (4°F) of reference values for calibration check).

Dry Gas Meter Thermometer

Was a pretest temperature correction made?  yes  no

If yes, temperature correction \_\_\_\_\_ (within ±3°C (5.4°F) of reference values for calibration and within ±6°C (10.8°F) of reference values for calibration check).

Barometer

Was the pretest field barometer reading correct?  yes  no  
(within ±2.5 mm (0.1 in) Hg of mercury-in-glass barometer)

\* Most significant items/parameters to be checked.

Figure 2.5. Pretest sampling checks.

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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 $\pm 1.0\%$	Calibrate initially and then yearly by liquid displacement	Adjust until specifications are met, or return to manufacturer
Dry gas meter	$Y_1 = Y + 0.02Y$ at a flow rate of about 1 l/min	Calibrate vs. wet test meter initially and when the posttest check is not within $Y \pm 0.05$	Repair and then recalibrate, or replace
Impinger thermometer	Within $\pm 1^\circ\text{C}$ ( $2^\circ\text{F}$ ) of true value	Calibrate each initially as a separate component against a mercury-in-glass thermometer; after train is assembled before each field test, compare with mercury-in-glass thermometer	Adjust, determine a constant correction factor, or reject
Dry gas meter thermometer	Within $+3^\circ\text{C}$ ( $5.4^\circ\text{F}$ ) of true value	As above	As above
Rotameter	Clean and maintain according to manufacturer's instructions (required); calibrate to $\pm 5\%$ (recommended)	Initially and after each field trip	Adjust and recalibrate, or reject
Barometer	Within $\pm 2.5$ 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

*Handwritten mark*



### 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<sub>2</sub> 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 Reference 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 Bubbler, 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.

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Apparatus check	Acceptable		Quantity required	Ready		Loaded and packed	
	Yes	No		Yes	No	Yes	No
<u>Probe</u>							
Type liner			3	✓		✓	
Glass <u>✓</u>	✓						
Stainless steel _____							
Other _____							
Heated properly	✓						
Leak checked on sampling train	✓						
<u>Filter</u>			Small Box	✓		✓	
Glass wool	✓						
Other _____							
<u>Glassware</u>							
Midget bubbler	✓		6	✓		✓	
Midget impinger	✓		18	✓		✓	
Size <u>Midget</u>							
Type <u>Std.</u>							
<u>Meter System</u>			2	✓		✓	
Leak-free pumps*	✓						
Rate meter*	✓						
Dry gas meter*	✓						
<u>Reagents</u>							
Distilled water	✓		2 gal	✓		✓	
H <sub>2</sub> O <sub>2</sub> , 30%	✓		1 liter	✓		✓	
Isopropanol, 100%*	✓		1 gal.	✓		✓	
Silica gel	✓		5 #	✓		✓	
<u>Other</u>							
Barometer	✓		1	✓		✓	
Drying tube	✓		10	✓		✓	

\* Most significant items/parameters to be checked.

Figure 3.1. Pretest preparations.

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3.1.4 Drying Tubes - Drying tubes should be packed with 6-to 16-mesh silica gel and sealed at both ends.

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 mo, or every 10th test (whichever comes first), or upon erratic behavior (nonuniform or insufficient pumping action).

3.1.7 Dry Gas Meter - A dry gas meter calibration check should be made in accordance with the procedure in Section 3.5.2. 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 the mercury-in-glass barometer or with a National Weather Service Station reading prior to each field trip.

### 3.2 Reagents and Equipment

3.2.1 Sampling - The midget bubbler solution is prepared by mixing 80 ml of reagent grade or certified ACS isopropanol (100%) with 20 ml of deionized distilled water. The midget impinger absorbing reagent (3% hydrogen peroxide) is prepared by diluting 100 ml of 30% hydrogen peroxide to 1 l with deionized distilled water. 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.

3.2.2 Sample Recovery - Deionized distilled water is required on site for quantitative transfer of impinger solutions to storage containers. This water and reagent grade 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 h.

3.3.3 Drying Tubes and Volumetric Glassware - A rigid container lined with polyethylene foam material protects drying tubes and assorted volumetric glassware.

3.3.4 Meter Box - The meter box--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).

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Table 3.1 ACTIVITY MATRIX FOR PRESAMPLING OPERATIONS

Operation	Acceptance limits	Frequency and method of measurement	Action if requirements are not met
<u>Apparatus</u>			
Probe	1. Probe liner free of contaminants  2. Probe leak free at 250 mm (10 in.) Hg  3. No moisture condensation	1. Clean probe internally by brushing with tap water, then deionized distilled water, then acetone; allow to dry in air before test  2. Visual check before test  3. Check out heating system initially and when moisture appears during testing	1. Retrace cleaning procedure and assembly  2. Replace  3. Repair or replace
Midget bubbler, midget impinger, 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 (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	Clean and within +2% of calibration factor	Calibrate according to Sec. 3.5.2; check for excess oil if oiler is used	As above
<u>Reagents</u>			
Sampling	Requires all ACS grade reagents	Prepare fresh daily and store in sealed containers	Prepare new reagent

(continued)



Table 3.1 (continued)

Operation	Acceptance limits	Frequency and method of measurement	Action if requirements are not met
Sample recovery	Requires deionized distilled water on site	Use water and reagent grade isopropanol to clean midget bubbler after test and before sampling	Prepare new reagent
<u>Package Equipment for Shipment</u>			
Probe	Protect with polyethylene foam	Prior to each shipment	Repack
Midget bubbler, impingers, connectors, and assorted glassware	Pack in rigid containers with polyethylene foam	As above	As above
Drying tubes, 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

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3.5.4

#### 4.0 ON-SITE MEASUREMENTS

On-site activities include transporting the equipment to the test site, unpacking and assembling, sampling for sulfur dioxide, and recording the data. The 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 bubbler and impingers, and for sample recovery.

##### 4.2 Preliminary Measurements and Setup

The Reference Method outlines the procedure used to determine the concentration of sulfur dioxide in the gas stream. The accuracy of the equipment that has been transported to the sampling site and that may have been handled roughly 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.,  $V_d = V_w$ ).  $Y_{ri}$  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 post-test 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 sampling data form, Figure 4.1.

##### 4.3 Sampling

The on-site sampling includes the following steps:

Plant name Acme Power Plant City Anywhere, USA  
 Sample location Boiler No. 3 Date 8/10/77  
 Operator Joe Smith Sample number 50-1  
 Barometric pressure, mm (in.) Hg 758 Probe length m (ft) 1.5  
 Probe material GLASS Probe heater setting 250°F  
 Meter box number JS-1 Meter calibration factor (Y) 1.01  
 Ambient temperature, °C (°F) 25 Sample point location 1.35 m in from Port A  
 Initial leak check 0.004 l/min @ 250 mm Hg Sample purge time, min 15  
 Final leak check 0.006 l/min @ 250 mm Hg Remarks Max. % Dev. < 10%

Sampling time, min	Clock time, 24 h	Sample volume, l ( <del>ft<sup>3</sup></del> )	Sample flow rate setting, l/min ( <del>ft<sup>3</sup>/min</del> )	Sample volume metered ( $\Delta V_m$ ), l ( <del>ft<sup>3</sup></del> )	Percent deviation, <sup>a</sup> %	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	1130	145.20	1.0	5.0	0	30	20
Total 25		Total 2500		$\Delta V_m$ avg 5.0	Avg dev 1.6	Avg 29	Max temp 20

$$^a \text{ Percent deviation} = \frac{\Delta V_m - \Delta V_m \text{ avg}}{\Delta V_m \text{ avg}} \times 100.$$

Figure 4.1. Field sampling data form for SO<sub>2</sub>.

1. Preparation and/or addition of the absorbing reagents to the midget bubbler and impingers.
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 3.5.3.

1. Use a pipette or a graduated cylinder to introduce 15 ml of 80% 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. 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.

2. Add 15 ml of 3% hydrogen peroxide to each of the first two midget impingers; leave the final midget impinger dry.

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

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

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

2. Leak check the sampling train just prior to use at the sampling site (not mandatory) by temporarily attaching a

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rotameter (capacity of 0 to 40 cm<sup>3</sup>/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 not  $\leq 2\%$  of the average sampling rate is acceptable. Note: Carefully release the probe inlet plug before turning off the pump. 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 precede the leak check of the sampling train. If after, the pump leak check shall follow the train leak check. To leak check the pump, proceed as follows: Disconnect the drying tube from the probe impinger assembly. Place a vacuum gauge at the inlet to either the drying tube or 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 s.

3. Place a loosely packed filter of glass wool in the end of the probe, and connect the probe to the bubbler.

4.3.3 Sampling (Constant Rate) - 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:

1. 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 be sure that no hydrogen peroxide has been allowed to back up and wet the glass wool.

2. 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<sub>2</sub>O while disconnected from the impinger, 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 isopropanol.

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3. Adjust the sample flow to a constant rate of approximately 1.0  $\ell$ /min as indicated by the rotameter.

4. Maintain this constant rate within 10% during the entire sampling run, and take readings (dry gas meter, temperatures at dry gas meter and at impinger outlet, and rate meter) at least every 5 min. 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.

5. 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 min and a minimum sampling volume of 20  $\ell$  corrected to standard conditions.) The total sample volume at meter conditions should be approximately 28  $\ell$  (1 ft<sup>3</sup>). 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 min.

6. 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.

7. Conduct a leak check, as described in Subsection 4.3.2 (mandatory).

8. 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 min at the sampling rate. To provide clean ambient air, pass air through a charcoal filter or through an extra midget impinger with 15 ml of 3% H<sub>2</sub>O<sub>2</sub>. The tester may opt to use ambient air without purification.

9. Calculate the sampling rate during the purging of the sample. The sample volume ( $\Delta V_m$ ) for each point should be within  $\pm 10\%$  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  $\pm 10\%$  of constant rate for a

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single sample should not have a significant effect on the final results of the test for noncyclic processes.

10. 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  $\text{SO}_2$  due to reactions with particulate matter.

#### 4.4 Sample Recovery

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

After completion of the purge, disconnect the impingers and transport them to the cleanup area. The contents of the midget bubbler (contains isopropanol) may be discarded. However, it is usually advisable to retain this fraction until analysis is performed on the  $\text{H}_2\text{O}_2$ . 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. Transfer the contents of the midget impingers into a labeled, leak-free polyethylene sample bottle. Rinse the three midget impingers a couple of times and the connecting tubes with 3 to 15 ml portions of distilled water. Add these washings to the same sample bottle, and mark the fluid level on the side. The total rinse and sample volume should be <100 ml; a 100-ml mark can be placed on the outside of the polyethylene containers as a guide. Place about 100 ml of the absorbing reagent (3%  $\text{H}_2\text{O}_2$ ) in a polyethylene bottle and label it for use as a blank during sample analysis. An example of a sample label is shown in Figure 4.2.

#### 4.5 Sample Logistics (Data) and Packing Equipment

The sampling and sample recovery procedures are followed until the required number of runs are completed. Log all data on the Sample Recovery and Integrity Data Form, Figure 4.3. If the bubbler, impingers, and connectors are to be used in the next test, they should be rinsed with distilled water, and the bubbler

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Plant	<u>Acme Power Plant</u>	City	<u>Anywhere, USA</u>	Remarks
Site	<u>Boiler No. 3</u>	Sample type	<u>SO<sub>2</sub></u>	
Date	<u>8/10/77</u>	Run number	<u>50-1</u>	
Front rinse	<input type="checkbox"/>	Front filter	<input type="checkbox"/>	
Front solution	<input type="checkbox"/>			
Back rinse	<input type="checkbox"/>	Back filter	<input type="checkbox"/>	
Back solution	<input checked="" type="checkbox"/>			
Solution	<u>H<sub>2</sub>O<sub>2</sub></u>	Level marked	<input checked="" type="checkbox"/>	
Volume: Initial	<u>30mL</u>	Final	<u>&lt; 100mL</u>	
Cleanup by	<u>WGD</u>			

Figure 4.2. Example of a sample label.

Plant Acme Power Plant Sample location Boiler No. 3

Field Data Checks

Sample recovery personnel Joe Smith

Person with direct responsibility for recovered samples \_\_\_\_\_

Sample number	Sample identification number	Date of recovery	Liquid level marked	Stored in locked container
1	50-1	8/10/77	Yes	Yes
2				
3				
4				
5				
6				
Blank				

Remarks Containers checked for leaks. Sample volume < 100 ml

Signature of field sample trustee Joe Smith

Laboratory Data Checks

Lab person with direct responsibility for recovered samples D. Jones

Date recovered samples received 8/11/77

Analyst D. Jones

Sample number	Sample identification number	Date of analysis	Liquid at marked level	Sample identified
1	50-1	8/12/77	Yes	Yes
2				
3				
4				
5				
6				
Blank				

Remarks \_\_\_\_\_

Signature of lab sample trustee Debbie Jones

Figure 4.3. Sample recovery and integrity data.

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should be rerinsed with isopropanol. A new drying tube 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. Record all data collected during the field test in duplicate by using carbon paper or by using data forms and a field laboratory notebook. One set of data should be mailed to the base laboratory, 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 quick check of the sampling and sample recovery procedures using the data form, Figure 4.4.

Sampling

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

Impinger Contents/Parameters\*

1st: 15 ml of 80% isopropanol ✓

2nd: 15 ml of 3% H<sub>2</sub>O<sub>2</sub> ✓

3rd: 15 ml of 3% H<sub>2</sub>O<sub>2</sub> ✓

Final impinger dry? ✓

Probe heat at proper level? ✓

Crushed ice around impingers? ✓

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

Leakage rate? 0.004 l/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? 0.006 l/min

Sample Recovery

System purged at least 15 min at test sampling rate?\* ✓

Contents of impingers placed in polyethylene bottles? ✓

Fluid level marked?\* ✓

Sample containers sealed and identified?\* ✓

\* Most significant items/parameters to be checked.

Figure 4.4 On-site measurements.

Table 4.1 ACTIVITY MATRIX FOR ON-SITE MEASUREMENT CHECKS

Activity	Acceptance limits	Frequency and method of measurement	Action if requirements are not met
Preparation and/or addition of absorbing reagents.	Add 15 ml of 80% isopropanol to midget bubbler and 15 ml of 3% H <sub>2</sub> O <sub>2</sub> to first two midget impingers	Prepare 3% H <sub>2</sub> O <sub>2</sub> 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  2. A leakage rate <2% of the average sampling rate	1. Before each sampling  2. Leak check before sampling (recommended) by attaching a rotameter to dry gas meter outlet, placing a vacuum gauge at or near probe inlet, and pulling a vacuum of >250 mm (10 in.) Hg	1. Reassemble  2. Correct the leak
Sampling (constant rate)	1. Within ±10% of a constant rate  2. Minimum acceptable time is 20 min and volume is 20 l corrected to STP or as specified by regulation  3. Less than 2% leakage rate at 250 mm (10 in.) Hg  4. Purge remaining SO <sub>2</sub> from isopropanol	1. Calculate % deviation for each sample using equation in Fig. 4.1  2. Make a quick calculation prior to completion and an exact calculation after completion  3. Leak check after sample run (mandatory); use same procedure as above  4. Drain ice and purge 15 min with clean air at the sample rate	1. Repeat the sampling, or obtain acceptance from a representative of the Administrator  2. As above  3. As above  4. As above

(continued)

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Table 4.1 (continued)

Activity	Acceptance limits	Frequency and method of measurement	Action if requirements are not met
Sample logistics (data) and packing of equipment	<ol style="list-style-type: none"> <li>1. All data are recorded correctly</li> <li>2. All equipment examined for damage and labeled for shipment</li> <li>3. All sample containers properly labeled and packaged</li> </ol>	<ol style="list-style-type: none"> <li>1. Visually check upon completion of each run and before packing</li> <li>2. As above</li> <li>3. Visually check upon completion of test</li> </ol>	<ol style="list-style-type: none"> <li>1. Complete the data form</li> <li>2. Redo test if damage occurred during testing</li> <li>3. Correct when possible</li> </ol>

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United States  
Environmental Protection  
Agency

Environmental Monitoring Systems  
Laboratory  
Research Triangle Park NC 27711

Research and Development



# Section 3.5

## Method 6—Determination of Sulfur Dioxide Emissions from Stationary Sources

### Outline

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12. Data Forms	3.5.12	13

### Summary

This Method 6 test procedure is applicable to the determination of sulfur dioxide emissions from stationary sources. A gas sample is extracted from the sampling point in the stack. The sulfur dioxide is separated from the sulfuric acid mist (including sulfur trioxide) and is measured by the barium-thorin titration method. The barium ions react preferentially with sulfate ions in solution to form a highly insoluble barium sulfate precipitate. When the barium has reacted with all sulfate ions, excess barium then reacts with the thorin indicator to form a metal salt of the indicator, resulting in a color change.

The minimum detectable limit of the method has been determined to be 3.4 mg SO<sub>2</sub>/m<sup>3</sup> (2.12 x 10<sup>-7</sup> lb SO<sub>2</sub>/ft<sup>3</sup>). Although no upper limit has been established, tests have shown

that concentrations as high as 80,000 mg SO<sub>2</sub>/m<sup>3</sup> can be collected efficiently in two midjet impingers, each containing 15 ml of 3% hydrogen peroxide and the sampling rate is 1.0 L/min for 20 min. Based on theoretical calculations, the upper concentration limit in a 20-L sample is about 93,300 mg SO<sub>2</sub>/m<sup>3</sup> if two such impingers are used. The limits may be extended by increasing the number of impingers or by increasing the peroxide concentration.

Interferences include free ammonia, water-soluble cations, and fluorides. The cations and fluorides are removed by glass-wool filters and an initial isopropanol bubbler, and hence do not affect the SO<sub>2</sub> analysis. When samples are being taken from a gas stream with high concentrations of very fine metallic fumes (such as from inlets to control devices), a high-efficiency glass-fiber filter must be

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used in place of the glass-wool plug in the probe to remove the cation interferences. Free ammonia interferes by reacting with SO<sub>2</sub> to form particulate sulfite and thus preventing it from reaching the peroxide impingers, and by reacting with the indicator. If free ammonia is present (as indicated by white particulate matter in the probe and the isopropanol bubbler), an alternative method, subject to the approval of the Administrator of the U.S. Environmental Protection Agency, is required.

The tester has the option of substituting sampling equipment described in Method 8 for the midget impinger equipment of Method 6. However, the Method 8 train must be modified to include a heated filter between the probe and the isopropanol impinger and must be operated at the flow rates defined in Method 8. The heated filter will help to eliminate the possibility of the SO<sub>2</sub> reacting with the particulate matter.

The tester also has the option of determining the emissions of SO<sub>2</sub> simultaneously with particulate matter and moisture determinations by (1) replacing the water in a Method 5 impinger system with 3% peroxide solution or (2) replacing the Method 5 water impinger system with a Method 8 isopropanol-filter-peroxide system. The analysis for SO<sub>2</sub> and the calibration of the metering system must be consistent with the procedure in Method 8.

The method description that follows is based on the Reference Method that was promulgated on August 18, 1977, and amended March 23, 1978.

Section 3.5.10 contains a complete copy of the Reference Method, and Section 3.5.12 provides blank data forms for the convenience of the Handbook user. References are in Section 3.5.11. Reference 1 was used in preparing the method description. References 2, 3, and 4 are collaborative test studies of this and other related methods. Data from these test studies were used in establishing quality control limits using the techniques of Reference 5. References 6 through 12 are included because of their potential value to the user.

The accuracy of Method 6 was checked using three standard gas mixtures containing 224, 1121, and 2082 mg SO<sub>2</sub>/m<sup>3</sup> (14, 70, and 130 x 10<sup>-6</sup> lb SO<sub>2</sub>/scf), respectively. The individual measurements by the participating laboratories were all within 24% of the true concentration.

The accuracy of the analytical phase of Method 6 was checked using standard sulfuric acid solutions of three concentrations that were equivalent to sampled concentrations of 281.9, 563.8, and 845.7 mg SO<sub>2</sub>/m<sup>3</sup> (17.6, 35.2, and 52.8 x 10<sup>-6</sup> lb SO<sub>2</sub>/scf), and a blank solution. The individual measurements by all of the participating laboratories were within 6% of the true concentration.

The estimated within-laboratory precision (relative standard deviation) was 4.0%. The between-laboratory precision was 5.8%. The relative standard deviation is the ratio of the standard deviation of the measurement to the mean measured value, expressed as a percentage of this mean value.

### Method Highlights

Specifications described in this Method 6 (Section 3.5) are only for the uses of midget impingers and midget bubblers with sample rates of about 1 liter per minute (l/min). If the tester opts to use the standard-sized impingers, the Method 8 description (Section 3.7) should be used as the reference for equipment calibration, sample setup, leak check, operation, and sample recovery. The only exceptions are that glass wool may be put in the U-tube between the isopropanol and peroxide impinger as an option to the filter, the sampling is to be conducted at a constant rate of about 0.02 scm/min (0.75 scfm) ( $\Delta H@$ , orifice pressure differential that gives 0.75 scfm of air at 70°F at 29.92 in. Hg); and the isopropanol need not be analyzed.

The five blank data forms at the end of this section may be removed from the Handbook and used in the pretest, test, and the posttest operations. Each form has a subtitle (e.g., Method 6, Figure 3.1) for helping the user find a similar filled-in form in the method description (Section 3.5.3). On the blank and the filled-in forms, the items/parameters that can cause the most significant errors are starred.

#### 1. Procurement of Equipment

Section 3.5.1 (Procurement of Apparatus and Supplies) gives the specifications, criteria, and design features of the equipment and material required to perform Method 6 tests with the midget impinger train. This section is designed to provide the tester with a guide for the procurement and initial check of equipment and supplies. The activity matrix (Table 1.1) at the end of Section 3.5.1 can be used as a quick reference,

and is a summary of the corresponding written descriptions.

#### 2. Pretest Preparations

Section 3.5.2 (Calibration of Apparatus) provides a step-by-step description of the recommended calibration procedures. The accuracy and precision for the equipment calibrations are the same as those for Methods 5 and 8, with the exception that there is no calibration requirement for the rotameter. The lower sampling rate required for the midget impinger train allows the use of a wet test meter with a capacity of 3 L/min or greater. The calibration section can be removed along with the corresponding sections for the other methods and used as a separate quality assurance reference manual by the calibration personnel. The calibration data are summarized on the pretest sampling checks form (Figure 2.5, Section 3.5.2).

Section 3.5.3 (Presampling Operations) provides the tester with a preparation guide for equipment and supplies for the field test. The pretest sampling checks and pretest preparation forms (Figure 3.1, Section 3.5.3) or appropriate substitutes should be used as equipment checkout and packing lists. The sample impingers may be charged in the base laboratory if the testing is to be performed within 24 h of charging. The recommended method described for packing the containers should help protect the equipment.

#### 3. On-Site Measurements

Section 3.5.4 (On-Site Measurements) contains step-by-step procedures to perform the sampling and sample recovery. A checklist (Figure 4.4, Section 3.5.4) is provided to assist the tester with a quick method of checking that the procedures have been completed satisfactorily. Section 3.5.4 may be taken to the field for reference but it would not normally be needed by an experienced crew. The most common problem with the midget impinger train is that the hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) solution can easily be backed up into the isopropanol solution. This causes the SO<sub>2</sub> to be removed in the first impinger or in the glass wool. For this reason, it is important to take precautions in preventing this

occurrence, and it is suggested that the isopropanol and glass-wool plug be saved. The isopropanol can then be analyzed if any of the SO<sub>2</sub> data indicate questionable results.

#### 4. *Posttest Operations*

Section 3.5.5 (Postsampling Operations) gives the posttest equipment check procedures and a step-by-step analytical procedure for determination of SO<sub>2</sub> concentration. The two posttest data forms (Figure 5.1, Section 3.5.5 and Figure 5.4, Section 3.5.5) or similar forms should be used and the posttest sampling checks form should be included in the emission test report to document the calibration checks. The step-by-step analytical procedure can be removed and made into a separate quality assurance analytical reference manual for the laboratory personnel. Analysis of a control sample is required prior to the analysis of the field

samples. This analysis of an independently prepared known standard will provide the laboratory with quality control checks on the accuracy and precision of the analytical techniques.

Section 3.5.6 (Calculations) provides the tester with the required equations, nomenclature, and significant digits. It is suggested that a programmed calculator be used, if available, to reduce the chance of calculation error.

Section 3.5.7 (Maintenance) provides the tester with a guide for maintenance procedures; these are not required, but should reduce equipment malfunctions.

#### 5. *Auditing Procedure*

Section 3.5.8 (Auditing Procedure) provides a description of activities necessary for conducting performance and system audits. The performance audit of the analytical phase can be performed using aqueous ammonium sulfate

solution. Performance audits for the analytical phase and the data processing are described in Section 3.5.8. A checklist for a systems audit is also included in this section.

Section 3.5.9 (Recommended Standards for Establishing Traceability) recommends the primary standards for establishing the traceability of the working standards. The volume measures are compared to a primary liquid displacement method, and the analysis of the SO<sub>2</sub> is traceable to primary standard grade potassium acid phthalate.

#### 6. *Reference Material*

Section 3.5.10 (Reference Method) is the reference method and thus the basis for the quality assurance method description.

Section 3.5.11 (References) is a listing of the references that were used in this method description.

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**Pretest Sampling Checks**  
**(Method 6, Figure 2.5)**

Date \_\_\_\_\_ Calibrated by \_\_\_\_\_

Meter Box Number \_\_\_\_\_  $\Delta H@$  \_\_\_\_\_

**Dry Gas Meter\***

Pretest calibration factor = \_\_\_\_\_ (within  $\pm 2\%$  of average factor for each calibration run).

**Impinger Thermometer**

Was a pretest temperature correction used? \_\_\_\_\_ yes \_\_\_\_\_ no

If yes, temperature correction \_\_\_\_\_ (within  $\pm 1^\circ\text{C}$  ( $2^\circ\text{F}$ ) of reference values for calibration and within  $\pm 2^\circ\text{C}$  ( $4^\circ\text{F}$ ) of reference values for calibration check).

**Dry Gas Meter Thermometer**

Was a pretest temperature correction made? \_\_\_\_\_ yes \_\_\_\_\_ no

If yes, temperature correction \_\_\_\_\_ (within  $\pm 3^\circ\text{C}$  ( $5.4^\circ\text{F}$ ) of reference values for calibration and within  $\pm 6^\circ\text{C}$  ( $10.8^\circ\text{F}$ ) of reference values for calibration check).

**Barometer**

Was the pretest field barometer reading correct? \_\_\_\_\_ yes \_\_\_\_\_ no  
(within  $\pm 2.5$  mm (0.1 in.) Hg of mercury-in-glass barometer).

\_\_\_\_\_  
\*Most significant items/parameters to be checked.

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- a. Prepare 0.5N  $H_2SO_4$  by adding approximately 1500 ml of distilled water to a 2-ℓ volumetric flask.
- b. Cautiously add 28 ml of concentrated sulfuric acid and mix.
- c. Cool if necessary.
- d. Dilute to 2 ℓ with distilled water.
- e. Prepare 0.01N  $H_2SO_4$  by first adding approximately 800 ml of distilled water to a 1-ℓ volumetric flask and then adding 20.0 ml of the 0.5N  $H_2SO_4$ .
- f. Dilute to 1 ℓ with distilled water and mix thoroughly.

5. Barium perchlorate solution 0.0100N. Dissolve 1.95 g of barium perchlorate trihydrate ( $Ba(ClO_4)_2 \cdot 3H_2O$ ) in 200 ml of distilled water and dilute to 1 ℓ with isopropanol. Alternatively, 1.22 g of barium chloride dihydrate ( $BaCl_2 \cdot 2H_2O$ ) may be used instead of the perchlorate. Standardize, as in Subsection 5.2.4, with 0.01N  $H_2SO_4$ . 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 deionized distilled water that has been determined to be acceptable as detailed in Subsection 5.2.4. When the 0.01N sulfuric acid is prepared in this manner, procedures in Subsections 5.2.2 and 5.2.3 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% w/w NaOH solution. Dilute 10 ml to 1 ℓ with deionized distilled water. Dilute 52.4 ml of the diluted solution to 1 ℓ with deionized distilled water.

2. Dry the primary standard grade potassium acid phthalate for 1 to 2 h at 110°C (230°F) and cool in desiccator.



4. Titrate a blank of 25 ml of deionized distilled water, using the same technique as step 3. The normality will be the average of the three independent values calculated using the following equation:

$$N_{\text{H}_2\text{SO}_4} = \frac{(\text{ml NaOH}_{\text{acid}} - \text{ml NaOH}_{\text{blank}}) \times N_{\text{NaOH}}}{25} \quad \text{Equation 5-4}$$

where

$N_{\text{H}_2\text{SO}_4}$  = calculated normality of sulfuric acid,  
ml NaOH<sub>acid</sub> = volume of titrant used for H<sub>2</sub>SO<sub>4</sub>, ml,  
ml NaOH<sub>blank</sub> = volume of titrant used for blank, ml, and  
 $N_{\text{NaOH}}$  = normality of sodium hydroxide.

5.2.4 Standardization of Barium Perchlorate (0.0100N) - 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 0.0100N 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 deionized distilled 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 or other polyvalent anions, then all reagents made with the distilled 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.

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Plant Acme Power Plant Date 8/12/77  
 Sample location Boiler No. 3 Analyst Debbie Jones  
 Volume and normality of barium perchlorate

1	24.52 ml	0.01019 N
2	24.50 ml	0.01020 N
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 ( $V_a$ ) <sup>a</sup> , ml	Volume of titrant ( $V_t$ ) <sup>b</sup> , ml		
				1st titration	2nd titration	Average
1	50-1	100	20	11.31	11.29	11.30
2						
3						
4						
5						
6						
Blank		N/A		0	0	$V_{tb} = 0$

<sup>a</sup> Volume for the blank must be the same as that of the sample aliquot.

<sup>b</sup>  $\frac{\text{1st titration}}{\text{2nd titration}} = 0.99 \text{ to } 1.01$  or  $|\text{1st titration} - \text{2nd titration}| < 0.2 \text{ ml}$ .

Signature of analyst Debbie Jones

Signature of reviewer or supervisor James Roberts

Figure 5.2 Sulfur dioxide analytical data form.

$$N_{\text{Ba}(\text{ClO}_4)_2} = \frac{N_{\text{H}_2\text{SO}_4} \times 25}{\text{ml Ba}(\text{ClO}_4)_2} \quad \text{Equation 5-5}$$

where

$N_{\text{Ba}(\text{ClO}_4)_2}$  = calculated normality of barium perchlorate,  
 $N_{\text{H}_2\text{SO}_4}$  = normality of standardized sulfuric acid, and  
 $\text{ml Ba}(\text{ClO}_4)_2$  = volume of barium perchlorate titrant, 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  $\text{H}_2\text{SO}_4$  into three 250-ml Erlenmeyer flasks.
2. Dilute to 25 ml with distilled water.
3. Add a 100-ml volume of 100% isopropanol and two to four drops of thorin indicator to each.
4. Titrate with barium perchlorate to become familiar with the endpoint.

5.2.5 Control Samples - The accuracy and precision of the sample analysis should be checked. The accuracy of the analytical technique is determined by control samples. The precision is checked by duplicate analyses of both the control and the field samples. Acceptable accuracy and precision should be demonstrated on the analysis of the control sample prior to the analysis of the field samples.

The control sample should be prepared and analyzed in the following manner:

1. Dry the primary standard grade ammonium sulfate ( $(\text{NH}_4)_2\text{SO}_4$ ) for 1 to 2 h 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.

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3. Dissolve the reagent in about 1800 ml of distilled water in a 2-ℓ volumetric flask.

4. Dilute to the 2-ℓ mark with distilled water. The resulting solution is 0.0100N ammonium sulfate.

5. Enter all data on the form shown in Figure 5.3.

6. Pipette 25 ml of the control sample into each of three 250-ml Erlenmeyer flasks, and pipette a 25-ml blank of distilled water into a fourth 250-ml Erlenmeyer flask. Note: Each control sample will contain 16.5 mg of ammonium sulfate.

7. Add 100 ml of reagent grade isopropanol to each flask and then two to four drops of thordin 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 distilled 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 s. All titrations should be done against a white background.

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 two 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% of the stated value, the technique

Plant Sulfuric Acid Plant Date analyzed 9/22/78  
 Analyst R. Kuntz  $N_{\text{Ba}(\text{ClO}_4)_2}$  0.010 N

Weight of ammonium sulfate is 1.3214 g? yes

Dissolved in 2 l of distilled water? yes

Titration of blank 0.0 ml  $\text{Ba}(\text{ClO}_4)_2$  (must be < 0.5-ml)

Control sample number	Time of analysis, 24 h	Titrant volume, <sup>a</sup> ml			
		1st	2nd	3rd	Avg
1	0930	25.0	25.0		25.0

<sup>a</sup> Two titrant volumes must agree within 0.2 ml.

$$\text{ml Ba}(\text{ClO}_4)_2 \times N_{\text{Ba}(\text{ClO}_4)_2} = \text{25 ml (control sample)} \times \text{0.01N (control sample)}$$

$$\underline{25.0} \text{ ml} \times \underline{0.010} \text{ N} = \underline{0.250}$$

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

Does value agree?  yes  no

Ronda Kuntz Signature of analyst

Craig Caldwell Signature of reviewer

Figure 5.3. Control sample analytical data form.

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and standard reactions are acceptable, and the field samples may be analyzed. When the 5% 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. The accuracy limit of  $\pm 5\%$  for intra-laboratory control samples is recommended based on the control limit of  $\pm 7\%$  for interlaboratory audit results discussed in Section 3.6.8.

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 flask, and dilute to exactly 100 ml with deionized distilled water.
3. Put water in the sample storage container to the initial sample mark, and measure the initial sample volume ( $V_{\text{soln}_i}$ ).
4. Put water in the sample storage container to the mark of the transferred sample, and measure the final volume ( $V_{\text{soln}_f}$ ).

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Reagents

Normality of sulfuric acid standard\* 0.0101 N  
Date purchased 10/26/78 Date standardized 11/16/78  
Normality of barium perchlorate titrant\* 0.0096 N  
Date standardized 11/16/78  
Normality of control sample\* 0.0100 N  
Date prepared 11/6/78  
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

Volume of aliquot analyzed\* 20 ml  
Do replicate titrant volumes agree within 1% or 0.2 ml? YES  
Number and normality of control samples analyzed 2 @ 0.100 N  
Are replicate control samples within 0.2 ml? YES  
Is accuracy of control sample analysis  $\pm 5\%$ ?\* YES  
All data recorded? ✓ Reviewed by WGD

\* Most significant items/parameters to be checked.

Figure 5.4. Posttest operations.

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5. If  $V_{\text{soln}_f}$  is  $< V_{\text{soln}_i}$ , correct the sample volume ( $V_{\text{soln}}$ ) by using Equation 5-6,

$$V_{\text{soln}'} = V_{\text{soln}} \frac{V_{\text{soln}_i}}{V_{\text{soln}_f}} \quad \text{Equation 5-6}$$

where

$V_{\text{soln}'}$  = sample volume to be used for the calculations, ml,

$V_{\text{soln}}$  = total volume of solution in which the sulfur dioxide is contained, ml,

$V_{\text{soln}_i}$  = initial sample volume placed in storage container, ml, and

$V_{\text{soln}_f}$  = 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 ( $V_{\text{soln}}$ ), 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% 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 ( $V_t$ ).

4. Repeat the above analysis on a new aliquot from the same sample. Replicate titrant volumes must be within 1% 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% or 0.2 ml, whichever is larger, 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 0.0100N barium perchlorate solution from evaporation at all times.

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Table 5.1. ACTIVITY MATRIX FOR POSTSAMPLING OPERATIONS

Activity	Acceptance limits	Frequency and method of measurement	Action if requirements are not met
<u>Sampling Apparatus</u>			
Dry gas meter	Within $\pm 5\%$ 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 $\pm 10\%$ of desired flow rate (recommended)	Make two independent runs during the check of the rate meter	Recalibrate
Meter thermometer	Within $\pm 6^\circ\text{C}$ ( $10.8^\circ\text{F}$ ) at ambient temperature	Compare with ASTM mercury-in-glass thermometer after each field test	Recalibrate and use higher temperature value for calculations
Barometer	Within $\pm 5.0$ 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
<u>Analysis</u>			
Reagents	Prepare according to requirements detailed in Subsec. 5.2	Prepare and/or standardize within 24 h of sample analysis	Prepare new solutions and/or re-standardize
Control Sample	Titriments differ by $< 0.2$ ml; analytical results within $\pm 5\%$ of stated value	Before and after analysis of field samples	Prepare new solutions and/or re-standardize
Sample analysis	Titriments volumes differ by $< 1\%$ or $< 0.2$ ml, whichever is greater	Titrate until two or more sample aliquots agree within $1\%$ or $0.2$ ml, whichever is greater; review all analytical data	Void sample if any two titriments 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 spot-checked, 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 6.1A and 6.1B, at the end of this section.

### 6.1 Nomenclature

The following nomenclature is used in the calculations.

$C_{SO_2}$  = concentration of sulfur dioxide, dry basis corrected to standard conditions, g/dscm (lb/dscf).

$N$  = normality of barium perchlorate titrant, meq/ml.

$P_{bar}$  = barometric pressure at the exit orifice of the dry gas meter, mm (in.) Hg.

$P_{std}$  = standard absolute pressure, 760 mm (29.92 in.) Hg.

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- $T_m$  = dry gas meter average absolute temperature, K ( $^{\circ}R$ ).
- $T_{std}$  = standard absolute temperature, 293K (528 $^{\circ}R$ ).
- $V_a$  = volume of sample aliquot titrated, ml.
- $V_m$  = 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.
- $Y$  = dry gas meter calibration factor.
- 32.03 = equivalent weight of sulfur dioxide.

## 6.2 Calculations

The following formulas for calculating the concentration of sulfur dioxide are to be used along with example calculation forms shown in Figures 6.1A and 6.1B.

### 6.2.1 Dry Sample Gas Volume, Corrected to Standard Conditions -

$$V_{m(std)} = V_m Y \frac{T_{std} P_{bar}}{T_m P_{std}} = K_1 Y \frac{V_m P_{bar}}{T_m} \quad \text{Equation 6-1}$$

where

$$K_1 = 0.3858 \text{ K/mm Hg for metric units, or} \\
= 17.64 \text{ }^{\circ}R/\text{in. Hg for English units.}$$

### 6.2.2 Sulfur Dioxide Concentration

$$C_{SO_2} = K_2 \frac{(V_t - V_{tb}) N \frac{V_{soln}}{V_a}}{V_{m(std)}} \quad \text{Equation 6-2}$$

where

$$\begin{aligned} K_2 &= 32.03 \text{ mg/meq for metric units, or} \\ &= 7.061 \times 10^{-5} \text{ lb/meq for English units.} \end{aligned}$$

Sample Volume<sup>a</sup>

$$V_m = 0.706 \text{ ft}^3, T_m = 544.2 \text{ }^\circ\text{R}, P_{\text{bar}} = 29.84 \text{ in. Hg}, Y = 1.010$$

$$V_{m(\text{std})} = 17.64 \frac{^\circ\text{R}}{\text{in. Hg}} \times \frac{Y V_m P_{\text{bar}}}{T_m} = 0.690 \text{ ft}^3$$

Equation 6-1

SO<sub>2</sub> Concentration

$$N = 0.0102 \text{ (g-eq)/ml}, V_t = 11.30 \text{ ml}, V_{\text{tb}} = 0.00 \text{ ml}$$

$$V_{\text{soln}} = 100.0 \text{ ml}, V_a = 20.0 \text{ ml}$$

$$C_{\text{SO}_2} = 7.06 \times 10^{-5} \frac{N (V_t - V_{\text{tb}})(V_{\text{soln}}/V_a)}{V_{m(\text{std})}} = 0.590 \times 10^{-4} \text{ lb/dscf}$$

Equation 6-2

<sup>a</sup> Calculation form for data collected using Method 6 type equipment. The alternative use of Method 5 or Method 8 equipment will change  $V_m$  and  $V_{m(\text{std})}$  to  $V_{m(\text{std})} = \dots \text{ ft}^3$ .

Figure 6.1A. Sulfur dioxide calculation form (English units).

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Sample Volume<sup>a</sup>

$$V_m = 20.00 \text{ l} \times 0.001 = 0.0200 \text{ m}^3$$

$$T_m = 302.0 \text{ K}, P_{\text{bar}} = 758. \text{ mm Hg}, Y = 1.010$$

$$V_{m(\text{std})} = 0.3858 \frac{\text{K}}{\text{mm Hg}} \times \frac{Y V_m P_{\text{bar}}}{T_m} = 0.0196 \text{ m}^3$$

Equation 6-1

SO<sub>2</sub> Concentration

$$N = 0.102 \text{ (g-eq)/ml}, V_t = 11.30 \text{ ml}, V_{\text{tb}} = 0.00 \text{ ml}$$

$$V_{\text{soln}} = 100.0 \text{ ml}, V_a = 20.0 \text{ ml}$$

$$C_{\text{SO}_2} = 32.03 \frac{N (V_t - V_{\text{tb}}) (V_{\text{soln}}/V_a)}{V_{m(\text{std})}} = 942. \text{ mg/dscm}$$

Equation 6-2

<sup>a</sup> Calculation form for data collected using Method 6 type equipment. The alternative use of Method 5 or Method 8 equipment will change  $V_m$  and  $V_{m(\text{std})}$  to  $V_{m(\text{std})} = \dots \text{ m}^3$ .

Figure 6.1B. Sulfur dioxide calculation form (metric units).

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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  $\ell$  (100 ft<sup>3</sup>) of operation, whichever is greater. 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 sample train, several types of pumps are used; the two 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 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 mo. 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.

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### 7.3 Rotameter

The rotameter should be disassembled and cleaned according to the manufacturer's instructions using only recommended cleaning fluids every 3 mo or upon erratic operation.

### 7.4 Sample Train

All remaining sample train components should be visually checked every 3 mo 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 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 measurements	Action if requirements are not met
Routine maintenance	No erratic behavior	Routine maintenance performed quarterly; 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 whenever meter dial runs erratically or whenever meter will not calibrate	Replace parts as needed or replace meter
Rotameter	Clean and no erratic behavior	Clean every 3 mo or whenever ball does not move freely	Replace
Sample 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

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## 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. In the case of a compliance test, the required performance audit will be conducted by the responsible enforcement agency. 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 collaborative tests<sup>2,3,4</sup> of Method 6, two specific performance audits are recommended:

1. Audit of the analytical phase of Method 6.
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 generally made to quantitatively evaluate 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. No performance audit is recommended at this time for the sampling phase. 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 6 analysis and should be performed at the discretion of the agency auditor, the laboratory supervisor, source test company, or quality assurance officer. The analytical phase of Method 6 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 Section 3.5.5 on control sample preparation.

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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 6 analysis procedure described in this Handbook.

To obtain pretest audit samples only, the testing laboratory should provide a notice 30 days prior to the time of the planned pretest audit to EPA's Environmental Monitoring Systems Laboratory, Quality Assurance Division, Source Branch, Mail Drop 77A, Research Triangle Park, North Carolina 27711. This request for known quality control samples from the Source Branch is different from and does not satisfy the required 30 day notice to the applicable enforcement agency as to the intent to conduct a compliance test. The laboratory can prepare their own quality control sample. The testing laboratory supervisor or quality assurance officer can then check the precision and accuracy of the analytical system prior to a compliance test with the use of the known value samples. All problems indicated by the audit should be eliminated prior to the audit by the agency.

The accuracy for each of two samples should be within 5 percent of true value. The relative error (RE) is a measure of the bias of the analytical phase of Method 6. Calculate RE using Equation 8-1.

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

Equation 8-1

where:

$C_d$  = Determined audit sample concentration, mg/dsm<sup>3</sup>.

$C_a$  = Actual audit sample concentration, mg/dsm<sup>3</sup>.

8.1.2 Audit of Analytical Phase of the Field Test (Required) - As stated in 40 CFR 60, Section 3.3.6 (49 FR 26522, 06/27/84), the testing laboratory should provide the responsible agency/organization requesting the performance test with a notification of the intent to test 30 days prior to the enforcement source test. The responsible agency obtains the audit samples from the appropriate EPA Regional Quality Assurance Coordinator shown in Table 5.1 of Section 3.0.5 of this Handbook. The responsible agency then provides the testing laboratory with two audit samples to be analyzed along with 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 two audit samples and the compliance samples should be concurrently analyzed in the same manner to evaluate the technique of the analyst and the standards preparation. (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 has been listed above.) The same analyst, analytical reagents, and analytical system shall be used both for compliance samples and the EPA audit samples; if this condition is met, auditing of subsequent compliance analyses for the same enforcement agency within 30 days 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  $\text{mg/dsm}^3$  using the specified sample volume in the audit instructions. (Note: Indication of acceptable results may be obtained immediately by reporting the audit results in  $\text{mg/dsm}^3$  and compliance results in total  $\text{mg NO}_2/\text{sample}$  by telephone to the responsible enforcement agency.) 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 (see Note in first paragraph of this section).

Failure to meet the 5-percent specification may require 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.

8.1.3 Audit of Data Processing - Calculation errors are prevalent in Method 6.<sup>3,4,5</sup> Data processing errors can be determined by auditing the recorded data on the field and laboratory forms. The original and audit (check) calculations should agree within round-off 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 audit may be reduced--for example, to 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 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. Purging the sampling train.

Figure 8.1 is a suggested checklist for the auditor.

Yes	No	Comment						
<input type="checkbox"/>  <input type="checkbox"/>	<input type="checkbox"/>  <input type="checkbox"/>		<p style="text-align: center;"><u>Presampling preparation</u></p> <p>1. Knowledge of process conditions</p> <p>2. Calibration of pertinent equipment, in particular, the dry gas meter, prior to each field test</p>					
			<input type="checkbox"/>  <input type="checkbox"/>  <input type="checkbox"/>  <input type="checkbox"/>  <input type="checkbox"/>  <input type="checkbox"/>	<input type="checkbox"/>  <input type="checkbox"/>  <input type="checkbox"/>  <input type="checkbox"/>  <input type="checkbox"/>  <input type="checkbox"/>		<p style="text-align: center;"><u>On-site measurements</u></p> <p>3. Leak testing of sampling train after sample run</p> <p>4. Preparation and addition of absorbing solutions to impingers</p> <p>5. Constant rate sampling (for Method 6A only)</p> <p>6. Purging of the sampling train and rinsing of the impingers and connecting tubes to recover the sample</p> <p>7. Recording of pertinent process conditions during sample collection</p> <p>8. Maintaining the probe at a given temperature</p>		
<input type="checkbox"/>  <input type="checkbox"/>  <input type="checkbox"/>  <input type="checkbox"/>  <input type="checkbox"/>  <input type="checkbox"/>  <input type="checkbox"/>  <input type="checkbox"/>	<input type="checkbox"/>  <input type="checkbox"/>  <input type="checkbox"/>  <input type="checkbox"/>  <input type="checkbox"/>  <input type="checkbox"/>  <input type="checkbox"/>  <input type="checkbox"/>					<p style="text-align: center;"><u>Postsampling</u></p> <p>9. Control sample analysis--accuracy and precision</p> <p>10. Sample aliquoting techniques</p> <p>11. Titration technique, particularly endpoint precision</p> <p>12. Use of detection blanks in correcting field sample results</p> <p>13. Audit results (+ 5%)</p> <p>14. Calculation procedure/check</p> <p>15. Calibration checks</p> <p>16. Standardized barium perchlorate solution</p>		
						<u>Comments</u>		

Figure 8.1. Method 6 checklist to be used by auditors.

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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 sulfate solution	<p>Measured RE of the pretest audit samples should be less than +5% for both audit results (optional)</p> <p>Measured RE for audit during test should be less than +5% for both audit results (required)</p>	<p><u>Frequency:</u> As considered necessary by the testing firm</p> <p><u>Method:</u> Measure reference samples and compare with true value</p> <p><u>Frequency:</u> Once during every enforcement source test (required)</p> <p><u>Method:</u> Measure audit samples and compare with true samples</p>	<p>Review operating techniques</p> <p>Review operating technique and repeat both the audit and field sample analyses</p>
Data processing errors (recommended)	<p>Original and check calculations within round-off error</p>	<p><u>Frequency:</u> Once during every enforcement source test</p> <p><u>Method:</u> Independent calculations, starting with recorded data</p>	<p>Check and correct all data for the source test</p>
System audit (recommended)	<p>Operation technique described in this section of the Handbook</p>	<p><u>Frequency:</u> Once during every enforcement test until experience gained, then every fourth test</p> <p><u>Method:</u> Observation of techniques, assisted by audit checklist, Fig. 8.1</p>	<p>Explain to team the deviations from recommended techniques and note on Fig. 8.1</p>

#### 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 repeat 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 3.5.2) 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.

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## 10.0 REFERENCE METHOD \*

### METHOD 6—DETERMINATION OF SULFUR DIOXIDE EMISSIONS FROM STATIONARY SOURCES

#### 1. Principle and Applicability

1.1 Principle. A gas sample is extracted from the sampling point in the stack. The sulfuric acid mist (including sulfur trioxide) and the sulfur dioxide are separated. The sulfur dioxide fraction is measured by the barium-chlorine titration method.

1.2 Applicability. This method is applicable for the determination of sulfur dioxide emissions from stationary sources. The minimum detectable limit of the method has been determined to be 3.4 milligrams (mg) of SO<sub>2</sub>/m<sup>3</sup> (2.12 x 10<sup>-6</sup> lb./ft.<sup>3</sup>). Although no upper limit has been established, tests have shown that concentrations as high as 10,000 mg/m<sup>3</sup> of SO<sub>2</sub> can be collected efficiently in two midge impingers, each containing 15 milliliters of 3 percent hydrogen peroxide, at a rate of 1.0 lpm for 30 minutes. Based on theoretical calculations, the upper concentration limit in a 30-liter sample is about 50,000 mg/m<sup>3</sup>.

Possible interferences are free ammonia, water-soluble cations, and fluorides. The cations and fluorides are removed by glass wool filters and an isopropanol bubbler, and hence do not affect the SO<sub>2</sub> analysis. When samples are being taken from a gas stream with high concentrations of very fine metallic fumes (such as in inlets to central drives), a high-efficiency glass fiber filter must be used in place of the glass wool plug (i.e., the one in the probe) to remove the cation interferences.

Free ammonia interferes by reacting with SO<sub>2</sub> to form particulate sulfate and by reacting with the indicator. If free ammonia is present (this can be determined by knowledge of the process and noticing white particulate matter in the probe and isopropanol bubbler), alternative methods, subject to the approval of the Administrator, U.S. Environmental Protection Agency, are required.

#### 2. Apparatus

2.1 Sampling. The sampling train is shown in Figure 6-1, and component parts are discussed below. The tester has the option of substituting sampling equipment described in Method 4 in place of the midge impinger equipment of Method 6. However, the Method 6 train must be modified to include a heated filter between the probe and isopropanol impinger, and the operation of the sampling train and sample analysis must be at the flow rate and solution volumes defined in Method 6.

The tester also has the option of determining SO<sub>2</sub> simultaneously with particulate matter and moisture determinations by (a) routing the water in a heated 3 impinger system with 3 percent peroxide solution, or (b) by modifying the Method 6 water impinger system with a Method 4 isopropanol-filter-peroxide system. The analysis for SO<sub>2</sub> must be consistent with the procedure in Method 6.

2.1.1 Probe. Borosilicate glass, or stainless steel (other materials of construction may be used, subject to the approval of the Administrator), approximately 6-cm inside diameter, with a heating system to prevent water condensation and a filter (glass wool or heated cartridge) to remove particulate matter, including sulfuric acid mist. A plug of glass wool is a satisfactory filter.

2.1.2 Bubbler and Impingers. One midge bubbler, with medium-coarse glass frit and borosilicate or quartz glass wool packed in top (see Figure 6-1) to prevent sulfuric acid mist carryover, and three 20-ml midge impingers. The bubbler and midge impingers must be connected in series with leak-free glass connectors. Gill-cose grease may be used, if necessary, to prevent leakage. At the option of the tester, a midge impinger may be used in place of the midge bubbler.

Other collection absorbents and flow rates may be used, but are subject to the approval of the Administrator. Also, collection efficiency must be shown to be at least 99 percent for each test gas and must be documented in the report. If the efficiency is found to be acceptable after a series of three tests, further documentation is not required. To conduct the efficiency test, an extra absorber must be added and analyzed separately. This extra absorber must not contain more than 1 percent of the total SO<sub>2</sub>.

2.1.3 Glass Wool. Borosilicate or quartz.

2.1.4 Stopcock Grease. Acetone-insoluble, heat-stable silicone grease may be used, if necessary.

2.1.5 Temperature Gauge. Dial thermometer, or equivalent, to measure temperature of gas leaving impinger train to within 1° C (3° F).

2.1.6 Drying Tube. Tube packed with 6- to 16-mesh indicating type silica gel, or equivalent, to dry the gas sample and to protect the meter and pump. If the silica gel has been used previously, dry at 175° C (350° F) for 2 hours. New silica gel may be used as received. Alternatively, other types of desiccant (anhydrous calcium chloride, or equivalent) may be used, subject to approval of the Administrator.

2.1.7 Valve. Needle valve, to regulate sample gas flow rate.

2.1.8 Pump. Leak-free diaphragm pump, or equivalent, to pull gas through the train. Install a small tank between the pump and rate meter to eliminate the pulsation effect of the diaphragm pump on the rotameter.

2.1.9 Rate Meter. Rotameter, or equivalent, capable of measuring flow rate to within 3 percent of the selected flow rate of about 1000 ac/min.

2.1.10 Volume Meter. Dry gas meter, sufficiently accurate to measure the sample volume within 2 percent, calibrated at the selected flow rate and conditions actually encountered during sampling, and equipped with a temperature gauge (dial thermometer, or equivalent) capable of measuring temperature to within 1° C (3.4° F).

2.1.11 Barometer. Mercury, aneroid, or other barometer capable of measuring atmospheric pressure to within 2.5 mm Hg (0.1 in. Hg). In many cases, the barometric reading may be obtained from a nearby national weather service station, in which case the station value (which is the absolute barometric pressure) shall be requested and an adjustment for elevation differences between the weather station and sampling point shall be applied at a rate of minus 2.5 mm Hg (0.1 in. Hg) per 30 m (100 ft) elevation increase or vice versa for elevation decrease.

2.1.12 Vacuum Gauge. At least 200 mm Hg (30 in. Hg) gauge, to be used for leak check of the sampling train.

#### 2.2 Sample Recovery

2.2.1 Wash bottles. Polyethylene or glass, 500 ml. two.

2.2.2 Storage Bottles. Polyethylene, 100 ml, to store impinger samples (one per sample).

#### 2.3 Analysis

2.3.1 Pipettes. Volumetric type, 5-ml, 20-ml (one per sample), and 25-ml (one per sample).

2.3.2 Volumetric Flasks, 100-ml size (one per sample) and 100-ml size.

2.3.3 Beakers, 5- and 60-ml size.

2.3.4 Erlenmeyer Flasks, 250 ml size (one for each sample, blank, and standard).

2.3.5 Dropping Bottle, 125-ml size, to add indicator.

2.3.6 Graduated Cylinder, 100-ml size.

2.3.7 Spectrophotometer. To measure absorbance at 253 nanometers.

#### 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

3.1.1 Water. Deionized, distilled to conform to ASTM specification D1582, Type 3. At the option of the analyst, the KMnO<sub>4</sub> test for oxidizable organic matter may be omitted when high concentrations of organic matter are not expected to be present.

3.1.2 Isopropanol, 99 percent. Mix 90 ml of isopropanol with 20 ml of deionized, distilled water. Check each lot of isopropanol for peroxide impurities as follows: shake 10 ml of isopropanol with 10 ml of freshly prepared 10 percent potassium iodide solution. Prepare a blank by similarly treating 10 ml of distilled water. After 1 minute, read the absorbance at 253 nanometers on a spectrophotometer. If absorbance exceeds 0.1, reject alcohol for use.

Peroxide may be removed from isopropanol by redistilling or by passage through a column of activated charcoal; however, reagent grade isopropanol with suitably low peroxide levels may be obtained from commercial sources. Rejection of contaminated lots may, therefore, be a more efficient procedure.

3.1.3 Hydrogen Peroxide, 3 Percent. Dilute 30 percent hydrogen peroxide 1:9 (v/v) with deionized, distilled water (90 ml is needed per sample). Prepare fresh daily.

3.1.4 Potassium Iodide Solution, 10 Percent. Dissolve 10.0 grams KI in deionized, distilled water and dilute to 100 ml. Prepare when needed.

3.1.5 Water. Deionized, distilled, as in 3.1.1.

3.1.6 Isopropanol, 99 Percent. Mix 90 ml of isopropanol with 20 ml of deionized, distilled water.

#### 3.2 Analysis

3.2.1 Water. Deionized, distilled, as in 3.1.1.

3.2.2 Isopropanol, 100 percent.

3.2.3 Thion Indicator. 1-(4-oxo-5-phosphoryl)-2-naphthol-6-sulfonic acid, sodium salt, or equivalent. Dissolve 0.20 g in 100 ml of deionized, distilled water.

3.2.4 Barium Perchlorate Solution, 0.005 N. Dissolve 1.00 g of barium perchlorate tetrahydrate [Ba(ClO<sub>4</sub>)<sub>2</sub>·4H<sub>2</sub>O] in 200 ml distilled water and dilute to 1 liter with isopropanol. Alternatively, 1.21 g of [BaCl<sub>2</sub>·2H<sub>2</sub>O] may be used instead of the perchlorate standard as in Section 3.1.

3.2.5 Sulfuric Acid Standard, 0.005 N. Purchase or standardize to ~0.005 N against 0.005 N NaOH which has previously been standardized against potassium acid phthalate (primary standard grade).

#### 4. Procedure

#### 4.1 Sampling

4.1.1 Preparation of collection train. Measure 15 ml of 99 percent isopropanol into the midge bubbler and 15 ml of 3 percent hydrogen peroxide into each of the first two midge impingers. Leave the final midge impinger dry. Assemble the train as shown in Figure 6-1. Adjust probe heater to a temperature sufficient to prevent water condensation. Place crushed ice and water around the impingers.

4.1.2 Leak-check procedure. A leak check prior to the sampling run is optional; however, a leak check after the sampling run is mandatory. The leak-check procedure is as follows:

With the probe disconnected, place a vacuum range at the inlet to the bubbler and pull a vacuum of 250 mm (10 in.) Hg; plug or mark off the outlet of the flow meter, and then turn off the pump. The vacuum shall remain stable for at least 30 seconds. Carefully release the vacuum gauge, before releasing the flow meter and to prevent back flow of the impinger fluid.

Other leak-check procedures may be used, subject to the approval of the Administrator, U.S. Environmental Protection Agency. This procedure used in Method 3 is not suitable for diaphragm pumps.

4.1.3 Sample collection. Record the local dry gas meter reading and barometric pressure. To begin sampling, position the tip of the probe at the sampling point, connect the probe to the bubbler, and start the pump. Adjust the sample flow to a constant rate of approximately 1.0 liter/min as indicated by the rotameter. Maintain this constant rate (+0.20 percent) during the entire sampling run. Take readings only gas meter, temperature at dry gas meter and at impinger outlet and rate meter) at least every 5 minutes. Add more ice during the run to keep the flow constant of the gas meter. At the conclusion of each run, turn off the pump, remove probe from the stack, and record the final reading. Conduct a leak check as in Section 4.1.2. (This leak check is mandatory.) If a leak is found, void the test run. Drain the ice bath and purge the remaining part of the train by drawing clean ambient air through the system for 15 minutes at the sampling rate.

Clean ambient air can be provided by passing air through a charcoal filter or through an ultra-midget impinger with 15 ml of 3 percent H<sub>2</sub>O<sub>2</sub>. The tester may opt to simply use ambient air, without purification.

4.2 Sample Recovery. Disconnect the impingers after purging. Discard the contents of the midge bubbler. Pour the contents of the midge impingers into a leak-free polyethylene bottle for shipment. Rinse the three midge impingers and the connecting tubes with deionized distilled water, and add the washings to the same storage container. Mark the final level. Seal and identify the sample container.

4.3 Sample Analysis. Note level of liquid in container, and confirm whether any sample was lost during shipment; note this on analytical data sheet. If a noticeable amount of leakage has occurred, either void the sample or use the methods, subject to the approval of the Administrator, to correct the loss.

Transfer the contents of the storage container to a 100-ml volumetric flask and dilute to exactly 100 ml with deionized, distilled water. Pipette a 20-ml aliquot of this solution into a 250-ml Erlenmeyer flask, add 80 ml of 100 percent isopropanol and two to four drops of thion indicator, and titrate to a pink endpoint using 0.005 N barium perchlorate. Repeat and average the titration volume. Run a blank with the washings in the same storage container. Titration must agree within 1 percent or 0.2 ml, whichever is larger.

(NOTE.—Protect the 0.005 N barium perchlorate solution from evaporation at all times.)

#### 5. Calibration

#### 5.1 Metering System

5.1.1 Initial Calibration. Before its initial use in the field, first leak check the metering system (drying tube, needle valve, pump, rotameter, and dry gas meter) as follows: place a vacuum gauge at the inlet to the drying tube and 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 shall remain stable for at least 30 seconds. Carefully release the vacuum gauge before releasing the flow meter and.

Next, calibrate the metering system at the sampling flow rate specified by the method) as follows: connect an appropriately sized wet test meter (0.5- to 1-liter gas revolutions) to the inlet of the drying tube. Make three independent calibration runs, using at least five revolutions of the dry gas meter per run. Calculate the calibration factor, Y (wet test meter calibration volume divided by the dry gas meter volume, both volumes adjusted to the same reference temperature and pressure, for each run, and average the results. If any Y value deviates by more than 1.1 percent from the mean, void the metering system. It is unacceptable for use. Otherwise, use the average of the calibration factor for subsequent test runs.

5.1.2 Post-Test Calibration Check. After each field test series, conduct a calibration check as in Section 5.1.1 above, except for the following variations: (a) the leak check is not to be conducted, (b) three, or more, revolutions of the dry gas meter may be used, and (c) 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 volume obtained during the test series are acceptable. If the calibration factor deviates by more than 5 percent, recalibrate the metering system as in Section 5.1.1. For the calibration factor, use the calibration factor (dry or non-hydrocarbon) that yields the lower gas volume for each test run.

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- 2. Thermometers. Calibrate against mercury-in-glass thermometers.
- 3. Rotameter. The rotameter need not be calibrated but should be cleaned and maintained according to the manufacturer's instruction.
- 4. Barometer. Calibrate against a mercury barometer.
- 5.5 Barium Perchlorate Solution. Standardize the barium perchlorate solution against 25 ml of standard sulfuric acid to which 100 ml of 100 percent isopropanol has been added.

4. Calculations  
 Carry out calculations, retaining at least one extra decimal figure beyond that of the acquired data. Round off figures after final calculation.

- 6.1 Nomenclature.
  - $C_{SO_2}$  = Concentration of sulfur dioxide, dry basis corrected to standard conditions, mg/dscm (lb/dscf).
  - $N$  = Normality of barium perchlorate titrant, milliequivalent/ml.
  - $P_{bar}$  = Barometric pressure at the exit orifice of the dry gas meter, mm Hg (in. Hg).
  - $P_{std}$  = Standard absolute pressure, 760 mm Hg (29.92 in. Hg).
  - $T_m$  = Average dry gas meter absolute temperature, °K (°R).
  - $T_{std}$  = Standard absolute temperature, 293° K (528° R).
  - $V_m$  = Volume of sample aliquot titrated, ml.
  - $V_{m(dry)}$  = Dry gas volume as measured by the dry gas meter, dcm (dct).

- $V_{m(dry)}$  = Dry gas volume measured by the 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, ml (average of replicate titrations).
- $V_{t0}$  = Volume of barium perchlorate titrant used for the blank, ml.
- $Y$  = Dry gas meter calibration factor.
- 22.03 = Equivalent weight of sulfur dioxide.
- 6.2 Dry sample gas volume, corrected to standard conditions.

$$V_{m(dry)} = V_m Y \left( \frac{T_{std}}{T_m} \right) \left( \frac{P_{bar}}{P_{std}} \right) = K_1 Y \frac{V_m P_{bar}}{T_m}$$

Equation 6-1

where:  
 $K_1 = 0.3858 \text{ } ^\circ\text{K/mm Hg for metric units.}$   
 $= 17.64 \text{ } ^\circ\text{R/in. Hg for English units.}$

- 6.3 Sulfur dioxide concentration.

$$C_{SO_2} = K_2 \frac{(V_t - V_{t0}) N \left( \frac{V_{soln}}{V_m} \right)}{V_{m(dry)}}$$

Equation 6-2

where:  
 $K_2 = 22.03 \text{ mg/meq, for metric units.}$   
 $= 7.061 \times 10^{-3} \text{ lb/meq, for English units.}$

7. Bibliography

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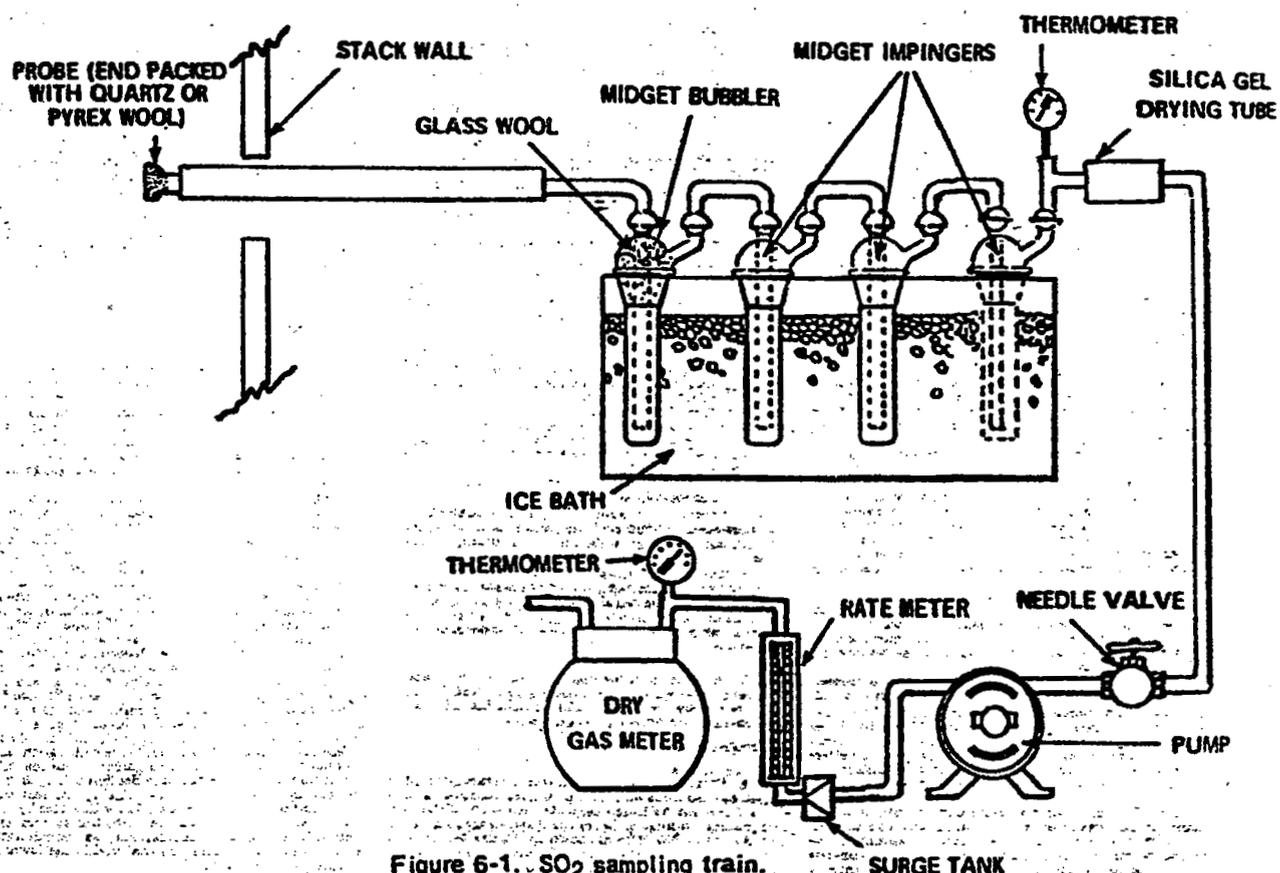


Figure 6-1. SO<sub>2</sub> sampling train.

In Method 8 of Appendix A, Sections 2.1, 2.1.6, 2.1.7, 2.1.8, 2.1.11, 2.1.12, 2.3.2, 3.3.4, 4.1.2, 4.1.3, and 5.1.1 are amended as follows:

1. In Section 2.1, the word "perioxide" in the fourth line of the second paragraph is corrected to read "peroxide."

2. In Section 2.1.6, the word "silac" in the third line is corrected to read "silica."

3. In Section 2.1.7, the word "value", which appears twice is corrected to read "valve."

4. In Section 2.1.8, the word "disphragm" is corrected to read "diaphragm" and the word "surge" is inserted between the words "small" and "tank."

5. In Section 2.1.11, the word "ameroid" is corrected to read "aneroid."

6. In Section 2.1.12, the phrase "and Rotameter." is inserted after the phrase "Vacuum Gauge" and the phrase "and 0-40 cc/min rotameter" is inserted between the words "gauge" and ", to."

7. In Section 2.3.2, the phrase "and 100-ml size" is corrected to read "and 1000-ml size."

8. In Section 3.3.4, the word "sopropanol" in the fourth line is corrected to read "isopropanol."

9. In Section 4.1.3, delete the last sentence of the last paragraph. Also delete the second paragraph and replace it with the following paragraphs:

Temporarily attach a suitable (e.g., 0-40 cc/min) rotameter to the outlet of the dry gas meter and place a vacuum gauge at or near the probe inlet. Plug the probe inlet, pull a vacuum of at least 250 mm Hg (10 in. Hg), and note the flow rate as indicated by the rotameter. A leakage rate not in excess of 2 percent of the average sampling rate is acceptable.

Note: Carefully release the probe inlet plug before turning off the pump.

It is suggested (not mandatory) that the pump be leak-checked separately, either prior to or after the sampling run. If done prior to the sampling run, the pump leak-check shall precede the leak check of the sampling train described immediately above; if done after the sampling run, the pump leak-check shall follow the train leak-check. To leak check the pump, proceed as follows: Disconnect the drying tube from the probe-impinger assembly. Place a vacuum gauge at the inlet to either the drying tube or 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.

10. In Section 4.1.3, the sentence "If a leak is found, void the test run" on the sixteenth line is corrected to read

"If a leak is found, void the test run, or use procedures acceptable to the Administrator to adjust the sample volume for the leakage."

11. In Section 5.1.1, the word "or" on the sixth line is corrected to read "of."

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## 11.0 REFERENCES

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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 M6-1.2 indicates that the form is Figure 1.2 in Section 3.5.1 of the Method 6 Handbook. Future revisions of these forms, if any, can be documented as 1.2A, 1.2B, etc. Thirteen of the blank forms listed below are included in this section. Five are in the Method Highlights subsection as shown by the MH following the form number.

<u>Form</u>	<u>Title</u>
1.2	Procurement Log
2.2	Wet Test Meter Calibration Log
2.4A and 2.4B	Dry Gas Meter Sample Calibration Data (English and metric units)
2.5 (MH)	Pretest Sampling Checks
3.1 (MH)	Pretest Preparations
4.1	Sampling Data Form for SO <sub>2</sub>
4.2	Sample Label
4.3	Sample Recovery and Integrity Data
4.4 (MH)	On-Site Measurements
5.1 (MH)	Posttest Sampling Checks
5.2	Sulfur Dioxide Analytical Data
5.3	Control Sample Analytical Data
5.4 (MH)	Posttest Operations

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6.1A and 6.1B

Sulfur Dioxide Calculation Forms  
(English and metric units)

8.1

Method 6 Checklist To Be Used by  
Auditors

**DRY GAS METER SAMPLE CALIBRATION DATA**  
(English units)

Date \_\_\_\_\_ Calibrated by \_\_\_\_\_ Meter box number \_\_\_\_\_  
 Barometer pressure,  $P_m =$  \_\_\_\_\_ in. Hg Wet test meter number \_\_\_\_\_  
 Dry test meter temperature correction factor \_\_\_\_\_<sup>°F</sup>

Wet test meter pressure drop ( $D_m$ ), <sup>a</sup> in. H <sub>2</sub> O	Rota-meter setting ( $R_s$ ), ft <sup>3</sup> /min	Wet test meter gas volume ( $V_w$ ), <sup>b</sup> ft <sup>3</sup>	Dry test meter gas volume ( $V_d$ ), <sup>b</sup> ft <sup>3</sup>		Wet test meter gas temp ( $t_w$ ), °F	Dry test meter						
			Initial	Final		Inlet gas temp ( $t_{d_i}$ ), °F	Outlet gas temp ( $t_{d_o}$ ), °F	Average gas temp ( $t_d$ ), <sup>c</sup> °F	Time of run ( $\Theta$ ), <sup>d</sup> min	Average ratio ( $Y_1$ ), <sup>e</sup>	( $Y_{r_1}$ ), <sup>f</sup>	

<sup>a</sup>  $D_m$  expressed as negative number.

<sup>b</sup> Volume passing through meter. Dry gas volume is minimum for at least five revolutions of the meter.

<sup>c</sup> The average of  $t_{d_i}$  and  $t_{d_o}$  if using two thermometers; the actual reading if using one thermometer.

<sup>d</sup> The time it takes<sup>1</sup> to complete the calibration run.

<sup>e</sup> With  $Y$  defined as the average ratio of volumes for the wet test and the dry test meters,  $Y_1 = Y \pm 0.02 Y$  for calibration and  $Y_1 = Y \pm 0.05 Y$  for the posttest checks, thus,

$$Y_1 = \frac{V_w (t_d + 460^{\circ}\text{F}) [P_m + (D_m/13.6)]}{V_d (t_w + 460^{\circ}\text{F}) (p_m)} \quad (\text{Eq. 1})$$

$$Y = \frac{Y_1 + Y_2 + Y_3}{3} = \underline{\hspace{2cm}} \quad (\text{Eq. 2})$$

<sup>f</sup> 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

$$Y_{r_1} = \frac{V_w (t_d + 460^{\circ}\text{F}) [P_m + (D_m/13.6)] (60)}{\Theta (t_w + 460^{\circ}\text{F}) (P_m) (0.035)} \quad (\text{Eq. 3})$$

$$Y_r = \frac{Y_1 + Y_2 + Y_3}{3} = \underline{\hspace{2cm}} \quad (\text{Eq. 4})$$

**DRY GAS METER SAMPLE CALIBRATION DATA**  
(metric units)

Date \_\_\_\_\_ Calibrated by \_\_\_\_\_ Meter box number \_\_\_\_\_  
 Barometer pressure,  $P_m =$  \_\_\_\_\_ mm Hg Wet test meter number \_\_\_\_\_  
 Dry test meter temperature correction factor \_\_\_\_\_ °C

Wet test meter pressure drop ( $D_m$ ), <sup>a</sup> mm H <sub>2</sub> O	Rota-meter setting ( $R_s$ ), l/min	Wet test meter gas volume ( $V_w$ ), <sup>b</sup> l	Dry test meter gas volume ( $V_d$ ), <sup>b</sup> l		Wet test meter gas temp ( $t_w$ ), °C	Dry test meter						
			Initial	Final		Inlet gas temp ( $t_{d_i}$ ), °C	Outlet gas temp ( $t_{d_o}$ ), °C	Average gas temp ( $t_d$ ), <sup>c</sup> °C	Time of run ( $\Theta$ ), <sup>d</sup> min	Average ratio ( $Y_i$ ), <sup>e</sup>	( $Y_{r_i}$ ), <sup>f</sup>	

<sup>a</sup>  $D_m$  expressed as negative number.

<sup>b</sup> Volume passing through meter. Dry gas volume is minimum for at least five revolutions of the meter.

<sup>c</sup> The average of  $t_{d_i}$  and  $t_{d_o}$  if using two thermometers; the actual reading if using one thermometer.

<sup>d</sup> The time it takes to complete the calibration run.

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

$$Y_i = \frac{V_w (t_d + 273^\circ\text{C}) [P_m + (D_m/13.6)]}{V_d (t_w + 273^\circ\text{C}) (P_m)} \quad (\text{Eq. 1})$$

$$Y = \frac{Y_1 + Y_2 + Y_3}{3} = \underline{\hspace{2cm}} \quad (\text{Eq. 2})$$

<sup>f</sup> With  $Y_r$  defined as the average ratio of volumetric measurement by wet test meter to rotameter. Tolerance  $Y_r = 1 \pm 0.05$  for calibration and  $Y \pm 0.1$  for posttest checks

$$Y_{r_i} = \frac{V_w (t_d + 273^\circ\text{C}) [P_m + (D_m/13.6)] (60)}{\Theta (t_w + 273^\circ\text{C}) (P_m) (0.035)} \quad (\text{Eq. 3})$$

$$Y_r = \frac{Y_1 + Y_2 + Y_3}{3} = \underline{\hspace{2cm}} \quad (\text{Eq. 4})$$

SAMPLING DATA FORM FOR SO<sub>2</sub>

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) \_\_\_\_\_ Sample point location \_\_\_\_\_  
 Initial leak check \_\_\_\_\_ Sample purge time, min \_\_\_\_\_  
 Final leak check \_\_\_\_\_ Remarks \_\_\_\_\_

Sampling time, min	Clock time, 24 h	Sample volume, l (ft <sup>3</sup> )	Sample flow rate setting, l/min (ft <sup>3</sup> /min)	Sample volume metered (ΔV <sub>m</sub> ), l (ft <sup>3</sup> )	Percent deviation, <sup>a</sup> %	Dry gas meter temp, °C (°F)	Impinger temp, °C (°F)
Total		Total		ΔV <sub>m</sub> avg	Avg dev	Avg	Max temp

<sup>a</sup> Percent deviation =  $\frac{\Delta V_m - \Delta V_{m \text{ avg}}}{\Delta V_{m \text{ avg}}} \cdot 100.$

SAMPLE LABEL

Plant _____	City _____	Remarks     	
Site _____	Sample type _____		
Date _____	Run number _____		
Front rinse <input type="checkbox"/>	Front filter <input type="checkbox"/>		Front solution <input type="checkbox"/>
Back rinse <input type="checkbox"/>	Back filter <input type="checkbox"/>		Back solution <input type="checkbox"/>
Solution _____	Level marked <input type="checkbox"/>		
Volume: Initial _____	Final _____		
Cleanup by _____			

**SAMPLE RECOVERY AND INTEGRITY DATA**

Plant \_\_\_\_\_ Sample location \_\_\_\_\_

**Field Data Checks**

Sample recovery personnel \_\_\_\_\_

Person with direct responsibility for recovered samples \_\_\_\_\_

Sample number	Sample identification number	Date of recovery	Liquid level marked	Stored in locked container
1				
2				
3				
4				
5				
6				
Blank				

Remarks \_\_\_\_\_

Signature of field sample trustee \_\_\_\_\_

**Laboratory Data Checks**

Lab person with direct responsibility for recovered samples \_\_\_\_\_

Date recovered samples received \_\_\_\_\_

Analyst \_\_\_\_\_

Sample number	Sample identification number	Date of analysis	Liquid at marked level	Sample identified
1				
2				
3				
4				
5				
6				
Blank				

Remarks \_\_\_\_\_

Signature of lab sample trustee \_\_\_\_\_

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**SULFUR DIOXIDE ANALYTICAL DATA**

Plant \_\_\_\_\_ Date \_\_\_\_\_  
 Sample location \_\_\_\_\_ Analyst \_\_\_\_\_  
 Volume and normality of barium perchlorate 1 \_\_\_\_\_ ml \_\_\_\_\_ N  
 2 \_\_\_\_\_ ml \_\_\_\_\_ N \_\_\_\_\_ N, avg  
 3 \_\_\_\_\_ ml \_\_\_\_\_ N

Sample number	Sample identification number	Total sample volume ( $V_{soln}$ ), ml	Sample aliquot volume ( $V_a$ ) <sup>a</sup> , ml	Volume of titrant ( $V_t$ ) <sup>b</sup> , ml		
				1st titration	2nd titration	Average
1						
2						
3						
4						
5						
6						
Blank		N/A				$V_{th} =$

<sup>a</sup> Volume for the blank must be the same as that of the sample aliquot.

<sup>b</sup>  $\frac{\text{1st titration}}{\text{2nd titration}} = 0.99 \text{ to } 1.01$  or  $|\text{1st titration} - \text{2nd titration}| < 0.2 \text{ ml}$ .

Signature of analyst \_\_\_\_\_

Signature of reviewer or supervisor \_\_\_\_\_

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, <sup>a</sup> ml			
		1st	2nd	3rd	Avg

<sup>a</sup> Two titrant volumes must agree within 0.2 ml.

$$ml Ba(ClO_4)_2 \times N_{Ba(ClO_4)_2} = \frac{25 ml}{(control\ sample)} \times \frac{0.01N}{(control\ sample)}$$

\_\_\_\_\_ ml × \_\_\_\_\_ N = \_\_\_\_\_

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

Does value agree?  yes  no

\_\_\_\_\_  
Signature of analyst

\_\_\_\_\_  
Signature of reviewer

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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, <sup>a</sup> mm H <sub>2</sub> O	Final volume ( $V_f$ ), ℓ	Initial volume ( $V_i$ ), ℓ	Total volume ( $V_m$ ) <sup>b</sup> , ℓ	Flask volume ( $V_s$ ), ℓ	Percent error, <sup>c</sup> %
1						
2						
3						

<sup>a</sup> Must be less than 10 mm (0.4 in.) H<sub>2</sub>O.

Calculations:

<sup>b</sup>  $V_m = V_f - V_i$ .

<sup>c</sup> % error =  $100 (V_m - V_s) / V_s =$  \_\_\_\_\_ (+1%).

\_\_\_\_\_  
Signature of calibration person

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METHOD 6 CHECKLIST TO BE USED BY AUDITORS

Presampling Preparation

Yes	No	Comment
_____	_____	_____
_____	_____	_____

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. Isokinetic sampling
6. Purging of the sampling train and rinsing of the impingers and connecting tubes to recover the sample
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. Calculation procedure/check
14. Calibration checks
15. Standardized barium perchlorate solution

General Comments

787

SULFUR DIOXIDE CALCULATION FORM  
(English units)

Sample Volume<sup>a</sup>

$$V_m = \text{---} \text{ ft}^3, T_m = \text{---} \text{ } ^\circ\text{R}, P_{\text{bar}} = \text{---} \text{ in. Hg}, Y = \text{---}$$

$$V_{m(\text{std})} = 17.64 \frac{^{\circ}\text{R}}{\text{in. Hg}} \times \frac{Y V_m P_{\text{bar}}}{T_m} = \text{---} \text{ ft}^3$$

Equation 6-1

SO<sub>2</sub> Concentration

$$N = \text{---} \text{ (g-eq)/ml}, V_t = \text{---} \text{ ml}, V_{tb} = \text{---} \text{ ml}$$

$$V_{\text{soln}} = \text{---} \text{ ml}, V_a = \text{---} \text{ ml}$$

$$C_{\text{SO}_2} = 7.06 \times 10^{-5} \frac{N (V_t - V_{tb}) (V_{\text{soln}}/V_a)}{V_{m(\text{std})}} = \text{---} \times 10^{-4} \text{ lb/dscf}$$

Equation 6-2

<sup>a</sup> Calculation form for data collected using Method 6 type equipment. The alternative use of Method 5 or Method 8 equipment will change  $V_m$  and  $V_{m(\text{std})}$  to  $V_{m(\text{std})} = \text{---} \text{ ft}^3$ .

785

SULFUR DIOXIDE CALCULATION FORM  
(metric units)

Sample Volume <sup>a</sup>

$$V_m = \text{---} \cdot \text{---} \ell \times 0.001 = \text{---} \cdot \text{---} \text{ m}^3$$

$$T_m = \text{---} \cdot \text{---} \text{ K}, P_{\text{bar}} = \text{---} \cdot \text{---} \text{ mm Hg}, Y = \text{---} \cdot \text{---}$$

$$V_{m(\text{std})} = 0.3858 \frac{K}{\text{mm Hg}} \frac{Y V_m P_{\text{bar}}}{T_m} = \text{---} \cdot \text{---} \text{ m}^3$$

Equation 6-1

SO<sub>2</sub> Concentration

$$N = \text{---} \cdot \text{---} (\text{g-eq})/\text{ml}, V_t = \text{---} \cdot \text{---} \text{ ml}, V_{tb} = \text{---} \cdot \text{---} \text{ ml}$$

$$V_{\text{soln}} = \text{---} \cdot \text{---} \text{ ml}, V_a = \text{---} \cdot \text{---} \text{ ml}$$

$$C_{\text{SO}_2} = 32.03 \frac{N (V_t - V_{tb}) (V_{\text{soln}}/V_a)}{V_{m(\text{std})}} = \text{---} \cdot \text{---} \text{ mg/dscm}$$

Equation 6-2

<sup>a</sup> Calculation form for data collected using Method 6 type equipment. The alternative use of Method 5 or Method 8 equipment will change  $V_m$  and  $V_{m(\text{std})}$  to  $V_{m(\text{std})} = \text{---} \cdot \text{---} \text{ m}^3$ .

(780)

