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**QUALITY ASSURANCE HANDBOOK
FOR
AIR POLLUTION MEASUREMENT SYSTEMS**

Volume III — Stationary Source Specific Methods

**U.S. ENVIRONMENTAL PROTECTION AGENCY
Office of Research and Development
Environmental Monitoring and Support Laboratory
Research Triangle Park, North Carolina 27711**

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VOLUME III

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PURPOSE AND OVERVIEW OF THE QUALITY ASSURANCE HANDBOOK

The purpose of this Quality Assurance Handbook for Air Pollution Measurement Systems is to provide guidelines and procedures for achieving quality assurance in air pollution measurement systems. It is intended to serve as a resource document for the design of quality assurance programs and to provide detailed method descriptions for certain measurement processes that can be used directly in implementing the quality assurance program.

This Handbook should be particularly beneficial to operators, project officers, and program managers responsible for implementing, designing, and coordinating air pollution emission source tests. The contents of each volume are briefly described in the following paragraphs.

Volume I - Principles

Volume I contains brief discussions of the elements of quality assurance. Expanded discussions of technical points and sample calculations are included in the Appendixes. The discussion of each element is structured to be brief and to highlight the most important features. Organizations developing and implementing their own quality assurance plans will find Volume I useful for general guidance.

Volume II - Ambient-Air-Specific Methods

Volume II contains quality assurance guidelines on ambient air measurement systems. Regardless of the scope and magnitude of ambient air measurement systems, there are a number of common considerations pertinent to the production of quality data. These considerations are discussed in Section 2.0 of Volume II, and include quality assurance guidelines in the areas of:

1. Sampling network design and site selection - monitoring objectives and spatial scales; representative sampling; meteorological and topographical constraints; and sampling schedules.

2. Sampling considerations - environmental controls; probe and manifold design; maintenance; and support services.

3. Data handling and reporting considerations - data recording systems, data validation, and systematic data management.

4. Reference and equivalent methods.

5. Recommended quality assurance program for ambient air measurements.

6. Chain-of-custody procedure for ambient air samples - sample collection; sample handling; analysis of the sample; field notes; and report as evidence.

7. Traceability protocol for establishing true concentrations of gases used for calibrations and audits - establishing traceability of commercial gas cylinders and of permeation tubes.

8. Calculations to assess monitoring data for precision and accuracy for SLAMS and PSD automated analyzers and manual methods.

9. Specific guidance for a quality control program for SLAMS and PSD for automated analyzers and manual methods - analyzer selection, calibration, zero and span checks; data validation and reporting; quality control program for gaseous standards and flow measurement devices.

10. EPA national performance audit program.

11. System audit criteria and procedures for ambient air monitoring programs.

12. Audit procedures for use by State and local air monitoring agencies.

The remainder of Volume II contains method and/or principle description and quality assurance guidelines for specific pollutants. Each pollutant-specific section contains the following information.

1. Procedures for procurement of equipment and supplies.
2. Calibration procedures.
3. Step-by-step descriptions of sampling, reagent preparation, and analysis procedures, as appropriate, depending upon the method or principle in the case of equivalencies.
4. Method of calculation and data processing checks.
5. Maintenance procedures.
6. Recommended auditing procedures to be performed during the sampling, analysis, and data processing.
7. Recommended procedure for routine assessment of accuracy and precision.
8. Recommended standards for establishing traceability.
9. Pertinent references.
10. Blank data forms for the convenience of the Handbook user (data forms are partially filled in within the text for illustration purposes).

Matrix tables at the ends of appropriate sections summarize the quality assurance functions therein. Each matrix includes the activities, the acceptance limits, method and frequency of the each quality assurance check, and the recommended action if the acceptance limits are not satisfied.

Volume II contains quality assurance guidelines for pollutant-specific measurement systems. The measurement systems planned for Volume II include:

1. Reference Method for the Determination of Sulfur Dioxide in the Atmosphere (Pararosaniline Method).
2. Reference Method for the Determination of Suspended Particulates in the Atmosphere (Hi-Vol Method).
3. Reference Method for the Determination of Nitrogen Dioxide in the Atmosphere (Chemiluminescence).
4. Equivalent Method for the Determination of Nitrogen Dioxide in the Atmosphere (Sodium Arsenite).
5. Equivalent Method for the Determination of Sulfur Dioxide in the Atmosphere (Flame Photometric Detector).

6. Reference Method for the Determination of Carbon Monoxide in the Atmosphere (Nondispersive Infrared Spectrometry).

7. Reference Method for the Determination of Ozone in the Atmosphere (Chemiluminescence).

8. Reference Method for the Determination of Lead in Suspended Particulate Matter Collected from Ambient Air (Atomic Absorption Spectrometry).

9. Method for the Determination of Sulfates in the Atmosphere (Methythymol Blue Automated Analysis).

As methods are added to Volume II, these will be sent to Handbook users through the document control system, as described in Section 1.4.1 of Volume I of this Handbook.

Volume III - Stationary-Source-Specific Methods

Volume III contains quality assurance guidelines on stationary-source-specific methods. The format for Volume III is patterned after that of Volume II.

Regardless of the scope and purpose of the emissions-testing plan, there are a number of general considerations pertinent to the production of quality data. These considerations are discussed in Section 3.0 of Volume III and include quality assurance guidelines in the areas of:

1. Planning the test program - preliminary plant survey; process information; stack data; location of sampling points; cyclonic gas flow.

2. General factors involved in stationary source testing -tools and equipment; standard data forms; and identification of samples.

3. Chain-of-custody procedures for source sampling - sample collection; sample analysis; field notes; and report as evidence.

4. Traceability protocol for establishing true concentrations of gases used for calibrations and audits of air pollution analyzers - establishing traceability of commercial gas cylinders.

The remainder of Volume III contains quality assurance guidelines for specific measurement methods. The measurement systems planned for Volume III include:

- Method 2 - Determination of Stack Gas Velocity and Volumetric Flow Rate (Type-S Pitot Tube).
- Method 3 - Gas Analysis for Carbon Dioxide, Oxygen, Excess Air, and Dry Molecular Weight.
- Method 4 - Determination of Moisture in Stack Gases.
- Method 5 - Determination of Particulate Emissions from Stationary Sources.
- Method 6 - Determination of Sulfur Dioxide Emissions from Stationary Sources.
- Method 7 - Determination of Nitrogen Oxide Emissions from Stationary Sources.
- Method 8 - Determination of Sulfuric Acid Mist and Sulfur Dioxide from Stationary Sources.
- Method 10 - Determination of Carbon Monoxide Emissions from Stationary Sources.
- Methods 13A - Determination of Fluoride Emissions from Stationary Sources (SPADNS and Specific Ion Electrode).
- Method 17 - Determination of Particulate Emissions from Stationary Sources (In-Stack Filtration Method).

As methods are added to Volume III, these will be sent to the users through the document control system used for the Handbook.

Section 3.1

METHOD 2 - DETERMINATION OF STACK GAS VELOCITY
AND VOLUMETRIC FLOW RATE

OUTLINE

<u>Section</u>	<u>Documentation</u>	<u>Number of Pages</u>
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METHOD HIGHLIGHTS	3.1	7
METHOD DESCRIPTION		
1. PROCUREMENT OF APPARATUS AND SUPPLIES	3.1.1	15
2. CALIBRATION OF APPARATUS	3.1.2	21
3. PRESAMPLING OPERATIONS	3.1.3	7
4. ON-SITE MEASUREMENTS	3.1.4	12
5. POSTSAMPLING OPERATIONS	3.1.5	3
6. CALCULATIONS	3.1.6	4
7. MAINTENANCE	3.1.7	1
8. AUDITING PROCEDURE	3.1.8	5
9. RECOMMENDED STANDARDS FOR ESTABLISHING TRACE- ABILITY	3.1.9	1
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11. REFERENCES	3.1.11	2
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SUMMARY

Method 2 outlines a procedure for determining stack gas velocity and volumetric flow rate from stationary sources. A Type S (stauscheibe or reverse) pitot tube or a standard pitot tube meeting the criteria in Section 3.1.1, calibrated according to the procedures outlined in Section 3.1.2, and operated in accordance with Section 3.1.4 is used to measure velocity pressure (Δp); this pressure measurement, along with gas density, is used to determine the stack gas velocity.

If the minimum criteria of Method 1 are not met or if the measurement site has a swirling or cyclonic gas stream, the procedures outlined in Method 2 for stack gas velocity and volumetric flow rate determination are not applicable. When unacceptable flow conditions exist, alternative procedures such as the use of flow-straightening devices or stack extensions must be employed as necessary to make accurate flow rate determinations. These alternative procedures are subject to approval by the administrator.

The Method Description which follows is based on the Reference Method published August 18, 1977. A complete copy of the Reference Method is contained in Section 3.1.10. Data forms are provided in Section 3.1.12 for the convenience of the Handbook user. Reference 1 was used extensively in preparing the Method Description and the data forms. References 2, 3, 4, and 5 summarize collaborative tests conducted to determine the usefulness and accuracy of this method.

METHOD HIGHLIGHTS

Section 3.1 describes specifications for determination of stack gas velocity and volumetric flow rate from stationary sources. The sampling apparatus consists of a pitot tube and a differential pressure gauge. Stack gas velocity and volumetric flow rate can be determined in conjunction with other EPA Reference Methods (i.e., Method 5) if the sampling components are mounted in an interference-free manner.

The results of collaborative tests have shown that the precision of this test method is adequate for use with other test methods in determining pollutant emission rates; collaborative tests also showed that the method is not subject to large biases from one user to another.^{2,5}

The blank data forms at the end of the highlights section may be removed from the Handbook and used in the pretest, test, and posttest operations. Each form has a subtitle (e.g., Method 2, Figure 2.4) to assist the user in finding a similar filled-in form in the Method Description (e.g., in Section 3.1.2). On the blank and filled-in forms, the items/parameters that can cause the most significant errors are indicated with an asterisk.

1. Procurement of Equipment

Section 3.1.1 (Procurement of Apparatus and Supplies) gives the specifications, criteria, and design features for equipment and materials required for performing Method 2 tests. The sampling apparatus can be used in conjunction with sampling equipment required for other methods such as Methods 5 and 8 presented in this Handbook. This section is designed as a guide in the procurement and initial check of equipment and supplies. The activity matrix (Table 1.1) at the end of Section 3.1.1 can be used as a quick reference; it follows the same order as the written description in the main text.

2. Pretest Preparations

Section 3.1.2 (Calibration of Apparatus) provides a step-by-step description of the required calibration procedures. Detailed methods and equipment are described for calibrating pitot tubes in the laboratory and in the field. The calibration section can be removed and compiled, along with calibration sections from all other methods, into a separate quality assurance reference manual for use by calibration personnel. A pretest checklist (Figure 3.1) or similar form should be used to summarize the calibration data.

Section 3.1.3 (Presampling Operations) provides the tester with a guide for supplies and equipment preparation for field tests. The pretest preparation form (Figure 3.2) can be used as an equipment checkout and packing list. The method for packing and the description of packing containers should help to protect the equipment, but are not required.

3. On-Site Measurements

Section 3.1.4 (On-Site Measurements) contains a step-by-step procedure for performing velocity measurements. Precautions must be taken to ensure that the pitot tube is aligned with the stack gas flow. Also a check for cyclonic flow must be made. The on-site measurement checklist (Figure 4.2) is provided to assist the tester with a quick method of checking requirements.

4. Posttest Operations

Section 3.1.5 (Postsampling Operations) gives the posttest equipment check procedures. Figure 5.1 or a similar form should be used to summarize the posttest calibration checks, and should be included in the emission test report.

Section 3.1.6 (Calculations) provides the tester with the required equations, nomenclature, and the suggested number of significant digits. It is suggested that a programmed calculator be used if available to reduce the chance of calculation error.

Section 3.1.7 (Maintenance) provides the tester with a guide for a routine maintenance program. This program is not required, but should reduce equipment malfunctions.

5. Auditing Procedure

Section 3.1.8 (Auditing Procedure) provides a description of necessary activities for conducting performance and system audits. The performance audits of the data processing and a systems audit of the on-site measurements should provide the independent assessment of the quality of data needed.

Section 3.1.9 (Recommended Standards for Establishing Traceability) recommends the primary standards to which the working standards should be traceable.

6. References

Sections 3.1.10 and 3.1.11 contain the Reference Method and the suggested references.

PRETEST SAMPLING CHECKS
(Method 2, Figure 3.1)

Date _____ Completed by _____

Pitot Tube

Identification number _____ Date _____

Dimension specifications checked?* _____ yes _____ no

Calibration required? _____ yes _____ no

Date _____ C_p _____

Temperature Sensor

Identification number _____

Calibrated?* _____ yes _____ no

Was a pretest temperature correction used? _____ yes _____ no
If yes, temperature correction _____ °C (°F)

Barometer

Was the pretest field barometer reading correct?* _____ yes _____ no

Differential Pressure Gauge

Was pretest calibration acceptable?* _____ yes _____ no

*Most significant items/parameters to be checked.

PRETEST PREPARATIONS
(Method 2, Figure 3.2)

Apparatus check	Acceptable		Quantity required	Ready		Loaded and packed
	Yes	No		Yes	No	
<u>Pitot Tube</u>						
Type S						
Standard						
Length _____ m(ft)						
Calibrated* _____						
<u>Differential Pressure Gauge</u>						
Inclined manom- eter sensitivity _____ cm (in.)						
Other _____						
<u>Stack Temperature Sensor</u>						
Type _____						
Calibrated* _____						
<u>Orsat Analyzer</u>						
Orsat _____						
Fyrite _____						
Other _____						

*Most significant items/parameters to be checked.

ON-SITE MEASUREMENTS CHECKLIST
(Method 2, Figure 4.2)

Sampling

Pitot tube, lines, and manometer assembled correctly?* _____

Pitot tube and components mounted in an interference free manner?* _____

Differential pressure gauge has correct sensitivity?* _____

Differential pressure gauge leveled and zeroed?* _____

Pretest leak check? ____ (optional) Cyclonic flow checked?* ____

Pitot tube parallel to gas flow?* _____

Static pressure measured? _____ Temperature measured? _____

Moisture content determined? _____ Method _____

Orsat samples taken? _____ If no, explain: _____

Posttest leak check performed?* _____ (mandatory)

Data recorded properly? _____

*Most significant items/parameters to be checked.

POSTTEST SAMPLING CHECKS
(Method 2, Figure 5.1)

Pitot Tube

Initial pitot tube coefficient _____
Was pitot tube damaged prior to start of any test runs? ____ yes
____ no
If yes, was pitot tube calibrated prior to repair?* ____ yes ____ no
Pitot tube coefficient (damaged) _____ (this value must
be used for runs started with the damaged pitot tube)

Temperature Sensor

Was a pretest temperature correction used? ____ yes ____ no
If yes, temperature correction _____ °C (°F) (within 1.5%
of readings in K (°R) over range)
Average stack temperature of compliance test (T_s) _____ K (°R)
Temperature of reference thermometer or solution for recalibra-
tion* _____ K (°R)
Temperature of stack thermometer for recalibration _____ K (°R)
Difference between reference and stack thermometer temperatures
(ΔT_s) _____ K (°R)
Do values agree within ±1.5%?* ____ yes ____ no
If yes, no correction necessary for calculations
If no, calculations must be done twice, once with recorded,
values and once with average stack temperature corrected to
correspond to reference temperature differential (ΔT_s). Both
values of final results must then be reported since there is no
way to determine which is correct

Barometer

Was pretest field barometer reading correct? ____ yes ____ no
Posttest comparison _____ mm (in.) Hg (within ±5.0 mm (0.2 in.)
Hg of mercury-in-glass barometer)
Was recalibration required? ____ yes ____ no
If yes, no correction needed when field barometer has the lower
reading
If mercury-in-glass reading is lower, subtract the difference
from the field data readings for the calculations

*Most significant items/parameters to be checked.

1.0 PROCUREMENT OF APPARATUS AND SUPPLIES

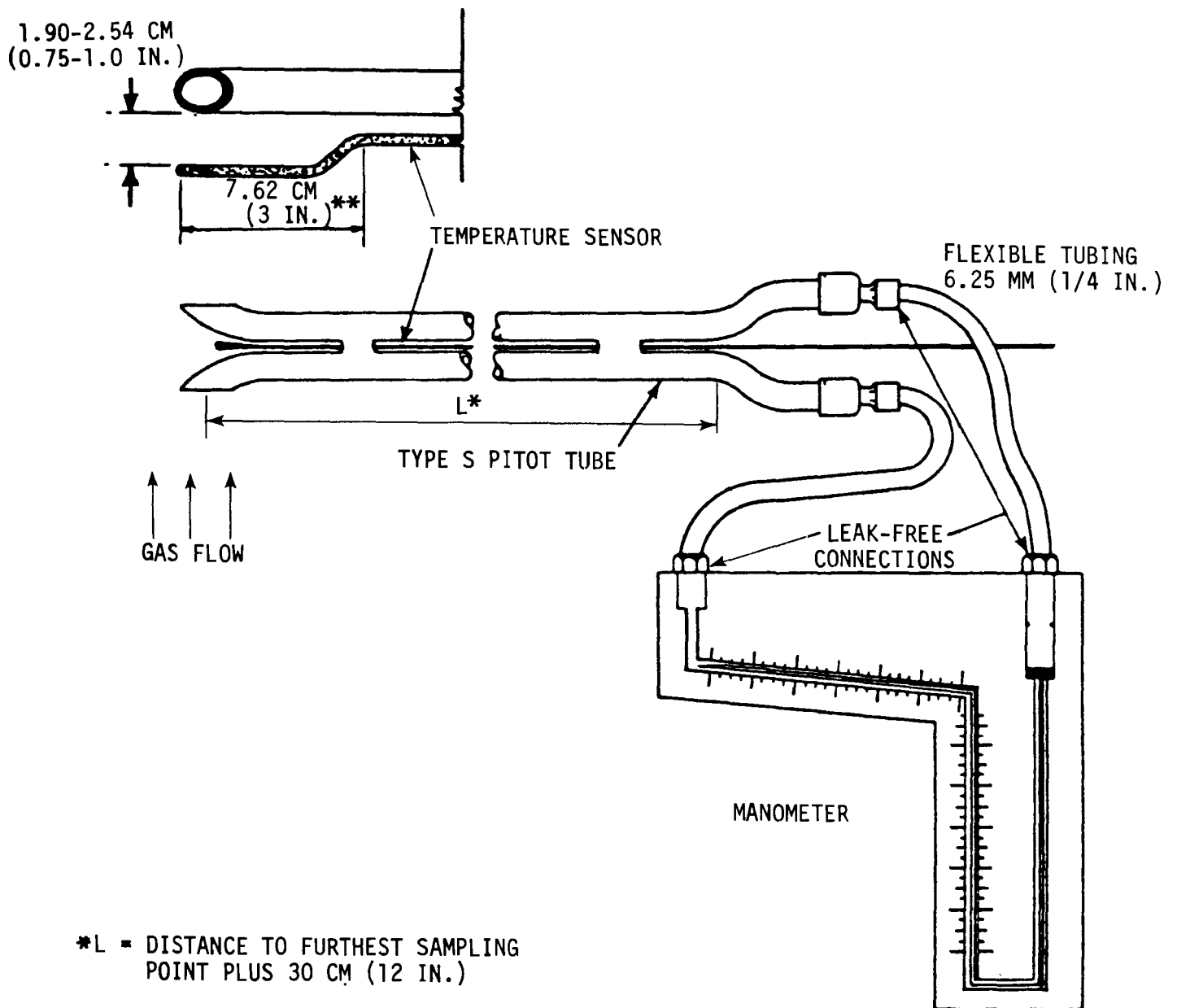
Figure 1.1 shows a diagram of the Type S pitot tube-manometer assembly used in this method. Specifications, criteria and/or applicable design features are given in this section to aid in the selection of equipment which will produce accurate data. Selection procedures and applicable limits for acceptance checks are also included. During procurement of equipment and supplies, it is suggested that a procurement log (Figure 1.2) be used to record the descriptive title of equipment; the identification number, if applicable; and the results of the acceptance check. Also, if calibration is required as part of the acceptance check, the data are to be recorded in the calibration log book. Table 1.1 at the end of this section contains a summary of quality assurance activities for procurement and acceptance of apparatus and supplies.

1.1 Pitot Tube

A Type S pitot tube shown in Figure 1.1 is required. The pitot tube should be constructed of metal tubing (e.g., 304 or 316 stainless steel) with an external tubing diameter (D_t) between 0.48 and 0.95 cm (3/16 and 3/8 in.). The major criteria in pitot tube construction material are durability and corrosion resistance. Upon receiving a new pitot tube, inspect it to determine if it was constructed according to the configuration in Figure 1.3. Repair, replace, or return to the manufacturer any Type S pitot tube which does not meet the face opening specifications outlined in Figure 1.4. One method of inspecting the construction details is as follows:

1. Obtain a section of angle aluminum approximately 20 cm (8 in.) long by 1.3 × 2.5 cm (0.5 × 1.0 in.). Mount a bull's eye level (with $\pm 1^\circ$ accuracy) to the angle aluminum, as shown in Figure 1.5.

2. Place the pitot tube in the angle aluminum as shown in Figure 1.5, and level the pitot tube as indicated by the bull's



*L = DISTANCE TO FURTHEST SAMPLING
POINT PLUS 30 CM (12 IN.)

**PITOT TUBE - TEMPERATURE SENSOR SPACING

Figure 1.1 Type S pitot tube-manometer assembly.

Item description	Quantity	Purchase order number	Vendor	Date		Cost	Disposition	Comments
				Ordered	Received			
Pitot tube	1	76-1308	Ace Metal	9-6-79	9-29-79	86.00	In Service	

Figure 1.2 Example of a procurement log.

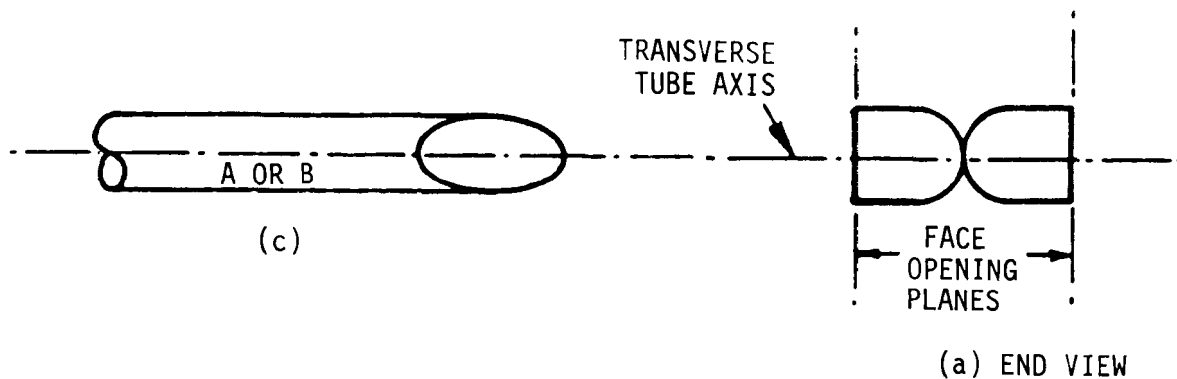
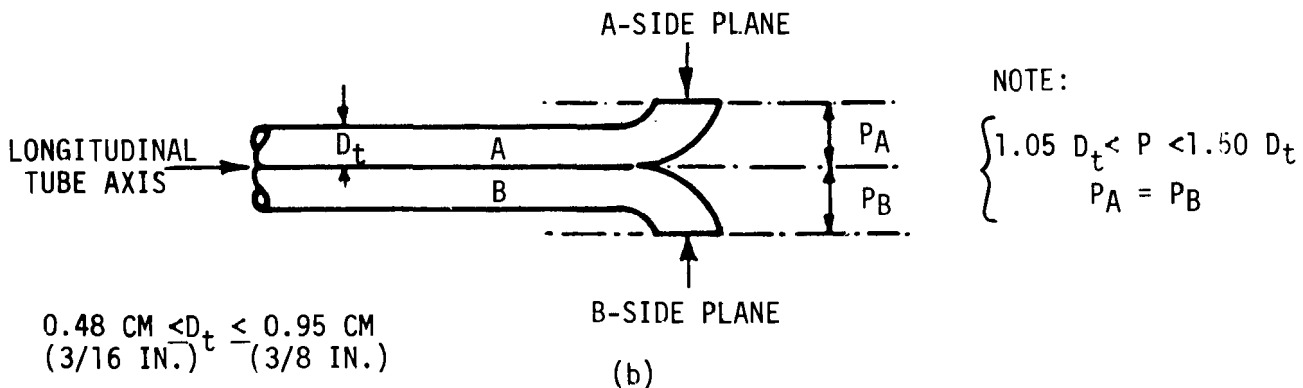


Figure 1.3. Properly constructed Type S pitot tube, shown in: (a) end view; face opening planes perpendicular to transverse axis; (b) top view; face opening planes parallel to longitudinal axis; (c) side view; both legs of equal length and centerlines coincident, when viewed from both sides. Baseline coefficient values of 0.84 may be assigned to pitot tubes constructed this way.

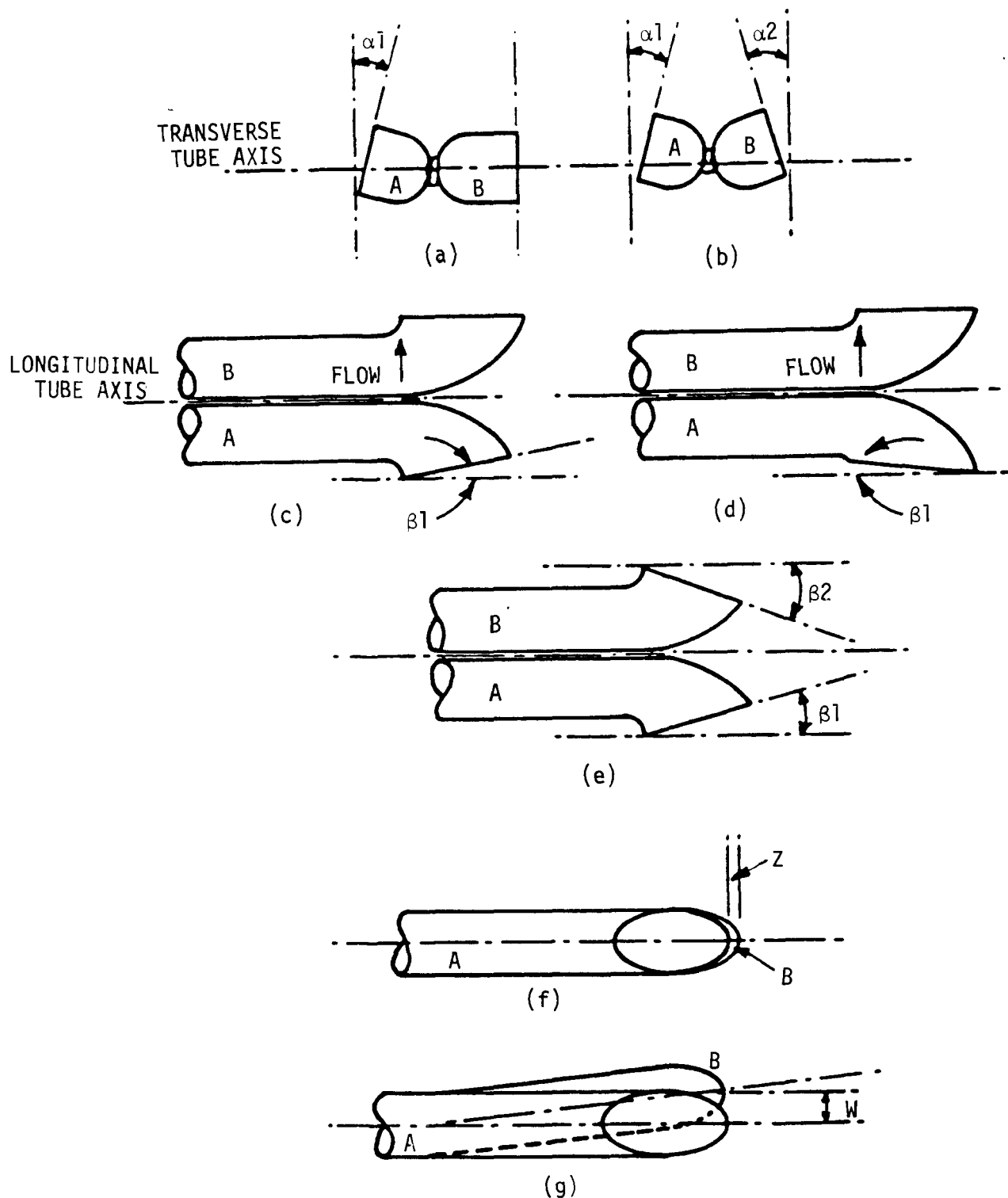


Figure 1.4. Types of face-opening misalignment that can result from field use or improper construction of Type S pitot tubes. These will not affect C_p so long as α_1 and $\alpha_2 < 10^\circ$, $\beta_2 < 5^\circ$, $z < 0.32$ cm (1/8 in.) and $w < 0.08$ cm (1/32 in.).

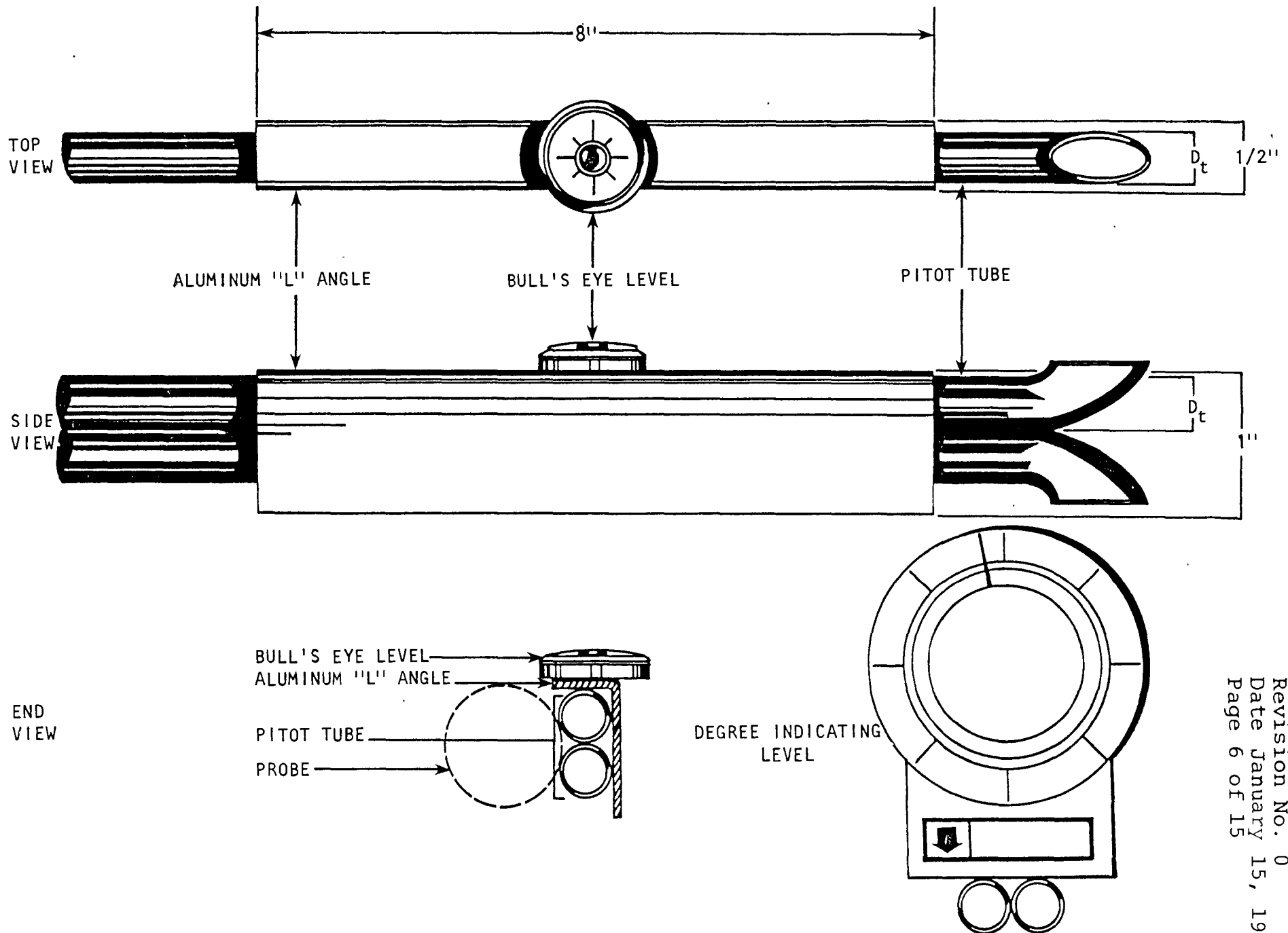


Figure 1.5 Type S pitot tube dimension specialization measurements.

eye level. A vise may be used to hold the angle aluminum and pitot tube. Note: A permanently mounted pitot tube and probe assembly may require a shorter section of angle aluminum to allow proper mounting on the assembly.

3. Place a degree indicating level in the various positions, as illustrated in Figure 1.6.

4. Measure distances P_a and P_b .

5. Measure the external tube diameter (D_t) with a micrometer. Record all data on a data form such as Figure 1.7.

6. Calculate dimensions w and z using the following equations:

$$z = A \sin \gamma \quad \text{Equation 2-1}$$

$$w = A \sin \theta \quad \text{Equation 2-2}$$

where,

z = alignment dimension, cm (in.)

w = alignment dimension, cm (in.)

A = distance between tips, ($P_a + P_b$), cm (in.)

γ = angle in degrees

θ = angle in degrees.

Note: Pitot tubes with bent or damaged tubing may be difficult to check using this procedure. If the Type S pitot tube meets the face alignment criteria, an identification number should be assigned and permanently marked or engraved on the body of the tube.

A standard pitot tube (Figure 1.8) may be used instead of a Type S for conducting velocity traverses. Upon receiving a new standard pitot tube, inspect it to determine if it meets the following design criteria:

1. The tip is of the hemispherical (shown in Figure 1.8), ellipsoidal, or conical design.

2. There is a minimum of six diameters straight run (based upon D_1 , the external diameter of the tube) between the tip and static pressure holes.

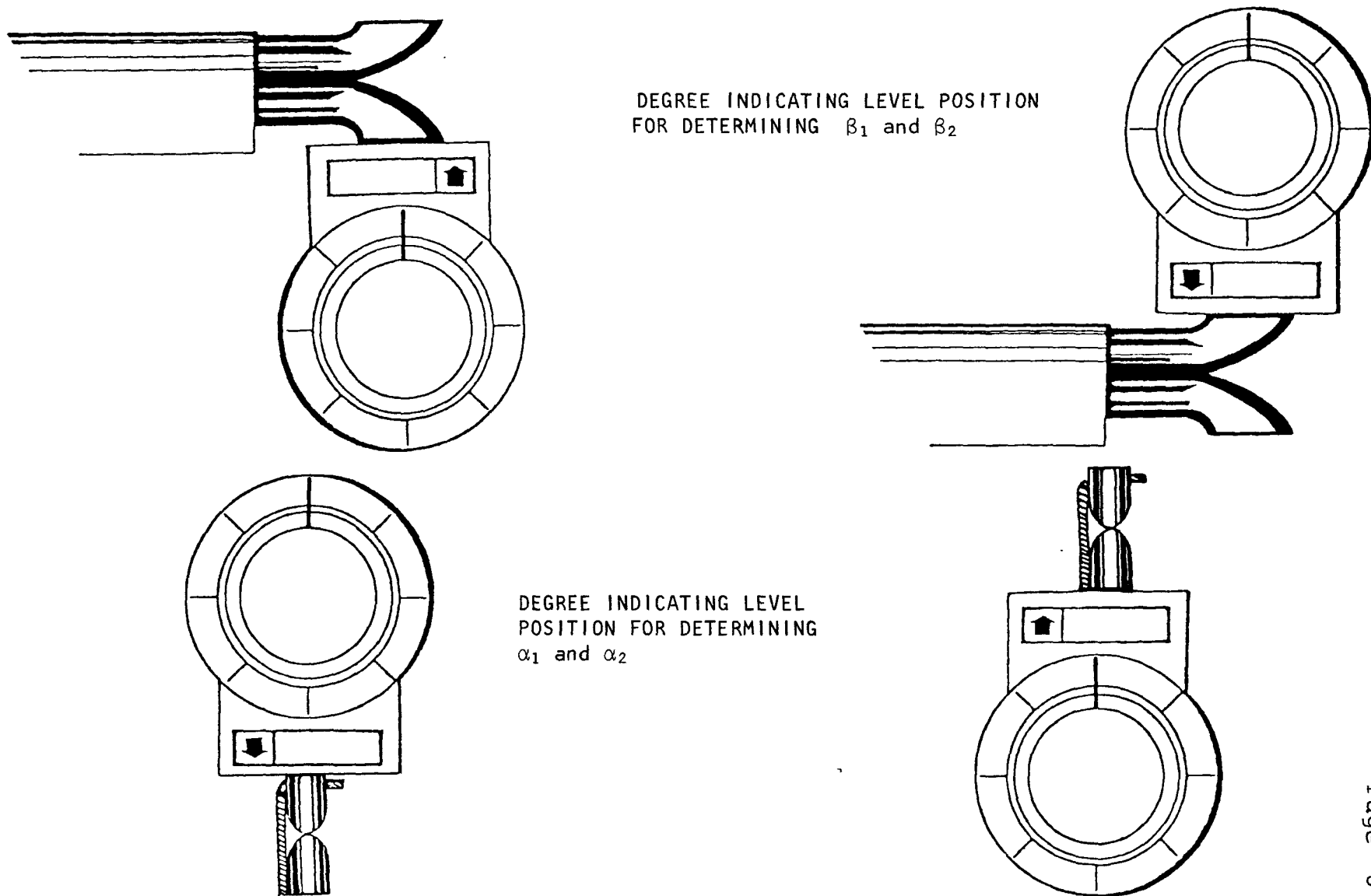
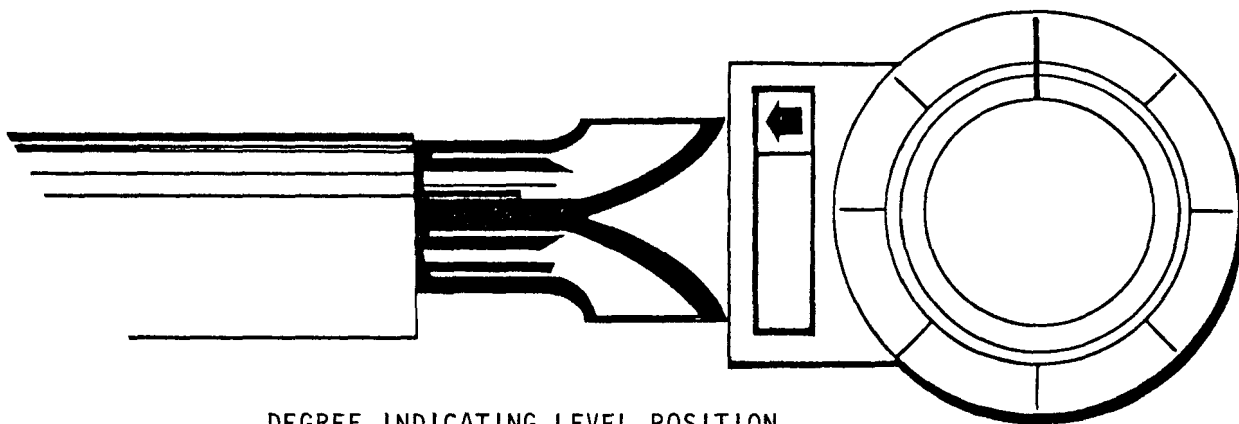
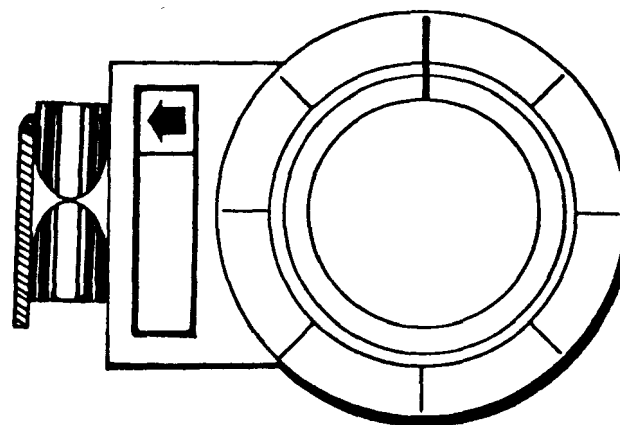


Figure 1.6 Position of dimension measurement.
(continued)



DEGREE INDICATING LEVEL POSITION
FOR DETERMINING γ , THEN CALCULATING Z



DEGREE INDICATING LEVEL POSITION
FOR DETERMINING θ , THEN CALCULATING W

Figure 1.6 (continued)

Pitot tube assembly level? ✓ yes _____ no

Pitot tube openings damaged? _____ yes (explain below) ✓ no

$\alpha_1 = \underline{2.5}^\circ (<10^\circ)$, $\alpha_2 = \underline{0.8}^\circ (<10^\circ)$, $\beta_1 = \underline{0.0}^\circ (<5^\circ)$,
 $\beta_2 = \underline{4.5}^\circ (<5^\circ)$

$\gamma = \underline{3.3}^\circ$, $\theta = \underline{1.5}^\circ$, $A = \underline{(0.921)}$ cm (in.)

$z = A \sin \gamma = \underline{(0.053)}$ cm (in.); <0.32 cm ($<1/8$ in.),

$w = A \sin \theta = \underline{(0.024)}$ cm (in.); <0.08 cm ($<1/32$ in.)

$P_A \underline{(0.461)}$ cm (in.) $P_b \underline{(0.460)}$ cm (in.)

$D_t = \underline{(0.289)}$ cm (in.)

Comments: _____

Calibration required? _____ yes ✓ no

Figure 1.7 Type S pitot tube inspection data form.

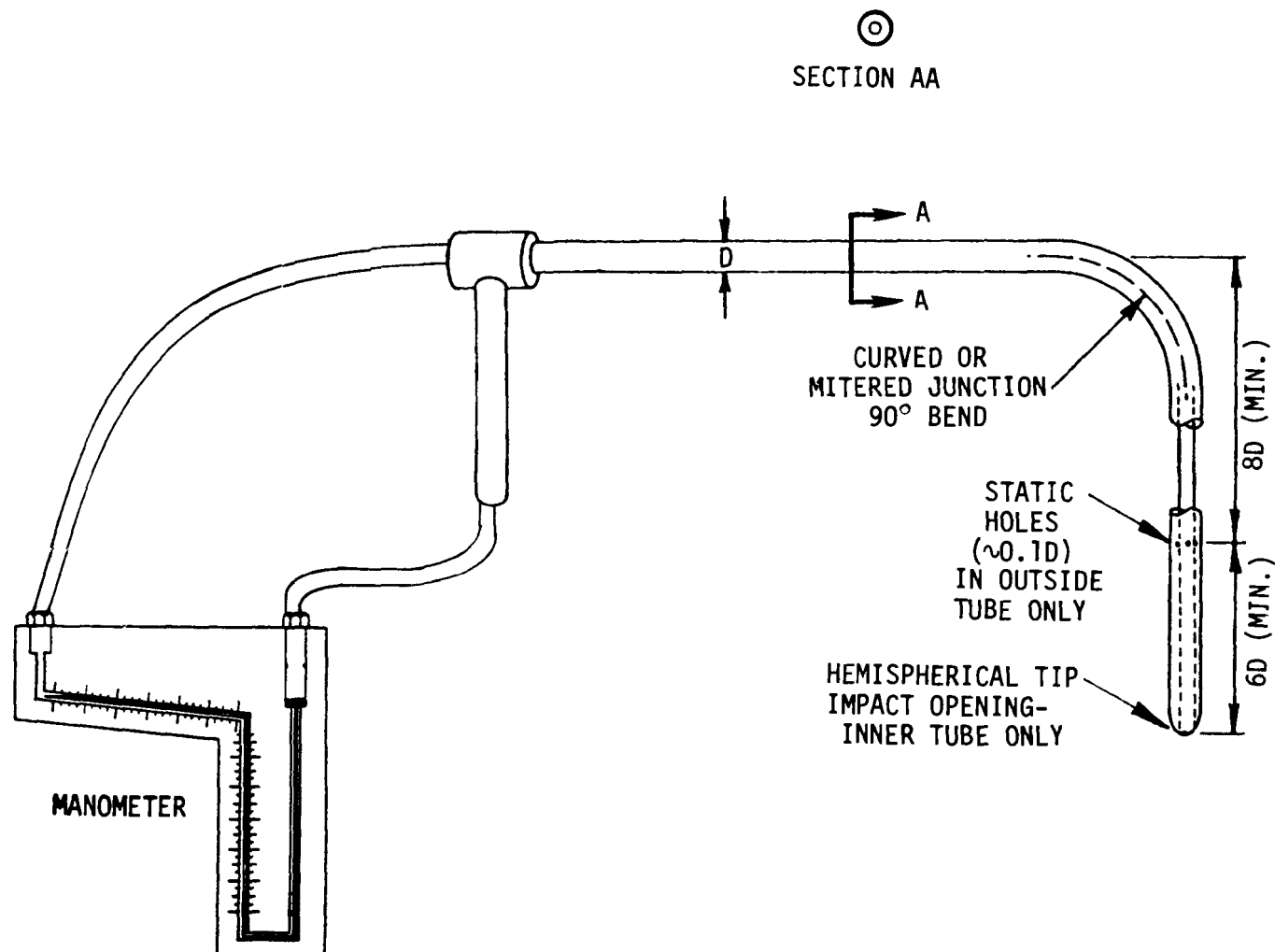


Figure 1.8 Standard pitot tube design specifications.

3. There is a minimum of eight diameters straight run between the static pressure holes and the centerline of the external tube, following the 90° bend.

4. The static pressure holes are of equal size (approximately 0.1 D), equally spaced in a piezometer ring configuration.

5. It has a 90° bend, with curved or mitered junction. Repair, replace or return to the manufacturer any standard pitot tube which does not meet the above criteria.

1.2 Differential Pressure Gauge

A liquid-filled inclined manometer or an equivalent device should be used to measure the velocity head. Most preassembled sampling trains are equipped with a 10-in. (water column) inclined-vertical manometer that has 0.01-in. divisions on the 0-to-1-in. inclined scale and 0.1-in. divisions on the 1-to-10-in. vertical scale. This type manometer (or other gauge of equivalent sensitivity) is satisfactory for measurements of Δp values as low as 1.3 mm (0.05 in.) H_2O . However, a gauge of greater sensitivity (e.g., with 6.4 mm (0.25 in.) H_2O full scale) is required for stacks with velocity pressures below 1.3 mm (0.05 in.) H_2O .

Upon receipt of a new manometer, leak check it using the following procedure:

1. Level and zero the manometer.
2. Vent both sides of the manometer to the atmosphere.
3. Place tygon tubing, or equivalent on the positive leg of the manometer, and blow into the tubing to displace the liquid to at least 30% of scale.
4. Close off the open end of the tubing, and observe the manometer for 15 s. If there is no change in the reading, the positive side of the manometer is leak free.
5. Repeat steps 3 and 4 for the negative side of the manometer, but use suction to produce the manometer reading.

Repair, replace, or return to the manufacturer any manometer which does not pass the leak check.

If differential pressure gauges other than inclined manometers are used (e.g., magnehelic or electronic gauges), calibrate the gauges upon receipt using the procedure in Section 3.1.2.

1.3 Temperature Gauge

A thermocouple, liquid-filled bulb thermometer, or other means capable of measuring temperature to within 1.5% of the minimum absolute stack temperature is required. Upon receipt, check the temperature gauge for damage, and then calibrate it according to the procedure in Section 3.1.2.

1.4 Pressure Probe and Gauge

Leak-free tubing and a mercury-or water-filled U-tube manometer capable of measuring stack pressure to within 2.5 mm (0.1 in.) Hg is required. The static tap of a standard type pitot tube or one leg of a Type S pitot tube with the face openings positioned parallel to the gas flow may also be used as the pressure probe. The differential pressure gauge used for velocity measurements can be used to measure static pressure.

Upon receipt of a U-tube manometer, leak check according to the procedure in Subsection 1.1.2.

1.5 Barometer

A mercury, aneroid, or other barometer capable of measuring atmospheric pressure to within 2.5 mm (0.1 in.) Hg is required. Upon receipt of a new barometer, check it against a mercury-in-glass barometer or the equivalent. If the barometer cannot be adjusted to agree within 2.5 mm (0.1 in.) Hg of the reference barometric pressure, it should be returned to the manufacturer.

1.6 Gas Analyzer

To analyze gas composition for determining dry molecular weight of the gases from combustion or other unknown streams, use Method 3. For processes emitting essentially air, use a dry molecular weight of 29.0. Use Method 4 or Method 5 for moisture content determinations.

1.7 Calibration Pitot Tube

Standard type, to calibrate the Type S pitot tube. The standard type pitot tube should have a known coefficient obtained from the National Bureau of Standards (NBS), Route 70 S, Quince Orchard Road, Gaithersburg, Maryland, or the standard pitot tube must be calibrated against another standard pitot tube with an NBS-traceable coefficient. Alternatively, a standard pitot tube designed according to the criteria given in Subsection 1.1.1 and illustrated in Figure 1.8 may be used. Be sure to inspect the standard type pitot tube for any damage upon receipt.

1.8 Differential Pressure Gauge

An inclined manometer or equivalent is used for Type S pitot tube calibration. This should be an easily readable, sensitive gauge for laboratory use. If the single-velocity calibration technique is used (Section 3.1.2), the calibration differential pressure gauge should be readable to the nearest 0.13 mm (0.005 in.) H_2O . For multivelocity calibrations, the gauge shall be readable to the nearest 0.13 mm (0.005 in.) H_2O for Δp values between 1.3 and 25 mm (0.05 and 1.0 in.) H_2O , and to the nearest 1.3 mm (0.05 in.) H_2O for Δp values above 25 mm (1.0 in.) H_2O . A special, more sensitive gauge will be required to read Δp values below 1.3 mm (0.05 in.) H_2O . Visually check and leak check the calibration differential pressure gauge upon receipt.

Table 1.1 ACTIVITY MATRIX FOR PROCUREMENT OF APPARATUS

Apparatus	Acceptance limits	Frequency and method of measurement	Action if requirements are not met
All apparatus	No visible damage	Visual check when purchased	Return to supplier immediately
Pitot tube (Type S or equivalent)	See Figs 1.3 and 1.4 for acceptance limits	Measure dimensions and alignment; identify upon receipt	Do not use if alignment is not within limits; repair or replace
Differential pressure gauge	No leaks	When purchased, visually inspect and leak check	Adjust or return to supplier
Temperature gauge	Capable of measuring temperature within 1.5% of minimum absolute stack temperature	Calibrate according to Section 3.1.2	Return to supplier or repair
Pressure probe and gauge	Capable of measuring stack pressure within 2.5 mm Hg (0.1 in.) Hg; no leaks	Visual inspection and leak check	Adjust to correct for error, or return to supplier
Calibration pitot tube	Meet design specifications with known coefficient from NBS, or see Sec 1.1	Visual check	Return to supplier
Calibration differential pressure gauge	No leaks; single point-capable of measuring Δp to within 0.13 mm (0.005 in.) H_2O ; multi-point readable within 0.13 mm (0.005 in.) H_2O for Δp values between 1.3 and 25 mm (0.05 and 1.0 in.) and to nearest 1.3 mm (0.05 in.) H_2O for Δp values >25 mm (110 in.); special sensitivity for values <1.3 mm (0.05 in.) H_2O	Visual check and leak check	Repair or replace

2.0 CALIBRATION OF APPARATUS

Calibration of apparatus is one of the most important functions in maintaining data quality. The detailed calibration procedures in this section are designed for the equipment specified by Method 2 and described in the previous section. A laboratory log book of all calibrations must be maintained. Table 2.1 at the end of this section summarizes the quality assurance activities for calibration.

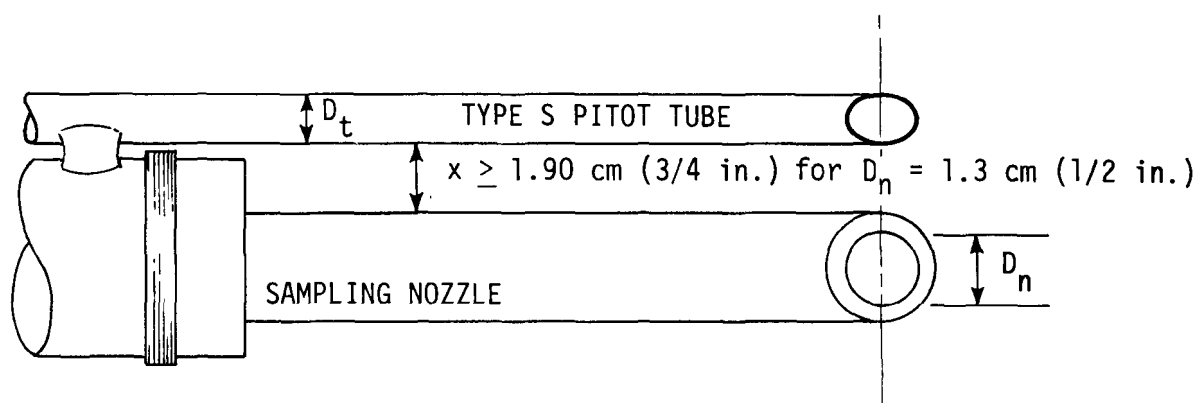
2.1 Type S Pitot Tube

A pitot tube that meets the face opening specifications in Section 3.1.1 (Figures 1.3 and 1.4) and that has the following dimensions--external tubing diameter (D_t) between 0.48 and 0.95 cm (3/16 and 3/8 in.) and P_A and P_B equal and between 1.05 and 1.50 D_t --either may be assigned a baseline (isolated tube) coefficient value of 0.84 or may be calibrated. Note, however, that if the pitot tube is mounted on a probe thermocouple assembly and if the components of the assembly do not meet the interference free criteria in (Subsection 2.1.1), calibration will be required despite knowledge of the baseline coefficient value.

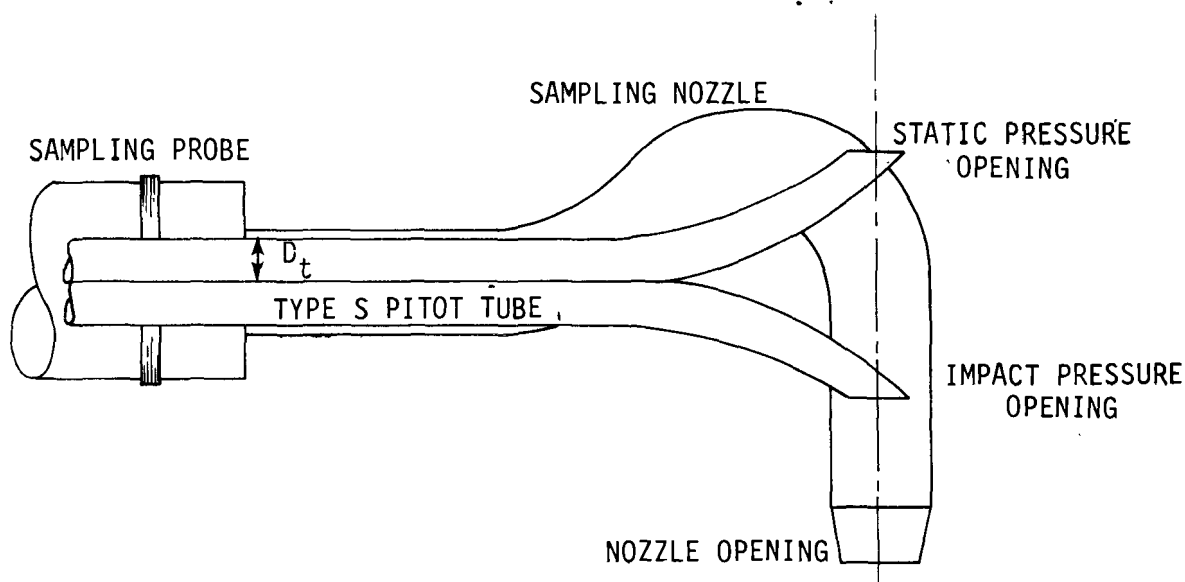
If D_t , P_A , and P_B are outside the specified limits, the pitot tube must be calibrated as outlined in Subsection 2.1.2.

2.1.1 Pitot Tube Assemblies - Interference-free assemblies--that is, pitot tubes mounted with a temperature sensor, probe, and nozzle--are shown in Figures 2.1 and 2.2. When the pitot tube meets the previously described dimensions and specifications and is mounted according to the specifications in Figures 2.1 and 2.2, no calibration is required and the baseline (isolated tube) coefficient of 0.84 may be used. Dimensions of the pitot tube - probe sampling assembly must be carefully measured with an internal caliper or a steel machinist's rule.

Note: Only pitot tubes constructed of 0.48 to 0.95 cm (3/16 to 3/8 in.) tubing can be used in interference-free assemblies. All other assemblies must be calibrated.



(a) BOTTOM VIEW: SHOWING MINIMUM PITOT-NOZZLE SEPARATION.



(b) SIDE VIEW: TO PREVENT PITOT TUBE FROM INTERFERING WITH GAS FLOW STREAMLINES APPROACHING THE NOZZLE, THE IMPACT PRESSURE OPENING PLANE OF THE PITOT TUBE SHALL BE EVEN WITH OR DOWNSTREAM FROM THE NOZZLE ENTRY PLANE

Figure 2.1 Required pitot tube-sampling nozzle configuration to prevent aerodynamic interference; buttonhook-type nozzle; centers of nozzle and pitot opening aligned; in respect to flow direction, D_t between 0.48 and 0.95 cm (3/16 and 3/8 in.).

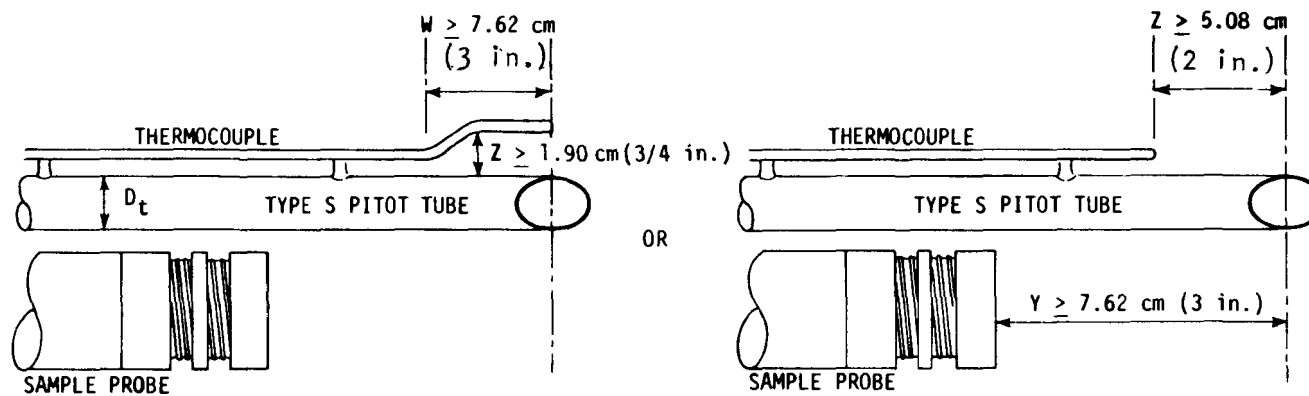


Figure 2.2 Required thermocouple and probe placement to prevent interference: D_t between 0.48 and 0.95 cm (3/16 and 3/8 in.).

2.1.2 Calibration Setup - A test setup for calibrating the pitot tube can be constructed in the laboratory from a straight section of duct that is 10 to 12 duct diameters long, as shown in Figure 2.3. The diameter of a circular duct must be at least 30.5 cm (12 in.), and the width (shorter side) of a rectangular duct of the same area must be at least 25.4 cm (10 in.). For a rectangular cross section, an equivalent circular diameter calculated from the following equation should be used to determine the required minimum length.

$$D_e = \frac{2 L W}{(L + W)} \quad \text{Equation 2-1}$$

where

D_e = equivalent diameter,

L = length of one side of duct, and

W = width of other side of duct

To ensure stable, fully developed flow patterns at the calibration site or at the "test section," this site must be located at least eight diameters downstream and two diameters upstream from any flow disturbance such as a bend, change in cross section, fan, or opening.

The eight- and two-diameter criteria are not absolute, and other test section locations may be used (subject to approval of the administrator), provided that the flow at the test site is stable and parallel to the duct axis. This may be achieved by using flow straighteners.

The flow system should generate a test section velocity of about 915 m/min (3000 ft/min); this velocity must be constant with time to guarantee steady flow during calibration. Type S pitot tube coefficients obtained by single-velocity calibration at 915 m/min (3000 ft/min) will generally be valid to within $\pm 3\%$ for the measurement of velocities above 305 m/min (1000 ft/min) and to within $\pm 6\%$ for those between 180 and 305 m/min (600 and

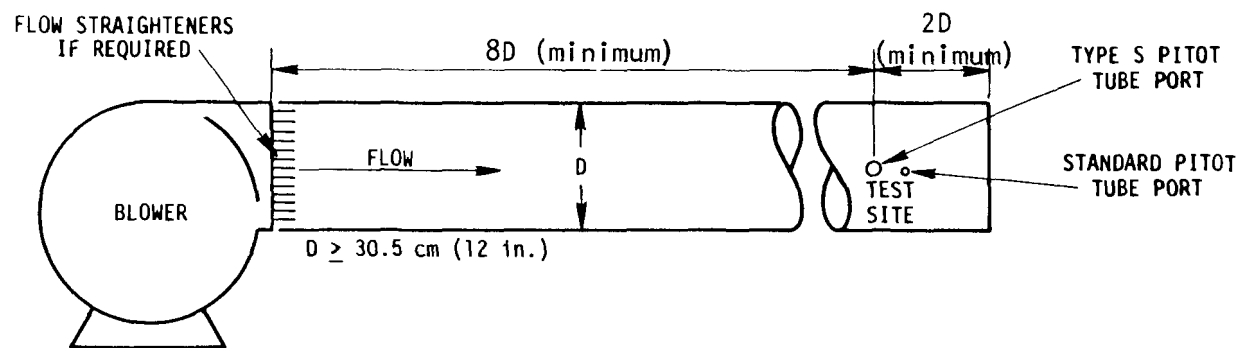


Figure 2.3 Pitot tube calibration system.

1000 ft/min). A more precise correlation between C_p and velocity can be obtained if at least four distinct velocities ranging from 180 to 1525 m/min (600 to 5000 ft/min) are used.^{7,8}

Two entry ports--one each for the standard and for the Type S pitot tubes--should be cut in the test section, as shown in Figure 2.4. The standard pitot entry port should be slightly downstream of the Type S port, so that the standard and Type S impact openings will lie in the same cross-sectional plane during calibration. The exact distance between openings depends on the standard pitot tube diameter. To facilitate alignment of the pitot tubes during calibration, the test section should be constructed of plastic or some transparent material.

A permanently mounted manometer should be provided near the calibration site. Plastic tubing and two-way valves will facilitate connecting the manometer to the pitot tubes and in switching from one pitot tube to another. Pitot tube holders should be used to maintain the alignment and location of each pitot tube during calibration.

2.1.3 Calibration Procedure - One leg of the Type S pitot tube should be marked with an "A" and the other with a "B." To obtain calibration data for both the A and B sides, proceed as follows:

1. Clean and fill the manometer with clean fluid of the proper density. Inspect and leak check all pitot lines and fittings; repair or replace if necessary.
2. Assemble the apparatus, as shown in Figure 2.4.
3. Level and zero the inclined manometer. Turn on the fan, and allow the flow to stabilize. Seal the Type S entry port with duct tape.
4. Position the standard type pitot tube near the center of the duct, and seal the entry port with duct tape or other means. Check to be sure that the pitot tube is properly aligned and perpendicular to the duct.

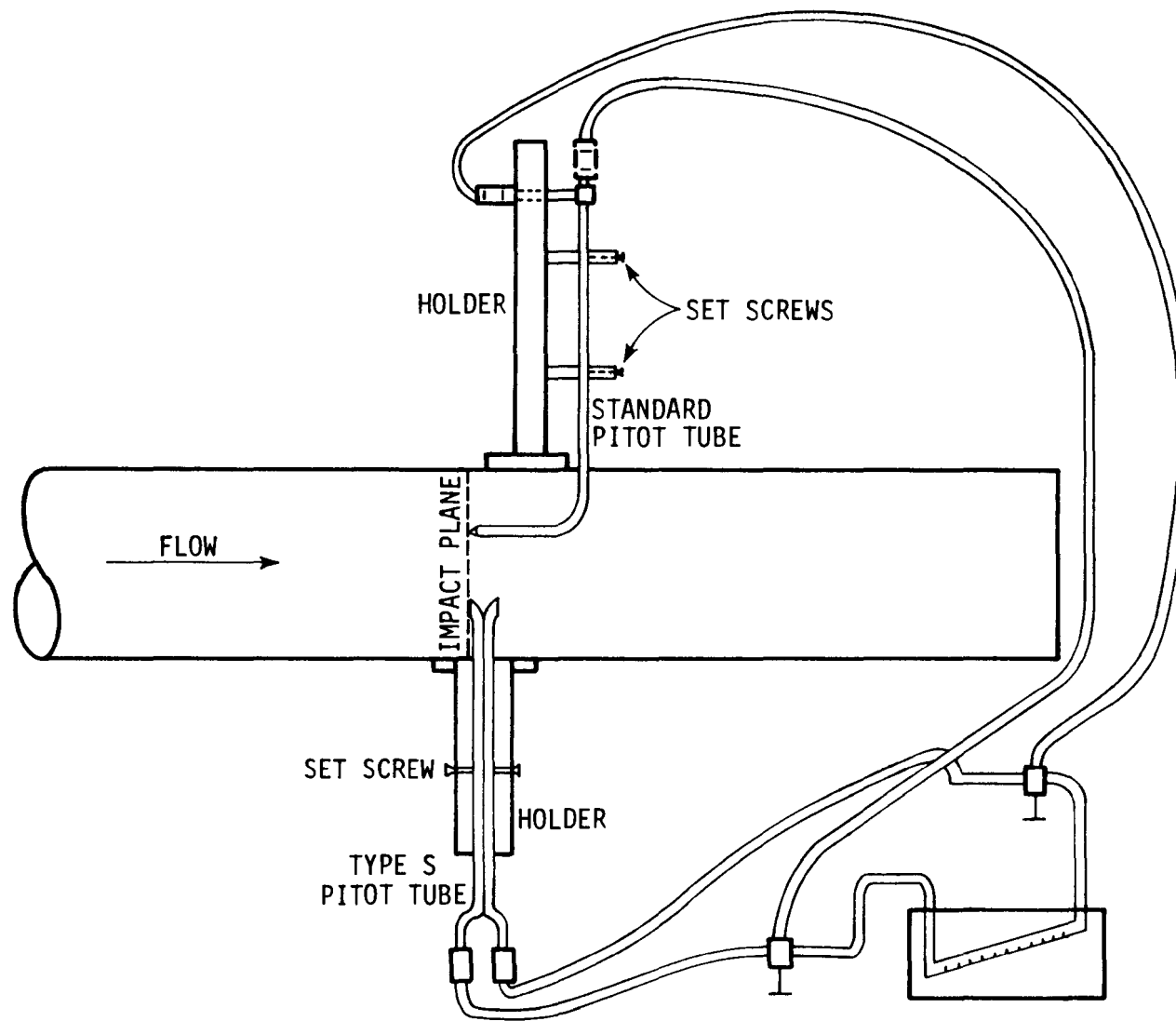


Figure 2.4 Pitot tube calibration set-up.

5. Adjust the fan speed or intake area to give a desired velocity head, as measured by the standard pitot tube, and record Δp_{std} on a form such as Figure 2.5. Check the reading again; withdraw this pitot tube; and seal the opening.

6. Connect the Type S pitot tube to the manometer. Insert the Type S tube, and locate the tip at the same point in the duct as that measured by the standard tube.

7. Align the Type S tube with leg A facing directly upstream. Alignment of the pitot tube along the roll and pitch axes is best accomplished by visually aligning it against the duct. Seal the entry port with a rag or duct tape. Figures 2.6 and 2.7 illustrate the magnitude and characteristics of measurement errors in C_p associated with varying degrees of nonalignment on the roll (yaw) and pitch axes, respectively.

8. Read and record the velocity head, Δp_s in Figure 2.5. Remove the Type S tube from the duct, and disconnect the manometer.

9. Repeat steps 4 through 8 above until three sets of velocity head measurements are obtained.

10. Repeat the complete procedure with leg B of the Type S pitot tube facing upstream.

11. Calculate the Type S pitot tube coefficient, $C_{p(s)}$, for each set of measurements, using Equation 2-2.

$$C_{p(s)} = C_{p(std)} \sqrt{\frac{\Delta p_{std}}{\Delta p_s}} \quad \text{Equation 2-2}$$

where

- $C_{p(s)}$ = Type S pitot tube coefficient,
- $C_{p(std)}$ = standard pitot tube coefficient (use 0.99 if coefficient is unknown and tube is designed according to guidelines in Section 3.1.1),
- Δp_{std} = velocity head measured by the standard pitot tube, cm (in.) H_2O , and
- Δp_s = velocity head measured by the Type S pitot tube, cm (in.) H_2O .

Calibration pitot tube: type S size (OD) 3/8" ID number FL-1
Type S pitot tube ID number 34 $C_{p(std)} =$ 0.99
Calibration: date Sept. 1, 1979 performed by H. Brown

A-Side Calibration

Δp_{std} cm (in.) H ₂ O	Δp_s cm (in.) H ₂ O	$C_{p(s)}^a$	DEV. ^b
0.060	0.085	0.832	0.008
0.075	0.105	0.837	0.003
0.090	0.125	0.840	0.0
Average		0.84	0.0037

B-Side Calibration

Δp_{std} cm (in.) H ₂ O	Δp_s cm (in.) H ₂ O	$C_{p(s)}^a$	DEV. ^b
0.065	0.09	0.841	0.001
0.080	0.11	0.844	0.004
0.095	0.13	0.846	0.006
Average		0.84	0.0037

$$^a C_{p(s)} = C_{p(std)} \sqrt{\frac{\Delta p_{std}}{\Delta p_s}} = \underline{0.84}.$$

$$^b DEV = C_{p(s)} - \bar{C}_p, \text{ (must be } \leq 0.01)$$

$$\bar{C}_p(A) - \bar{C}_p(B) = \underline{0} \text{ (must be } \leq 0.01)$$

Figure 2.5 Pitot tube calibration data.

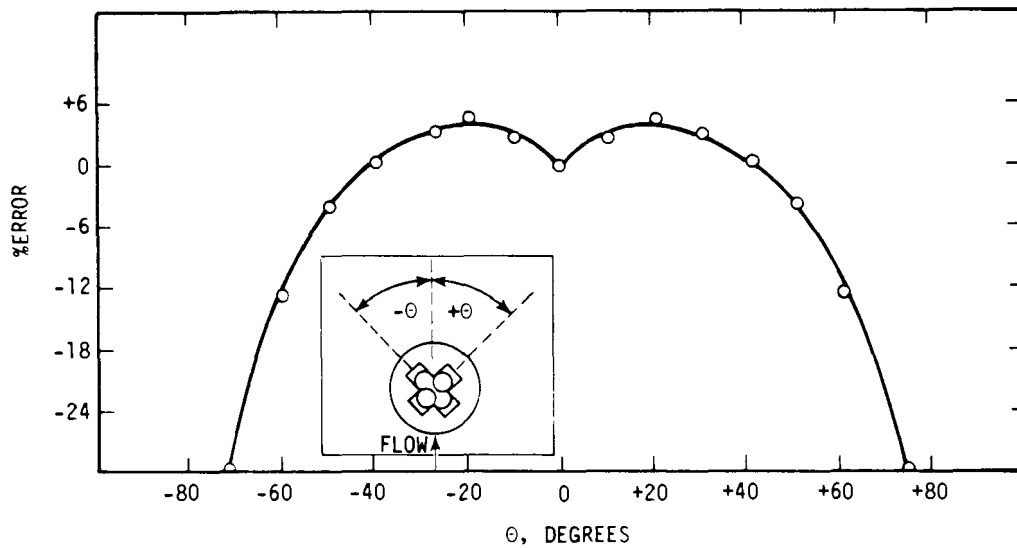


Figure 2.6 Example of error in measured stack gas velocity as a function of tube misalignment along its roll axis (yaw).

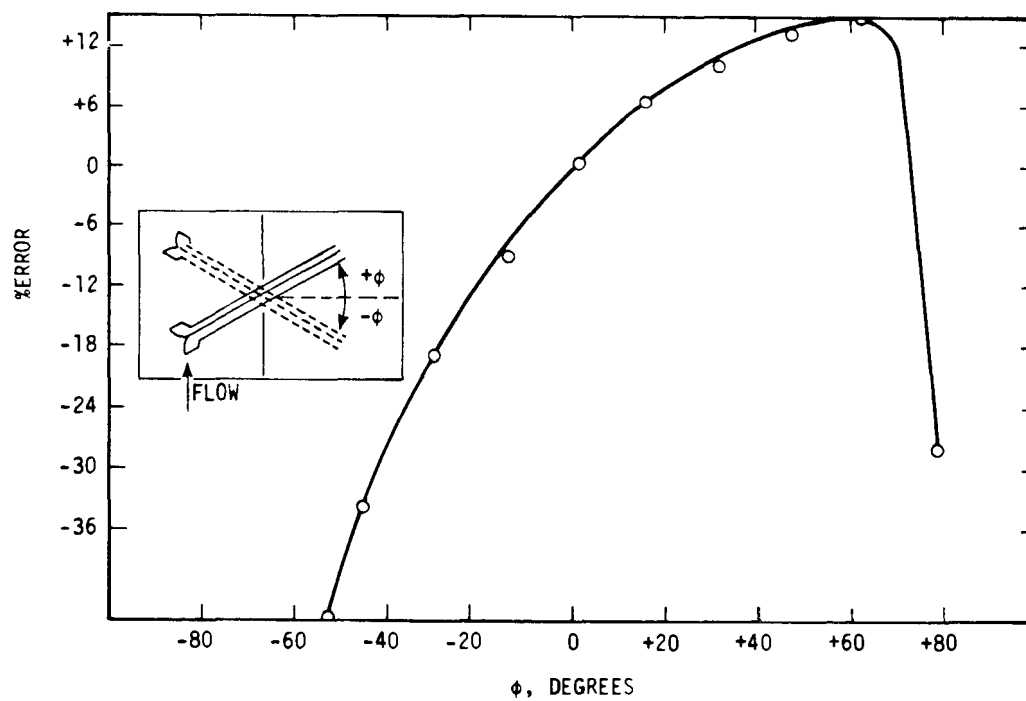


Figure 2.7 Example of error in measured stack gas velocity as a function of tube misalignment along its pitch axis.

12. Calculate $\bar{C}_p(A)$ and $\bar{C}_p(B)$, the average A-side and B-side coefficients, and the difference between these two averages.

13. Calculate the deviation of each of the three A-side values of $C_{p(S)}$ from $\bar{C}_p(A)$, and the deviation of each B-side value of $C_{p(S)}$ from $\bar{C}_p(B)$, using Equation 2-3.

$$\text{Deviation} = C_{p(S)} - \bar{C}_p \text{ (A or B)}. \quad \text{Equation 2-3}$$

14. Calculate s , the estimated standard deviation of the deviations from the mean for both the A and B sides of the pitot tube using Equation 2-4.

$$s \text{ (A or B)} = \left(\frac{\sum_{i=1}^3 [C_{p(S)} - \bar{C}_p \text{ (A or B)}]^2}{2} \right)^{1/2}. \quad \text{Equation 2-4}$$

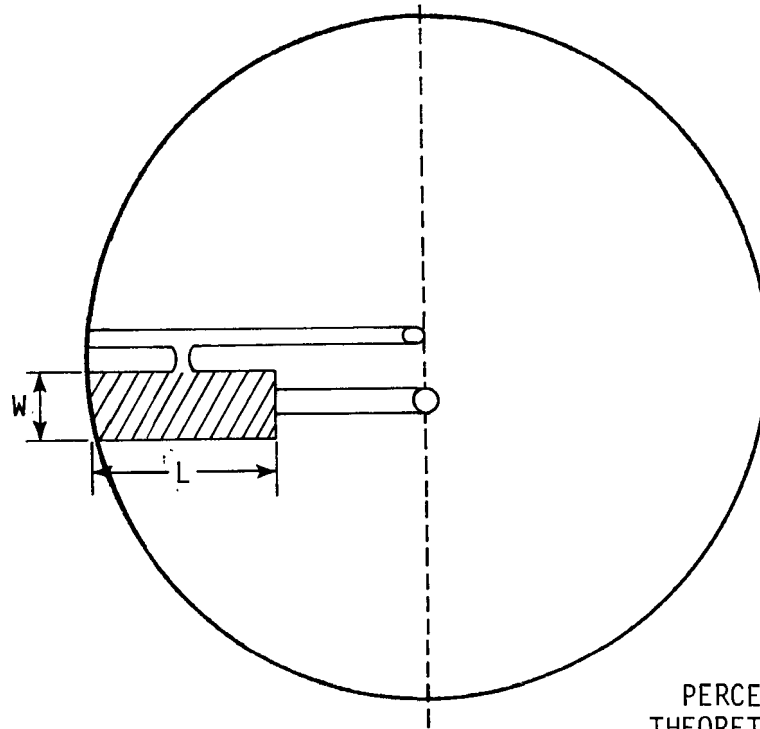
Use the Type S pitot tube assembly only if the values of s for both A and B are ≤ 0.02 and if the absolute value of the difference between $\bar{C}_p(A)$ and $\bar{C}_p(B)$ is ≤ 0.01 .

2.1.4 Special Calibration Considerations - The pitot tube-probe assembly may block a significant part of the flow in ducts < 91 cm (36 in.) in diameter. This blockage, in turn, affects the pitot tube calibration factor. To check for any blockage effects, use the following procedure:

1. Make a projected-area model of the pitot tube assembly with the Type S pitot tube impact opening positioned at the center of the duct (Figure 2.8). This model represents the approximate "average blockage" of the duct cross section during calibration or during a sample traverse. Although the actual blockage will be less than this for sample points close to the near stack wall and more than this for points close to the far wall, the model approximates the average condition.

2. Calculate the theoretical average blockage by taking the ratio of the projected area of the probe sheath to the cross

NOTE: A PITOT TUBE ASSEMBLY WITH
NO EXTERNAL SHEATH IS SHOWN.



$$\text{PERCENT THEORETICAL BLOCKAGE} = \left[\frac{L \times W}{\text{DUCT AREA}} \right] \times 100.$$

Figure 2.8. Projected-area model for sampling of small ducts with pitot tube assemblies.

sectional area of the duct (use consistent units of measure), and multiply by 100. If the theoretical blockage is either $\leq 2\%$ for an assembly with an external sheath or $\leq 3\%$ for an assembly without an external sheath, the decrease in C_p will be $< 1\%$ and no adjustment in the pitot tube coefficients will be necessary. If the theoretical blockage exceeds these values, apply a correction factor, as shown in Figure 2.9. During calibration, the blockage effect can be minimized by keeping the pitot tube approximately halfway between the near side wall and the center.

2.1.5 Recalibration - After each field use, the isolated pitot tubes must be carefully examined and their dimensions checked, as specified in Section 3.1.1. If damaged, a tube must either be repaired to conform with the acceptable dimensions or be discarded. Pitot tube assembly dimensions must also be carefully checked. If the component spacings have not changed and if alignment is intact, the assembly may be reused with the same correction factor. If the spacings have changed, either restore the original spacing or recalibrate. No correction to the field data is required for runs that were started with acceptable pitot tubes. If the pitot tube is damaged, it may be replaced using an interference-free spacing, as shown in Section 2.1; otherwise, the assembly should be recalibrated.

Standard pitot tubes need not be recalibrated. If they are damaged, they should be replaced.

2.2 Stack Temperature Sensor

The stack temperature sensor should be calibrated upon receipt or checked before field use. Each sensor should be uniquely marked for identification. The calibration should be performed at three points and then extrapolated over the range of temperatures anticipated during actual sampling. For the three point calibration, a reference mercury-in-glass thermometer should be used.

The following procedure is recommended for calibrating stack temperature sensors (thermocouples and thermometers) for field use.¹¹

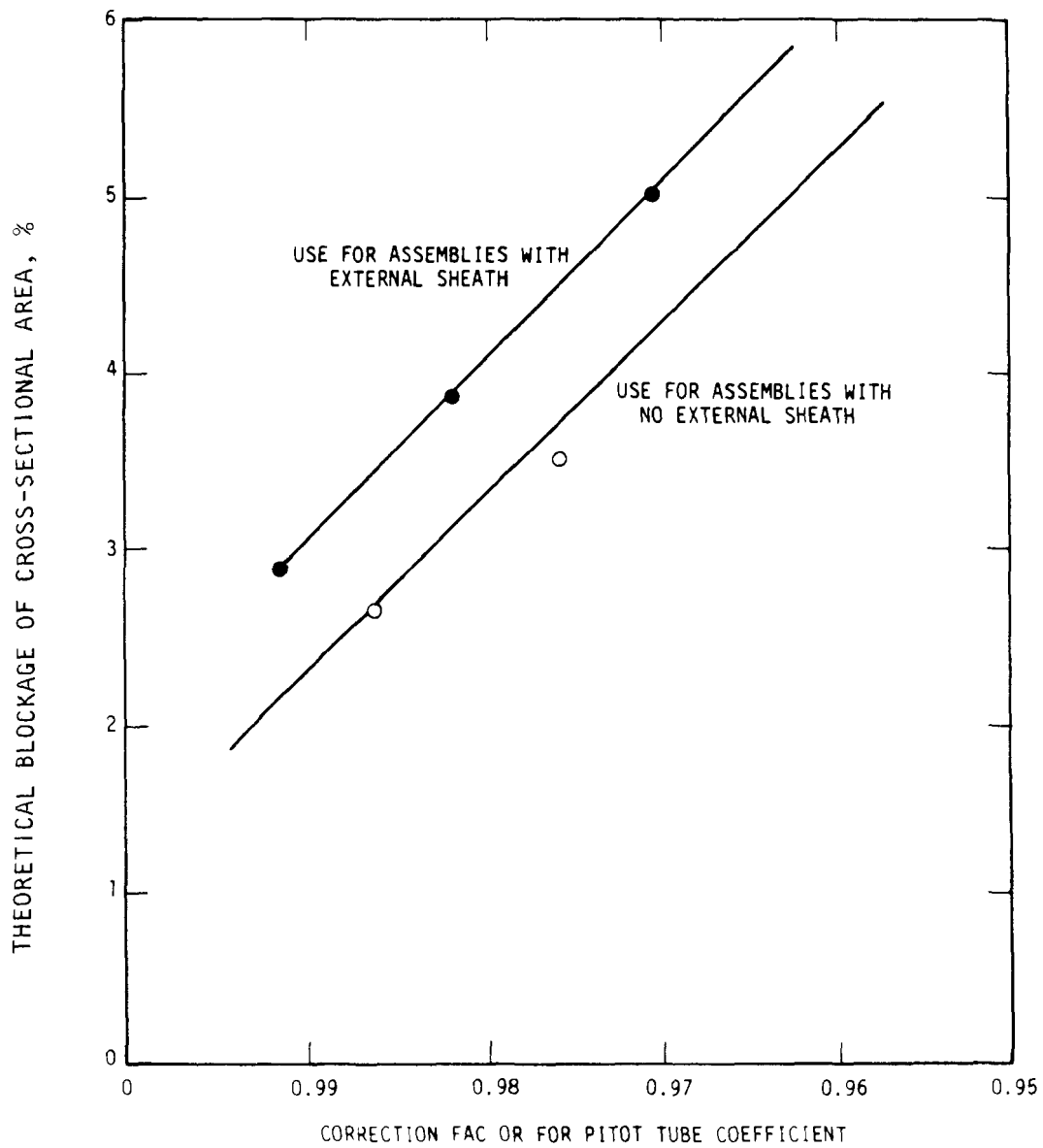


Figure 2.9 Adjustment of Type S pitot tube coefficients to account for blockage effects in duct <91 cm in diameter.

1. For the ice point calibration, form a slush from crushed ice and liquid water (preferably deionized, distilled) in an insulated vessel such as a Dewar flask.

Taking care that they do not touch the sides of the flask, insert the stack temperature sensor into the slush to a depth of at least 2 in. Wait 1 min to achieve thermal equilibrium, and record the readout on the potentiometer. Obtain three readings taken in 1-min intervals. Note: Longer times may be required to attain thermal equilibrium with thick-sheathed thermocouples.

2. Fill a large Pyrex beaker with water to a depth ≥ 4 in. Place several boiling chips in the water, and bring the water to a full boil using a hot plate as the heat source. Insert the stack temperature sensor(s) in the boiling water to a depth of at least 2 in., taking care not to touch the sides or bottom of the beaker.

Alongside the sensor(s), an ASTM reference thermometer should be placed. If the entire length of the mercury shaft in the thermometer cannot be immersed, a temperature correction will be required to give the correct reference temperature.

After 3 min, both instruments will attain thermal equilibrium. Simultaneously record temperatures from the ASTM reference thermometer and the stack temperature sensor three times at 1-min intervals.

3. For thermocouple, repeat Step 2 with a liquid that has a boiling point (such as cooking oil) in the $150^{\circ} - 250^{\circ}\text{C}$ ($300^{\circ} - 500^{\circ}\text{F}$) range. Record all data on Figure 2.10. For thermometers, other than thermocouples, repeat Step 2 with a liquid that boils at the maximum temperature that the thermometer is to be used, or place the stack thermometer and reference thermometer in a furnace or other device to reach the required temperature. Note: If the thermometer is to be used at temperatures higher than the reference thermometers will record, the stack thermometer may be calibrated with a thermocouple previously calibrated with the above procedure.

Reference point number ^a	Source ^b (specify)	Reference thermometer temperature, °C	Thermocouple potentiometer temperature, °C	Temperature difference, °C %
0°	ice water	1°C	1°C	—
100°	boiling water	101.5°C	101.0°C	0.1%
—	boiling cooking oil	205.5°C	205°C	0.5%

^bType of calibration system used.

$$C \left[\frac{(\text{ref temp, } ^\circ\text{C} + 273) - (\text{test thermom temp, } ^\circ\text{C} + 273)}{\text{ref temp, } ^\circ\text{C} + 273} \right] 100 \leq 1.5\%.$$

Figure 2.10 Stack temperature sensor calibration data form.

4. If the absolute temperature values of the reference thermometer and thermocouple(s) agree within $\pm 1.5\%$ at each of the three calibration points, plot the data on linear graph paper and draw the best-fit line between the points or calculate the linear equation using the least-squares method. The data may be extrapolated above and below the calibration points and cover the entire manufacturer's suggested range for the thermocouple. For the portion of the plot or equation that agrees within 1.5% of the absolute reference temperature, no correction need be made. For all other portions that do not agree within $\pm 1.5\%$ use the plot or equation to correct the data.

If the absolute temperature values of the reference thermometer and stack temperature sensor (other than the thermocouple) agree within $\pm 1.5\%$ at each of the three points, the thermometer may be used over the range of calibration points for testing without applying any correction factor. The data cannot be extrapolated outside the calibration points.

2.3 Barometer

The field barometer should be adjusted initially and before each test series to agree within 2.5 mm (0.1 in.) Hg of the mercury-in-glass barometer or the station pressure value reported by a nearby National Weather Service station corrected for elevation. The correction for elevation difference between the weather station and sampling point should be applied at a rate of -2.5 mm (0.1 in.) Hg/30 m (100 ft). Record the results on the pretest sampling check form or on a similar form, as shown in Section 3.1.3.

2.4 Differential Pressure Gauge

Differential pressure gauges other than inclined manometers must be calibrated initially, and their calibration must be checked after each test series. Calibrate and check the differential pressure gauge using the following procedure:

1. Connect the differential pressure gauge to a gauge-oil manometer, as illustrated in Figure 2.11.

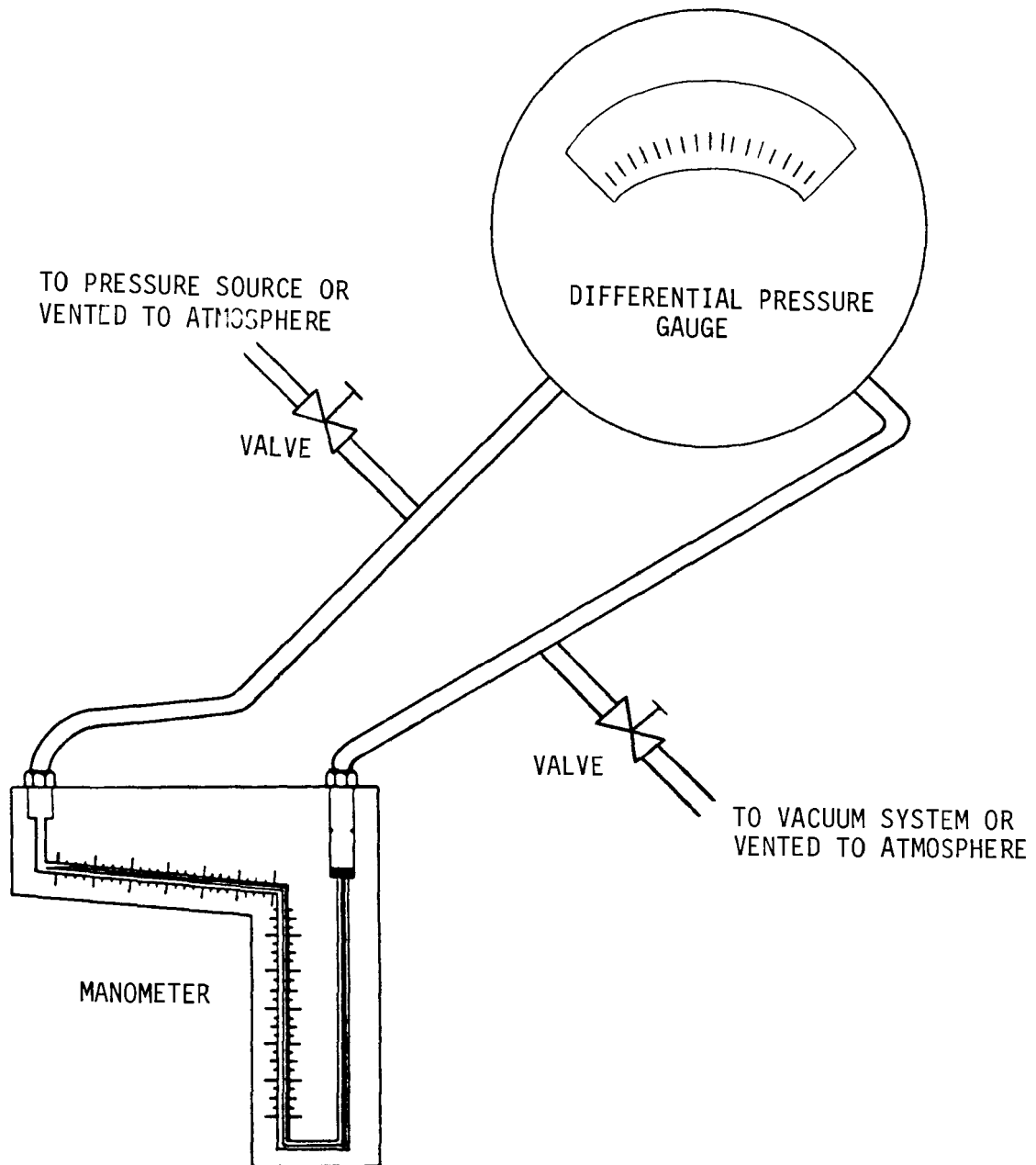


Figure 2.11 Differential pressure gauge check.

2. Vent the vacuum side to the atmosphere, and place a pressure on each system.

3. Compare Δp readings of the differential pressure gauge with those of the gauge-oil manometer at a minimum of three points representing approximately the range of Δp values to be encountered. Follow the same procedures on the vacuum side by venting the pressure side to the atmosphere and by putting a vacuum on the system.

4. The posttest calibration should be performed at the average Δp . If the agreement is within $\pm 5\%$ the calibration is acceptable; if not, void the data or consult the administrator to determine acceptability.

5. Record the data on a form such as Figure 2.12. If, at each point, the value of Δp as read by the differential pressure gauge and the gauge-oil manometer agree within 5%, the differential pressure gauge should be considered properly calibrated.

Gauge type MAGNETIC Serial or ID number 0074

Scale 0-1"

Gauge-oil manometer Δp		Differential pressure gauge Δp	Pressure difference %
Side A	0.1	0.1	0
	0.15	0.15	0
	0.20	0.20	0
Side B	0.1	0.1	0
	0.15	0.15	0
	0.20	0.20	0

Calibration: initial _____ posttest ✓

Date calibrated August 4, 1979 by T. WATKINS

Figure 2.12 Differential pressure gauge calibration data form.

Table 2.1 ACTIVITY MATRIX FOR CALIBRATION OF APPARATUS

Apparatus	Acceptance limits	Frequency and method of measurement	Action if requirements are not met
Type S pitot tube and/or probe assembly	All dimension specifications met, or calibrate according to Sec 3.1.2, and mount in an interference free manner	When purchased, use method in Secs 3.1.1 and 3.1.2; visually inspect after each field test	Do not use pitot tubes that do not meet face opening specifications; repair or replace as required
Stack gas temperature measurement system	Capable of measuring within 1.5% of minimum stack temperature (absolute)	When purchased and after each field test, calibrate against ASTM 3C or 3F thermometer	Adjust to agree with Hg bulb thermometer, or construct a calibration curve to correct the readings
Barometer	Agrees within 2.5 mm (0.1 in.) Hg of mercury-in-glass barometer	Initially and after every field use, compare to a liquid-in-glass barometer	Adjust, repair, or discard
Differential pressure gauge (does not include inclined manometers)	Agree within $\pm 5\%$ of inclined manometers	Initially and after each field use	Reject test results, or consult administrator if post-test calibration is out of specification

3.0 PRESAMPLING OPERATIONS

The quality assurance activities for presampling preparations 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

Figures 3.1 and 3.2 or similar forms are recommended to aid the tester in recording calibration data and in preparing an equipment checklist, status form, and packing list.

3.1.1 Type S Pitot Tube and Differential Pressure Gauge - For the Type S pitot tube and inclined manometer assembly illustrated in Figure 1.2, the following checks should be made before each field test.

1. Visually inspect the pitot tube openings for damage such as a scratch, nick, or dent that would tend to disrupt the air flow pattern. Check for proper alignment; that is, the centers of the two openings should be in a straight line such that when one opening is directed upstream, the other will be exactly 180° opposite, pointing downstream. If the damage or misalignment is obvious when visually inspected, the pitot tube should be replaced or repaired. Check the weld spots holding the two legs together; if broken, repair. Calibration must be checked after repair if the pitot tube does not conform to specifications.

2. Check the quick disconnects on the pitot tube and check the connecting lines for proper operation. Clean the small metal parts of the disconnect. Lubricate sparingly to help to keep them free.

3. Blow out the pitot tube legs from the line ends with compressed air, rinse with distilled water then with acetone, and dry with compressed air.

4. Visually inspect the differential pressure gauge for damage. Repair or replace as necessary. Level the inclined

Date August 1, 1979 Completed by T. WATKINS

Pitot Tube

Identification number 34 Date August 1, 1979

Dimension specifications checked?* ✓ yes no

Calibration required? yes ✓ no

Date C_p 0.84

Temperature Sensor

Identification number 16

Calibrated?* ✓ yes no

Was a pretest temperature correction used? yes ✓ no
If yes, temperature correction °C (°F)

Barometer

Was the pretest field barometer reading correct?* ✓ yes no

Differential Pressure Gauge

Was pretest calibration acceptable?* ✓ yes no

*Most significant items/parameters to be checked.

Figure 3.1 Pretest sampling checks.

Apparatus check	Acceptable		Quantity required	Ready		Loaded and packed
	Yes	No		Yes	No	
<u>Pitot Tube</u>						
Type S	✓		3	✓		yes
Standard						
Length <u>5</u> m(ft)						
Calibrated* <u>✓</u>						
<u>Differential Pressure Gauge</u>						
Inclined manometer sensitivity	✓		3	✓		yes
<u>0-25</u> cm (in.)						
Other _____						
<u>Stack Temperature Sensor</u>						
Type <u>thermocouple</u>	✓		3	✓		yes
Calibrated* <u>yes</u>						
<u>Orsat Analyzer</u>						
Orsat <u>✓</u>	✓		2	✓		yes
Fyrite <u>✓</u>	✓		2	✓		yes
Other _____						

*Most significant items/parameters to be checked.

Figure 3.2 Pretest preparation check.

manometer (if used as the differential pressure gauge), and fill with the proper specific gravity fluid; this recommended fluid is usually inscribed on the manometer. Check for leaks, especially around the fluid level plunger and drain screws. Replace the fluid level plunger or O-rings if leaks are detected. Clean the manometer when it is dirty and change the fluid at any sign of fading. If other differential pressure gauges are used, follow the manufacturer's check-out instructions.

5. Connect the pitot tube and differential pressure gauge with the pitot tube lines. Check for obstructions by blowing lightly on one pitot tube leg and then the other; watch the responses of the gauge. Also check for leaks by blowing into the downstream leg, sealing the opening, and noting any drop in the pressure gauge reading. Check the upstream leg by drawing a slight vacuum, sealing, and noting the gauge. If there are no leaks, the gauge readings will remain constant. No change in the differential pressure gauge reading should occur.

6. Check the manometer fluid reservoir for proper adjustment. A standard 0-254 mm (0-10 in.) H₂O manometer should be able to adjust ± 1.3 mm (0.05 in.) H₂O.

3.1.2 Temperature Measurement System - The following temperature gauge checks should be made before each field test:

1. Visually check the readout device, sensor, and inter-connecting lines or wires as applicable for general appearance. If damage is detected, repair or replace as necessary.

2. Compare the ambient temperature readings made with the temperature measuring system to those made with a mercury-in-glass thermometer. If the system does not agree within $\pm 4^{\circ}\text{C}$ (this is less than $\pm 1.5\%$ at about 293K, which is near room temperature) of the thermometer, the temperature measuring system should be calibrated as directed in Section 3.1.2. Otherwise, record the two readings in the calibration log book and date and initial the entries.

3.1.3 Barometer - Check the field barometer reading against that of a mercury barometer. If they disagree more than ± 2.3 mm

(0.1 in.) of mercury, adjust the field barometer until it agrees with the mercury barometer. Record the two readings in the calibration log book; date and initial the entries.

3.2 Packing Equipment for Shipment

The logistics, time of sampling, and quality of data of any source testing method are dependent upon the packing of equipment in regards to (1) accessibility, (2) ease of movement, and (3) optimum functioning of measurement devices in the field. Equipment should be packed under the assumption that it will receive severe treatment during shipping and field operation.

3.2.1 Type S Pitot Tube - Pack the pitot tube in a case protected by styrofoam or other suitable packing material. The case should have handles which can withstand hoisting and should be rigid enough to prevent bending or twisting of the pitot tube during shipping and handling.

3.2.2 Differential Pressure Gauge - Close all valves on the pressure gauge and pack it in a suitable case for shipment. Pack spare parts such as O-rings and operating fluid (for inclined manometer).

3.2.3 Temperature Measurement System - Proper packing of the temperature measuring systems depends on the type of system used. In general, the sensor and leads can be protected from breakage or other damage during shipment by securing them to the pitot tube and enclosing them with suitable packing material. The readout device, if detachable from the sensor, should be packed in a separate packing case. Check batteries and include spares prior to shipment if applicable.

3.2.4 Barometer - The barometer should be packed in a shock-mounted (spring system) carrying case.

Table 3.1 ACTIVITY MATRIX FOR PRE-SAMPLING

Operation	Acceptance limits	Frequency and method of measurement	Action if requirements are not met
Type S pitot tube assembly	1. No evidence of damage/misalignment 2. Proper operation 3. Cleaned according to procedure 4. No leaks 5. No visual damage or leaks 6. Proper response of the gauge 7. Sensitivity ± 1.3 mm (0.05 in.) H_2O	1. Visually check for damage, alignment 2. Check quick disconnects for proper operation 3. Blow out tube legs; rinse first with distilled H_2O and then with acetone; dry with compressed air 4. Check for leaks 5. Visually check differential pressure gauge for damage or leaks 6. Check for obstruction by blowing lightly 7. Check reservoir for proper adjustment range	1. Replace or repair, and then recalibrate 2. Clean, and use a drop of penetrating oil Reclean 4. Repair or replace as necessary 5. Repair or replace as necessary 6. Remove obstruction, and repeat test 7. Add or remove fluid
Temperature measurement system	Agreement within $\pm 4^\circ C$ ($7^\circ F$) ($< 1.5\%$ at 293K) ($530^\circ R$); \approx room temperature	Before each field test, compare absolute ambient readings to those with a Hg-in-glass thermometer	Recalibrate the system

(continued)

Table 3.1 (continued)

Operation	Acceptance limits	Frequency and method of measurement	Action if requirements are not met
Barometer	Agreement within (2.5 mm) 0.1 in. Hg	Before each field test, check against a Hg barometer	Adjust until agreement attained
Packing equipment for shipment	Packed according to specified conditions	Visually check	Correct the packing procedure

4.0 ON-SITE MEASUREMENTS

The on-site measurement activities include transporting equipment to the test site, unpacking and assembling equipment, making duct measurements, measuring velocity, determining molecular weight, and recording data. Table 4.1 at the end of this section summarizes the quality assurance activities for on-site measurements. A copy of all field data forms mentioned are in Section 3.1.12.

4.1 Transport of Equipment to the Sampling Site

The most efficient means of transporting the equipment from ground level to the sampling site should be decided during the preliminary site visit (or prior correspondence). Care should be exercised to prevent damage to the test equipment or injury to test personnel during the moving phase.

4.2 Velocity Measurement

On-site measurements include the following steps:

1. Preliminary measurements and setup; this includes a determination of acceptable flow conditions, as described in Method 1 (Section 3.0.1).
2. Leak checking the pitot tube and differential pressure gauge.
3. Insertion of the pitot assembly into the stack.
4. Sealing the port.
5. Measuring velocity pressure and temperature at designated points.
6. Measuring the static pressure of the stack.
7. Determining the moisture content according to Method 4.
8. Determining the molecular weight according to Method 3.

A final leak check of the pitot tube and differential pressure gauge assembly must always be performed upon completion of sampling. Record all data on Figure 4.1 or similar form.

Plant and city	Run date
Lakeland Paper Co., Columbus, Ohio	01/15/80

Sampling location	Clock time
Main stack	9:50

Run number	Operator	Amb. temp., °F	Bar. press., in. Hg	Static press., in. H ₂ O
1	B. Blanton	79	29.54	-0.05

Molecular wt.				Stack inside dimension, in.								Pitot tube (C _p)					
				Diam. of side 1				side 2									
3	0	.	25					4	8					0	.	8	4

Field data						
Traverse point number	Position, in.	Velocity head (Δp_s), in. H ₂ O	Stack temp., °F	Cyclonic flow determination		
				Δp_s at 0° reference	Angle (α) which yields a null Δp	
1	2.1	1.2	287	0.1	1	
2	7.0	1.2	287	0.3	2	
3	14.2	1.2	287	0.5	3	
4	33.8	1.3	288	0.5	3	
5	41.0	1.2	288	0.7	5	
6	45.9	1.1	288	0.6	5	
7						
8						
9						
10						
11						
12						
13						
14						
15						
16						
17						
18						
19						
20						
Average angle (α) ^a						3

^a Average of α must be <10 degrees to be acceptable.

Figure 4.1 Method 2 gas velocity and volume data form.

4.2.1 Preliminary Measurements and Setup - An accurate determination of the stack's cross-sectional area is important when calculating volumetric flow rate. Also, the inside dimensions must be known to properly mark the pitot tube for making a velocity traverse and to calculate a total flow rate. Field team members must use good judgement and experience in selecting the best method of measuring stack dimensions for each particular situation.

Two commonly used methods of measuring stack dimensions are:

1. Inserting a rigid rod made of metal or other material that will, in most instances, withstand stack conditions through a sampling port, is the easiest and most accurate method of measuring the dimensions (i.e., diameter or length and width) of small stacks. Caution: When testing a stack that has hot and/or noxious gases at a positive pressure, use a packing gland to prevent the gases from escaping from the sampling port. Also, wear asbestos gloves when working around a hot stack.

Because all circular stacks are not perfect circles and because all sides of a rectangular stack are not straight, best results are obtained if the dimensions are measured from as many sampling ports as available at the sampling site. Calculate the average value for use in subsequent calculation of the volumetric flow rate. Sketch the cross-sectional area of the stack on the sample data form (Figure 4.1), and show all measured dimensions and their values. Record the average value on the same form in the blank space designated for stack dimension. (If the stack is rectangular, record the average length and width in this space, and mark out the diameter.) Determine all dimensions to the nearest 3 mm (1/8 in.).

2. For stacks too large or too inconvenient for measuring with a rod as described in (1) above, the next best method may be to measure the outside circumference and to calculate the inside diameter (d):

$$d = (C/\pi) - 2t$$

Equation 4-1

where

d = inside diameter of the stack,
C = outside circumference of stack,
 $\pi \simeq 3.1416 \simeq 22/7$, and
t = stack wall thickness.

For rectangular stacks, measure the outside dimensions and subtract the (2t) wall thickness; measure all lengths to the nearest 3 mm (1/8 in). Note: In horizontal ducts, particulate buildup may occur on the bottom of the duct; this buildup (determined visually or by probing with a rod) should be subtracted from the duct cross section. Select the sampling site location in accordance with Method 2; if this is not possible due to duct configuration or other reasons, have the sampling site location approved by the administrator. Determine the minimum number of traverse points by Method 1, or check the traverse points determined from the preliminary site visit (Section 3.0 of this Handbook). Record all data on the traverse point location form, as shown in Section 3.0. Use these measurements to locate the pitot tube and the sampling probe during preliminary measurements and actual sampling.

4.2.2 Stack Parameters - Check the sampling site for cyclonic or nonparallel flow, as described in Method 1 (Section 3.0.1). The sampling site must be acceptable before a valid measurement can be made. Be sure that the proper differential pressure gauge is chosen for the range of velocity heads encountered.

4.2.3 Velocity Measurement - Determine the number and location of traverse points and sampling ports by Method 1. For circular stacks <3 m (10 ft) in diameter, two ports along diameters at right angles to each other and in the same plane are sufficient; however, when the stack diameter is >3 m (10 ft), four ports--one at each end of the two diameters--are desirable to avoid the use of extra long pitot tubes. If it is necessary to use a Type S pitot tube >3 m (10 ft) in length, it should be structurally reinforced to prevent bending of the tube and resulting in the type

error illustrated in Figure 2.7. Each sampling port and traverse point should be identified by a number or letter and should be so-designated on the sketch.

Measure the velocity head and temperature at each traverse point accessible from a given port by measuring each point once as the pitot tube is inserted into the stack and moved across the stack's diameter. To prevent damage or clogging, be careful to avoid touching the pitot tube tip to the side of the stack wall.

A standard pitot tube may be used instead of a Type S, for conducting velocity traverses; however, the static and impact pressure holes of standard pitot tubes are susceptible to plugging in particulate-laden or moist gas streams. Therefore, whenever a standard pitot tube is used to perform a traverse, adequate proof must be furnished to show that the openings of the pitot tube did not plug up during the traverse period.

The following procedure will provide sufficient evidence that plugging did not occur.

1. Measure the velocity head (Δp) reading at the final traverse point.

2. Clean out the impact and static holes of the standard pitot tube by "back purging" with pressurized air, and then re-measure the Δp at the final point. If the Δp readings before and after the air purge are the same ($\pm 5\%$), the traverse is acceptable. Note: If Δp at the final point is unsuitably low, another point may be selected.

If "back purging" at regular intervals is part of the procedure, comparative Δp readings should be taken (as above) for the last two back purges at which suitably high Δp readings are observed.

3. Record the clock time, Δp , and T_s for each traverse point on the data form (Figure 4.1).

4. After the traverse, check the differential pressure gauge zero setting and local indicator. If either has shifted, reset and repeat the traverse.

If a more sensitive differential pressure gauge is required after making a traverse because the velocity head readings were <1.3 mm (0.05 in.), use a more sensitive manometer, as discussed in Section 3.1.1. After completing the traverse, check the pitot tube differential pressure gauge assembly again for leaks, as described in Subsection 4.2.5.

4.2.4 Measurement of Low Velocities - A Type S pitot tube can be used to measure velocities as low as 122 m/min (400 ft/min) without affecting the calibration coefficient.

Most sampling trains are equipped with a 10-in. (H₂O column) inclined vertical manometer that has 0.01-in. divisions on the 0-to-1-in. inclined scale and 0.1-in. divisions on the 1-to-10-in. vertical scale. This type of manometer (or other gauge of equivalent sensitivity) is satisfactory for the measurement of Δp values as low as 1.3 mm (0.05 in.) H₂O. However, a differential pressure gauge of greater sensitivity should be used (subject to the approval of the administrator) if any of the following is found to be true:

1. The arithmetic average of all Δp readings at the traverse points in the stack is <1.3 mm (0.05 in.) H₂O;
2. More than 10% of the individual Δp readings are <1.3 mm (0.05 in.) H₂O points, for traverses of 12 or more points;
3. More than one Δp reading is <1.3 mm (0.05 in.) H₂O for traverses of fewer than 12 points.

As an alternative to criteria (1) through (3) above, the following calculation may be performed to determine the necessity of using a more sensitive differential pressure gauge:

$$T = \frac{\sum_{i=1}^n \sqrt{\Delta p_i + K}}{\sum_{i=1}^n \sqrt{\Delta p_i}}$$

where

Δp_i = individual velocity head reading at a traverse point,
mm (in.) H_2O ,

n = total number of traverse points, and

K = 0.13 mm (0.005 in.) H_2O .

If T is >1.05, the velocity head data are unacceptable, and a more sensitive differential pressure gauge must be used.

4.2.5 Special Precautions - Before and during the traverse, a number of precautions should be taken:

1. The pitot tube should be short enough for easy handling from outside the stack when held at any traverse point for safety reasons and for efficiency in the measurement process.

2. The alignment should be made visually with reference to the stack geometry and not by rolling or tipping the pitot tube until a maximum response is observed.

3. If the gas stream contains a significant concentration of particulates, both legs of the pitot tube should be blown out frequently during the velocity traverse.

4. All unused sampling ports must be plugged, and the port being used should be sealed as tightly as possible to minimize any disturbance on the gas flow pattern when making a velocity measurement. The port being used can be sealed with asbestos material, precut sponge, or duct tape depending on the temperature of the stack gas.

5. If liquid droplets are present in the gas stream, a liquid trap should be inserted in the gauge line leading to the upstream pitot tube leg (impact opening). A trap may be required for both legs.

6. When testing a stack that has hot and/or noxious gases under positive pressure, a packing gland and gate valve assembly should be used to prevent the gases from escaping from the sampling port. Caution: Asbestos gloves should be worn when working around a hot stack. Always wear safety glasses and under hazardous conditions, fullface shields.

7. Damage or suspected damage to any item of equipment, such as a pitot tube or an inclined manometer, during the test should be fully documented at the time it occurs or at the first awareness of its occurrence. The item should be replaced by a spare if available. If it is necessary to continue using the damaged item, a posttest calibration (as described in Section 3.1.2) should be performed, and the new calibration should be used for the data collected after the damage occurred.

4.2.6 Measurement of the Static Pressure in the Stack - Three acceptable methods for measuring static pressure are given in the order of decreasing acceptability:

1. Install a tap perpendicular to the stack gas flow, or insert a 6-mm (0.25-in.) steel tube into the sampling port while maintaining a good seal. Connect one side of a U-tube manometer to the tap, and vent the other side of the manometer to the atmosphere. If the pressure is expected to be >63-75 cm (25-30 in.) H_2O , a mercury-filled U-tube manometer should be used instead of a water-filled U-tube.

2. Use the static pressure tap of a standard pitot tube connected to one side of a manometer. (If the stack pressure is obviously negative, connect the static pressure tap to the other side of the manometer; otherwise trial and error will have to suffice.) Vent the remaining side of the manometer to the atmosphere. Point the pitot tube pressure opening (the unconnected end) directly into the flow and seal the port around the tube.

3. Use a Type S pitot tube with the pitot tube openings facing perpendicular to the gas stream. Connect only one leg of the pitot tube to the manometer; vent the other side of the manometer to the atmosphere. Take extreme care to align the probe properly and to seal the port around the pitot tube.

One static pressure reading is usually adequate for all points within a stack; however, this must be confirmed by randomly moving the pressure probe over the stack to see if there are any significant variations--that is, a range of pressure

values >100 mm (4 in.) H_2O . If there are significant variations, visually check the location for physical flow disturbances. If none are found, measure and record the static pressure at each traverse point.

4. Measure the atmospheric pressure at the test site using the barometer.

Record the static pressure, P_g , (be sure to include the plus or minus sign for positive or negative pressure respectively) as read from the manometer on the velocity data form, Figure 4.1.

4.2.7 Pitot Tube Calibration Check - If the pitot tube coefficient were based on an acceptable geometry standard, be sure that the pitot meets these standards prior to each run and that no posttest data correction is required from any pitot tube damages that may have occurred during testing.

4.2.8 Dry Stack Gas Molecular Weight Determination - For combustion processes, use Method 3. For processes emitting essentially air, an analysis need not be conducted and a molecular weight of 29 should be used. Moisture content can be measured by using Method 4. For other processes, consult the administrator.

4.3 Sample Logistics (Data) and Packing of Equipment - Follow the above procedures until the required number of runs are completed. Log all data on the form shown previously in Figure 4.1.

The following are recommended at the completion of the test series:

1. Record and duplicate all data recorded during the field test by the best means available. One set of data can then be either mailed to the base laboratory, given to another team member, or to the Agency; the original data should be hand-carried.

2. Examine all sampling equipment for damage, and then properly pack it for shipment to the base laboratory. All shipping containers should be properly labeled to prevent loss of equipment.

3. Quickly check sampling procedures using the data form, Figure 4.2.

Sampling

Pitot tube, lines, and manometer assembled correctly?* YES

Pitot tube and components mounted in an interference free manner?* YES

Differential pressure gauge has correct sensitivity?* YES

Differential pressure gauge leveled and zeroed?* YES

Pretest leak check? YES (optional) Cyclonic flow checked? YES

Pitot tube parallel to stack walls?* YES

Static pressure measured? YES Temperature measured? YES

Moisture content determined? YES Method REFERENCE METHOD 4

Orsat samples taken? YES If no explain: _____

Posttest leak check performed?* YES (mandatory)

Data recorded properly? YES

*Most significant items/parameters to be checked.

Figure 4.2 On-site measurements checklist.

Table 4.1 ACTIVITY MATRIX FOR ON-SITE MEASUREMENTS

Activity	Acceptance limits	Frequency and method of measurement	Action if requirements are not met
Type S pitot tube and differential pressure gauge	Leak-free connections; manometer properly leveled; oil column zeroed	Visually check before taking measurements at each field test	Take corrective action
Temperature measurement system	No physical damage	Visually check for damage	Take corrective action prior to taking measurements
Cross sectional area of stack	All measurements made to the nearest 3 mm (1/8 in.)	During each field test, measure inside diameter (or width) and/or circumference (perimeter)	Obtain data as specified
Velocity measurements	1. Number and location of traverse points (Method 1) 2. No leaks for 15 s	1. Check before taking measurements 2. Apparatus leak checked upon completion of tests	Repeat traverse
Static pressure	Variation in static pressure $P_g < 100$ mm (3.9 in.) H_2O to make a single point measurement	Use one of three means given in Subsec 4.8; move probe over cross section to determine if variation is significant	Check the location for disturbances; if none, measure and record the static pressure at each point

(continued)

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	1. All data recorded correctly 2. All equipment examined for damage and labeled for shipment	1. Upon completion of each traverse and before packing for shipment 2. As above	1. Complete required number of runs 2. Repeat the sampling if damage occurred during testing

5.0 POSTSAMPLING OPERATIONS

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

5.1 Apparatus Checks

Disassemble, clean, and visually check each component of the sample apparatus upon completion of sampling. Posttest calibration must be performed on the pitot tube if damaged, and the temperature sensor.

5.1.1 Pitot Tube - If the pitot tube is damaged, do not repair if the sample runs were started with the unacceptable pitot tube. Calibrate the pitot tube according to Section 3.1.2. For calibration purposes, the pitot tube posttest coefficient should be used for all data obtained using the damaged pitot tube only. For any runs that started with an acceptable pitot tube no data correction is required. After calibration, repair the pitot tube and calibrate as initially (by dimensional specifications or calibration). Record posttest calibration data on Figure 5.1. If all runs were started with an acceptable pitot, and repairs can be made, no field data correction is required.

5.1.2 Temperature Sensor - The stack temperature sensor readings should be compared with the reference thermometer readings.

For thermocouples(s), compare the thermocouple and reference thermometer values at ambient temperature. If the values agree within $\pm 1.5\%$ of the absolute temperature, the calibration is considered valid. If the values do not agree within $\pm 1.5\%$, recalibrate the thermocouple as described in Section 3.1.2 to determine the difference (ΔT_s) at the average stack temperature (T_s). Note: This comparison may be done in the field immediately following the tests.

For thermometers, compare the reference thermometer (1) at ambient temperatures for average stack temperature below 100°C (212°F), (2) in boiling water for stack temperatures from 100° - 200°C (212° - 390°F), and (3) in a boiling liquid with a boiling

Pitot Tube

Initial pitot tube coefficient 0.84
Was pitot tube damaged prior to start of any test runs? no yes
✓ no
If yes, was pitot tube calibrated prior to repair?* no yes
Pitot tube coefficient (damaged) _____ (this value must
be used for runs started with the damaged pitot tube)

Temperature Sensor

Was a pretest temperature correction used? _____ yes ✓ no
If yes, temperature correction _____ °C (°F) (within 1.5%
of readings in K (°R) over range)
Average stack temperature of compliance test (T_s) 612 K (°R)
Temperature of reference thermometer or solution for recalibra-
tion* 528 K (°R)
Temperature of stack thermometer for recalibration 523 K (°R)
Difference between reference and stack thermometer temperatures
(ΔT_s) 5 K (°R)
Do values agree within ±1.5%?* ✓ yes _____ no
If yes, no correction necessary for calculations
If no, calculations must be done twice, once with recorded,
values and once with average stack temperature corrected to
correspond to reference temperature differential (ΔT_s). Both
values of final results must then be reported since there is no
way to determine which is correct

Barometer

Was pretest field barometer reading correct? ✓ yes _____ no
Posttest comparison 29.61 mm (in.) (Hg within (±5.0 mm (0.2 in.)
Hg) of mercury-in-glass barometer)
Was recalibration required? _____ yes ✓ no
If yes, no correction needed when field barometer has the lower
reading
If mercury-in-glass reading is lower, subtract the difference
from the field data readings for the calculations

*Most significant items/parameters to be checked.

Figure 5.1 Posttest sampling checks.

point $>200^{\circ}$ (390°F) for stack temperatures between 200° - 405°C (390° - 760°F). For stack temperatures $>405^{\circ}$ (760°F), compare the stack thermometer with a thermocouple at a temperature within $\pm 10\%$ of the average absolute stack temperature. If the absolute values agree within $\pm 1.5\%$, the calibration is considered valid. If not, determine the error (ΔT_s) to correct the average stack temperature.

5.1.3 Barometer - The field barometers are acceptable if they agree within ± 5 mm (0.2 in.) Hg when compared with the mercury-in-glass barometer. When the comparison is not within this range, the lesser calibration value should be used for the calculations. If the field barometer reads lower, no correction is necessary. When the mercury-in-glass barometer gives the lower reading, subtract the difference from the field data readings for the calculations.

Table 5.1 ACTIVITY MATRIX FOR POST-SAMPLING OPERATIONS

Apparatus	Acceptance limits	Frequency and method of measurement	Action if requirements are not met
Pitot tube	If damaged, recalibrate according to Sec 3.1.2	After every field test, visually inspect for damage	Recalibrate, and use calibration factor for data obtained by using damaged pitot tube or repeat the tests
Temperature sensor	Within $\pm 1.5\%$ of absolute temperature	Calibrate with ASTM mercury-in-glass thermometer	Use correction factor on temperature data
Barometer	Within ± 2.5 mm (0.1 in.) Hg at ambient pressure	Compare with mercury-in-glass barometer after each test	Recalibrate, and use lower barometric values for calculations

6.0 CALCULATIONS

Calculation errors due to procedural or mathematical mistakes can be a large 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 roundoff error is detected, the calculations should be checked step-by-step until the source of error is found and corrected. A computer program that prints the input data so that it can be checked is advantageous in reducing calculation errors. If a standardized computer program is used, the original data entry should 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 retaining at least one significant digit beyond that of the acquired data and then should be rounded off after final calculation to two significant digits for each run or sample. All rounding off of numbers should be in accordance with the ASTM 380-76 procedures. Record all calculations on Figures 6.1A or B and on Figures 6.2A or B, or on similar forms.

6.1 Nomenclature

The nomenclature used in the calculations that follow are listed alphabetically.

A = Cross-sectional area of stack, m^2 (ft^2)

B_{ws} = Water vapor in the gas stream (Method 5 or Method 4), proportion by volume

C_p = Pitot tube coefficient, dimensionless

K_p = Pitot tube constant,

$$34.97 \frac{\text{m}}{\text{s}} \left[\frac{(\text{g/g-mole})(\text{mm Hg})}{(^{\circ}\text{K})(\text{mm H}_2\text{O})} \right]^{1/2} \text{ for the metric system, and}$$

$$85.49 \frac{\text{ft}}{\text{s}} \left[\frac{(\text{lb/lb-mole})(\text{in. Hg})}{(^{\circ}\text{R})(\text{in. H}_2\text{O})} \right]^{1/2} \text{ for the English system}$$

M_d = Molecular weight of stack gas, dry basis, g/g-mole
(lb/lb-mole)

M_s = Molecular weight of stack gas, wet basis, g/g-mole
(lb/lb-mole), or

$$M_d(1 - B_{ws}) + 18.0 B_{ws} \quad \text{Equation 6-1}$$

Δp = Velocity head of stack gas, mm (in.) H_2O

P_{bar} = Barometric pressure at measurement site, mm (in.) Hg

P_g = Stack static pressure, mm (in.) Hg

P_s = Absolute stack gas pressure, mm (in.) Hg, or

$$P_{\text{bar}} + P_g \quad \text{Equation 6-2}$$

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

Q_{std} = Dry volumetric stack gas flow rate corrected to standard conditions, dsm^3/h (dscf/h)

t_s = Stack temperature, $^{\circ}\text{C}$ ($^{\circ}\text{F}$)

T_s = Absolute stack temperature, K ($^{\circ}\text{R}$), or

$$273 + t_s \text{ for metric system} \quad \text{Equation 6-3}$$

$$460 + t_s \text{ for English system} \quad \text{Equation 6-4}$$

T_{std} = Standard absolute temperature, 293K (528 $^{\circ}\text{R}$)

v_s = Average stack gas velocity, m/s (ft/s)

3600 = Conversion factor, s/h

18.0 = Molecular weight of water, g/g-mole (lb/lb-mole)

6.2 Calculations

The following are the equations used to calculate the stack gas velocity and the volumetric flow rate.

6.2.1 Average Stack Gas Velocity - Equation 6-5 is used to calculate the average stack gas velocity at stack conditions.

$$v_s = K_p C_p (\sqrt{\Delta p})_{avg} \sqrt{\frac{(T_s)_{avg}}{P_s M_s}} \quad \text{Equation 6-5}$$

This equation assumes that T_s , P_s , and M_s do not change appreciably (i.e., <1%) with cross-sectional distance and with time. If they do, consult the administrator to determine an acceptable procedure.

The $(\sqrt{\Delta p})_{avg}$ term is the average square root of each individual velocity head (Δp). Additionally, it should be noted here that to be technically correct the term $(\sqrt{T_s})_{avg}$ should be used. However, since T_s is large, (usually $\geq 289K$ ($515^\circ R$)), the term $\sqrt{(T_s)_{avg}}$ can be used with <1% error if the range of t_s is not $\geq 10^\circ C$ ($50^\circ F$).

6.2.2 Average Stack Gas Dry Volumetric Flow Rate - Calculate Q_{std} using Equation 6-6,

$$Q_{std} = 3600(1 - B_{ws})v_s A \left(\frac{T_{std}}{(T_s)_{avg}} \right) \left(\frac{P_s}{P_{std}} \right) \quad \text{Equation 6-6}$$

Table 6.1 ACTIVITY MATRIX FOR CALCULATION CHECKS

Characteristic	Acceptance limits	Frequency and method of measurement	Action if requirements are not met
Data analysis form	All data and calculations given	Visually check	Complete the missing data values
Calculations	Difference between check and original calculations within round-off error; at least one decimal figure retained beyond that of acquired data	Repeat all calculations, starting with raw data for hand calculations; check all raw data input to computer calculations; hand calculate one sample per test	Indicate errors on analysis data form

7.0 MAINTENANCE

The normal use of emission testing equipment subjects it to corrosive gases, extremes in temperature, vibrations, and shocks. Keeping the equipment in good operating order over an extended period of time requires a knowledge of the equipment and a program of routine maintenance which is performed quarterly. Maintenance procedures for the various components are summarized in Table 7.1 below.

The following procedures are not required, but are recommended to increase the reliability of the equipment.

7.1 Pitot Tube

The pitot tube should be checked for dents, corrosion, and dirt that may cause a complete restriction of pressure or cause a leak in the system.

7.2 Inclined Manometer

The fluid in the inclined manometer should be changed whenever there is discoloration or visible matter in the fluid, and during the yearly disassembly. No other routine maintenance is required since the inclined manometers will be leak checked during both the leak check of the pitot tube and the leak check of the entire control console.

Table 7.1 ACTIVITY MATRIX FOR EQUIPMENT MAINTENANCE CHECKS

Apparatus	Acceptance limits	Frequency and method of measurement	Action if requirements are not met
Pitot tube	Check for dents, corrosion, other damage, or broken welds	Visually check before and after each test run	Use another pitot tube or clean, repair, and calibrate
Inclined manometer	No discoloration or visible matter in the fluid	Check periodically during disassembly	Replace parts as needed

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 those used by the regular field crew. 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 activities for auditing, and Figure 8.1 suggest a checklist for the auditor.

Based on the results of a collaborative test of Method 2,² two specific performance audits are recommended:

1. Audit of the measurement phase of Method 2, and
2. Audit of data processing.

In addition to these performance audits, a systems audit may be conducted as specified by the quality assurance coordinator. The performance audits and the systems audit are described in Subsections 8.1 and 8.2, respectively.

8.1 Performance Audits

Performance audits quantitatively evaluate the quality of data produced by the total measurement system (sample collection, data processing, etc.). 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.

8.1.1 Audit of Measurement Systems - A performance audit should be performed on the geometric standards for the Type S pitot tube, as described in Section 3.1.1.

8.1.2 Audit of Data Processing - Calculation errors are prevalent in Method 2. Data processing errors can be determined by auditing the data recorded on the field and laboratory forms.

The original and audit (check) calculations should agree within roundoff; 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 occur 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, 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--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 in the following:

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 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. Determining stack dimensions and selecting the number and position of traverse points.

2. Checking the geometry criteria in the field using the devices described in the calibration section.
3. Marking the pitot tube to ensure measurements at the correct traverse points.
4. Checking for cyclonic flow.
5. Aligning the pitot tube properly along its roll and pitch axes throughout the velocity traverse.
6. Clearing the pitot tube frequently when measuring in a dust-laden gas.
7. Leak checking the sample apparatus.

Yes	No	Operation
		<u>Presampling preparation</u>
<input checked="" type="checkbox"/>	<input type="checkbox"/>	1. Knowledge of process conditions
<input checked="" type="checkbox"/>	<input type="checkbox"/>	2. Calibration of pertinent equipment prior to each field tests
		<u>On-site measurements</u>
<input checked="" type="checkbox"/>	<input type="checkbox"/>	3. Pitot tube meets geometry requirements
<input checked="" type="checkbox"/>	<input type="checkbox"/>	4. Manometer should be carefully leveled and the liquid column set exactly on zero
<input checked="" type="checkbox"/>	<input type="checkbox"/>	5. Check for cyclonic flow
<input checked="" type="checkbox"/>	<input type="checkbox"/>	6. Leak check after sample run
<input checked="" type="checkbox"/>	<input type="checkbox"/>	7. Sampling port adequately plugged
<input checked="" type="checkbox"/>	<input type="checkbox"/>	8. Process at correct operating level
<input checked="" type="checkbox"/>	<input type="checkbox"/>	9. Pitot tube properly aligned along its roll and pitch axes throughout the traverse
<input checked="" type="checkbox"/>	<input type="checkbox"/>	10. Pitot tube frequently cleared when measuring in a dust-laden gas
<input checked="" type="checkbox"/>	<input type="checkbox"/>	11. Manometer has the correct sensitivity
<input checked="" type="checkbox"/>	<input type="checkbox"/>	12. Staying at each traverse point long enough for the system to stabilize
<input checked="" type="checkbox"/>	<input type="checkbox"/>	13. Measuring the stack gas static pressure and temperature
		<u>Postsampling</u>
<input checked="" type="checkbox"/>	<input type="checkbox"/>	14. All information recorded on data form as obtained
<input checked="" type="checkbox"/>	<input type="checkbox"/>	15. Any unusual conditions recorded
<input checked="" type="checkbox"/>	<input type="checkbox"/>	16. Independent check of calculations
<input checked="" type="checkbox"/>	<input type="checkbox"/>	17. Temperature sensor calibrated
COMMENTS		

Figure 8.1 Stack gas velocity and volumetric flow rate determination checklist to be used by auditor.

Table 8.1 ACTIVITY MATRIX FOR AUDITING PROCEDURE

Audit	Acceptance limits	Frequency and method of measurement	Action if requirements are not met
Data processing errors	Original and check calculations agree within roundoff error	Once during every enforcement source test, perform independent calculations, starting with recorded data	Check and correct all data for the source test
Systems audit	Operation technique described in this section of the Handbook	Once during every enforcement test until experience gained; then every fourth test; observation of technique, assisted by audit checklist, Fig 8.1	Explain to team its deviations from recommended techniques, and note on Fig 8.1

9.0 RECOMMENDED STANDARDS FOR ESTABLISHING TRACEABILITY

To achieve data of desired quality, two considerations are necessary: (1) the measurement process must be in a state of statistical control at the time of the measurement, and (2) the systematic errors, when combined with the random variation (errors of measurement), must result in a small uncertainty.

To ensure good quality data, it is necessary to perform quality control checks and independent audits of the measurement process; to document these checks and audits by recording the results, as appropriate; and to use materials, instruments, and measurement procedures that can be traced to an appropriate standard of reference.

Working calibration standards should be traceable to standards that are considered to be primary. Two primary standards recommended for establishing traceability are:

1. Calibrate pitot tubes against a standard pitot tube with a known coefficient obtained from the National Bureau of Standards or standard measurement which has been shown to have given acceptable coefficients.

2. Compare the stack temperature sensor to an ASTM reference thermometer.

10.0 REFERENCE METHOD^{*}

METHOD 2—DETERMINATION OF STACK GAS VELOCITY AND VOLUMETRIC FLOW RATE (TYPE S PITOT TUBE)

1. Principle and Applicability

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

1.2 Applicability. This method is applicable for measurement of the average velocity of a gas stream and for quantifying gas flow.

This procedure is not applicable at measurement sites which fail to meet the criteria of Method 1, Section 2.1. Also, the method cannot be used for direct measurement in cyclonic or swirling gas streams. Section 2.4 of Method 1 shows how to determine cyclonic or swirling flow conditions. When unacceptable conditions exist, alternative procedures, subject to the approval of the Administrator, U.S. Environmental Protection Agency, must be employed to make accurate flow rate determinations; examples of such alternative procedures are: (1) to install straightening vanes, (2) to calculate the total volumetric flow rate stoichiometrically, or (3) to move to another measurement site at which the flow is acceptable.

2. Apparatus

Specifications for the apparatus are given below. Any other apparatus that has been demonstrated (subject to approval of the Administrator) to be capable of meeting the specifications will be considered acceptable.

^{*} Taken from the Federal Register, Vol. 42, No. 160--Thursday, August 18, 1977, pp.41758-41768.

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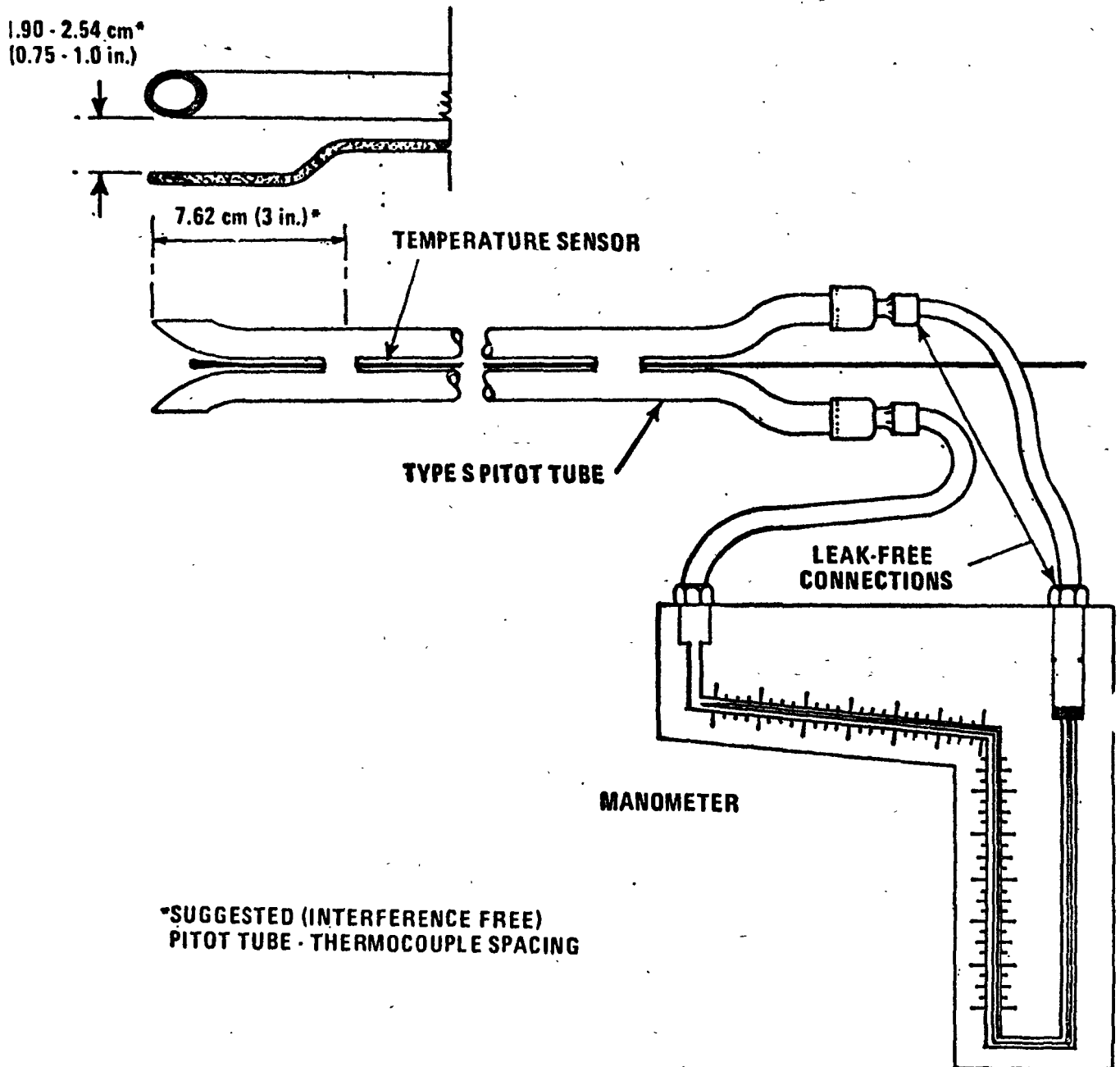


Figure 2-1. Type S pitot tube manometer assembly.

2.1 Type S Pitot Tube. The Type S pitot tube (Figure 2-1) shall be made of metal tubing (e.g., stainless steel). It is recommended that the external tubing diameter (dimension D , Figure 2-2b) be between 0.48 and 0.95 centimeters ($\frac{3}{16}$ and $\frac{3}{8}$ inch). There shall be an equal distance from the base of each leg of the pitot tube to its face-opening plane (dimensions P_1 and P_2 , Figure 2-2b); it is recommended that this distance be between 1.05 and 1.50 times the external tubing diameter. The face openings of the pitot tube shall, preferably, be aligned as shown in Figure 2-2; however, slight misalignments of the openings are permissible (see Figure 2-3). The Type S pitot tube shall have a known coefficient, determined as outlined in Section 4. An identification number shall be assigned to the pitot tube; this number shall be permanently marked or engraved on the body of the tube.

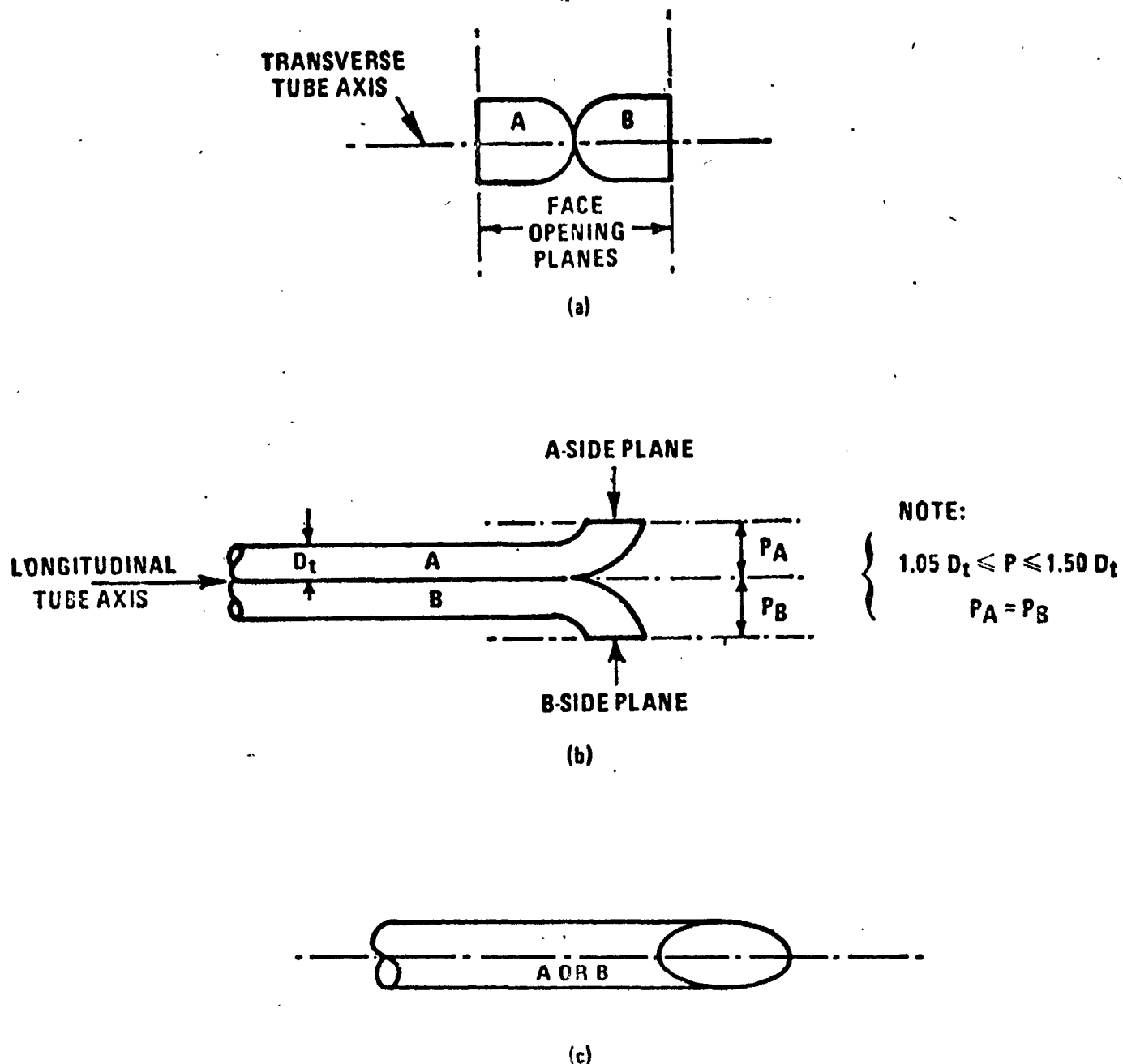


Figure 2-2. Properly constructed Type S pitot tube, shown in: (a) end view; face opening planes perpendicular to transverse axis; (b) top view; face opening planes parallel to longitudinal axis; (c) side view; both legs of equal length and centerlines coincident, when viewed from both sides. Base-line coefficient values of 0.84 may be assigned to pitot tubes constructed this way.

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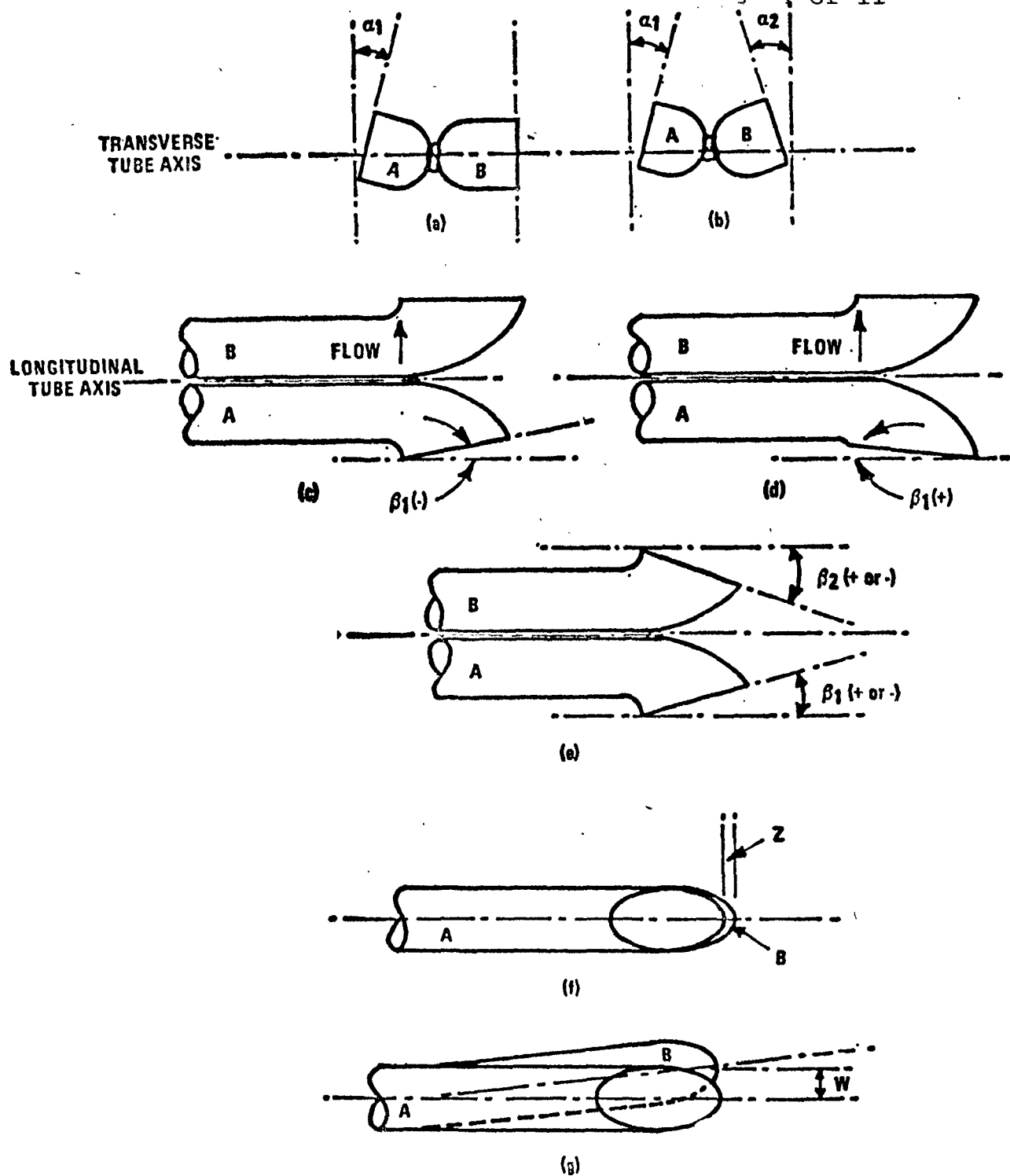


Figure 2-3. Types of face-opening misalignment that can result from field use or improper construction of Type S pitot tubes. These will not affect the baseline value of $\bar{C}_p(s)$ so long as α_1 and $\alpha_2 < 10^\circ$, β_1 and $\beta_2 < 5^\circ$, $z < 0.32 \text{ cm}$ (1/8 in.) and $w < 0.09 \text{ cm}$ (1/32 in.) (citation 11 in Section 6).

A standard pitot tube may be used instead of a Type 8, provided that it meets the specifications of Sections 2.7 and 4.2; note, however, that the static and impact pressure holes of standard pitot tubes are susceptible to plugging in particulate-laden gas streams. Therefore, whenever a standard pitot tube is used to perform a traverse, adequate proof must be furnished that the openings of the pitot tube have not plugged up during the traverse period; this can be done by taking a velocity head (Δp) reading at the final traverse point, cleaning out the impact and static holes of the standard pitot tube by "back-purging" with pressurized air, and then taking another Δp reading. If the Δp readings made before and after the air purge are the same (± 5 percent), the traverse is acceptable. Otherwise, reject the run. Note that if Δp at the final traverse point is unsuitably low, another point may be selected. If "back-purging" at regular intervals is part of the procedure, then comparative Δp readings shall be taken, as above, for the last two back purges at which suitably high Δp readings are observed.

2.2 Differential Pressure Gauge. An inclined manometer or equivalent device is used. Most sampling trains are equipped with a 10-in. (water column) inclined-vertical manometer, having 0.01-in. H_2O divisions on the 0- to 1-in. inclined scale, and 0.1-in. H_2O divisions on the 1- to 10-in. vertical scale. This type of manometer (or other gauge of equivalent sensitivity) is satisfactory for the measurement of Δp values as low as 1.3 mm (0.05 in.) H_2O . However, a differential pressure gauge of greater sensitivity shall be used (subject to the approval of the Administrator), if any of the following is found to be true: (1) the arithmetic average of all Δp readings at the traverse points in the stack is less than 1.3 mm (0.05 in.) H_2O ; (2) for traverses of 12 or more points, more than 10 percent of the individual Δp readings are below 1.3 mm (0.05 in.) H_2O ; (3) for traverses of fewer than 12 points, more than one Δp reading is below 1.3 mm (0.05 in.) H_2O . Citation 18 in Section 6 describes commercially available instrumentation for the measurement of low-range gas velocities.

As an alternative to criteria (1) through (3) above, the following calculation may be performed to determine the necessity of using a more sensitive differential pressure gauge:

$$T = \frac{\sum_{i=1}^n \sqrt{\Delta p_i + K}}{\sum_{i=1}^n \sqrt{\Delta p_i}}$$

where:

Δp_i = Individual velocity head reading at a traverse point, mm H_2O (in. H_2O).

n = Total number of traverse points.

K = 0.13 mm H_2O when metric units are used and 0.005 in. H_2O when English units are used.

If T is greater than 1.05, the velocity head data are unacceptable and a more sensitive differential pressure gauge must be used.

NOTE.—If differential pressure gauges other than inclined manometers are used (e.g., magnelic gauges), their calibration must be checked after each test series. To check the calibration of a differential pressure gauge, compare Δp readings of the gauge with those of a gauge-oil manometer at a minimum of three points, approximately representing the range of Δp values in the stack. If, at each point, the values of Δp as read by the differential pressure gauge and gauge-oil manometer agree to within 5 percent, the differential pressure gauge shall be considered to be in proper calibration. Otherwise, the test series shall either be voided, or procedures to adjust the measured Δp values and final results shall be used, subject to the approval of the Administrator.

2.3 Temperature Gauge. A thermocouple, liquid-filled bulb thermometer, bimetallic thermometer, mercury-in-glass thermometer, or other gauge capable of measuring temperature to within 1.5 percent of the minimum absolute stack temperature shall be used. The temperature gauge shall be attached to the pitot tube such that the sensor tip does not touch any metal; the gauge shall be in an interference-free arrangement with respect to the pitot tube face openings (see Figure 2-1 and also Figure 2-7 in Section 4). Alternate positions may be used if the pitot tube-temperature gauge system is calibrated according to the procedure of Section 4. Provided that a difference of not more than 1 percent in the average velocity measurement is introduced, the tem-

perature gauge need not be attached to the pitot tube; this alternative is subject to the approval of the Administrator.

2.4 Pressure Probe and Gauge. A piezometer tube and mercury- or water-filled U-tube manometer capable of measuring stack pressure to within 2.5 mm (0.1 in.) Hg is used. The static tap of a standard type pitot tube or one leg of a Type X pitot tube with the face opening planes positioned parallel to the gas flow may also be used as the pressure probe.

2.5 Barometer. A mercury, aneroid, or other barometer capable of measuring atmospheric pressure to within 2.5 mm Hg (0.1 in. Hg) may be used. 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 the sampling point shall be applied at a rate of minus 2.5 mm (0.1 in.) Hg per 30-meter (100 foot) elevation increase, or vice-versa for elevation decrease.

2.6 Gas Density Determination Equipment. Method 3 equipment, if needed (see Section 3.6), to determine the stack gas dry molecular weight, and Reference Method 4 or Method 5 equipment for moisture content determination; other methods may be used subject to approval of the Administrator.

2.7 Calibration Pitot Tube. When calibration of the Type 8 pitot tube is necessary (see Section 4), a standard pitot tube is used as a reference. The standard pitot tube shall, preferably, have a known coefficient, obtained either (1) directly from the National Bureau of Standards, Route 270, Quince Orchard Road, Gaithersburg,

Maryland, or (2) by calibration against another standard pitot tube with an NBS-traceable coefficient. Alternatively, a standard pitot tube designed according to the criteria given in 2.7.1 through 2.7.5 below and illustrated in Figure 2-4 (see also Citations 7, 8, and 17 in Section 6) may be used. Pitot tubes designed according to these specifications will have baseline coefficients of about 0.99 ± 0.01 .

2.7.1 Hemispherical (shown in Figure 2-4), ellipsoidal, or conical tip.

2.7.2 A minimum of six diameter's straight run (based upon D , the external diameter of the tube) between the tip and the static pressure holes.

2.7.3 A minimum of eight diameter's straight run between the static pressure holes and the centerline of the external tube, following the 90 degree bend.

2.7.4 Static pressure holes of equal size (approximately 0.1 D), equally spaced in a piezometer ring configuration.

2.7.5 Ninety degree bend, with curved or mitered junction.

2.8 Differential Pressure Gauge for Type 8 Pitot Tube Calibration. An inclined manometer or equivalent is used. If the single-velocity calibration technique is employed (see Section 4.1.2.3), the calibration differential pressure gauge shall be readable to the nearest 0.13 mm H_2O (0.005 in. H_2O). For multiveLOCITY calibrations, the gauge shall be readable to the nearest 0.13 mm H_2O (0.005 in. H_2O) for Δp values between 1.3 and 25 mm H_2O (0.05 and 1.0 in. H_2O), and to the nearest 1.3 mm H_2O (0.05 in. H_2O) for Δp values above 25 mm H_2O (1.0 in. H_2O). A special, more sensitive gauge will be required to read Δp values below 1.3 mm H_2O [0.05 in. H_2O] (see Citation 18 in Section 6).

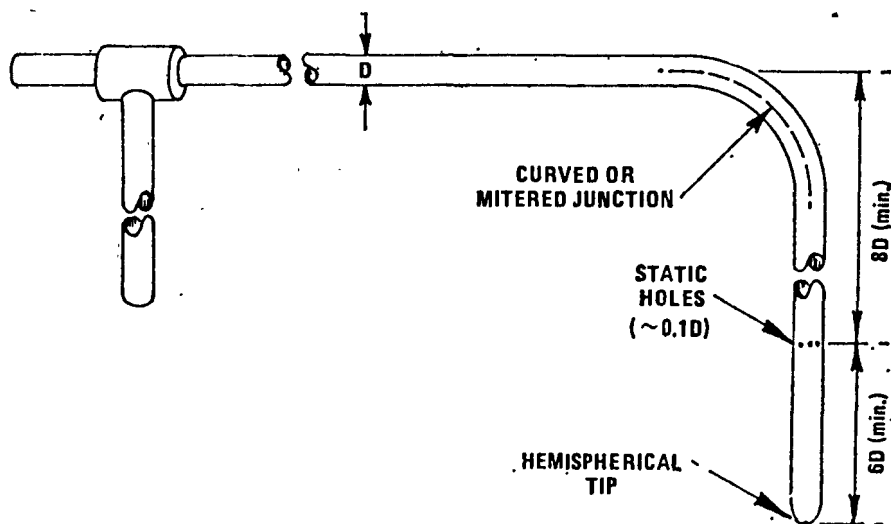


Figure 2-4. Standard pitot tube design specifications.

3. Procedure

3.1 Set up the apparatus as shown in Figure 2-1. Capillary tubing or surge tanks installed between the manometer and pitot tube may be used to dampen Δp fluctuations. It is recommended, but not required, that a pretest leak-check be conducted, as follows: (1) blow through the pitot impact opening until at least 7.6 cm (3 in.) H_2O velocity pressure registers on the manometer; then, close off the impact opening. The pressure shall remain stable for at least 15 seconds; (2) do the same for the static pressure side, except using suction to obtain the minimum of 7.6 cm (3 in.) H_2O . Other leak-check procedures, subject to the approval of the Administrator, may be used.

3.2 Level and zero the manometer. Because the ma-

nometer level and zero may drift due to vibrations and temperature changes, make periodic checks during the traverse. Record all necessary data as shown in the example data sheet (Figure 2-5).

3.3 Measure the velocity head and temperature at the traverse points specified by Method 1. Ensure that the proper differential pressure gauge is being used for the range of Δp values encountered (see Section 2.2). If it is necessary to change to a more sensitive gauge, do so, and remeasure the Δp and temperature readings at each traverse point. Conduct a post-test leak-check (mandatory), as described in Section 3.1 above, to validate the traverse run.

3.4 Measure the static pressure in the stack. One reading is usually adequate.

3.5 Determine the atmospheric pressure.

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[illegible]

Figure 2-5. Velocity traverse data.

3.6 Determine the stack gas dry molecular weight. For combustion processes or processes that emit essentially CO_2 , O_2 , CO , and N_2 , use Method 3. For processes emitting essentially air, an analysis need not be conducted; use a dry molecular weight of 29.0. For other processes, other methods, subject to the approval of the Administrator, must be used.

3.7 Obtain the moisture content from Reference Method 4 (or equivalent) or from Method 5.

3.8 Determine the cross-sectional area of the stack or duct at the sampling location. Whenever possible, physically measure the stack dimensions rather than using blueprints.

4. Calibration

4.1 Type S Pitot Tube. Before its initial use, carefully examine the Type S pitot tube in top, side, and end views to verify that the face openings of the tube are aligned within the specifications illustrated in Figure 2-3 or 2-3. The pitot tube shall not be used if it fails to meet these alignment specifications.

After verifying the face opening alignment, measure and record the following dimensions of the pitot tube:

(a) the external tubing diameter (dimension D_t , Figure 2-2b); and (b) the base-to-opening plane distances (dimensions P_A and P_B , Figure 2-2b). If D_t is between 0.48 and 0.95 cm ($\frac{3}{16}$ and $\frac{3}{8}$ in.) and if P_A and P_B are equal and between 1.05 and 1.50 R_t , there are two possible options: (1) the pitot tube may be calibrated according to the procedure outlined in Sections 4.1.2 through 4.1.5 below, or (2) a baseline (isolated tube) coefficient value of 0.84 may be assigned to the pitot tube. Note, however, that if the pitot tube is part of an assembly, calibration may still be required, despite knowledge of the baseline coefficient value (see Section 4.1.1).

If D_t , P_A , and P_B are outside the specified limits, the pitot tube must be calibrated as outlined in 4.1.2 through 4.1.5 below.

4.1.1 Type S Pitot Tube Assemblies. During sample and velocity traverses, the isolated Type S pitot tube is not always used; in many instances, the pitot tube is used in combination with other source-sampling components (thermocouple, sampling probe, nozzle) as part of an "assembly." The presence of other sampling components can sometimes affect the baseline value of the Type S pitot tube coefficient (Citation 9 in Section 6); therefore an assigned (or otherwise known) baseline coefficient

value may or may not be valid for a given assembly. The baseline and assembly coefficient values will be identical only when the relative placement of the components in the assembly is such that aerodynamic interference effects are eliminated. Figures 2-6 through 2-8 illustrate interference-free component arrangements for Type S pitot tubes having external tubing diameters between 0.48 and 0.95 cm ($\frac{3}{16}$ and $\frac{3}{8}$ in.). Type S pitot tube assemblies that fail to meet any or all of the specifications of Figures 2-6 through 2-8 shall be calibrated according to the procedure outlined in Sections 4.1.2 through 4.1.5 below, and prior to calibration, the values of the inter-component spacings (pitot-nozzle, pitot-thermocouple, pitot-probe sheath) shall be measured and recorded.

Note.—Do not use any Type S pitot tube assembly which is constructed such that the impact pressure opening plane of the pitot tube is below the entry plane of the nozzle (see Figure 2-6b).

4.1.2 Calibration Setup. If the Type S pitot tube is to be calibrated, one leg of the tube shall be permanently marked A, and the other, 3. Calibration shall be done in a flow system having the following essential design features:

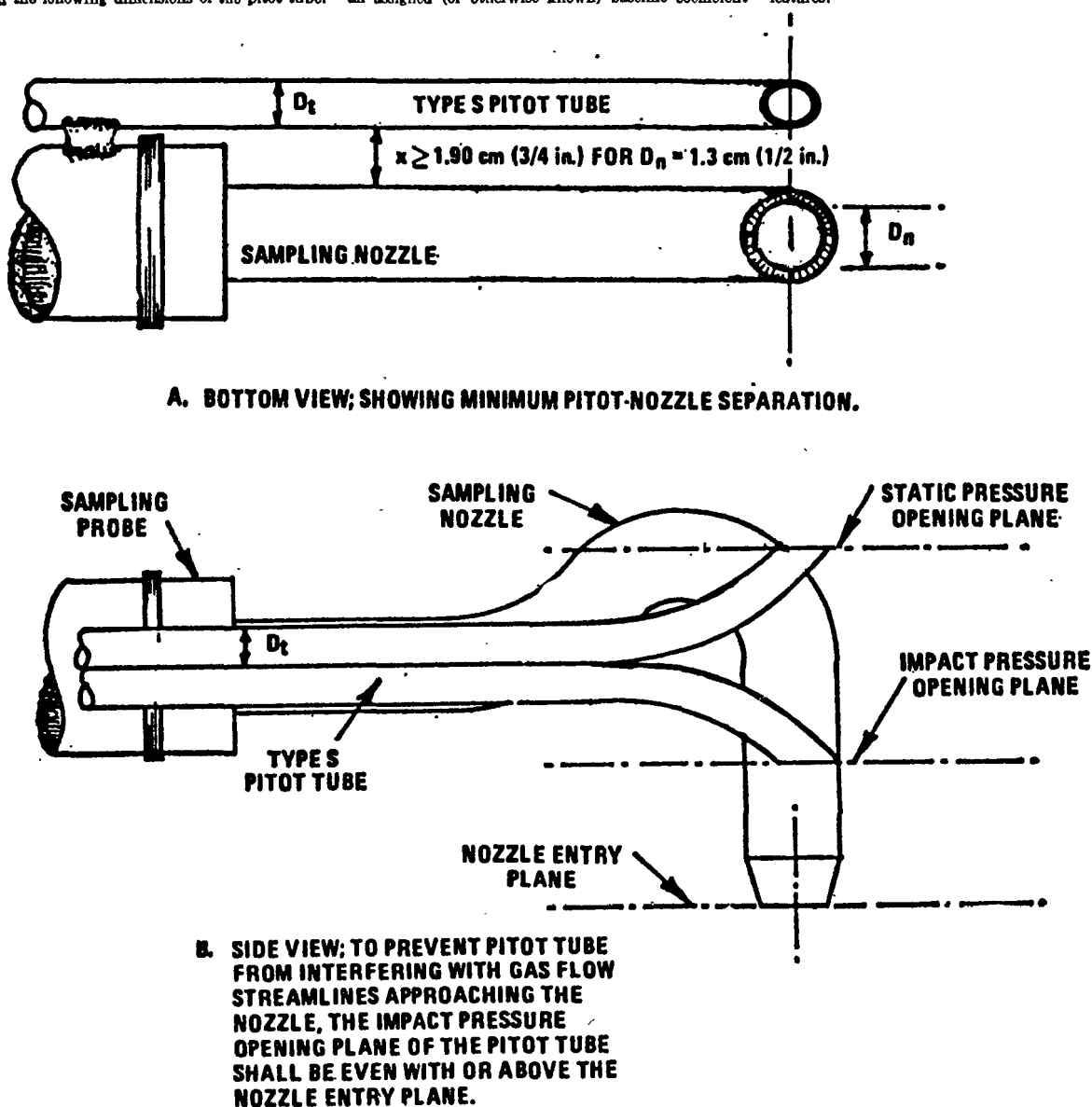


Figure 2-6. Proper pitot tube - sampling nozzle configuration to prevent aerodynamic interference; buttonhook - type nozzle; centers of nozzle and pitot opening aligned; D_t between 0.48 and 0.95 cm ($\frac{3}{16}$ and $\frac{3}{8}$ in.).

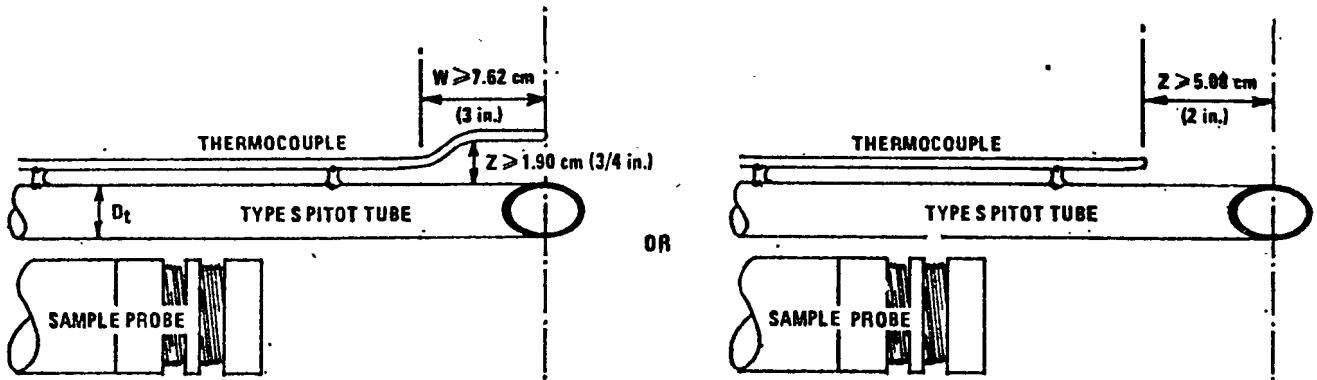


Figure 2-7. Proper thermocouple placement to prevent interference; D_t between 0.48 and 0.95 cm (3/16 and 3/8 in.).

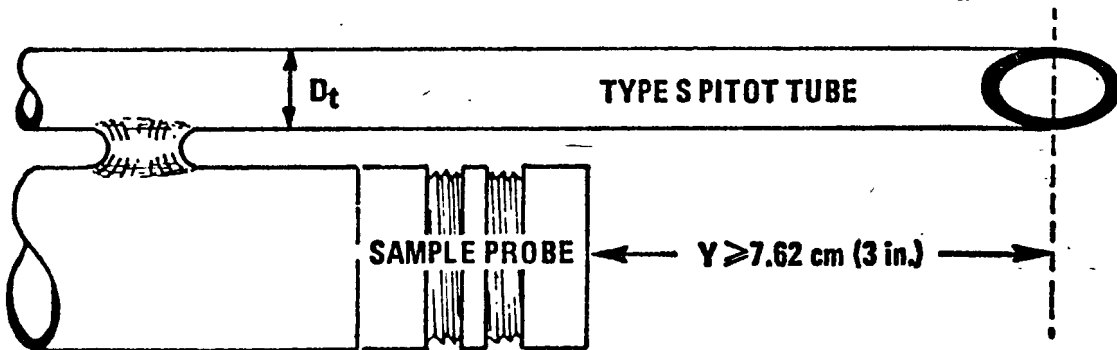


Figure 2-8. Minimum pitot-sample probe separation needed to prevent interference; D_t between 0.48 and 0.95 cm (3/16 and 3/8 in.).

4.1.2.1 The flowing gas stream must be confined to a duct of definite cross-sectional area, either circular or rectangular. For circular cross-sections, the minimum duct diameter shall be 30.5 cm (12 in.); for rectangular cross-sections, the width (shorter side) shall be at least 25.4 cm (10 in.).

4.1.2.2 The cross-sectional area of the calibration duct must be constant over a distance of 10 or more duct diameters. For a rectangular cross-section, use an equivalent diameter, calculated from the following equation, to determine the number of duct diameters.

$$D_e = \frac{2LW}{(L+W)}$$

Equation 2-1

where:

D_e = Equivalent diameter
 L = Length
 W = Width

To ensure the presence of stable, fully developed flow patterns at the calibration site, or "test section," the site must be located at least eight diameters downstream and two diameters upstream from the nearest disturbances.

NOTE.—The eight- and two-diameter criteria are not absolute; other test section locations may be used (subject to approval of the Administrator), provided that the flow at the test site is stable and demonstrably parallel to the duct axis.

4.1.2.3 The flow system shall have the capacity to generate a test-section velocity around 915 m/min (3,000

ft/min). This velocity must be constant with time to guarantee steady flow during calibration. Note that Type S pitot tube coefficients obtained by single-velocity calibration at 915 m/min (3,000 ft/min) will generally be valid to within ± 3 percent for the measurement of velocities above 305 m/min (1,000 ft/min) and to within ± 5 to 6 percent for the measurement of velocities between 180 and 305 m/min (600 and 1,000 ft/min). If a more precise correlation between C_p and velocity is desired, the flow system shall have the capacity to generate at least four distinct, time-invariant test-section velocities covering the velocity range from 180 to 1,525 m/min (600 to 5,000 ft/min), and calibration data shall be taken at regular velocity intervals over this range (see Citations 9 and 14 in Section 6 for details).

4.1.2.4 Two entry ports, one each for the standard and Type S pitot tubes, shall be cut in the test section; the standard pitot entry port shall be located slightly downstream of the Type S port, so that the standard and Type S impact openings will lie in the same cross-sectional plane during calibration. To facilitate alignment of the pitot tubes during calibration, it is advisable that the test section be constructed of plexiglas or some other transparent material.

4.1.3 Calibration Procedure. Note that this procedure is a general one and must not be used without first referring to the special considerations presented in Section 4.1.5. Note also that this procedure applies only to single-velocity calibration. To obtain calibration data for the A and B sides of the Type S pitot tube, proceed as follows:

4.1.3.1 Make sure that the manometer is properly filled and that the oil is free from contamination and is of the proper density. Inspect and leak-check all pitot lines; repair or replace if necessary.

4.1.3.2 Level and zero the manometer. Turn on the fan and allow the flow to stabilize. Seal the Type S entry port.

4.1.3.3 Ensure that the manometer is level and zeroed. Position the standard pitot tube at the calibration point (determined as outlined in Section 4.1.5.1), and align the tube so that its tip is pointed directly into the flow. Particular care should be taken in aligning the tube to avoid yaw and pitch angles. Make sure that the entry port surrounding the tube is properly sealed.

4.1.3.4 Read Δp_{std} and record its value in a data table similar to the one shown in Figure 2-9. Remove the standard pitot tube from the duct and disconnect it from the manometer. Seal the standard entry port.

4.1.3.5 Connect the Type S pitot tube to the manometer. Open the Type S entry port. Check the manometer level and zero. Insert and align the Type S pitot tube so that its A side impact opening is at the same point as was the standard pitot tube and is pointed directly into the flow. Make sure that the entry port surrounding the tube is properly sealed.

4.1.3.6 Read Δp_s and enter its value in the data table. Remove the Type S pitot tube from the duct and disconnect it from the manometer.

4.1.3.7 Repeat steps 4.1.3.3 through 4.1.3.6 above until three pairs of Δp readings have been obtained.

4.1.3.8 Repeat steps 4.1.3.3 through 4.1.3.7 above for the B side of the Type S pitot tube.

4.1.3.9 Perform calculations, as described in Section 4.1.4 below.

4.1.4 Calculations.

4.1.4.1 For each of the six pairs of Δp readings (i.e., three from side A and three from side B) obtained in Section 4.1.3 above, calculate the value of the Type S pitot tube coefficient as follows:

PITOT TUBE IDENTIFICATION NUMBER: _____ DATE: _____
 CALIBRATED BY: _____

"A" SIDE CALIBRATION				
RUN NO.	ΔP_{std} cm H ₂ O (in. H ₂ O)	$\Delta P(s)$ cm H ₂ O (in. H ₂ O)	$C_p(s)$	DEVIATION $C_p(s) - \bar{C}_p(A)$
1				
2				
3				
			\bar{C}_p (SIDE A)	

"B" SIDE CALIBRATION				
RUN NO.	ΔP_{std} cm H ₂ O (in. H ₂ O)	$\Delta P(s)$ cm H ₂ O (in. H ₂ O)	$C_p(s)$	DEVIATION $C_p(s) - \bar{C}_p(B)$
1				
2				
3				
			\bar{C}_p (SIDE B)	

$$\text{AVERAGE DEVIATION} = \sigma \text{ (A OR B)} = \frac{1}{3} \sum_{i=1}^3 |C_p(s) - \bar{C}_p(A \text{ OR } B)| \quad \leftarrow \text{MUST BE } \leq 0.01$$

$$|\bar{C}_p(\text{SIDE A}) - \bar{C}_p(\text{SIDE B})| \quad \leftarrow \text{MUST BE } \leq 0.01$$

Figure 2-9. Pitot tube calibration data.

$$C_{p(s)} = C_{p(std)} \sqrt{\frac{\Delta P_{std}}{\Delta P_s}}$$

Equation 2-2

where:

 $C_{p(s)}$ = Type S pitot tube coefficient $C_{p(std)}$ = Standard pitot tube coefficient; use 0.99 if the coefficient is unknown and the tube is designed

according to the criteria of Sections 2.7.1 to 2.7.5 of this method.

 ΔP_{std} = Velocity head measured by the standard pitot tube, cm H₂O (in. H₂O) ΔP_s = Velocity head measured by the Type S pitot tube, cm H₂O (in. H₂O)4.1.4.2 Calculate \bar{C}_p (side A), the mean A-side coefficient, and \bar{C}_p (side B), the mean B-side coefficient; calculate the difference between these two average values.
 4.1.4.3 Calculate the deviation of each of the three A-side values of $C_p(s)$ from \bar{C}_p (side A), and the deviation of each B-side value of $C_p(s)$ from \bar{C}_p (side B). Use the following equation:

$$\text{Deviation} = C_{p(s)} - \bar{C}_p(A \text{ or } B)$$

Equation 2-3

 4.1.4.4 Calculate σ , the average deviation from the mean, for both the A and B sides of the pitot tube. Use the following equation:

$$\sigma \text{ (side A or B)} = \frac{\sum_{i=1}^3 |C_{p(s)} - \bar{C}_p(A \text{ or } B)|}{3}$$

Equation 2-4

 4.1.4.5 Use the Type S pitot tube only if the values of σ (side A) and σ (side B) are less than or equal to 0.01 and if the absolute value of the difference between \bar{C}_p (A) and \bar{C}_p (B) is 0.01 or less.

4.1.5 Special considerations.

4.1.5.1 Selection of calibration point.

 4.1.5.1.1 When an isolated Type S pitot tube is calibrated, select a calibration point at or near the center of the duct, and follow the procedures outlined in Sections 4.1.3 and 4.1.4 above. The Type S pitot coefficients so obtained, i.e., \bar{C}_p (side A) and \bar{C}_p (side B), will be valid, so long as either: (1) the isolated pitot tube is used; or (2) the pitot tube is used with other components (nozzle, thermocouple, sample probe) in an arrangement that is free from aerodynamic interference effects (see Figures 2-6 through 2-8).

4.1.5.1.2 For Type S pitot tube-thermocouple combinations (without sample probe), select a calibration point at or near the center of the duct, and follow the procedures outlined in Sections 4.1.3 and 4.1.4 above. The coefficients so obtained will be valid so long as the pitot tube-thermocouple combination is used by itself or with other components in an interference-free arrangement (Figures 2-6 and 2-8).

4.1.5.1.3 For assemblies with sample probes, the calibration point should be located at or near the center of the duct; however, insertion of a probe sheath into a small duct may cause significant cross-sectional area blockage and yield incorrect coefficient values (Citation 9 in Section 6). Therefore, to minimize the blockage effect, the calibration point may be a few inches off-center if necessary. The actual blockage effect will be negligible when the theoretical blockage, as determined by a projected-area model of the probe sheath, is 2 percent or less of the duct cross-sectional area for assemblies without external sheaths (Figure 2-10a), and 3 percent or less for assemblies with external sheaths (Figure 2-10b).

 4.1.5.2 For those probe assemblies in which pitot tube-nozzle interference is a factor (i.e., those in which the pitot-nozzle separation distance fails to meet the specification illustrated in Figure 2-6a), the value of $C_p(s)$ depends upon the amount of free-space between the tube and nozzle, and therefore is a function of nozzle size. In these instances, separate calibrations shall be performed with each of the commonly used nozzle sizes in place. Note that the single-velocity calibration technique is acceptable for this purpose, even though the larger nozzle sizes (>0.635 cm or 1/4 in.) are not ordinarily used for isokinetic sampling at velocities around 915 m/min (3,000 ft/min), which is the calibration velocity; note also that it is not necessary to draw an isokinetic sample during calibration (see Citation 19 in Section 6).

 4.1.5.3 For a probe assembly constructed such that its pitot tube is always used in the same orientation, only one side of the pitot tube need be calibrated (the side which will face the flow). The pitot tube must still meet the alignment specifications of Figure 2-2 or 2-3, however, and must have an average deviation (σ) value of 0.01 or less (see Section 4.1.4.4).

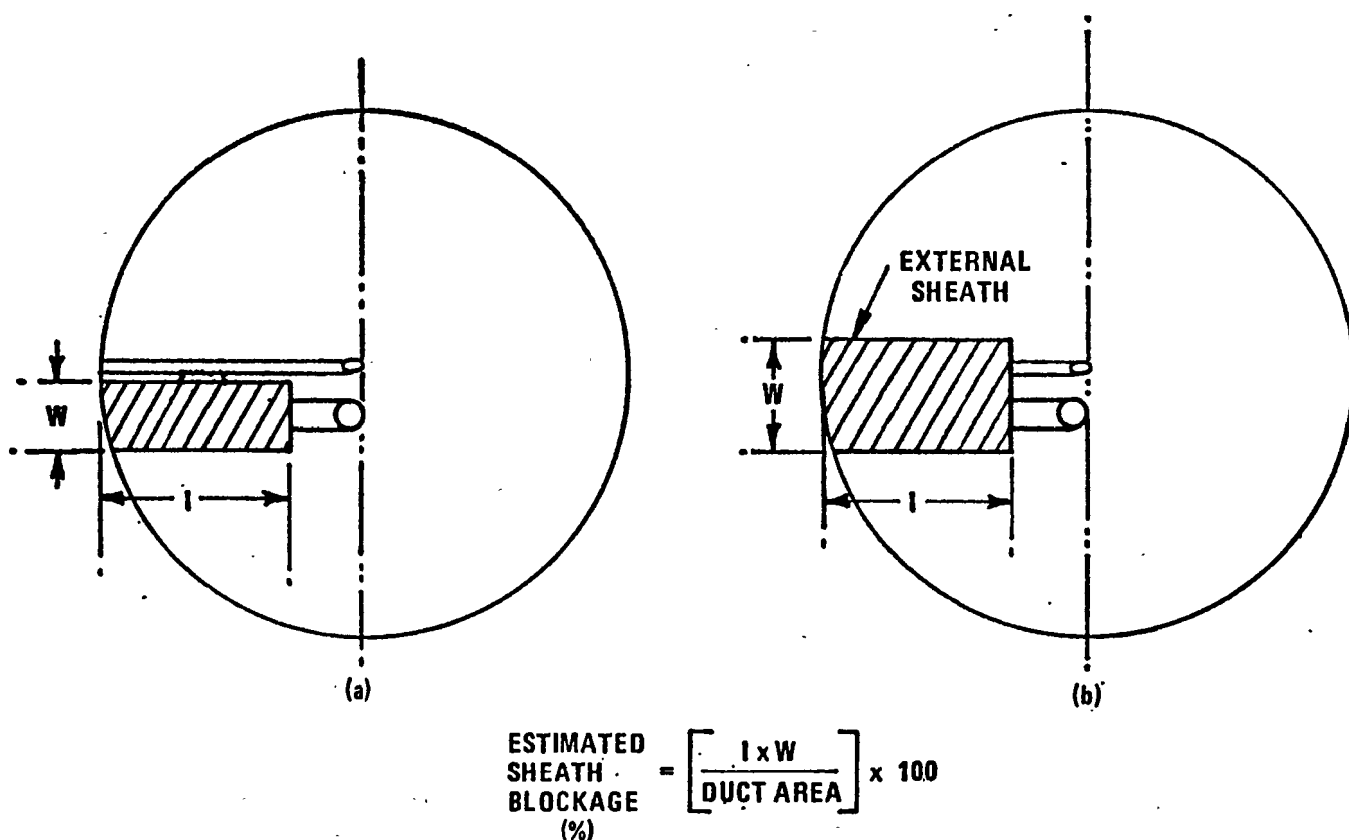


Figure 2-10. Projected-area models for typical pitot tube assemblies.

4.1.6 Field Use and Recalibration.

4.1.6.1 Field Use.

4.1.6.1.1 When a Type S pitot tube (isolated tube or assembly) is used in the field, the appropriate coefficient value (whether assigned or obtained by calibration) shall be used to perform velocity calculations. For calibrated Type S pitot tubes, the A side coefficient shall be used when the A side of the tube faces the flow, and the B side coefficient shall be used when the B side faces the flow; alternatively, the arithmetic average of the A and B side coefficient values may be used, irrespective of which side faces the flow.

4.1.6.1.2 When a probe assembly is used to sample a small duct (12 to 36 in. in diameter), the probe sheath sometimes blocks a significant part of the duct cross-section, causing a reduction in the effective value of C_p . Consult Citation 9 in Section 6 for details. Conventional pitot-sampling probe assemblies are not recommended for use in ducts having inside diameters smaller than 12 inches (Citation 16 in Section 6).

4.1.6.2 Recalibration.

4.1.6.2.1 Isolated Pitot Tubes. After each field use, the pitot tube shall be carefully reexamined in top, side, and end views. If the pitot face openings are still aligned within the specifications illustrated in Figure 2-2 or 2-3, it can be assumed that the baseline coefficient of the pitot tube has not changed. If, however, the tube has been damaged to the extent that it no longer meets the specifications of Figure 2-2 or 2-3, the damage shall either be repaired to restore proper alignment of the face openings or the tube shall be discarded.

4.1.6.2.2 Pitot Tube Assemblies. After each field use, check the face opening alignment of the pitot tube, as in Section 4.1.6.2.1; also, remeasure the intercomponent spacings of the assembly. If the intercomponent spacings have not changed and the face opening alignment is acceptable, it can be assumed that the coefficient of the assembly has not changed. If the face opening alignment is no longer within the specifications of Figures 2-2 or 2-3, either repair the damage or replace the pitot tube (calibrating the new assembly, if necessary). If the intercomponent spacings have changed, restore the original spacings or recalibrate the assembly.

4.2 Standard pitot tube (if applicable). If a standard pitot tube is used for the velocity traverse, the tube shall be constructed according to the criteria of Section 2.7 and shall be assigned a baseline coefficient value of 0.99. If the standard pitot tube is used as part of an assembly,

the tube shall be in an interference-free arrangement (subject to the approval of the Administrator).

4.3 Temperature Gauges. After each field use, calibrate dial thermometers, liquid-filled bulb thermometers, thermocouple-potentiometer systems, and other gauges at a temperature within 10 percent of the average absolute stack temperature. For temperatures up to 405° C (761° F), use an ASTM mercury-in-glass reference thermometer, or equivalent, as a reference; alternatively, either a reference thermocouple and potentiometer (calibrated by NBS) or thermometric fixed points, e.g., ice bath and boiling water (corrected for barometric pressure) may be used. For temperatures above 405° C (761° F), use an NBS-calibrated reference thermocouple-potentiometer system or an alternate reference, subject to the approval of the Administrator.

If, during calibration, the absolute temperatures measured with the gauge being calibrated and the reference gauge agree within 1.5 percent, the temperature data taken in the field shall be considered valid. Otherwise, the pollutant emission test shall either be considered invalid or adjustments (if appropriate) of the test results shall be made, subject to the approval of the Administrator.

4.4 Barometer. Calibrate the barometer used against a mercury barometer.

5. Calculations

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

5.1 Nomenclature.

A = Cross-sectional area of stack, m² (ft²).
B_w = Water vapor in the gas stream (from Method 5 or Reference Method 4), proportion by volume.
C_p = Pitot tube coefficient, dimensionless.
K_p = Pitot tube constant,

$$34.97 \frac{\text{m}}{\text{sec}} \left[\frac{(g/g\text{-mole})(\text{mm Hg})}{(^{\circ}\text{K})(\text{mm H}_2\text{O})} \right]^{1/2}$$

for the metric system and

$$85.49 \frac{\text{ft}}{\text{sec}} \left[\frac{(\text{lb/lb-mole})(\text{in. Hg})}{(^{\circ}\text{R})(\text{in. H}_2\text{O})} \right]^{1/2}$$

for the English system.

M_d = Molecular weight of stack gas, dry basis (see Section 3.6) g/g-mole (lb/lb-mole).

M_w = Molecular weight of stack gas, wet basis, g/g-mole (lb/lb-mole).

$$= M_d (1 - B_w) + 18.0 B_w \quad \text{Equation 2-5}$$

P_{bar} = Barometric pressure at measurement site, mm Hg (in. Hg).

P_s = Stack static pressure, mm Hg (in. Hg).

P_{st} = Absolute stack gas pressure, mm Hg (in. Hg):

$$= P_{bar} + P_s \quad \text{Equation 2-6}$$

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

Q_{sd} = Dry volumetric stack gas flow rate corrected to standard conditions, dscf/hr (dscf/hr).

t_s = Stack temperature, °C (°F).

T_s = Absolute stack temperature, °K (°R).

$$= 273 + t_s \text{ for metric} \quad \text{Equation 2-7}$$

$$= 460 + t_s \text{ for English} \quad \text{Equation 2-8}$$

T_{std} = Standard absolute temperature, 293°K (528°R)

v_s = Average stack gas velocity, m/sec (ft/sec).

Δp = Velocity head of stack gas, mm H₂O (in. H₂O).

3,600 = Conversion factor, sec/hr.

18.0 = Molecular weight of water, g/g-mole (lb-lb-mole).

5.2 Average stack gas velocity.

$$v_s = K_p C_p (\sqrt{\Delta p})_{avg} \sqrt{\frac{T_{s(ave)}}{P_s M_s}}$$

$$\text{Equation 2-9}$$

5.3 Average stack gas dry volumetric flow rate.

$$Q_{sd} = 3,600 (1 - B_{ws}) v_s A \left(\frac{T_{std}}{T_{s(ave)}} \right) \left(\frac{P_s}{P_{std}} \right) \quad \text{Equation 2-10}$$

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12.0 DATA FORMS

Blank data forms are provided on the following pages for the convenience of the Handbook user. Many of these forms are taken or adapted from EPA forms, Reference 1, and other references. No documentation is given on these forms as it would detract from their usefulness. The titles are also placed at the top of the figure as is customary for a data form. In order to relate the form to the text, a form number is given in the lower right-hand corner, e.g., Form M2 - 2.5, indicates that the form is Figure 2.5, the fifth figure in Section 3.1.2, of the written description for Method 2 (M2). Future revisions of these forms, if any, can be documented by 2.5A, 2.5B, etc. Seven of the data forms listed below are included in this section. Four are in the Method Highlights subsection as shown by the (MH) following the form number.

<u>Form</u>	<u>Title</u>
1.2	Example of a Procurement Log
1.7	Type S Pitot Tube Inspection Data Form
2.5	Pitot Tube Calibration Data
2.10	Stack Temperature Sensor Calibration Data Form
2.12	Differential Pressure Gauge Calibration Data Form
3.1 (MH)	Pretest Sampling Checks
3.2 (MH)	Pretest Preparations
4.1	Method 2 Gas Velocity and Volume Data Form
4.2 (MH)	On-Site Measurements Checklist
5.1 (MH)	Posttest Sampling Checks
8.1	Stack Gas Velocity and Volumetric Flow Rate Determination Checklist to be Used by Auditor

PROCUREMENT LOG

Item description	Quantity	Purchase order number	Vendor	Date		Cost	Dispo- sition	Comments
				Ordered	Received			

TYPE S PITOT TUBE INSPECTION DATA FORM

Pitot tube assembly level? _____ yes _____ no

Pitot tube openings damaged? _____ yes (explain below) _____ no

$\alpha_1 =$ _____ $^{\circ}$ ($<10^{\circ}$), $\alpha_2 =$ _____ $^{\circ}$ ($<10^{\circ}$), $\beta_1 =$ _____ $^{\circ}$ ($<5^{\circ}$),

$\beta_2 =$ _____ $^{\circ}$ ($<5^{\circ}$)

$\gamma =$ _____ $^{\circ}$, $\theta =$ _____ $^{\circ}$, $A =$ _____ cm (in.)

$z = A \sin \gamma =$ _____ cm (in.); <0.32 cm ($<1/8$ in.),

$w = A \sin \theta =$ _____ cm (in.); $<.08$ cm ($<1/32$ in.)

P_A _____ cm (in.) P_b _____ cm (in.)

$D_t =$ _____ cm (in.)

Comments: _____

Calibration required? _____ yes _____ no

PITOT TUBE CALIBRATION DATA

Calibration pitot tube: type _____ size (OD) _____ ID number _____

Type S pitot tube ID number _____ $C_{p(Std)}$ = _____

Calibration: date _____ performed by _____

A-Side Calibration

$\Delta p_{std'}$ cm (in.) H_2O	$\Delta p_{S'}$ cm (in.) H_2O	$C_{P(S)}^a$	DEV. ^b
Average			

B-Side Calibration

$\Delta p_{std'}$ cm (in.) H ₂ O	$\Delta p_{s'}$ cm (in.) H ₂ O	$C_{p(S)}^a$	DEV. ^b
Average			

$$a_{C_p(S)} = C_{p(std)} \sqrt{\frac{\Delta p_{std}}{\Delta p_s}} = \underline{\hspace{2cm}}$$

$$b_{DEV} = c_{p(S)} - \bar{c}_p, \text{ (must be } \leq 0.01)$$

$$\bar{C}_p(A) - \bar{C}_p(B) = \underline{\hspace{2cm}} \text{ (must be } \leq 0.01 \text{)}.$$

STACK TEMPERATURE SENSOR CALIBRATION DATA FORM

Date _____ Thermocouple number _____

Ambient temperature _____ °C Barometric pressure _____ in. Hg

Calibrator _____ Reference: mercury-in-glass _____
other _____

Reference point number ^a	Source ^b (specify)	Reference thermometer temperature, °C	Thermocouple potentiometer temperature, °C	Temperature difference, °C %

^aEvery 30°C (50°F) for each reference point.

^bType of calibration system used.

$$C \left[\frac{(\text{ref temp, } ^\circ\text{C} + 273) - (\text{test thermom temp, } ^\circ\text{C} + 273)}{\text{ref temp, } ^\circ\text{C} + 273} \right] 100 \leq 1.5\%.$$

DIFFERENTIAL PRESSURE GAUGE CALIBRATION DATA FORM

Gauge type _____ Serial or ID number _____

Scale _____

Gauge-oil manometer Δp	Differential pressure gauge Δp	Pressure difference %

Calibration: _____ initial _____ posttest

Date calibrated _____ by _____

METHOD 2 GAS VELOCITY AND VOLUME DATA FORM

Plant and city	Run date					

Sampling location	Clock time

Run number	Operator	Amb. temp., °F	Bar. press., in. Hg	Static press., in. H ₂ O

Molecular wt.	Stack inside dimension, in.												Pitot tube (C _p)	
	Diam. of side 1						side 2							

Field data					
Traverse point number	Position, in.	Velocity head (Δp), in. H ₂ O	Stack temp., °F	Cyclonic flow determination	
				Δp_s at 0° reference	Angle (α) which yields a null Δp
Average angle (α) ^a					

^a Average of α must be <10 degrees to be acceptable.

STACK GAS VELOCITY AND VOLUMETRIC FLOW RATE
DETERMINATION CHECKLIST TO BE USED BY AUDITOR

Yes	No	Operation
		<u>Presampling preparation</u>
_____	_____	1. Knowledge of process conditions
_____	_____	2. Calibration of pertinent equipment prior to each field tests
		<u>On-site measurements</u>
_____	_____	3. Pitot tube meets geometry requirements
_____	_____	4. Manometer should be carefully leveled and the liquid column set exactly on zero
_____	_____	5. Check for cyclonic flow
_____	_____	6. Leak check after sample run
_____	_____	7. Sampling port adequately plugged
_____	_____	8. Process at correct operating level
_____	_____	9. Pitot tube properly aligned along its roll and pitch axes throughout the traverse
_____	_____	10. Pitot tube frequently cleared when measuring in a dust-laden gas
_____	_____	11. Manometer has the correct sensitivity
_____	_____	12. Staying at each traverse point long enough for the system to stabilize
_____	_____	13. Measuring the stack gas static pressure and temperature
		<u>Postsampling</u>
_____	_____	14. All information recorded on data form as obtained
_____	_____	15. Any unusual conditions recorded
_____	_____	16. Independent check of calculations
_____	_____	17. Temperature sensor calibrated
COMMENTS		

Section 3.2

METHOD 3 - DETERMINATION OF CARBON DIOXIDE, OXYGEN,
EXCESS AIR, AND DRY MOLECULAR WEIGHT

OUTLINE

<u>Section</u>	<u>Documentation</u>	<u>Number of Pages</u>
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METHOD HIGHLIGHTS	3.2	5
METHOD DESCRIPTION		
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2. CALIBRATION OF APPARATUS	3.2.2	4
3. PRESAMPLING OPERATIONS	3.2.3	6
4. ON-SITE MEASUREMENTS	3.2.4	12
5. POSTSAMPLING OPERATIONS	3.2.5	2
6. CALCULATIONS	3.2.6	3
7. MAINTENANCE	3.2.7	1
8. AUDITING PROCEDURE	3.2.8	5
9. RECOMMENDED STANDARDS FOR ESTABLISHING TRACEABILITY	3.2.9	1
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SUMMARY

In this procedure, a gas sample is extracted from a stack by one of the following methods: single-point grab sampling; single-point integrated sampling; or multipoint integrated sampling. The gas sample is then analyzed for carbon dioxide (CO_2), oxygen (O_2), and if necessary carbon monoxide (CO). Depending on the desired accuracy of the subsequent analysis, either an Orsat or other type of gas absorption analyzer such as a Fyrite⁺ analyzer may be used for the analysis.

This method is used for determining CO_2 and O_2 concentrations $>0.2\%$ by volume and for calculating excess air and the dry molecular weight of gas streams from combustion processes. The method may also be applicable to other processes where it has been determined that compounds other than CO_2 , O_2 , CO , and nitrogen (N_2) are not present in concentrations sufficient to affect the results. Sulfur dioxide (SO_2), for example, can affect CO_2 readings since it would be absorbed with the CO_2 .

Other methods and modifications to measure these constituents include: a multipoint sampling method using an Orsat apparatus to directly analyze individual grab samples obtained at each point; assigning a value of 30.0 for dry molecular weight, in lieu of actual measurements for processes burning natural gas, coal, or oil; or a method using CO_2 or O_2 and stoichiometric calculations to determine dry molecular weight and excess air. These methods and modifications may be used, but are subject to the approval of the administrator, U.S. Environmental Protection Agency.

The Method Description which follows is based on the Reference Method promulgated on August 18, 1977. A complete copy

⁺Mention of trade names or specific products does not constitute endorsement by the Environmental Protection Agency.

of the Reference Method is in Section 3.2.10 of this document, and data forms are provided in Section 3.2.12 for the convenience of the user. Reference 1 was largely used in preparing the Method Description. References 2 through 5 summarize collaborative test studies of the method and other related methods. Data from these test studies are used to the extent possible in establishing quality control limits.

METHOD HIGHLIGHTS

Specifications described in this method (Section 3.2) are for determining excess air and dry molecular weight of gas streams from fossil-fuel combustion processes. This method may also be applicable to other processes where it has been determined that compounds other than CO_2 , O_2 , CO , and N_2 are not present in sufficient concentrations to affect the results. A gas sample is extracted from a stack by one of the following methods: (1) single-point grab sampling; (2) single-point integrated sampling; or (3) multipoint integrated sampling. The gas sample is analyzed for percent CO_2 , percent O_2 , and if necessary percent CO .

Determination of dry molecular weight can be made using either an Orsat or Fyrite¹ analyzer and any of the three sampling methods listed above. When using the single-point grab sampling or single-point integrated sampling methods, the sampling point should either be at the centroid of the cross section or at a point >1.00 m (3.3 ft) from the stack wall, unless otherwise specified by the administrator. The sample collected for molecular weight determination must be analyzed within 8 h of collection.

Excess air or emission rate correction factors must be determined using an Orsat analyzer and the sample collection procedure specified in the applicable subpart of the standard. When using the single-point grab or single-point integrated sampling method, the sampling point should be located as specified above for molecular weight determinations. When using the multipoint integrated sampling method, a minimum of eight and nine traverse points should be used for circular and rectangular stacks,

¹Mention of trade names or specific products does not constitute endorsement by the Environmental Protection Agency.

respectively, with diameters <0.61 m (24 in.). A minimum of 12 traverse points shall be used for all other cases. The sampling run must be simultaneous with and for the same total length of time as the pollutant emission rate determination. The Orsat analyzer must be leak checked before and after the analysis. When analyzing low concentrations of CO_2 ($<4.0\%$) or high concentrations of O_2 ($>15.0\%$), the measuring burette of the Orsat must have at least 0.1% subdivisions. The sample must be analyzed within 4 h of collection.

The Method Highlights checklist at the end of this section may be removed from the Handbook and used in pretest, test, and posttest operations. Each form has a subtitle (i.e., Method 3, Figure 3.1) to aid the user in finding a similar filled-in form in the Method Description. Each item on the checklist that can cause significant errors are designated with an asterisk. Most of the Method Description and forms are designed for use in calculating excess air corrections, and therefore contain many more controls than would be required for molecular weight determination only.

1. Procurement of Equipment

Section 3.2.1 (Procurement of Apparatus and Supplies) gives the specifications, criteria, and design features of the equipment and materials required to perform Method 3 tests. This subsection 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 3.2.1 can be used as a quick reference, and is a summary of the corresponding written descriptions.

2. Pretest Preparations

Section 3.2.2 (Calibration of Apparatus) provides a step-by-step description of the recommended calibration procedure for the Orsat analyzer and the flow rate meter.

Section 3.2.3 (Presampling Operations) provides the tester with a guide for supplies and equipment preparation for field

tests. The method for packing and the description of packing containers should help protect the equipment but are not required.

3. On-site Measurements

Section 3.2.4 (On-site Measurements) contains procedures for sampling and analysis. Subsection 4.1 outlines the step-by-step procedure for determination of dry molecular weight. Subsection 4.2 outlines the step-by-step procedure for determination of excess air and emission rate correction factor. Subsection 4.3 includes a list of precautions that will aid in using the Orsat analyzer and improve the validity of the results.

4. Posttest Operations

Section 3.2.5 (Postsampling Operations) outlines a data comparison procedure which will allow detection of gross measurement error. A visual inspection procedure is also included to detect any change in the sampling and analysis apparatus that could have adversely affected the measured values.

Section 3.2.6 (Calculations) provides the tester with the required equations and nomenclature for calculating percent excess air and dry molecular weight.

Section 3.2.7 (Maintenance) outlines the necessary equipment maintenance which will help ensure high quality data.

5. Auditing Procedure

Section 3.2.8 (Auditing Procedure) provides a description of necessary activities for conducting performance and system audits. The performance audit of the analytical phase can be conducted using certified gas samples. Auditing procedures for the analytical, data processing, and systems phases are described in this section. A checklist for a systems audit is also included in this section.

Section 3.2.9 (Recommended Standards for Establishing Traceability) recommends the primary standards for use in assessing the accuracy of test data.

6. References

Sections 3.2.10 and 3.2.11 contain the Reference Method and the suggested references.

PRETEST PREPARATIONS
(Method 3, Figure 3.1)

Apparatus check	Acceptable		Quantity required	Ready		Loaded and packed	
	Yes	No		Yes	No	Yes	No
Probe type: Borosilicate glass _____ Stainless steel _____ Other _____							
Filter In-stack _____ Out-stack _____ Glass wool _____ Other _____							
Pump One-way squeeze _____ Diaphragm _____ Other _____ Leak checked* _____							
Condenser Type _____							
Flexible Bag Tedlar _____ Mylar _____ Teflon _____ Other _____ Leak checked* _____							
Pressure Gauge Type _____							
Analyzer Orsat _____ Fyrite _____ Other _____ Leak checked* _____ Spare reagents _____							

*Most significant items/parameters to be checked.

ON-SITE MEASUREMENTS CHECKLIST
(Method 3, Figure 4.1)

Sampling

Method: single-point grab _____ single-point integrated _____
 multipoint integrated _____
Is a filter used to remove particulate matter? _____
*Sampling train leak checked? _____
*Orsat analyzer leak checked? _____
All connections tight and leak free? _____
Sampling port properly sealed? _____
Sampling rate held constant? _____
Sampling train purged? _____

Analysis

Molecular Weight Determination

Analyzer: Orsat _____ Fyrite _____ Other _____

Fyrite:

Reagent at proper level and zeroed?* _____
Leak-free connection between analyzer and sample line? _____
Sampling line purged?* _____

Orsat:

Reagents at proper level?* _____
Analyzer level? _____
Leak checked?* _____
Sample analyzed within 8 h?* _____
Sample lines purged?* _____

Excess Air-Emission Rate Correction

Orsat analyzer leak checked?* Before _____ After _____
Reagents at proper level?* _____
Sampling lines purged?* _____
Analysis repeated by drawing a new sample until the following
criteria are met?

CO₂ - any three analyses differ by
a) $\leq 0.3\%$ when CO₂ $\geq 4.0\%$ _____
b) $\leq 0.2\%$ when CO₂ $\leq 4.0\%$ _____

O₂ - any three analyses differ by
a) $\leq 0.3\%$ when O₂ $\leq 15.0\%$ _____
b) $\leq 0.2\%$ when O₂ $\geq 15.0\%$ _____

CO - any three analyses differ by $\leq 0.3\%$ _____

All readings averaged and reported to nearest 0.1% _____

*Most significant items/parameters to be checked.

1.0 PROCUREMENT OF APPARATUS AND SUPPLIES

Diagrams of the sampling trains used in the method are shown in Figures 1.1 and 1.2. Specifications, criteria, and/or applicable design features are given in this section to aid in the selection of equipment to assure the collection of good quality data. 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 equipment, the identification number (if applicable), and the results of acceptance checks. An example procurement log is shown in Figure 1.3; a blank form is given in Section 3.2.12 for the user. If calibration data are required as part of the acceptance check, the data should be recorded in a calibration log. Table 1.1 at the end of this section contains a summary of the quality assurance activities for procurement and acceptance of apparatus and supplies.

As alternatives to the sampling systems described herein, others (e.g., liquid displacement) may be used if they are capable of obtaining a representative sample, maintaining a constant sampling rate, and yielding acceptable results. Use of such systems is subject to the approval of the administrator.

1.1 Grab Sample (Figure 1.1)

1.1.1 Probe - The probe or probe liner should be made of stainless steel or borosilicate glass tubing and should be equipped with an in-stack (preferred) or an out-stack filter to remove particulate matter. A plug of glass wool is generally a satisfactory filter. The probe tip should be designed to prevent the glass-wool filter from being drawn from the probe when sampling a source that has a substantial negative pressure. Any material inert to O₂, CO₂, CO, and N₂ and resistant to temperature at the sampling conditions may be used for the probe; examples of such

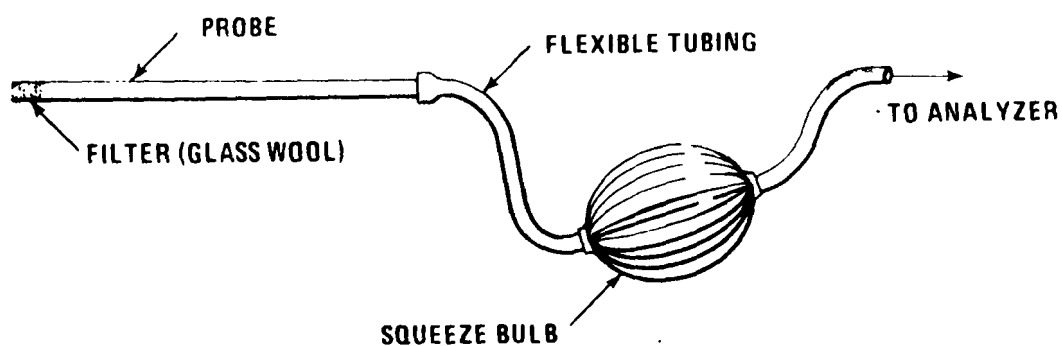


Figure 1.1 Grab sampling train.

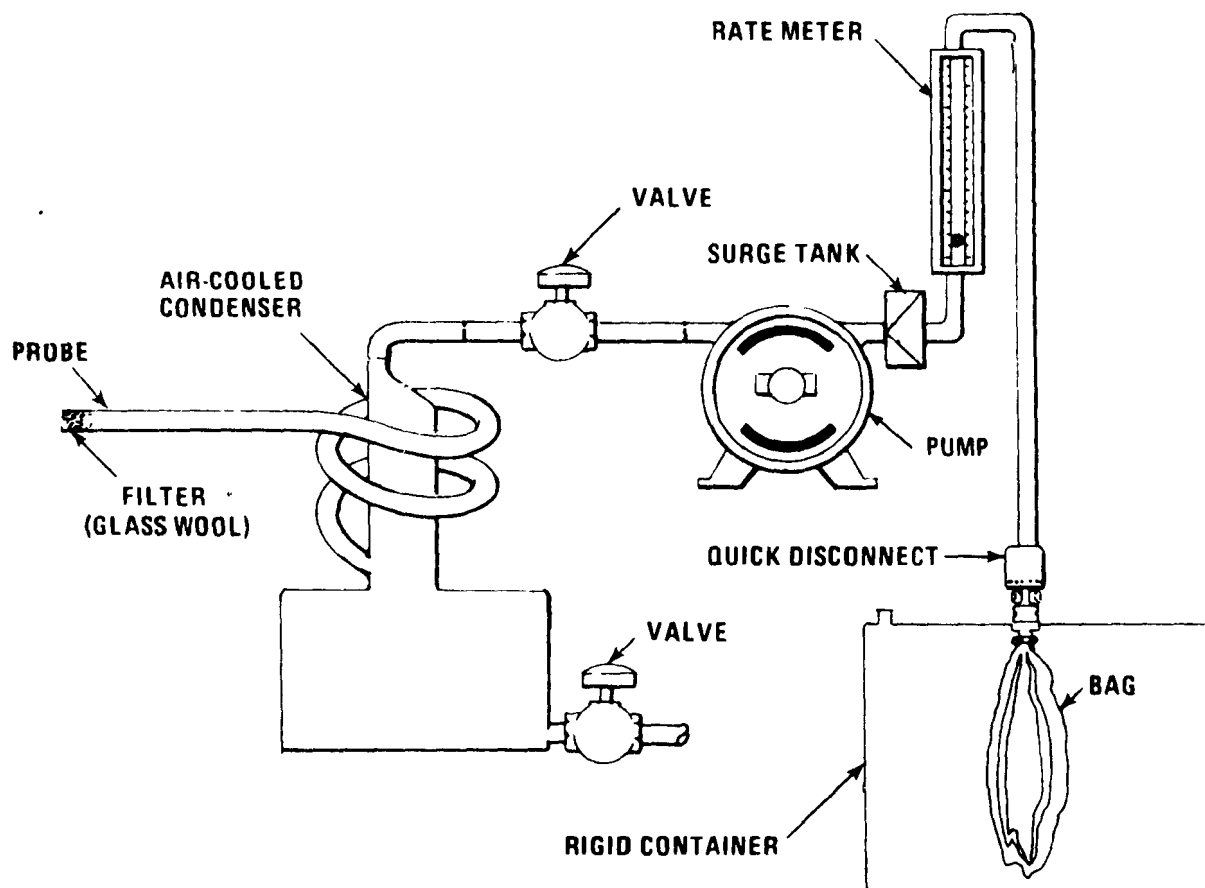


Figure 1.2 Integrated gas sampling train.

Item description	Quantity	Purchase order number	Vendor	Date		Cost	Disposition	Comments
				Ordered	Received			
Orsat Analyzer	1	22481A	Lacy Inc.	7/29/79	8/15/79	\$2100	In service	

Figure 1.3 Example of a procurement log.

materials are aluminum, steel, glass, PVC plastic, and Teflon^R. Since the gases to be sampled are relatively inert, the key criterion in probe selection is the stack gas temperature.

1.1.2 Pump - A one-way squeeze bulb, or the equivalent, is used to draw the gas sample into the analyzer.

1.2 Integrated Sample (Figure 1.2)

1.2.1 Probe - A probe equipped in the manner just described in Subsection 1.1.1 is suitable.

1.2.2 Condenser - An air or water-cooled condenser that will not remove O₂, CO₂, CO, and N₂ should be used to remove excess moisture if the gas stream contains >2% moisture by volume. (This includes most combustion processes.) The main consideration is that the condenser volume be kept to the minimum size necessary to sufficiently cool the sample gas, because the larger the volume the more difficult it is to completely purge the sampling train before collecting a sample. A 0.63-cm (0.25-in.) stainless steel coil or equivalent connected to a water collection chamber with a capacity of about 40 ml is sufficient.

1.2.3 Valve - Needle valves are needed to adjust the sample gas flow rate.

1.2.4 Pump - A leak-free diaphragm pump, or the equivalent, is needed to transport the sample gas to the flexible bag. A small surge tank should be installed between the pump and the rate meter to eliminate the pulsation effect of the pump on the rate meter. Upon receipt, the pump, surge tank, and rate meter (Subsection 1.2.5 below) should be checked in the following manner:

1. Assemble the pump, surge tank, and rate meter.
2. Place a needle valve and vacuum gauge at the pump inlet using a T-connector.
3. Turn on the pump and close the needle valve until a vacuum of 125 mm (5 in.) Hg is obtained. The pumping rate at this vacuum is suggested to be at least 1 l/min (0.035 ft³/min),

^RRegistered trademark.

and the rate meter when the flow is adjusted between 0.5 and 1.0 ℓ/min (0.018 and 0.035 ft^3/min) should yield steady readings.

If the pump capacity is insufficient, repair, replace, or return it to the manufacturer. If rotameter readings fluctuate >2% of the full-scale reading, use a larger surge tank. Be sure that the rotameter is clean and dry.

1.2.5 Rate Meter - A rotameter or an equivalent rate meter, capable of measuring flow rates within $\pm 2\%$ of the selected flow rate should be used.

The calibration curve (Figure 1.4) supplied by the manufacturer should be checked by comparing the rotameter readings against the wet test meter readings. If the rotameter is not within $\pm 5\%$ of the manufacturer's calibration curve, recalibrate and construct a new curve.

Changes in sample gas pressure, density, and viscosity will affect the sampling rate. However, since sampling is performed at a constant rate and since the total volume sampled need not be measured accurately, these changes are not significant.

1.2.6 Flexible Bag - Any leak-free inert plastic (e.g., Tedlar^R, Mylar^R, Teflon^R) bag, or the equivalent, having a capacity adequate for the selected flow rate and time length of the test run may be used. A capacity of 90 ℓ (3.2 ft^3) is usually required. To leak check the bag (Figure 1.5):

1. Connect it to a manometer and pressurize the bag to from 5 to 10 cm (2 to 4 in.) H_2O .
2. Allow it to stand for 10 min.

Any displacement in the water manometer will indicate a leak and a need to repair the bag. An alternative leak check is to pressurize the flexible bag to 5 to 10 cm (2 to 4 in.) H_2O and allow it to stand overnight. A deflated bag indicates a leak.

1.2.7 Pressure Gauge - A water-filled U-tube manometer, or the equivalent, of about 28 cm (12 in.) is needed for the flexible

^R Registered trademark.

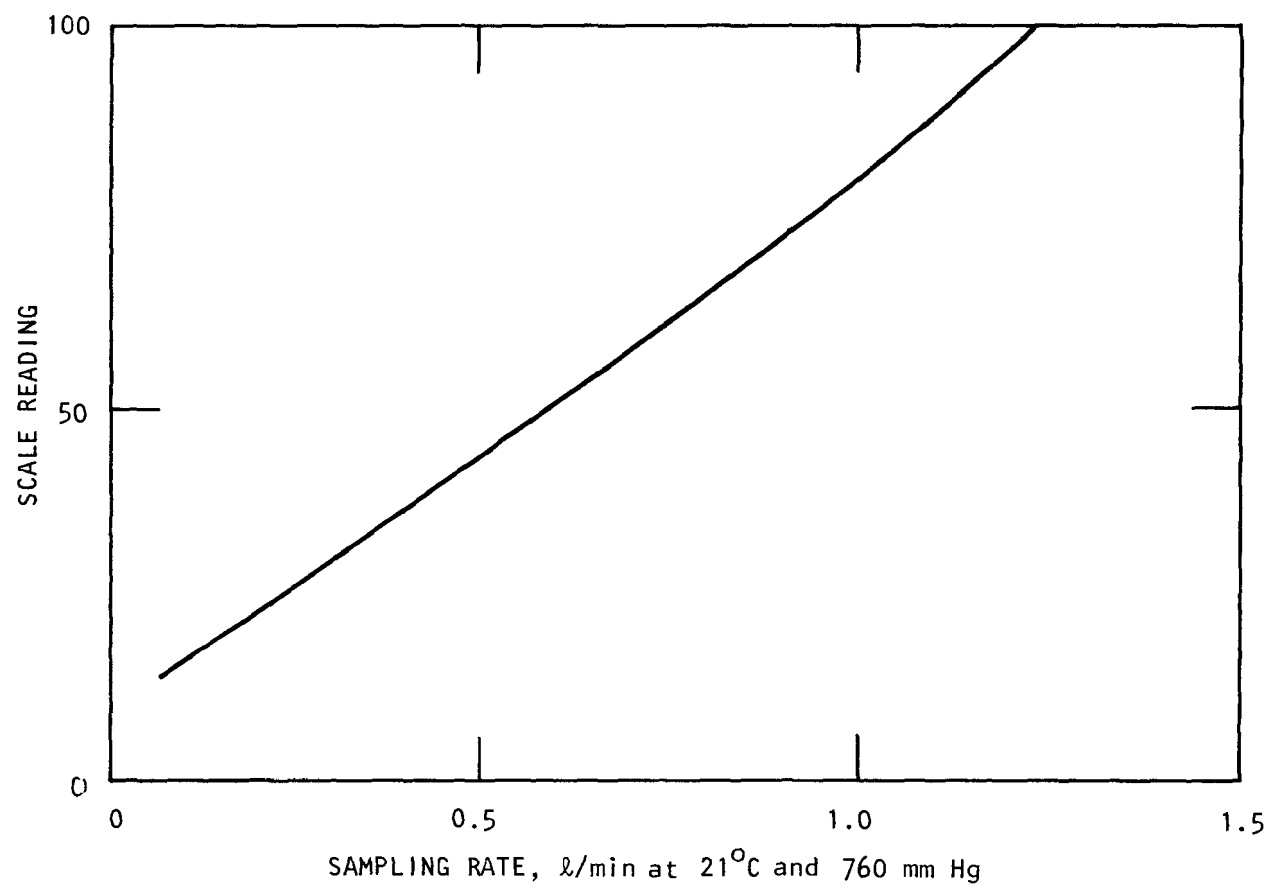


Figure 1.4 Example rotameter calibration curve.

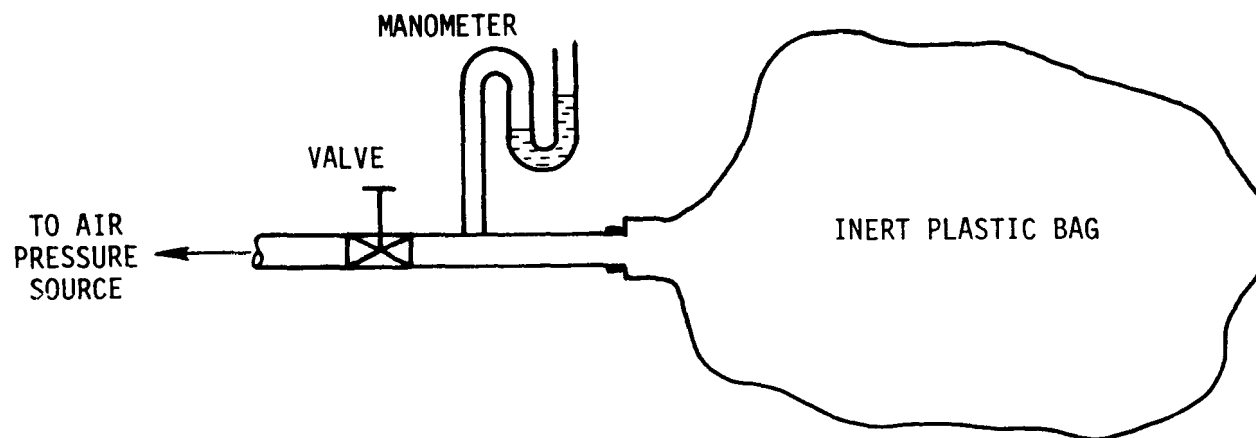


Figure 1.5 Plastic bag leak-check system.

bag leak check. The gauge should be leak checked upon receipt as follows:

1. Place a flexible tube on the gauge opening.
2. Apply a positive pressure of from 5 to 10 cm (2 to 4 in.) H₂O on the gauge by blowing on and then pinching off the tube. The pressure reading should remain stable for 10 min.
3. Check each side of the gauge separately.

If a deflection is noted, repair, replace, or return the gauge to the manufacturer.

1.2.8 Vacuum Gauge - A mercury manometer, or the equivalent, of at least 760 mm (30 in.) Hg is needed for the sampling train leak check. If a mercury manometer is used, leak check the system by pulling a 380 mm (15 in.) Hg vacuum on the gauge and then pinching off the tube. No deflection should be noted in the reading over a 10-min period. If another type of gauge is used, compare the gauge reading with a mercury manometer reading at about 380 mm (15 in.) Hg. The gauge reading should be within ± 25 mm (1 in.) Hg of the mercury manometer reading. If the gauge fails the leak check or the comparison with the mercury manometer, repair, replace, or return the manometer to the manufacturer.

1.3 Analyzer

An Orsat or a similar absorption type analyzer is required for measuring constituents of combustion gases. The latter is used only for molecular weight determinations, since it is less accurate than the Orsat.

1.3.1 Orsat Gas Analyzer - The Orsat analyzer^{6,7} is used to determine the CO₂, O₂, and CO stack gas concentrations. A sample is analyzed by successively passing it through absorbents that remove specific gaseous components. The difference in gas volume before and after the absorption represents the amount of the constituent gas in the sample. Constant pressure and temperature must be maintained throughout the analysis. Results are reported as dry volume percentages.

The Orsat analyzer illustrated in Figure 1.6 includes a glass burette to accurately measure the gas volume, a water

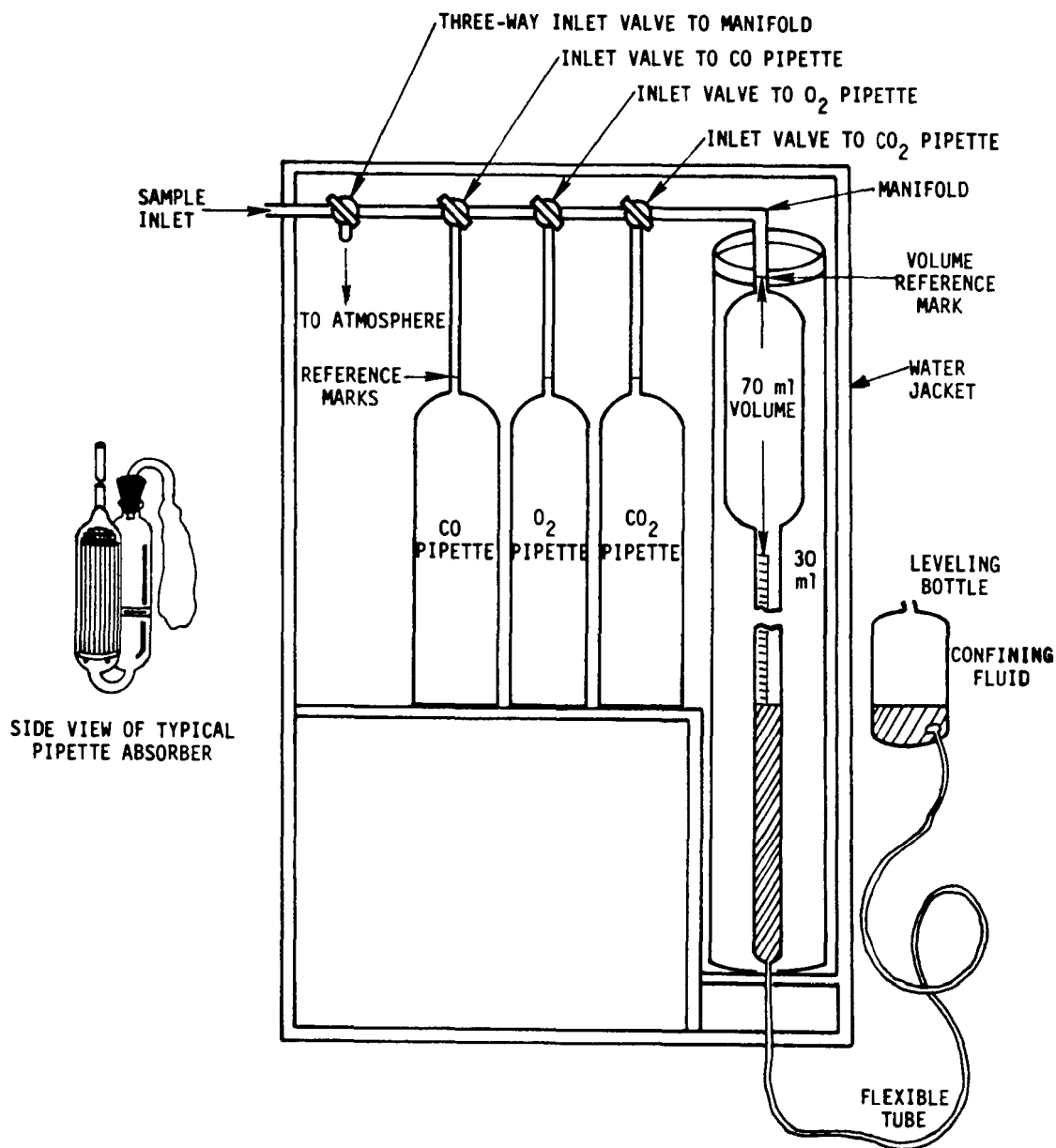


Figure 1.6 Orsat apparatus.

jacket to maintain constant temperature, a manifold to control the gas flow, three absorption pipettes (CO , O_2 , and CO_2), rubber expansion bags, and a liquid-filled leveling bottle to move the gases. The apparatus is usually assembled inside a case that has front and rear doors and a carrying handle.

For expected CO_2 readings $>4.0\%$, a standard Orsat analyzer containing a burette with 0.2-ml divisions and spacings between divisions of about 1 mm (0.04 in.) is satisfactory. For lower CO_2 values or for O_2 values $>15\%$, an analyzer equipped with a burette having 0.1-ml divisions with spacings of ≥ 1 mm (0.04 in.) should be used.

Upon receipt of the analyzer, wash and dry all components and assemble the apparatus according to the manufacturer's instructions. Then properly lubricate all glass valves with silicone stopcock lubricant. If the apparatus is to be used promptly, add the liquid reagents and check for leaks as follows:

1. Allow the apparatus to reach ambient temperature with the manifold valve open and the three pipette valves closed.
2. Bring the liquid in each absorption pipette up to the reference mark by opening the pipette valves one at a time and by slowly lowering the leveling bottle. Pinch off the rubber tube to the leveling bottle with the heel of the hand to quickly stop liquid flow. Close the pipette valves.
3. Displace the indicating fluid until a reading is obtained in the narrow part of the burette, and quickly close the manifold inlet valve.
4. Place the leveling bottle on top of the Orsat case, and read the meniscus in the burette.
5. Wait at least 4 min; then read the meniscus again. A change of ≥ 0.2 ml in the reading indicates a leak in the system which must be repaired. A drop in reagent level to below the capillary tube over a 4-min period indicates a leak in that pipette.

If leaks are detected, correct them so that the above criteria will be met.

Desirable Design Qualities - There is a variety of Orsat analyzer designs on the market. Some design features increase the precision and accuracy. Some of these desirable features are described below.

Precision and probably accuracy are improved with a glass burette configuration as shown in Figure 1.6; that is, the burette column has a large diameter having a volume of about 70 ml joined onto a narrow 30-ml burette graduated in 0.1-ml divisions.⁺ Such designs result in less error in reading the gas volume than with designs having larger graduations and less spacing between divisions. To further reduce reading error, the volume line should be scribed completely around the burette at the reference point. For processes in which CO₂ is released from the product (e.g., in a limestone kiln), the cumulative total of O₂ and CO₂ may be >25%. For these processes, the graduated portion of the burette must be long enough to provide a reading. (Graduated burettes are available up to 100 ml.) A burette with a vertical dark line behind the graduations is easier to read.

The volume reference mark should be on the capillary tube at the top of the glass burette, not on the larger diameter burette. Having the mark on the small capillary tube increases the precision from test to test and increases the accuracy of the burette calibration--both for a more accurate sample volume determination.

The connecting manifold should have as small a volume as possible to reduce the possibility of diluting the sample due to incomplete purging of the manifold. It also minimizes the increase in sample volume; the volume of gas in the manifold between the reference mark on the burette and that on the pipette is small.

⁺ These burettes are commercially available.

The Orsat apparatus and case should be designed so that the leveling bottle and the glass burette can be viewed side by side when leveling the liquid. The liquid levels in both the burette and the bottle must be at the same height when reading the volumes; otherwise, the sample gas will not be at atmospheric pressure.

The inlet manifold valve should be three-way to allow purging of the manifold without causing the sample bag or the inlet gas to be diluted by ambient air.

Reagents - Four reagents are required by a standard Orsat apparatus for analyzing flue gas. These are the gas-confining solution, the CO₂ absorbent, the O₂ absorbent, and the CO absorbent. Due to the solubility of CO₂ in water, a colored aqueous acidic salt solution is used as the confining solution; it contains sodium sulfate, sulfuric acid, and methyl orange. The CO₂ absorbent is a solution of potassium or sodium hydroxide, and the O₂ absorbent is a solution of alkaline pyrogalllic acid or chromous chloride. The CO absorbent is usually a cuprous chloride or sulfate solution, but other solutions may be used.⁶ All of these solutions can be purchased from most chemical suppliers. Note the shelf-life requirements, since some reagents deteriorate with time.

1.3.2 Other Absorption Type Analyzers - Absorption type analyzers which determine CO₂ or O₂ concentrations are also available. These devices are simpler and easier to use than an Orsat, and they are more rugged. However, they provide less precision and can thus be used only for molecular weight determinations of the gases. These devices operate similarly to the Orsat by absorbing the gas in a colored solution; then the volume absorbed is read directly on a scale as percentage by volume. A commonly used O₂ analyzer is shown in Figure 1.7. The use of continuous monitors for determining O₂ content must be approved by the administrator.

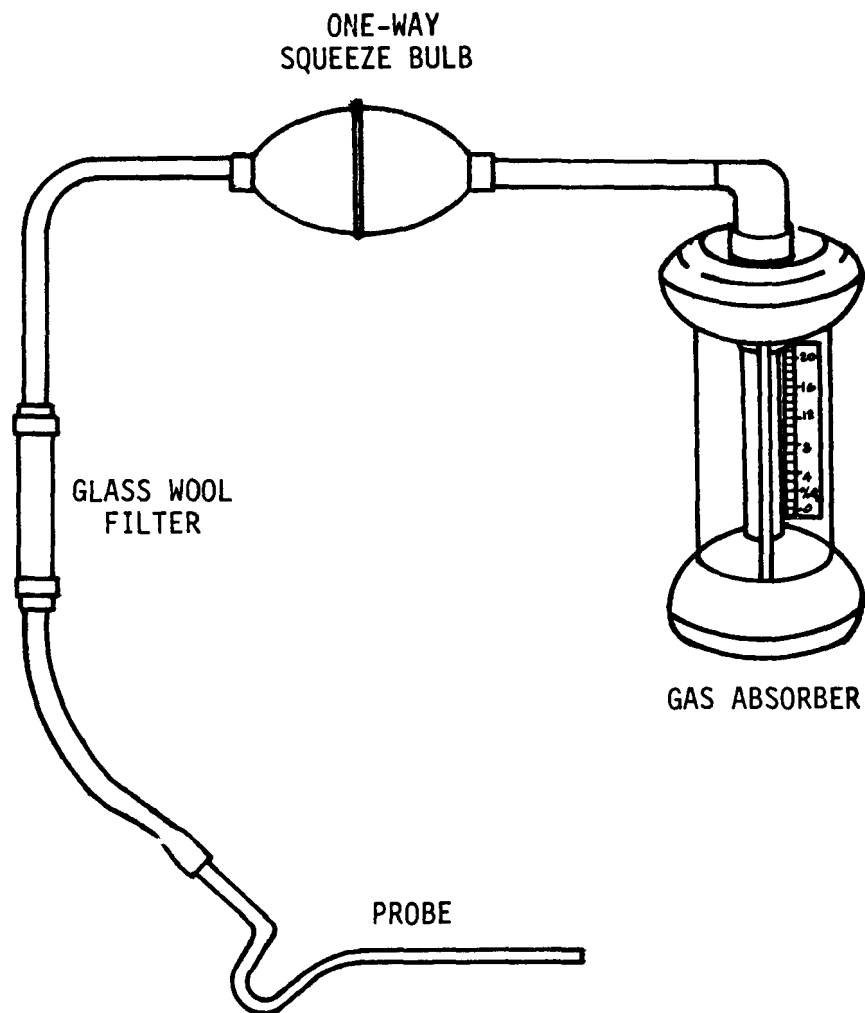


Figure 1.7 Absorption type analyzer.

Table 1.1 ACTIVITY MATRIX FOR PROCUREMENT OF APPARATUS AND SUPPLIES

Characteristics	Acceptance limits	Frequency and method of measurement	Action if requirements are not met
<u>Grab Sampling Train</u>			
Probe	Stainless steel, boro-silicate glass, or equivalent; not damaged or corroded; no leakage	Visual observation upon receipt	Discard or return defective equipment to supplier, as appropriate
Pump	One-way squeeze bulb or equivalent; not damaged or corroded	As above, plus manual operating check	As above
<u>Integrated Gas Sampling Train</u>			
Probe	Stainless steel, boro-silicate glass, or equivalent; no leakage	As above	As above
Air-cooled condenser	No leakage; keep the condenser volume to a minimum necessary to cool the sample with air	As above	As above
Valve	Needle valve	As above	As above
Pump	Diaphragm type, leak frge, and 1 ℓ /min (0.035 ft^3 /min) capacity	Check for leaks and capacity upon receipt	As above
Rate meter (rotameter)	Check flow range from 0 to 1 ℓ /min (0 to 0.035 ft^3 /min) must be accurate to within $\pm 2\%$ of selected flow rate	Check upon receipt for damage; calibrate against WTM	Recalibrate and construct new calibration curve
Flexible bag	Capacity of 55 to 90 ℓ (1.9 to 3.2 ft^3); leak test not mandatory	Check for leaks and capacity	Return to supplier

(continued)

Table 1.1 (continued)

Characteristics	Acceptance limits	Frequency and method of measurement	Action if requirements are not met
Pressure gauge	28-cm (12-in.) water-filled U-tube or equivalent for flexible bag leak check	Visually observe and leak check upon receipt	As above
Vacuum gauge	At least 760-mm (30-in.) Hg gauge for the sampling train leak check	Check against a mercury U-tube manometer and leak check	As above
<u>Orsat Analyzer</u>			
Glass burette	0.1-ml divisions with spacings of about 1mm	Visually inspect upon receipt	Return to supplier
Pipettes, manifolds, etc.	Air tight	Initially and before tests	Repair or discard
Leveling bottle	Can be viewed side-by-side with glass burette	Visually check for damages	As above
<u>Other Analyzers</u>	<0.5% divisions	Visually check for damage and leaks	As above

2.0 CALIBRATION OF APPARATUS

Calibration of sampling apparatus is one of the most important functions in maintaining data quality. Only limited initial calibration is required for gas absorption using an analyzer such as an Orsat. Continued maintenance, reagent checks, and most importantly, the operator's technique and diligence are required for good quality data. Table 2.1 at the end of this section summarizes the quality assurance activities for calibration.

2.1 Analyzers

Calibration is recommended upon receipt, before every third field test, and before any field test in which the Orsat or other absorption type analyzer has not been checked during the previous 3 mo.

To check the O₂-absorbing reagent and the operator's technique, the percentage of O₂ in air should be determined. The average of three replicates should be 20.8 ±0.7% when using the standard Orsat. A measured average value >21.5% generally indicates poor operator technique, while a value <20.1% generally indicates leaking valves, spent absorbing reagent (for O₂ only), and/or poor operator technique. (See Section 4.1 of Reference 1 for the derivation of the above limits.) The three replicates and their averages should be reported on an \bar{X} and R chart, as illustrated by Figure 2.1; a blank copy of this form is in Section 3.2.12.

A more thorough check, if required equipment is available, would be to take a sample from a manifold containing a known mixture of CO₂ and O₂. This is applicable to grab samples or to the integrated samples. In both cases, the sample is analyzed for CO₂ and O₂ using the Orsat. The average of three replicates should be ±0.5% (absolute) of the known concentration of each gas. Again, high measured values indicate poor operator technique, while low values indicate leaking valves, spent absorbing reagent, and/or poor operator technique.

If the above limits are exceeded, corrective action should be equipment maintenance and/or operator training.

2.2 Rate Meter

Clean and calibrate the rate meter in the integrated gas sampling train every 6 mo and at any sign of erratic behavior. Calibrate using either a wet test meter or a volume meter which has been recently calibrated against a primary standard.

1. Place the calibrated volume meter or wet test meter in series with the rate meter.

2. Adjust the flow rate to 1 ℓ/min ($0.035 \text{ ft}^3/\text{min}$) on the rate meter.

3. Take readings with the wet test meter and stopwatch. If the flow rate is not near the desired 1 ℓ/min ($0.035 \text{ ft}^3/\text{min}$) on the rate meter, adjust the valve and repeat the reading with the wet test meter and stopwatch; repeat until the desired flow rate is obtained for the rate meter setting.

4. Take readings at 0.5, 0.75, and 1.0 ℓ/min (0.18, 0.027, and $0.035 \text{ ft}^3/\text{min}$) on the rate meter. Record the readings from the calibrated meter and the rate meter in the calibration log.

5. Construct a calibration curve of rate meter reading versus flow rate for the meter using corrected wet test meter stopwatch readings.

6. Number each rate meter and include the number and the date of calibration on the calibration curve.

Table 2.1 ACTIVITY MATRIX FOR THE CALIBRATION OF APPARATUS

Characteristics	Acceptance limits	Frequency and method of measurement	Action if requirements are not met
Orsat analyzer	Average of three replicates should be 20.8 $\pm 0.5\%$ (absolute) or known concentration ± 0.5 (absolute)	Upon receipt and before any test in which the analyzer has not been checked during the previous 3 mo; determine % O_2 in ambient air, or use a calibration gas with known CO , CO_2 , O_2 concentrations	Check Orsat analyzer for leaking valves, spent absorbing reagent, and/or operator techniques; take corrective action
Rotameter or rate meter	Smooth curve of rotameter actual flow rates with no evidence of error	Check with wet test meter or volume meter at 6-mo intervals or at indication of erratic behavior	Repeat calibration steps until limits are attained

3.0 PRESAMPLING OPERATIONS

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

3.1 Apparatus and Calibration Checks

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 Grab Sample Train - The grab sample train (Figure 1.1) should be checked before each field test as follows:

1. Clean the probe with soap and water, rinse it with water, and allow it to dry. Check it visually for leaks indicated by cracks or corrosion. Cap both ends of the probe tightly to prevent contaminants from entering while it is not in use. If particulates are expected, insert a plug of glass wool into the sampling end of the probe.

2. Check the pump--either a one-way squeeze bulb or a leak-free diaphragm type pump--to see if it is operating properly. Check all connectors and tubes for leaks; do this by slightly pressurizing the system and by applying soap to the connections and joints and watching for bubbles.

3.1.2 Integrated Sample Train - The integrated gas sampling train (Figure 1.2) should be checked before each field test as follows:

1. Clean the probe with soap and water, rinse it with water, and allow it to dry. Visually check it for leaks indicated by cracks or corrosion. Cap both ends of the probe tightly to prevent contaminants from entering it while it is not in use. If particulates are expected, insert a plug of glass wool into the sampling end of the probe.

2. Clean the air-cooled condenser, or equivalent, and leak check it by slightly pressurizing the unit, applying soap to joints and connections, and watching for bubbles.

Apparatus check	Acceptable		Quantity required	Ready		Loaded and packed	
	Yes	No		Yes	No	Yes	No
<u>Probe type:</u> Borosilicate glass _____ Stainless steel <input checked="" type="checkbox"/> _____ Other _____	<input checked="" type="checkbox"/>		2	<input checked="" type="checkbox"/>		<input checked="" type="checkbox"/>	
<u>Filter</u> In-stack <input checked="" type="checkbox"/> _____ Out-stack _____ Glass wool _____ Other _____	<input checked="" type="checkbox"/>		2	<input checked="" type="checkbox"/>		<input checked="" type="checkbox"/>	
<u>Pump</u> One-way squeeze _____ Diaphragm <input checked="" type="checkbox"/> _____ Other _____ Leak checked* _____	<input checked="" type="checkbox"/>		2	<input checked="" type="checkbox"/>		<input checked="" type="checkbox"/>	
<u>Condenser</u> Type <u>air cooled</u>	<input checked="" type="checkbox"/>		2	<input checked="" type="checkbox"/>		<input checked="" type="checkbox"/>	
<u>Flexible Bag</u> Tedlar _____ Mylar <input checked="" type="checkbox"/> _____ Teflon _____ Other _____ Leak checked* <u>yes</u>	<input checked="" type="checkbox"/>		6	<input checked="" type="checkbox"/>		<input checked="" type="checkbox"/>	
<u>Pressure Gauge</u> Type <u>1/2" tube</u>	<input checked="" type="checkbox"/>			<input checked="" type="checkbox"/>		<input checked="" type="checkbox"/>	
<u>Analyzer</u> Orsat <input checked="" type="checkbox"/> _____ Fyrite <input checked="" type="checkbox"/> _____ Other _____ Leak checked* <u>yes</u> Spare reagents <input checked="" type="checkbox"/> _____	<input checked="" type="checkbox"/> <input checked="" type="checkbox"/> <input checked="" type="checkbox"/>		2 2 1	<input checked="" type="checkbox"/> <input checked="" type="checkbox"/> <input checked="" type="checkbox"/>		<input checked="" type="checkbox"/> <input checked="" type="checkbox"/> <input checked="" type="checkbox"/>	

*Most significant items/parameters to be checked.

Figure 3.1 Pretest preparation.

3. Disassemble, clean, and reassemble the needle valve and rate meter at any sign of foreign matter in the rotameter or erratic behavior of the rotameter.

4. Leak check the flexible bag by pressurizing and by observing for any loss in pressure as described in Section 3.2.1.

3.1.3 Orsat Gas Analyzer - The Orsat apparatus should be checked and serviced before each field test in the following manner:

1. Check the confining fluid levels in the leveling bottle and the burette. Be sure the approximately 300 ml of fluid in the leveling bottle is clear, orange, and sufficient to fill the burette. Be sure the solution in the leveling bottle is distilled water containing approximately 5% by volume of concentrated sulfuric acid and 2 to 3 ml of methyl orange acidic indicator; then saturate the solution with a salt, usually sodium sulfite or sodium chloride, at the temperature at which the Orsat is expected to operate. (The sulfuric acid acts as a drying agent to remove any moisture from the sample, and the saturated salt solution prevents the absorption of sample gases by the leveling solution.) This leveling bottle solution should be prepared as a stock solution and taken to the field in case it is needed.

2. Remove and clean the stopcocks. Carefully apply stopcock grease to prevent system leaks, and do it without plugging the air passages. Stopcocks are generally not interchangeable, so replace each one in the same port from which it was originally taken.

3. Change the absorbing solutions if >10 passes are needed to obtain a constant reading for any gas component. If in doubt, change the solution (following the manufacturer's instructions) by emptying the absorber and adding fresh absorbing reagents. Add new reagents when required, 6 to 8 h prior to field use. Prior to adding the O₂ reagent, flush the absorbing pipette and the expansion bag with N₂, and pass N₂ over the reagent while adding it to the pipette.

4. Leak check the Orsat analyzer thoroughly on site before using it, since moving an Orsat to the site may have caused it to leak. (Use the procedure in Section 3.2.1) If there are leaks, check all connections and stopcocks until the cause of the leak is identified. Leaking stopcocks must be disassembled, cleaned, and regreased; leaking rubber connections must be replaced. After the analyzer is reassembled, the leak-check procedure must be repeated.

3.1.4 Fyrite Gas Analyzer - Check the absorption analyzer visually for leaking of reagents prior to each test.

3.2 Equipment Packaging

Logistics of the method, time of sampling, and quality of data are dependent on the packing of the sampling and analytical equipment for (1) accessibility in the field, (2) ease of movement on site, and (3) optimum functioning in the field. Equipment should be packed to withstand severe treatment during shipment and field operations.

1. Pack probes, pumps, and condenser in cases or wooden boxes filled with packing material or lined with styrofoam. The cases should have handles or hooks that can withstand hoisting and should be rigid enough to prevent bending or twisting during shipping and handling.

2. Pack rate meters, needle valves, and all small glassware individually in shipping containers.

3. Use the rigid container with the integrated sampling bag for its shipping container.

4. Disassemble the Orsat and pack each item individually in suitable packing material and rigid containers for long trips or for shipping as freight. Ship the spare parts and the absorbent solutions in separate containers.

Table 3.1 ACTIVITY MATRIX FOR PRESAMPLING OPERATIONS

Characteristics	Acceptance limits	Frequency and method of measurement	Action if requirements are not met
<u>Grab Sample Train</u>	No visual sign of breakage	Visual observation before each field test	Replace as necessary
Probe	As above	As above	As above
Pump	As above	As above	As above
<u>Integrated Gas Sampling Train</u>			
Probe	As above	As above	As above
Air-cooled condenser	As above	As above	Clean and replace as necessary
Needle valve and rotameter	No foreign matter or erratic behavior	As above	Clean and reassemble as necessary
Flexible bag	No visual indication of leakage	As above	Replace as necessary
Pump	According to manufacturer's criteria	Before each field test, use manufacturer's directions	Service or return to supplier as necessary
<u>Gas Analyzer Orsat</u>			
Leveling solution	Distilled water containing approximately 5% by volume of concentrated H_2SO_4 and saturated with a salt		Prepare fresh solution
Absorbing solution	<10 passes needed for constant readings with any component gas	Performance check using any component gas	Use fresh reagent

(continued)

Table 3.1 (continued)

Characteristics	Acceptance limits	Frequency and method of measurement	Action if requirements are not met
Stopcocks	No leakage	Visual observation	Remove, clean, regrease as necessary
Assembly	No leaks present	See text	Eliminate leaks before test
<u>Gas Analyzer</u> <u>(Fyrite)</u>	Fill with reagents; no leaks	Visual observation	Add fresh reagent; re- pair as neces- sary
<u>Package Equip-</u> <u>ment for Ship-</u> <u>ment</u>	Not applicable	See packing instruc- tions	Not applicable

4.0 ON-SITE MEASUREMENTS

The choice of procedure to be used at the sampling site depends on whether an emission rate factor (F-factor), an excess air determination, or a molecular weight determination is required. The applicable measurement is specified in the emission standard, and the quality assurance activities are summarized in Table 4.1 in this section. In any case, the equipment is unpacked at the sampling site and visually inspected for damage during shipment from the laboratory; the Orsat analyzer, especially, is carefully checked for reagent levels and leaks as described in Section 3.2.1. Figure 4.1 (On-site Measurement Checklist) can be used as a guide for sampling and analysis of molecular weight, excess air, and emission rate determination.

4.1 Determination of CO₂ and O₂ for Dry Molecular Weight Calculations

Three methods are described in the Federal Register for measuring a gas stream's dry molecular weight. These are discussed in order of increasing complexity, and their uses are determined by the applicable standards or by expected variations in gas composition.

4.1.1 Single-Point Grab Sampling and Analysis - Set up the grab sampling train as depicted in Figure 1.1. Visually check each connection for leaks.

1. Be sure the sampling point in the duct is either at the centroid of the cross section or at a point ≥ 1 m (3.28 ft) from the walls of larger ducts, unless otherwise specified by the administrator.

2. Place the probe securely in the stack at the sampling point.

3. Seal the sampling port as well as possible with a sponge or rag to prevent dilution of the stack gas by ambient air if the stack pressure is negative.

Sampling

Method: single-point grab ☒ single-point integrated _____
multipoint integrated _____

Is a filter used to remove particulate matter? yes

*Sampling train leak checked? yes

*Orsat analyzer leak checked? yes

All connections tight and leak free? yes

Sampling port properly sealed? yes

Sampling rate held constant? N/A

Sampling train purged? yes

Analysis

Molecular Weight Determination

Analyzer: Orsat ☒ Fyrite _____ Other _____

Fyrite:

Reagent at proper level and zeroed?* _____

Leak-free connection between analyzer and sample line? _____

Sampling line purged?* _____

Orsat:

Reagents at proper level?* yes

Analyzer level? yes

Leak checked?* yes

Sample analyzed within 8 h?* yes

Sample lines purged?* yes

Excess Air-Emission Rate Correction N/A

Orsat analyzer leak checked?* Before _____ After _____

Reagents at proper level?* _____

Sampling lines purged?* _____

Analysis repeated by drawing a new sample until the following criteria are met?

CO₂ - any three analyses differ by

a) $<0.3\%$ when CO₂ $>4.0\%$ _____

b) $\leq 0.2\%$ when CO₂ $\leq 4.0\%$ _____

O₂ - any three analyses differ by

a) $<0.3\%$ when O₂ $<15.0\%$ _____

b) $\leq 0.2\%$ when O₂ $\geq 15.0\%$ _____

CO - any three analyses differ by $\leq 0.3\%$ _____

All readings averaged and reported to nearest 0.1% _____

*Most significant items/parameters to be checked.

Figure 4.1 On-site measurement checklist.

4. Check the Orsat analyzer for leaks as described in Section 3.2.1. (Though this step is not mandatory, it is highly recommended.) If another gas absorption device is used, it must be zeroed before use.

5. Purge the sampling line several times by squeezing the one-way squeeze bulb and then attaching the gas analyzer (either the Orsat or another gas absorption device).

6. Draw a gas sample into the analyzer and immediately analyze it for CO_2 and O_2 . Record the data on data form shown in Figure 4.2 or on a similar form.

7. Calculate the molecular weights as described in Section 3.2.6.

8. Repeat steps 5 through 7 until the calculated molecular weights of any three samples differ from their mean by ≤ 0.3 g/mole.

4.1.2 Single-Point Integrated Sampling and Analysis - Set up the sampling train as shown in Figure 1.2. Visually check for leaks.

1. Be sure the sampling point in the duct is either at the centroid of the cross section or at a point ≥ 1 m (3.28 ft) from the walls of larger ducts, unless otherwise specified by the administrator.

2. Place the probe securely in the stack at the sampling point.

3. Seal the sampling port as well as possible with a sponge or rag to prevent dilution of the stack gas by ambient air if the stack pressure is negative.

4. Leak check the flexible bags as described in Section 3.2.1, and then evacuate the selected bag. Leak check the sampling system by attaching a vacuum gauge to the condenser inlet, drawing a vacuum of 250 mm (10 in.) Hg, and plugging the outlet fitting where the bag is usually attached. Turn off the pump and observe the vacuum reading for 30 s; it should remain stable. If the vacuum drops, check the system for leaks, then repair if necessary, and finally recheck. (These leak checks are optional, but highly recommended.)

PLANT Valley Power Company
 DATE 8-1-79 TEST NO 0-1
 SAMPLING TIME (24-hr CLOCK) 1335-1454
 SAMPLING LOCATION ESP Outlet
 SAMPLE TYPE (BAG, INTEGRATED, CONTINUOUS) Integrated bag
 ANALYTICAL METHOD Orsat
 AMBIENT TEMPERATURE 60°F
 OPERATOR T. Clark

COMMENTS:

<div> <div>RUN 0-1</div> <div>GAS</div> </div>	1		2		3		AVERAGE NET VOLUME	MULTIPLIER	MOLECULAR WEIGHT OF STACK GAS (DRY BASIS) M_d
	ACTUAL READING	NET	ACTUAL READING	NET	ACTUAL READING	NET			
CO ₂	8.0	8.0	8.0	8.0	8.0	8.0	8.0	⁴⁴ /100	3.52
O ₂ (NET IS ACTUAL O ₂ READING MINUS ACTUAL CO ₂ READING)	19.2	11.2	19.2	11.2	19.2	11.2	11.2	³² /100	3.58
CO (NET IS ACTUAL CO READING MINUS ACTUAL O ₂ READING)	19.2	0	19.2	0	19.2	0	0	²⁸ /100	0
N ₂ (NET IS 100 MINUS ACTUAL CO READING)	80.8		80.8	80.8	80.8	80.8	80.8	²⁸ /100	22.62
TOTAL									29.72

Figure 4.2 Gas analysis data form.

5. Connect the probe, open the quick disconnect at the bag connection, and purge the sampling system with stack gas by running the pump for about 1 min at a high rate. Make sure that the condenser drain valve is closed tightly.

6. Connect the evacuated flexible bag, and begin the sampling. Record the time, flow rate, and other appropriate data on a form like the one shown in Figure 4.3.

7. Sample at a constant rate so that about 30 to 90 l (1 to 3 ft³) of gas are collected simultaneously with the pollutant emission rate test.

8. Disconnect, seal, and remove the flexible sampling bag to a suitable area for performing the analysis. Allow the collected sample to sit for about 30 min to ensure thorough mixing and temperature equilibrium. It is recommended that the analysis be performed as soon as practical after the 30-min waiting period, but not more than 8 h after sampling. If an Orsat analyzer is used, leak check it as described in Section 3.2.1. (Though not mandatory, this step is highly recommended.) If a gas absorption device is used, zero it before use.

9. Calculate the molecular weights as described in Section 3.2.6. A data form similar to the one shown in Figure 4.2 can be used for recording the results of the calculations.

10. Repeat steps 8 and 9 until the calculated molecular weights of any three analyses differ from their mean by ≤ 0.3 g/mole.

4.1.3 Multipoint Integrated Sampling and Analysis - This procedure is similar to the single-point integrated sampling procedure, but it is used when the stack cross section is traversed.

1. Locate the sampling points according to the procedures described in Method 1. Determine the minimum number of traverse points, as follows:

a. 8 points for a round stack with < 0.61 m (24 in.) diameter,

b. 9 points for a rectangular stack with an equivalent diameter of < 0.61 m (24 in.), or

Run number 0-1
Date January 9, 1980 Plant Valley Power Company
Sampling location CSP Outlet
Barometric pressure 29.57 in.
Ambient temp. °C 30.5 Stack temp. °C 152
Operator B. C. Blagum

Time	Traverse point	Rate meter flow rate (Q), cm ³ /min	% Dev. ^a
13:00	W-1	500	0
13:05	2	500	0
13:10	3	500	0
13:15	4	500	0
13:20	5	500	0
13:25	6	500	0
13:45	N-1	500	0
13:50	2	500	0
13:55	3	500	0
14:00	4	500	0
14:05	5	500	0
14:10	6	500	0
Avg = 500			0

^a

$$\% \text{ Dev.} = \left(\frac{Q - Q_{\text{avg}}}{Q_{\text{avg}}} \right) 100; \text{ must be } \leq 10\%.$$

Figure 4.3 Integrated bag sampling field data.

c. 12 points for a larger stack.

2. Leak check and purge the bag and the sampling train as described in Subsection 4.1.2.

3. Sample each point at the same rate and for the same time increment. Record the sampling data as shown in Figure 4.3. Collect from 30 to 90 l (1 to 3 ft³) of gas simultaneously with the pollutant emission rate test.

4. Disconnect, seal, and remove the bag to a suitable area for performing the analysis within 8 h, as described in Subsection 4.1.2.

5. Calculate the molecular weight, and repeat the analysis until the results from any three analyses differ from their mean by ≤ 0.3 g/mole.

4.2 Determination of Gas Composition for Emission Rate Factor or Excess Air Calculations

The same three sampling procedures may be used as previously described (Subsections 4.1.1, 4.1.2, and 4.1.3), but in all cases the Orsat analyzer must be used for analysis, and it must be leak checked before and after analysis. In addition, the integrated sampling train (when used) and the flexible bags must be leak checked prior to sampling. Care in using the Orsat and in assuring the accuracy of the results is also required, as described in this section.

4.2.1 Single-Point Grab Sampling and Analysis - Set up, check, and purge the system as described in Subsection 4.1.1. Perform the Orsat analysis immediately according to the manufacturer's instructions and as follows:

1. Draw sample gas into the Orsat and flush (i.e., allow to bubble through the burette) at least three times to saturate the liquid in the burette with the gas being analyzed and to ensure that the air remaining in the manifold is of the same composition as the sample to be analyzed. Caution: Once the flushing has begun, ambient air must not be allowed to enter the manifold.

2. Draw in a fixed volume (usually 100 ml) of the sample gas, following the manufacturer's instructions. Allow a minimum of 5 min for the sample gas to come to temperature equilibrium with the water jacket around the burette (unless the sample and the analyzer have both been at the same temperature for at least 5 min).

3. Proceed with the sequential determinations of CO_2 , O_2 , and CO as directed by the instructions supplied by the manufacturer of the gas analyzer. Make repeated analyses of each component until two consecutive readings are identical. Always make two or three passes through the absorbing solution between readings. Note: If more than three readings of two or three passes are required to reach a constant reading for any component gas, replace the absorbing reagent and repeat the entire sampling sequence.

4. Record the readings on the data form (Figure 4.1), and determine the average value for each component of interest.

5. Leak check the Orsat after analysis. If it does not pass the leak test, repair it and repeat the analysis.

4.2.2 Integrated Single-Point and Multipoint Sampling and Analysis - The sampling procedures are identical to those described in Subsections 4.1.2 and 4.1.3. The flexible bag and the sampling train must be checked for leaks prior to sampling, and the Orsat must be leak checked before and after analysis.

After taking the sample, remove the flexible bag to the analysis area and let it remain there for at least 30 min before analyzing with the Orsat. Analysis must be completed within 4 h of sampling. Perform the analysis according to the manufacturer's instructions and as outlined in Subsection 4.2.1. Repeat the analyses by drawing in new samples of CO_2 , O_2 , or CO from the bag until the following criteria are met:

For CO_2 - Repeat until any three analyses differ by $\leq 0.3\%$ (absolute) when CO_2 is $> 4.0\%$, or by $\leq 0.2\%$ (absolute) when CO_2 is $\leq 4.0\%$. Average the three acceptable readings, and report to the nearest 0.1%.

For O₂ - Repeat until any three analyses differ by $\leq 0.3\%$ when the O₂ is $\leq 15.0\%$, or by $\leq 0.2\%$ when the O₂ is $> 15.0\%$. Average the three acceptable readings and repeat to the nearest 0.1%.

For CO, if required - Repeat until any three results differ by $\leq 0.3\%$.

4.3 Special Precautions

The Orsat analyzer is a simple instrument, but the validity of results depends on operator technique, care, and patience. Special precautions for using an Orsat analyzer include:

1. Do not allow ambient air to enter the Orsat analyzer during testing.

2. Always perform the analysis in the following sequence: absorber No. 1 - CO₂, absorber No. 2 - O₂, and absorber No. 3 - CO. This sequence is necessary because absorber No. 2 will also absorb CO₂, and absorber No. 3 will absorb O₂ and possibly CO₂; double absorption will yield erroneous data.

3. Be sure to saturate the indicating solution in the burette with salt at the operating temperature to prevent absorption of sample gases prior to analysis. Be sure the solution is acidic (as indicated by methyl orange) to enable it to absorb any moisture in the sample gas.

4. Keep the absorber solution from entering the capillary column manifold. Void the test if any absorber solution enters the manifold, and clean the sample manifold with acetone.

5. Allow a minimum of 5 min for gas samples to come to temperature equilibrium with the water jacket before the analysis.

6. Operate the Orsat analyzer under constant temperature and pressure. Be sure that the levels of solutions in the burette and the leveling bottle are the same to ensure equal pressures before taking a reading from the Orsat. The water jacket acts as a buffer for temperature changes.

7. Measure SO₂ concentrations quantitatively (Method 6) if the source being tested is known to have or is suspected of

having high SO_2 concentrations, and subtract the value from that of the CO_2 determination. Measure and correct the values when the SO_2 concentration is suspected to be $\geq 3\%$ (relative) of the CO_2 concentration and when the data are to be used to correct emission rates or to calculate gas flows. If the data are to be used for calculating just the molecular weight (M_d), then SO_2 interferences as high as 0.5% (absolute) or 5000 ppm are acceptable; this level of interference will result in an error of only about 0.1 g/g-mole (0.1 lb/lb-mole) in M_d .

Table 4.1 ACTIVITY MATRIX FOR ON-SITE MEASUREMENTS

Characteristics	Acceptance limits	Frequency and method of measurement	Action if requirements are not met
<u>Grab Sampling</u>			
Sampling train	No leaks	Visually check before each field test	Eliminate leaks before proceeding with test
Sampling points	At the centroid of the cross section or at a point >1 m (3.28 ft) from the walls	Not applicable	Not applicable
<u>Integrated Sampling</u>			
Locate sampling points	8-12 points; see Sub-sec 4.1.3	Not applicable	Not applicable
Flexible bag	No leaks	Check before each field test; see Sec 3.2.1	Replace as necessary
Train	No leaks; vacuum stable for >30 s	Pull vacuum of at least 250 mm (10 in.) Hg	Check all connections, replace items as necessary
Sampling rate	Constant rate	Check using Fig 4.2	Repeat sampling to meet 10% deviation limit
<u>Orsat Analyzer</u>			
Leak check	No leaks for 4 min	Varies with test method; mandatory for emission rate factor and excess air calculations; Sec 3.2.1	Check rubber connections and stopcocks until cause of leak is identified; leak check after repair and reassembly

(continued)

Table 4.1 (continued)

Characteristics	Acceptance limits	Frequency and method of measurement	Action if requirements are not met
<u>Test Results</u>			
For M_d	M_d from each of three grab samples and analyses differ from their mean by <0.3 g/g mole (0.3 lb/lb mole)	For each field test, compare calculated M_d 's to their means	Repeat analysis, perhaps by another operator
For emission rate factor or excess air calculations	<p>1. Make repeated passes thru the absorbing solution until two consecutive readings are the same; compare three readings</p> <p>2. Make repeated analyses; see Subsec 4.2.2 for criteria</p>	<p>1. Compare readings</p> <p>2. Compare analyses of component gases</p>	<p>1. Replace absorbing solution</p> <p>2. Repeat analyses by another operator; check the apparatus and technique</p>

5.0 POSTSAMPLING OPERATIONS

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

5.1 Compare Measured Values Against Theoretical Values

After the analyses have been performed and before the apparatus is disassembled, the measured and the theoretical results (if available) should be compared as a quick check for gross measurement errors.

Combustion nomographs are available for estimating the percentages by volumes of CO_2 and O_2 when the fuel composition is known.^{8,9} Also the nomograph can be used to calculate the molecular weight of the stack gas.

Perform the calculations on the measured data as directed in Section 3.2.6 and perform the following comparison:

$$D_{\text{CO}_2} = \% \text{CO}_{2(\text{m})} - \% \text{CO}_{2(\text{e})}$$

where

D_{CO_2} = difference in measured and estimated values, %,

$\% \text{CO}_{2(\text{m})}$ = measured CO_2 (average of r replicates), %, and

$\% \text{CO}_{2(\text{e})}$ = estimated or theoretical CO_2 , %.

Accept the measured value if D_{CO_2} is $< 2\%$ (absolute); otherwise, check the apparatus, the technique, and the estimating procedures before collecting and analyzing more samples.

Record the estimated or theoretical values on a form similar to Figure 4.1. (Theoretical values may have been calculated and recorded before the field test if sufficient knowledge of the process was available.)

A second method to help eliminate gross errors is the use of the Fyrite sampler at several points during the test. This will indicate whether a problem does exist, but will not reveal which value is indeed correct.

5.2 Disassemble and Inspect Apparatus

When disassembling the apparatus, visually inspect the sampling train components and the Orsat analyzer for damages that could have adversely affected the measured values. Any identified damage that was not detected during the test should be documented on the field data form and thoroughly evaluated by the appropriate apparatus check in the laboratory. After checking if it is concluded that the damage could have biased the measurements, a description of potential bias in the data should be included in the field test report. If possible, repeat the field test.

5.3 Pack Apparatus for Shipment to Laboratory

Pack the apparatus for shipment to the laboratory as described in Section 3.2.3. Return the data forms, prepared in duplicate, to the laboratory--one copy should be sent by mail, and one copy handcarried.

Table 5.1 ACTIVITY MATRIX FOR POSTSAMPLING OPERATIONS

Characteristics	Acceptance limits	Frequency and method of measurement	Action if requirements are not met
Compare measured vs. estimated values of %CO ₂	%CO _{2(m)} - %CO _{2(e)} ≤2% (absolute) suggested	As suggested by administrator; e.g., for each incinerator test when an estimate of %CO ₂ is to be used to correct particulate emission levels	Repeat the analysis for additional samples
Disassemble and inspect apparatus	No damage that could have adversely affected the measurement	Visual inspection	Report damage and its possible bias on measurements to the administrator; use Fig 4.1
Pack apparatus for shipment	Follow specified packing instructions	After each field test	Not applicable

6.0 CALCULATIONS

Table 6.1 at the end of this section summarizes the quality assurance checks pertaining to calculations.

6.1 Excess Air

Use Equation 6-1 to calculate the percentage of excess air. Use the average value for each of the component gases, as follows:

$$\%EA = \left(\frac{\%O_2 - 0.5 \%CO}{0.264 \%N_2 (\%O_2 - 0.5 \%CO)} \right) 100 \quad \text{Equation 6-1}$$

where

$\%EA$ = percent excess air, %,

$\%O_2$ = percent O_2 by volume (dry basis), average of three O_2 values, %,

$\%CO$ = percent CO by volume (dry basis), average of three CO values, %,

$\%N_2$ = percent N_2 by volume (dry basis), average of three N_2 values, %, and

0.264 = ratio of O_2 to N_2 in air, v/v.

The average value for each of the gases is computed from the Orsat analyses satisfying the criteria in Section 3.2.4. Round each average to the nearest 0.1%. In many cases, $\%CO$ will be close to zero and can be dropped to simplify Equation 6-1. Equation 6-1 is applicable whenever most of the N_2 in the flue gas comes from N_2 in the combustion air, as is the case with most fuel and refuse combustion processes. If the fuel contains appreciable amounts of N_2 or if O_2 enrichment is used, Equation 6-1 cannot be used; alternate methods, subject to the approval by the administrator, are required.

6.2 Dry Molecular Weight

Use Equation 6-2 to calculate the dry molecular weight from data in Figure 4.1--i.e., the average values of the component gases reported to the nearest 0.1%.

$$M_d = 0.44 (\%CO_2) + 0.32 (\%O_2) + 0.28 (\%N_2 + \%CO) \quad \text{Equation 6-2}$$

where

M_d = dry molecular weight, g/g-mole (lb/lb-mole),

$\%CO_2$ = percent CO_2 by volume (dry basis), average of three analyses, and

$\%O_2$, $\%N_2$, and $\%CO$ are previously defined.

Round M_d to the nearest 0.1, and record the value Figure 4.1.

6.3 Data Reporting

A copy of Figure 4.1 or an equivalent form should be filed in the laboratory log, and the original should be forwarded either to the home laboratory for further internal review or to the user. An independent check of the calculations should be performed, and the corrected values should be indicated on the form if the differences are more than the acceptable roundoff error. The checking analyst should initial the data form.

Table 6.1 ACTIVITY MATRIX FOR CALCULATIONS

Characteristics	Acceptance limits	Frequency and method of measurement	Action if requirements are not met
Calculations	<p>1. Data form Fig 4.1 contains all data required for calculations of %EA, M_d, and emission rate factor</p> <p>2. Average concentrations calculated to the nearest 0.1%; final calculations rounded to nearest 0.1%</p> <p>3. Independent calculation agrees to the nearest 0.1%</p>	<p>1. Visual observation at each field test</p> <p>2. For each field test, compute the average concentration of three analyses that meet test requirements</p> <p>3. For each field test, repeat calculations starting with raw data</p> <p>4. Visual check</p>	<p>1. Obtain necessary data to complete the form</p> <p>2. Recalculate all results for which computations not consistent with procedure</p> <p>3. Report corrected values of the calculations in Fig 4.1</p> <p>4. Correct calculations</p>
Data reporting	Data report complete with indication of calculation check	Visual observation of each field test	Perform necessary calculation checks

7.0 MAINTENANCE

Little periodic maintenance is required for the Orsat apparatus--other than visual checks of the glassware, tubes, and expansion bulbs. Keep the valves closed during storage, and avoid freezing temperatures. If the Orsat is to be stored over an extended period, it is generally better to remove all of the absorbing reagents. The flexible bags are generally subjected to extensive wear, and require repair or replacement when leaks occur. The pump and rotameter should be kept clean and should be maintained in accordance with manufacturers' instructions.

Table 7.1 ACTIVITY MATRIX FOR MAINTENANCE

Characteristics	Acceptance limits	Frequency and method of measurement	Action if requirements are not met
Glassware, connecting tubing, expansion bulbs	No damage	Visually check before each use	Replace if damaged
Flexible bags	As above	As above	Repair or replace as required
Pump and rotameter	Clean and maintained in accordance with manufacturer's instructions	According to manufacturer's instructions	Adjust/repair or request assistance of supplier

8.0 AUDITING PROCEDURE

An audit is an independent assessment of data quality. It is independent because it is conducted by personnel other than the field crew and by using apparatus and measurement standards that are different from those used by the regular field crew. In the field, routine quality assurance checks are necessary for obtaining good quality data from a series of test runs at one source, but they are not part of the auditing procedure. Table 8.1 at the end of this section summarizes the quality assurance activities for auditing. Based on the results of collaborative tests, three performance audits and a systems audit are recommended in Subsections 8.1 and 8.2. Both types are to be conducted by auditors.

8.1 Performance Audits

Performance audits are quantitative evaluations of the quality of the data produced and recorded by the total measurement system (sample collection, sample analysis, and data processing). These audits should be conducted by the responsible control agency once during every enforcement source test, regardless of whether the test is conducted by a control agency or by a private company personnel. A source test for enforcement comprises a series of runs at one source.

8.1.1 Audit of M_d - Because the maximum relative error in M_d is approximately 4%, it is not practical to audit M_d unless directed by the administrator.

8.1.2 Audit of Analytical Phase Using Certified Gas Mixtures for Emission Rate Correction Factor and Excess Air Determination - Analyzer operation and operator technique can be checked by providing audit samples of certified gas mixtures to be analyzed prior to or along with field samples. One sample should contain concentrations of 2-4% O_2 and 14-18% CO_2 , and another sample should contain concentrations of 2-4% CO_2 and about 15% O_2 .

These gas samples can be transferred from their pressurized storage containers to flexible bags and delivered to the test team on site by the auditor. Replicate samples of the audit gas containing O₂ and CO₂ concentrations similar to the concentrations expected during the test and one sample of the other audit gas should be sufficient for audit of the analytical phase.

The error of the analytical phase can be calculated using Equation 8-1, and should be $\leq 1.0\%$ for CO₂ and O₂.

$$D = \overline{\%V_a} - \%V_c \quad \text{Equation 8-1}$$

where

D = difference in the field test results and the certified audit value, %,

$\overline{\%V_a}$ = field team's value as the average of r replicates, %, and

$\%V_c$ = certified value of audit gas, %.

The emission rate correction factor is not directly proportional to the Orsat analyzer error. Therefore, the standard calculation of %D is not applicable. The results of the calculated %D should be included in the enforcement source test report as an assessment of accuracy of the analytical phase of Method 3 during the actual enforcement source test.

8.1.3 Audit of Data Processing - Data processing errors can be detected by auditing the data recorded on the field and the laboratory forms. The original and the field check calculations should agree; if not, all of the remaining data should be rechecked by the auditor, and any errors should be clearly explained to the team to prevent or minimize reoccurrence. The data processing errors may also be detected in copies of data sets compiled and filed in the field and in copies of manual data reductions (or computer printouts, if used) forwarded to the evaluator for audit. Calculation errors are prevalent among users of Method 3.

8.2 Systems Audit

A systems audit is an on-site qualitative inspection and review of the quality assurance checks used by the team for the total measurement system (sample collection, sample analysis, data processing, etc.). Initially, a systems audit specified by a quality assurance coordinator should be conducted for each enforcement source test, which by definition comprises three runs at one source. After the team gains experience with the procedure, the frequency of audit may be reduced, for example, to once for every four tests. The auditor should have extensive experience in source sampling--more specifically, with the characterization technique being audited.

The functions of the auditor are summarized as follows:

1. Observe procedures and techniques of the field team during sample collection.
2. Check/verify the records of apparatus calibration and the quality control charts used in the laboratory analysis.
3. Record the results of the audit and forward them with comments on source team management to the quality assurance coordinator so that any needed corrective actions may be implemented.

8.2.1 Collecting On-Site Information - While on-site, the auditor should observe the field team's overall performance of the source test. Specific operations to observe should include, but not be limited to:

1. Setting up and leak testing the sampling train.
2. Purging the sampling train with stack gas prior to collecting the sample.
3. Proportional sampling.
4. Transferring of the sample from the collapsible bag to the Orsat analyzer.

Table 8.1 is a suggested form for use by the auditor.

8.2.2 Collecting Laboratory Information - When visiting the field team's home laboratory, the auditor should check the records to verify that the performance criteria in Table 4.3 (Section 3.2.4) have been met since the last audit was performed.

Yes	No	OPERATION
<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	<p>Presampling Operation</p> <p>1. Availability of theoretical value</p> <p>2. Use of modified Orsat analyzer (0.1-ml divisions)</p>
<input checked="" type="checkbox"/> <input checked="" type="checkbox"/> <input checked="" type="checkbox"/> <input checked="" type="checkbox"/> <input checked="" type="checkbox"/> <input type="checkbox"/> <input type="checkbox"/>	<input type="checkbox"/> <input type="checkbox"/> <input type="checkbox"/> <input type="checkbox"/> <input type="checkbox"/> <input checked="" type="checkbox"/> <input checked="" type="checkbox"/>	<p>On-Site Measurements</p> <p>3. Setting up and leak testing the sampling train</p> <p>4. Purging the sampling train with stack gas prior to collecting the sample</p> <p>5. Constant rate sampling</p> <p>6. Transfer of sample from collapsible bag to the Orsat analyzer</p> <p>7. Maintaining constant pressure throughout the test</p> <p>8. Exposing the sample to ambient air</p> <p>9. Spent absorbing reagent</p>
<input checked="" type="checkbox"/> <input checked="" type="checkbox"/> <input checked="" type="checkbox"/> <input checked="" type="checkbox"/> <input checked="" type="checkbox"/>	<input type="checkbox"/> <input type="checkbox"/> <input type="checkbox"/> <input type="checkbox"/> <input type="checkbox"/>	<p>Postsampling Measurements</p> <p>10. Perform independent calculations using data from audit</p> <p>11. Compare the audit value with the field team's test value</p> <p>12. Make sufficient passes for complete absorption of a component gas</p> <p>13. Minimize volumetric reading error</p> <p>14. Check/verify applicable records of apparatus calibration checks and quality control charts in the field team's home laboratory</p>
General Comments		

Figure 8.1 Checklist for Method 3 for use by the auditor.

Table 8.1 ACTIVITY MATRIX FOR AUDITING PROCEDURES

Audit	Acceptance limits	Frequency and method of measurement	Action if requirements are not met
Analytical audit	$D = \overline{\%V}_a - \%V_c$ <p>$\overline{\%V}_a$ = mean value of measurements by field team</p> <p>$\%V_c$ = certified value of audit gas</p>	As designated by the administrator	Advise team of sources of errors, and request they seek additional training; rerun test if necessary for determination of compliance
Data processing audit	Agreement of original and check calculations	Once during each enforcement source test; independent calculations starting with raw data	Check and correct all data
Systems audit	Technique described in this section	Once during each enforcement test until experience gained, then every fourth test; observe techniques; use audit checklist Fig 8.1	Explain to team the deviations from recommended techniques, and note deviations on Fig 8.1

9.0 RECOMMENDED STANDARDS FOR ESTABLISHING TRACEABILITY

To acquire data of good quality, two considerations are essential: (1) the measurement process must be in a state of statistical control at the time of the measurement, and (2) the systematic errors combined with the random variations (errors of measurement) must result in an acceptable level of uncertainty. As evidence of good quality, it is necessary to perform quality control checks and independent audits of the measurement process, to use materials and measurement procedures which can be traced to an appropriate reference standard, and to document data from the checks and audits (e.g., by means of a quality control chart).

Data must be routinely obtained by repeat measurements of standard reference samples, primary, secondary, and/or working standards. The working calibration standards should be traceable to either primary or higher order standards.

In the case of absorption type gas analyzers, operator techniques and analyzer operations can be checked by sampling two certified mixtures of bottled gas containing 2-4% O₂ and 14-18% CO₂, or 2-4% CO₂ and about 15% O₂. Bottled gases used for audit purposes should be traceable to NBS standards.

10.0 REFERENCE METHOD ^a

METHOD 3—GAS ANALYSIS FOR CARBON DIOXIDE, OXYGEN, EXCESS AIR, AND DRY MOLECULAR WEIGHT

1. Principle and Applicability

1.1 Principle. A gas sample is extracted from a stack, by one of the following methods: (1) single-point, grab sampling; (2) single-point, integrated sampling; or (3) multi-point, integrated sampling. The gas sample is analyzed for percent carbon dioxide (CO₂), percent oxygen (O₂), and, if necessary, percent carbon monoxide (CO). If a dry molecular weight determination is to be made, either an Orsat or a Fyrite analyzer may be used for the analysis, for excess air or emission rate correction factor determination, an Orsat analyzer must be used.

1.2 Applicability. This method is applicable for determining CO₂ and O₂ concentrations, excess air, and dry molecular weight of a sample from a gas stream of a fossil-fuel combustion process. The method may also be applicable to other processes where it has been determined that components other than CO₂, O₂, CO, and nitrogen (N₂) are not present in concentrations sufficient to affect the results.

Other methods, as well as modifications to the procedure described herein, are also applicable for some or all of the above determinations. Examples of specific methods and modifications include: (1) a multi-point sampling method using an Orsat analyzer to analyze individual grab samples obtained at each point; (2) a method using CO₂ or O₂ and stoichiometric calculations to determine dry molecular weight and excess air; (3) assigning a value of 39.0 for dry molecular weight, in lieu of actual measurements, for processes burning natural gas, coal, or oil. These methods and modifications may be used, but are subject to the approval of the Administrator.

2. Apparatus

As an alternative to the sampling apparatus and systems described herein, other sampling systems (e.g., liquid displacement) may be used provided such systems are capable of obtaining a representative sample and maintaining a constant sampling rate, and are otherwise capable of yielding acceptable results. Use of such systems is subject to the approval of the Administrator.

2.1 Grab Sampling (Figure 3-1).

2.1.1 Probe. The probe should be made of stainless steel or borosilicate glass tubing and should be equipped with an in-stack or out-stack filter to remove particulate matter (a plug of glass wool is satisfactory for this purpose). Any other material inert to O₂, CO₂, CO, and N₂ and resistant to temperature at sampling conditions may be used for the probe; examples of such material are aluminum, copper, quartz glass and Teflon.

2.1.2 Pump. A one-way squeeze bulb, or equivalent, is used to transport the gas sample to the analyzer.

2.2 Integrated Sampling (Figure 3-2).

2.2.1 Probe. A probe such as that described in Section 2.1.1 is suitable.

^a Mention of trade names or specific products does not constitute endorsement by the Environmental Protection Agency.

2.2.2 Condenser. An air-cooled or water-cooled condenser, or other condenser that will not remove O₂, CO₂, CO, and N₂, may be used to remove excess moisture which would interfere with the operation of the pump and flow meter.

2.2.3 Valve. A needle valve is used to adjust sample gas flow rate.

2.2.4 Pump. A leak-free, diaphragm-type pump, or equivalent, is used to transport sample gas to the flexible bag. Install a small surge tank between the pump and flow meter to eliminate the pulsation effect of the diaphragm pump on the rotameter.

2.2.5 Rate Meter. The rotameter, or equivalent rate meter, used should be capable of measuring flow rate to within ± 2 percent of the selected flow rate. A flow rate range of 500 to 1000 cm³/min is suggested.

2.2.6 Flexible Bag. Any leak-free plastic (e.g., Tedlar, Mylar, Teflon) or plastic-coated aluminum (e.g., aluminumized Mylar) bag, or equivalent, having a capacity consistent with the selected flow rate and time length of the test run, may be used. A capacity in the range of 55 to 90 liters is suggested.

To leak-check the bag, connect it to a water manometer and pressurize the bag to 5 to 10 cm H₂O (2 to 4 in. H₂O). Allow to stand for 10 minutes. Any displacement in the water manometer indicates a leak. An alternative leak-check method is to pressurize the bag to 5 to 10 cm H₂O (2 to 4 in. H₂O) and allow to stand overnight. A deflated bag indicates a leak.

2.2.7 Pressure Gauge. A water-filled U-tube manometer, or equivalent, of about 28 cm (12 in.) is used for the flexible bag leak-check.

2.2.8 Vacuum Gauge. A mercury manometer, or equivalent, of at least 760 mm Hg (30 in. Hg) is used for the sampling train leak-check.

2.3 Analysis. For Orsat and Fyrite analyzer maintenance and operation procedures, follow the instructions recommended by the manufacturer, unless otherwise specified herein.

2.3.1 Dry Molecular Weight Determination. An Orsat analyzer or Fyrite type combustion gas analyzer may be used.

2.3.2 Emission Rate Correction Factor or Excess Air Determination. An Orsat analyzer must be used. For low CO₂ (less than 4.0 percent) or high O₂ (greater than 15.0 percent) concentrations, the measuring burette of the Orsat must have at least 0.1 percent subdivisions.

3. Dry Molecular Weight Determination

Any of the three sampling and analytical procedures described below may be used for determining the dry molecular weight.

3.1 Single-Point, Grab Sampling and Analytical Procedure.

3.1.1 The sampling point in the duct shall either be at the centroid of the cross section or at a point no closer to the walls than 1.00 m (3.3 ft), unless otherwise specified by the Administrator.

3.1.2 Set up the equipment as shown in Figure 3-1, making sure all connections ahead of the analyzer are tight and leak-free. If an Orsat analyzer is used, it is recommended that the analyzer be leak-checked by following the procedure in Section 5; however, the leak-check is optional.

3.1.3 Place the probe in the stack, with the tip of the probe positioned at the sampling point; purge the sampling line. Draw a sample into the analyzer and immediately analyze it for percent CO₂ and percent O₂. Determine the percentage of the gas that is N₂ and CO by subtracting the sum of the percent CO₂ and percent O₂ from 100 percent. Calculate the dry molecular weight as indicated in Section 6.3.

3.1.4 Repeat the sampling, analysis, and calculation procedures, until the dry molecular weights of any three grab samples differ from their mean by no more than 0.3 g/g-mole (0.3 lb/lb-mole). Average these three molecular weights, and report the results to the nearest 0.1 g/g-mole (lb/lb-mole).

3.2 Single-Point, Integrated Sampling and Analytical Procedure.

3.2.1 The sampling point in the duct shall be located as specified in Section 3.1.1.

3.2.2 Leak-check (optional) the flexible bag as in Section 2.2.6. Set up the equipment as shown in Figure 3-2. Just prior to sampling, leak-check (optional) the train by placing a vacuum gauge at the condenser inlet, pulling a vacuum of at least 2.0 mm Hg (10 in. Hg), plugging the outlet at the quick disconnect, and then turning off the pump. The vacuum should remain stable for at least 0.5 minute. Evacuate the flexible bag. Connect the probe and place it in the stack, with the tip of the probe positioned at the sampling point; purge the sampling line. Next, connect the bag, and make sure that all connections are tight and leak-free.

3.2.3 Sample at a constant rate. The sampling run should be simultaneous with, and for the same total length of time as, the pollutant emission rate determination. Collection of at least 5 liters (100 ft³) of sample gas is recommended; however, smaller volumes may be collected, if desired.

3.2.4 Obtain one integrated fine gas sample during each pollutant emission rate determination. Within 8 hours after the sample is taken, analyze it for percent CO₂ and percent O₂ using either an Orsat analyzer or a Fyrite-type combustion gas analyzer. If an Orsat analyzer is used, it is recommended that the Orsat leak-check described in Section 5 be performed before this determination; however, the check is optional. Determine the percentage of the gas that is N₂ and CO by subtracting the sum of the percent CO₂ and percent O₂

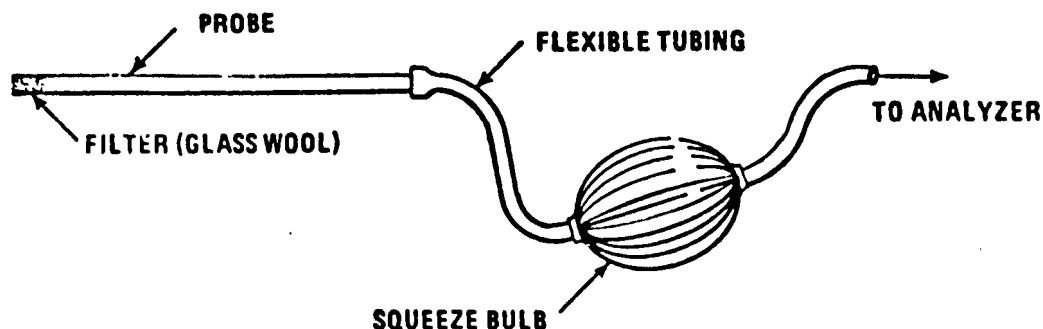


Figure 3-1. Grab-sampling train.

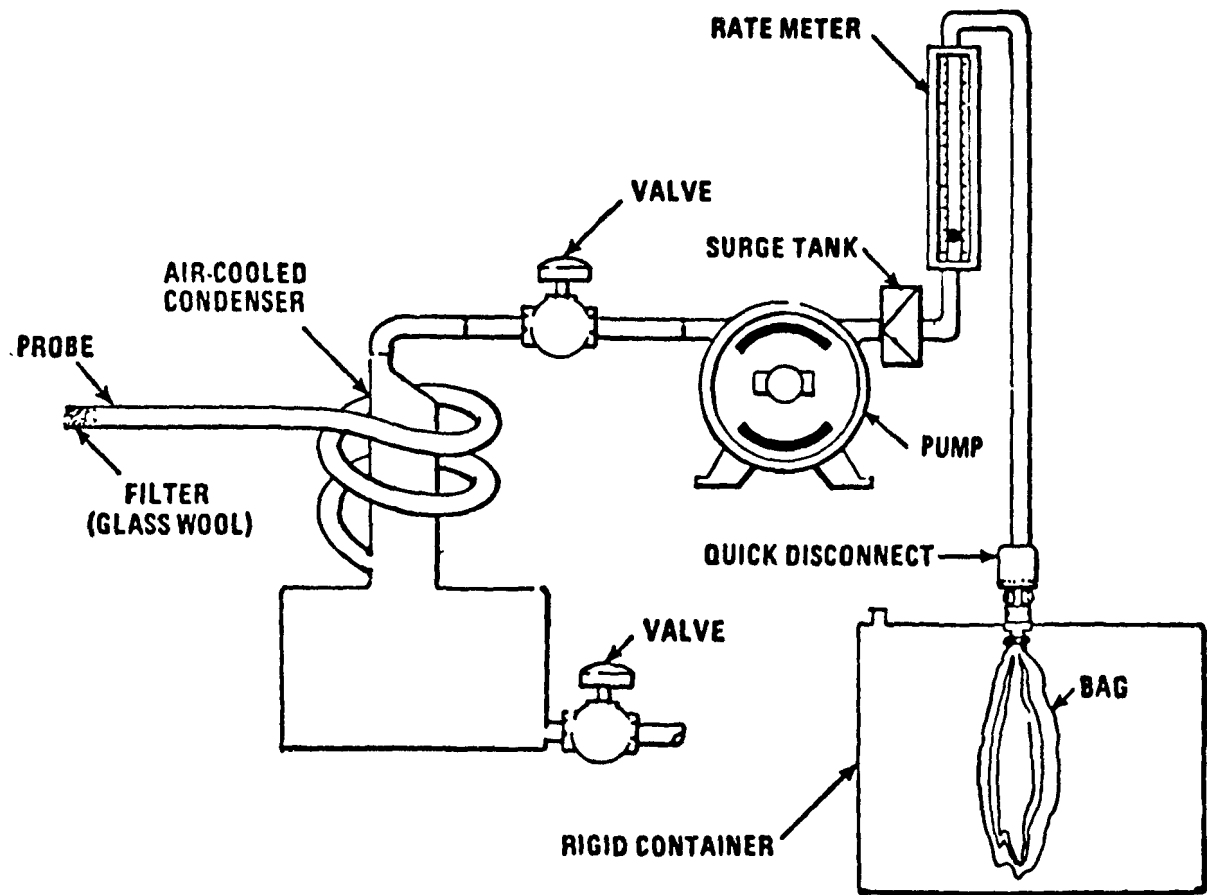


Figure 3-2. Integrated gas-sampling train.

TIME	TRAVERSE PT.	Q 1pm	% DEV. ^a
AVERAGE			

^a % DEV = $\left(\frac{Q \cdot Q_{avg}}{Q_{avg}} \right) 100$ (MUST BE ≤ 10%)

Figure 3-3. Sampling rate data.

from 100 percent. Calculate the dry molecular weight as indicated in Section 6.3.

3.2.5 Repeat the analysis and calculation procedures until the individual dry molecular weights for any three analyses differ from their mean by no more than 0.3 g/g-mole (0.3 lb/lb-mole). Average these three molecular weights, and report the results to the nearest 0.1 g/g-mole (0.1 lb/lb-mole).

3.3 Multi-Point, Integrated Sampling and Analytical Procedure

3.3.1 Unless otherwise specified by the Administrator, a minimum of eight traverse points shall be used for circular stacks having diameters less than 0.61 m (24 in.), a minimum of nine shall be used for rectangular stacks having equivalent diameters less than 0.61 m (24 in.), and a minimum of twelve traverse points shall be used for all other cases. The traverse points shall be located according to Method 1. The use of fewer points is subject to approval of the Administrator.

3.3.2 Follow the procedures outlined in Sections 3.2.2 through 3.2.5, except for the following: traverse all sampling points and sample at each point for an equal length of time. Record sampling data as shown in Figure 3-3.

4. Emission Rate Correction Factor or Excess Air Determination

NOTE.—A Fyrite-type combustion gas analyzer is not acceptable for excess air or emission rate correction factor determination, unless approved by the Administrator. If both percent CO_2 and percent O_2 are measured, the analytical results of any of the three procedures given below may also be used for calculating the dry molecular weight.

Each of the three procedures below shall be used only when specified in an applicable subpart of the standards. The use of these procedures for other purposes must have specific prior approval of the Administrator.

4.1 Single-Point Grab Sampling and Analytical Procedure

4.1.1 The sampling point in the duct shall either be at the centroid of the section or at a point no closer to the walls than 1.3 ft (0.4 m), unless otherwise specified by the Administrator.

4.1.2 Set up the equipment as shown in Figure 3-1, making sure all connections ahead of the analyzer are tight and leak-free. Leak-check the Orsat analyzer according to the procedure described in Section 5. This leak-check is mandatory.

4.1.3 Place the probe in the stack, with the tip of the probe positioned at the sampling point, purge the sampling line. Draw a sample into the analyzer. For emission rate correction factor determination, immediately analyze the sample, as outlined in Sections 4.1.4 and 4.1.5, for percent CO_2 or percent O_2 . If excess air is desired, proceed as follows: (1) immediately analyze the sample, as in Sections 4.1.4 and 4.1.5, for percent CO_2 , O_2 , and CO ; (2) determine the percentage of the gas that is N_2 by subtracting the sum of the percent CO_2 , percent O_2 , and percent CO from 100 percent; and (3) calculate percent excess air as outlined in Section 6.2.

4.1.4 To ensure complete absorption of the CO_2 , O_2 , or if applicable, CO , make repeated passes through each absorbing solution, until two consecutive readings are the same. Several passes (three or four) should be made between readings. (If constant readings cannot be obtained after three consecutive readings, replace the absorbing solution.)

4.1.5 After the analysis is completed, leak-check (mandatory) the Orsat analyzer once again, as described in Section 5. For the results of the analysis to be valid, the Orsat analyzer must pass this leak test before and after the analysis. **NOTE.**—Since this single-point, grab sampling and analytical procedure is normally conducted in conjunction with a single-point, grab sampling and analytical procedure for a pollutant, only one analysis is ordinarily conducted. Therefore, great care must be taken to obtain a valid sample and analysis. Although in most cases only CO_2 or O_2 is required, it is recommended that both CO_2 and O_2 be measured, and that Citation 5 in the Bibliography be used to validate the analytical data.

4.2 Single-Point, Integrated Sampling and Analytical Procedure

4.2.1 The sampling point in the duct shall be located as specified in Section 4.1.1.

4.2.2 Leak-check (mandatory) the flexible bag as in Section 2.2.6. Set up the equipment as shown in Figure 3-2. Just prior to sampling, leak-check (mandatory) the train by placing a vacuum gauge at the condenser inlet, pulling a vacuum of at least 250 mm Hg (10 in. Hg), plugging the outlet at the quick disconnect, and then

turning off the pump. The vacuum shall remain stable for at least 0.5 minute. Evacuate the flexible bag. Connect the probe and place it in the stack, with the tip of the probe positioned at the sampling point; purge the sampling line. Next, connect the bag and make sure that all connections are tight and leak free.

4.2.3 Sample at a constant rate, or as specified by the Administrator. The sampling run must be simultaneous with, and for the same total length of time as, the pollutant emission rate determination. Collect at least 30 liters (1.00 ft³) of sample gas. Smaller volumes may be collected, subject to approval of the Administrator.

4.2.4 Obtain one integrated flue gas sample during each pollutant emission rate determination. For emission rate correction factor determination, analyze the sample within 4 hours after it is taken for percent CO_2 or percent O_2 (as outlined in Sections 4.2.5 through 4.2.7). The Orsat analyzer must be leak-checked (see Section 5) before the analysis. If excess air is desired, proceed as follows: (1) within 4 hours after the sample is taken, analyze it (as in Sections 4.2.5 through 4.2.7) for percent CO_2 , O_2 , and CO ; (2) determine the percentage of the gas that is N_2 by subtracting the sum of the percent CO_2 , percent O_2 , and percent CO from 100 percent; (3) calculate percent excess air, as outlined in Section 6.2.

4.2.5 To ensure complete absorption of the CO_2 , O_2 , or if applicable, CO , make repeated passes through each absorbing solution until two consecutive readings are the same. Several passes (three or four) should be made between readings. (If constant readings cannot be obtained after three consecutive readings, replace the absorbing solution.)

4.2.6 Repeat the analysis until the following criteria are met:

4.2.6.1 For percent CO_2 , repeat the analytical procedure until the results of any three analyses differ by no more than (a) 0.3 percent by volume when CO_2 is greater than 4.0 percent or (b) 0.2 percent by volume when CO_2 is less than or equal to 4.0 percent. Average the three acceptable values of percent CO_2 and report the results to the nearest 0.1 percent.

4.2.6.2 For percent O_2 , repeat the analytical procedure until the results of any three analyses differ by no more

than (a) 0.3 percent by volume when O_2 is less than 15.0 percent or (b) 0.2 percent by volume when O_2 is greater than 15.0 percent. Average the three acceptable values of percent O_2 and report the results to the nearest 0.1 percent.

4.2.6.3 For percent CO , repeat the analytical procedure until the results of any three analyses differ by no more than 0.3 percent. Average the three acceptable values of percent CO and report the results to the nearest 0.1 percent.

4.2.7 After the analysis is completed, leak-check (mandatory) the Orsat analyzer once again, as described in Section 5. For the results of the analysis to be valid, the Orsat analyzer must pass this leak test before and after the analysis. **NOTE.**—Although in most instances only CO_2 or O_2 is required, it is recommended that both CO_2 and O_2 be measured, and that Citation 5 in the Bibliography be used to validate the analytical data.

4.3 Multi-Point, Integrated Sampling and Analytical Procedure

4.3.1 Both the minimum number of sampling points and the sampling point location shall be as specified in Section 3.3.1 of this method. The use of fewer points than specified is subject to the approval of the Administrator.

4.3.2 Follow the procedures outlined in Sections 4.2.2 through 4.2.7, except for the following: Traverse all sampling points and sample at each point for an equal length of time. Record sampling data as shown in Figure 3-3.

5. Leak-Check Procedure for Orsat Analyzers

Moving an Orsat analyzer frequently causes a leak. Therefore, an Orsat analyzer should be thoroughly leak-checked on site before the flue gas sample is introduced into it. The procedure for leak checking an Orsat analyzer is:

5.1.1 Bring the liquid level in each pipette up to the reference mark on the capillary tubing and then close the pipette stopcock.

5.1.2 Raise the leveling bulb sufficiently to bring the confining liquid meniscus past the graduated portion of the burette and then close the manifold stopcock.

5.1.3 Record the meniscus position.

5.1.4 Observe the meniscus in the burette and the liquid level in the pipette for movement over the next 4 minutes.

5.1.5 For the Orsat analyzer to pass the leak-check, two conditions must be met.

5.1.5.1 The liquid level in each pipette must not fall below the bottom of the capillary tubing during this 4-minute interval.

5.1.5.2 The meniscus in the burette must not change by more than 0.2 ml during this 4-minute interval.

5.1.6 If the analyzer fails the leak-check procedure, all rubber connections and stopcocks should be checked until the cause of the leak is identified. Leaking stopcocks must be disassembled, cleaned, and regreased. Leaking rubber connections must be replaced. After the analyzer is reassembled, the leak-check procedure must be repeated.

6. Calculations

6.1 Nomenclature.

M_d = Dry molecular weight, g/g-mole (lb/lb-mole).

%EA = Percent excess air.

% CO_2 = Percent CO_2 by volume (dry basis).

% O_2 = Percent O_2 by volume (dry basis).

%CO = Percent CO by volume (dry basis).

% N_2 = Percent N_2 by volume (dry basis).

0.264 = Ratio of O_2 to N_2 in air, v/v.

0.280 = Molecular weight of N_2 or CO , divided by 100.

0.320 = Molecular weight of O_2 divided by 100.

0.440 = Molecular weight of CO_2 divided by 100.

6.2 Percent Excess Air. Calculate the percent excess air (if applicable), by substituting the appropriate values of percent O_2 , CO , and N_2 (obtained from Section 4.1.3 or 4.2.6) in Equation 3-1.

$$\%EA = \left[\frac{\%O_2 - 0.5\%CO}{0.264\%N_2 - (\%O_2 - 0.5\%CO)} \right] 100$$

Equation 3-1

NOTE.—The equation above assumes that ambient air is used as the source of O_2 and that the fuel does not contain appreciable amounts of N_2 (as do coke oven or blast furnace gases). For those cases when appreciable amounts of N_2 are present (coal, oil, and natural gas do not contain appreciable amounts of N_2) or when oxygen enrichment is used, alternate methods, subject to approval of the Administrator, are required.

6.3 Dry Molecular Weight. Use Equation 3-2 to calculate the dry molecular weight of the stack gas.

$$M_d = 0.10(\%CO) + 0.32(\%O_2) + 0.280(\%N_2 + \%CO)$$

Equation 3-2

NOTE.—The above equation does not consider argon in air (about 0.9 percent, molecular weight of 39.7). A negative error of about 0.4 percent is introduced. The tester may opt to include argon in the analysis using procedures subject to approval of the Administrator.

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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 M3-1.3 indicates that the form is Figure 1.3 in Section 3.2.1 of the Method 3 Handbook. Future revisions of these forms, if any, can be documented by 1.3A, 1.3B, etc. Five of the blank forms listed below are included in this section. Two are in the Methods Highlights Section as shown by the MH following the form number.

<u>Form</u>	<u>Title</u>
1.3	Procurement Log
2.1	\bar{X} and R Chart
3.1 (MH)	Pretest Preparations
4.1 (MH)	On-Site Measurements Checklist
4.2	Gas Analysis Data Form
4.3	Integrated Bag Sampling Data Form
8.1	Checklist for Method 3 for Use by the Auditor

PROCUREMENT LOG

[illegible]

\bar{X} AND R CHART

PROJECT NAME		MEASUREMENT PERFORMED										MEASUREMENT UNITS											
DATE																							
MEASUREMENT	RESULT CODE	1																					
		2																					
		3																					
		4																					
SUM																							
AVERAGE, \bar{X}																							
RANGE, R																							
AVERAGES, \bar{X}																							
RANGES, R																							
Comments (Correct Action, etc.)																							

GAS ANALYSIS DATA FORM

PLANT _____ COMMENTS: _____
 DATE _____ TEST NO _____
 SAMPLING TIME (24-hr CLOCK) _____
 SAMPLING LOCATION _____
 SAMPLE TYPE (BAG, INTEGRATED, CONTINUOUS) _____
 ANALYTICAL METHOD _____
 AMBIENT TEMPERATURE _____
 OPERATOR _____

<div style="display: inline-block; transform: rotate(-45deg);"> RUN GAS </div>	1		2		3		AVERAGE NET VOLUME	MULTIPLIER	MOLECULAR WEIGHT OF STACK GAS (DRY BASIS) M_d
	ACTUAL READING	NET	ACTUAL READING	NET	ACTUAL READING	NET			
CO ₂								44/100	
O ₂ (NET IS ACTUAL O ₂ READING MINUS ACTUAL CO ₂ READING)								32/100	
CO (NET IS ACTUAL CO READING MINUS ACTUAL O ₂ READING)								28/100	
N ₂ (NET IS 100 MINUS ACTUAL CO READING)								28/100	
								TOTAL	

INTEGRATED BAG SAMPLING DATA FORM

Run number _____

Date	Plant
------	-------

Sampling location

Barometric pressure _____

Ambient temp. °C Stack temp. °C

Operator

[illegible]

a

$$\% \text{ Dev.} = \left(\frac{Q - Q_{\text{avg}}}{Q_{\text{avg}}} \right) 100; \text{ must be } \leq 10\%.$$

CHECKLIST FOR METHOD 3 FOR USE BY THE AUDITOR

Yes	No	OPERATION
		Presampling Operation
— —	— —	1. Availability of theoretical value 2. Use of modified Orsat analyzer (0.1-ml divisions)
		On-Site Measurements
— — — — — — — —	— — — — — — — —	3. Setting up and leak testing the sampling train 4. Purging the sampling train with stack gas prior to collecting the sample 5. Constant rate sampling 6. Transfer of sample from collapsible bag to the Orsat analyzer 7. Maintaining constant pressure throughout the test 8. Exposing the sample to ambient air 9. Spent absorbing reagent
		Postsampling Measurements
— — — — —	— — — — —	10. Perform independent calculations using data from audit 11. Compare the audit value with the field team's test value 12. Make sufficient passes for complete absorption of a component gas 13. Minimize volumetric reading error 14. Check/verify applicable records of apparatus calibration checks and quality control charts in the field team's home laboratory
General Comments		

Section 3.3

METHOD 4--DETERMINATION OF MOISTURE IN STACK GASES

OUTLINE

<u>Section</u>	<u>Documentation</u>	<u>Number of Pages</u>
SUMMARY	3.3	2
METHOD HIGHLIGHTS	3.3	8
METHOD DESCRIPTION		
1. PROCUREMENT OF APPARATUS AND SUPPLIES	3.3.1	9
2. CALIBRATION OF APPARATUS	3.3.2	19
3. PRESAMPLING OPERATIONS	3.3.3	7
4. ON-SITE MEASUREMENTS	3.3.4	10
5. POSTSAMPLING OPERATIONS	3.3.5	4
6. CALCULATIONS	3.3.6	8
7. MAINTENANCE	3.3.7	3
8. AUDITING PROCEDURE	3.3.8	4
9. RECOMMENDED STANDARDS FOR ESTABLISHING TRACEABILITY	3.3.9	1
10. REFERENCE METHOD	3.3.10	5
11. REFERENCES	3.3.11	1
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SUMMARY

A gas sample is extracted at a constant rate from the source; moisture is removed from the sample stream and determined either volumetrically or gravimetrically.

This Reference Method is used for the accurate determination of moisture content (as needed to calculate emission data) of stack gas. The Reference Method is often conducted simultaneously with a pollutant emission measurement run; when it is, calculation of percent isokinetic, pollutant emission rate, etc., for the run shall be based upon the results of the Reference Method or its equivalent. Alternative methods capable of yielding results within 1% water of the Reference Method may be used, subject to the approval of the administrator.

Note: The Reference Method may yield questionable results when applied to saturated gas streams or to gas streams that contain water droplets. Therefore, when these conditions exist or are suspected, a second method for determining the moisture content shall be used simultaneously with the Reference Method, as follows. Assume that the gas stream is saturated. Attach a temperature sensor capable of measuring to $\pm 1^{\circ}\text{C}$ (2°F) to the Reference Method probe. Measure the stack gas temperature at each traverse point during the Reference Method traverse; calculate the average stack gas temperature. Next, determine the moisture percentage either by using a psychrometric chart and making appropriate corrections if stack pressure is different from that of the chart or by using saturation vapor pressure tables. In cases where the psychrometric chart or the saturation vapor pressure tables are not applicable (based on evaluation of the process), alternate methods, subject to the approval of the administrator, shall be used.

The procedure described in Method 5 for determining moisture content is acceptable as a Reference Method.

The Method Description which follows is based on the method promulgated in the Federal Register, Vol. 42, No. 160, August 18, 1977.

A complete copy of the Reference Method is contained in Section 3.3.10. References 1 and 2 in Section 3.3.11 were used in the subsections concerning the description, calibration, and maintenance of the sampling train. Data forms are provided in Section 3.3.12 for the convenience of the Handbook user.

METHOD HIGHLIGHTS

Method 4 is a gaseous sampling method for the determination of water vapor content of stack gas. This method requires fewer quality control activities than the other methods in this Handbook. Since moisture is collected as a gas, the analysis is not easily biased; furthermore, water vapor is not a regulated pollutant. However, an accurate determination of moisture content is usually needed to set and determine the isokinetic sampling rate and also to perform emission data calculations. The accuracy and precision³ of the method have been demonstrated to be acceptable except when applied to saturated gas streams or to streams that contain water droplets.

The blank data forms at the end of this section may be removed from the Handbook and used as checklists during the pretest, field sampling, and posttest operations. Each form has a subtitle (e.g., Method 4, Figure 2.5) to aid the user in locating a similar filled-in form in the Method Description. Items/parameters that can cause significant error are designated with an asterisk on each form.

1. Procurement of Equipment - Section 3.3.1 (Procurement of Apparatus and Supplies) gives the specifications, criteria, and design features for equipment and materials required for performing Method 4 tests. The sampling apparatus has the same design criteria as Method 5 with the exception that a pitot tube system and sample nozzle are not required for collecting the sample. This section is designed as a guide in the procurement and initial check of equipment and supplies. The activity matrix (Table 1.1) at the end of Section 3.3.1 can be used as a quick reference, and follows the same order as the written descriptions in the main text.

2. Pretest Preparations - Section 3.3.2 (Calibration of Apparatus) provides a step-by-step description of the required calibration procedures. The calibration of the Method 4 equipment is similar to that of Method 5 with the exception that

Method 4 sampling is performed at a constant rate not in excess of $0.021 \text{ m}^3/\text{min}$ ($0.75 \text{ ft}^3/\text{min}$). The calibration section can be removed and compiled, along with calibration sections for all other methods, into a separate quality assurance reference manual for use by calibration personnel. A pretest checklist (Figure 2.5) or similar form should be used to summarize the calibration data.

Section 3.3.3 (Presampling Operations) provides the tester with a guide for supplies and equipment preparation for field tests. Sample impingers may be charged in the base laboratory as long as the water-filled impinger section and silica gel impinger are each tightly capped. The pretest preparation form (Figure 3.1) can be used as an equipment checkout and packing list. An important item in the pretest preparation is the determination of stack gas saturation or water droplet content. Under these conditions, a specially calibrated stack gas temperature sensor is required for moisture determination. The methods for packing and the descriptions of packing containers should help protect the equipment, but are not required.

3. On-Site Measurements - Section 3.3.4 (On-Site Measurements) contains a step-by-step procedure for performing sampling and sample recovery. Testing is performed at a constant rate not to exceed $0.02 \text{ m}^3/\text{min}$ ($0.75 \text{ ft}^3/\text{min}$). When the stack gas is suspected of being saturated or having water droplets, the additional procedure for accurately measuring the stack temperature to determine the moisture content with the saturated vapor pressure and absolute stack temperature must be performed and compared with the Reference Method. The on-site measurement checklist (Figure 4.4) is provided to assist the tester with a quick method for checking requirements.

4. Posttest Operations - Section 3.3.5 (Postsampling Operations) gives the posttest equipment check procedures. Figure 5.1 or a similar form should be used to provide a summary of the posttest calibration checks, and should be included in the emission test report. No control samples are required for

analysis since the analysis is only a gravimetric or volumetric determination of a sample which is large enough to provide an easy determination.

Section 3.3.6 (Calculations) provides the tester with the required equations, nomenclature, and suggested number of significant digits. It is suggested that a programmable calculator be used if available to reduce the chance of calculation error.

Section 3.3.7 (Maintenance) provides the tester with a guide for a routine maintenance program. This program is not required, but if performed, should reduce malfunctions.

5. Auditing Procedure - Section 3.3.8 (Auditing Procedure) provides a description of necessary activities for conducting performance and system audits. A performance audit of the data processing and a systems audit of the on-site measurements should provide independent assessments of the quality of data needed to allow the collaborative test results to be used in the final data evaluation.

PRETEST SAMPLING CHECKS
(Method 4, Figure 2.5)

Date _____ Calibrated by _____
Meter box number _____ $\Delta H@$ _____

Dry Gas Meter*

Pretest calibration factor _____ (within 2% of the average factor for each calibration run)

Impinger Thermometer

Was a pretest temperature correction used? _____ yes _____ no
If yes, temperature correction _____ (within 2°C (4°F) of reference value)

Dry Gas Meter Thermometer

Was a pretest temperature correction made? _____ yes _____ no
If yes, temperature correction _____ (within 6°C (10.8°F) of reference value)

Barometer

Was the pretest field barometer reading correct? ____ yes ____ no

Stack Gas Temperature Sensor (if required)*

Was a temperature sensor required for moisture determination purposes? _____ yes _____ no

Was a pretest temperature correction used? _____ yes _____ no
If yes, temperature correction _____ (within $\pm 1^\circ\text{C}$ (2°F) over the entire range)

Did the temperature sensor agree with the reference thermometer (within $\pm 1^\circ\text{C}$ (2°F) over the range of 10° to 82°C (50° to 180°F))? _____ yes _____ no

*Most significant items/parameters to be checked.

PRETEST PREPARATION CHECKLIST
(Method 4, Figure 3.1)

Apparatus check	Acceptable		Quantity required	Ready		Packed and loaded	
	Yes	No		Yes	No	Yes	No
<u>Probe type</u>							
Borosilicate glass _____							
Quartz glass _____							
Other _____							
Heater and leak checked* _____							
<u>Filter</u>							
In-stack _____							
Out-stack _____							
Glass wool _____							
Other _____							
<u>Condenser</u>							
Impingers _____							
Other _____							
<u>Cooling System</u>							
Ice bath _____							
Other _____							
<u>Metering System</u>							
Vacuum gauge _____							
Checked* _____							
Pump _____							
Leak checked* _____							
Thermometers _____							
Calibrated* _____							
Dry gas meter _____							
Calibrated* _____							
Other _____							

*Most significant items/parameters to be checked.

(continued)

Figure 3.1 (continued)

Apparatus check	Acceptable		Quantity required	Ready		Packed and loaded	
	Yes	No		Yes	No	Yes	No
<u>Barometer</u>							
Mercury _____							
Aneroid _____							
Other _____							
Calibrated* _____							
<u>Quantitative Instrument</u>							
Graduated cylinder _____							
Trip balance _____							
Calibrated* _____							
<u>Stack Temperature Sensor*</u>							
Type _____							
Calibrated _____							

*Most significant items/parameters to be checked.

ON-SITE MEASUREMENT CHECKLIST
(Method 4, Figure 4.1)

Procedure used: Reference _____ Approximate _____

Reference Method

Conducted simultaneously with pollutant emission test? _____

Impingers properly placed?* _____

Impinger content: 1st _____ 2nd _____ 3rd _____

4th _____ Modifications _____

Cooling System: Crushed ice _____ Other _____

Sampling time per point _____

Probe heater (if applicable) on? _____ Temp _____

Crushed ice in ice bath? _____

Leak check? (optional) _____ Leakage rate _____

Sampling rate constant (within 10%)*? _____

All data properly recorded?* _____

Posttest leak check?* (mandatory) _____

Leakage rate* _____

Analysis - Impinger Content

Method: Volumetric _____ Gravimetric _____

Measurement of volume of water condensed:

Graduated cylinder _____ Other _____

Measurement of silica gel: Balance _____ Other _____

Color of silica gel? _____ Condition _____

All analytical data properly recorded? _____

*Most significant items/parameters to be checked.

POSTTEST EQUIPMENT CHECKS
(Method 4, Figure 5.1)

Dry Gas Meter

Pretest calibration factor Y _____ (must be within $\pm 2\%$)*
Posttest checks, Y_1 _____ Y_2 _____ (must be within $\pm 5\%$ of
pretest)
Recalibration required? _____ yes _____ no
If yes, recalibration factor Y _____ (must be within $\pm 2\%$)*
Lower calibration factor Y _____ for calculations (pretest
or posttest)*

Dry Gas Thermometer

Was a pretest meter temperature correction used? _____ yes _____ no
If yes, temperature correction _____ (within $\pm 3^\circ\text{C}$ (5.4°F)
over range)*
Posttest comparison with mercury-in-glass thermometer _____
_____ (within $\pm 6^\circ\text{C}$ (10.8°F) at room temperature)
Recalibration required? _____ yes _____ no
Recalibration temperature correction, if used _____ (within
 $\pm 3^\circ\text{C}$ (5.4°F) over range)*
If yes, no correction is necessary for calculations when meter
thermometer temperature is higher
If recalibration temperature is higher, add correction to aver-
age meter temperature for calculations

Barometer

Was pretest field barometer reading correct? _____ yes _____ no
Posttest comparison _____ mm (in.) Hg [within ± 2.5 mm
(0.1 in.) Hg of mercury-in-glass barometer reading]
Was recalibration required? _____ yes _____ no
If yes, no correction is necessary for calculations when the
field barometer has the lower reading
If the mercury-in-glass reading is lower, then subtract the
difference from the field data readings for the calculation

Stack Gas Temperature Sensor (if required)

Posttest comparison _____ [within $\pm 2^\circ\text{C}$ (4°F) of reference
values]*
Was recalibration required? _____ yes _____ no

*Most significant items/parameters to be checked.

1.0 PROCUREMENT OF APPARATUS AND SUPPLIES

A schematic of the sampling train used in Method 4 is shown in Figure 1.1. Commercial models of this train are available. For those who desire to build their own, construction details are published in APTD-0581.¹ Allowable modifications are described in the following sections.

The operating, maintenance, and calibrating procedures for the sampling train are in APTD-0576.² Since correct usage is important to obtaining valid results, all users should read the document and adopt the procedures unless alternatives are outlined herein.

Applicable specifications, criteria, and/or design features are in this section to aid in the selection of equipment which assures collection of data of good quality. Procedures and limits (where applicable) for acceptance checks are given. The descriptive title, the identification number (if applicable), and the results of the acceptance check are recorded in the procurement log, which is dated and signed by the individual performing the check. An example of a procurement log is shown in Figure 1.2, and a blank copy of the log is in Section 3.3.12 for the convenience of the Handbook user. If calibration is required as part of the acceptance check, the data are to be recorded in a calibration log. Table 1.1 at the end of this section is a summary of the quality assurance activities for the procurement and acceptance of apparatus and supplies.

1.1 Sampling Apparatus

1.1.1 Probe - The sampling probe should be a borosilicate (Pyrex), quartz glass, or stainless steel tubing with an outside diameter (OD) of about 16 mm (0.625 in.), and it should be encased in a stainless steel sheath with an OD of 25.4 mm (1 in.). Alternatively, other metals or plastic tubing may be used if approved by the administrator.

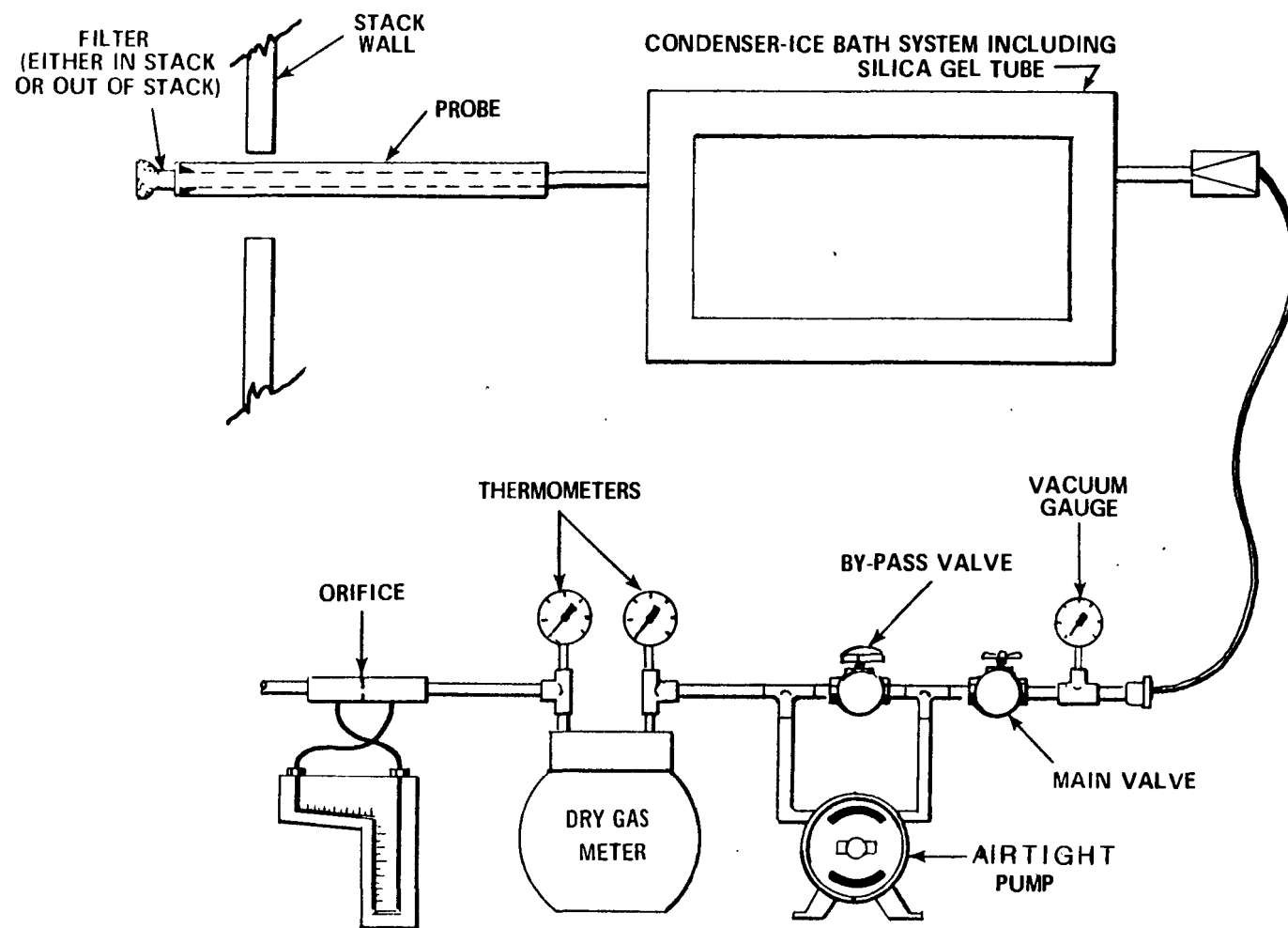


Figure 1.1 Moisture sampling train (Reference Method).

Item description	Quantity	Purchase order number	Vendor	Date		Cost	Disposition	Comments
				Ordered	Received			
Meter Box	2	4687-Q	Acme Testing Equipment	6/2/79	8/5/79	\$2,500/ea	Calibrated + Ready	Calibrated By WGD 8/10/79

Figure 1.2 Example of a procurement log.

Either borosilicate or quartz glass liners may be used for stack temperatures up to about 480°C (900°F), but quartz glass liners should be used from 480° to 900°C (900° to 1650°F). Either type of liner may be used at the higher temperatures for short periods of time with administrator approval. However, the absolute upper limits--the softening temperatures of 820°C (1508°F) and 1500°C (2732°F)--for borosilicate and quartz respectively must be observed.

A heating system is required which will maintain an exit gas temperature of 120° ±14°C (248° ±25°F) during sampling. Other temperatures may be specified by a subpart of the regulations and must be approved by the administrator for a particular application. Since the actual probe outlet temperature is not usually monitored during the sampling, probes constructed in accordance to APTD-0581¹ and utilizing the calibration procedures in APTD-0576² will be acceptable.

Upon receiving a new probe, the user should visually check it for specifications: that is, is it the length and composition ordered? The probe should be visually checked for breaks or cracks, and it should be checked for leaks on a sampling train (Figure 1.1). The probe heating system should be checked as follows:

1. Connect the probe with a nozzle attached to the inlet of the pump.

2. Electrically connect and turn on the probe heater for 2 or 3 min. The probe should become warm to the touch.

3. Start the pump and adjust the needle valve until a flow rate of about 0.02 m³/min (0.75 ft³/min) is achieved.

4. Be sure the probe remains warm to the touch. The heater should 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 repaired, returned to the supplier, or rejected.

1.1.2 Condenser - Four impingers should be connected in series with leak-free ground-glass fittings or any similarly leak-free

noncontaminating fittings. The first, third, and fourth impingers must be the Greenburg-Smith design modified by replacing the inserts with an unstricted 13 mm (0.5 in.) ID glass tube extending to within 13 mm (0.5 in.) of the flask bottom. The second impinger must be a Greenburg-Smith with the standard tip and plate. Modifications--for example, using flexible connections between impingers, using materials other than glass, or using a flexible vacuum hose to connect the filter holder to the condenser--may be used if approved by the administrator. The fourth impinger outlet connection must allow insertion of a thermometer capable of measuring $\pm 1^{\circ}\text{C}$ (2°F) of true value in the range of 0° to 25°C (32° to 77°F).

Alternatively, any system that cools the gas stream and allows measurement of the condensed water and the water vapor leaving the condenser, each to within 1 ml or 1 g, may be used with approval of the administrator.

Upon receipt of a standard Greenburg-Smith impinger, the user should fill the inner tube with water. If the water does not drain through the orifice in ≤ 6 to 8 s, the impinger tip should be replaced or enlarged to prevent an excessive pressure drop in the sampling system. Each impinger should be checked visually for damage--breaks, or cracks, or manufacturing flaws such as poorly shaped connections.

1.1.3 Temperature Gauge - A thermometer capable of measuring within 1°C (2°F) is located at the outlet of the fourth impinger. The thermometer should be checked upon receipt for damage--for example, dents, bent stem, broken face.

1.1.4 Cooling System - An ice bath container and crushed ice (or equivalent) are needed for condensing the moisture.

1.1.5 Metering System - The metering system should consist of a vacuum gauge; a leak-free vacuum pump; thermometers capable of measuring $\pm 3^{\circ}\text{C}$ (5.4°F) of true value in the range of 0° to 90°C (32° to 194°F); a dry gas meter with 2% accuracy at the required sampling rate; and related equipment as shown in Figure 1.1. Other metering systems capable of maintaining sampling rates

within 10% of constant rate and capable of determining sample volumes to within 2% may be used if approved by the administrator. Sampling trains with metering systems designed for sampling rates higher than that described in APTD-0581¹ and APTD-0576² may be used if the above specifications can be met.

Upon receipt or after construction of the equipment, the user should perform both positive and negative pressure leak checks before beginning the system calibration procedure described in Section 3.3.2. Any leakage requires repair or replacement of the malfunctioning item.

1.1.6 Differential Pressure Gauge - The differential pressure gauge should be an inclined manometer or the equivalent to measure the orifice pressure differential.

Initially, check the gauge against a gauge-oil manometer at a minimum of three points: 0.64 mm (0.025 in.); 12.7 mm (0.5 in.); and 25.4 mm (1.0 in.) H₂O. The gauge should agree within 5% of the gauge-oil manometer. Repair or return to the supplier any gauge which does not meet these requirements.

1.1.7 Barometer - A mercury, aneroid, or other barometer capable of measuring atmospheric pressure to within 2.5 mm (0.1 in.) Hg is required.

A preliminary check of a new barometer should be made against a mercury-in-glass barometer or the equivalent. In lieu of this, the absolute barometric pressure may be obtained from a nearby weather service station and adjusted for the elevation difference between the station and the sampling point. Either subtract 2.5 mm Hg/30 m (0.1 in. Hg/100 ft) for an elevation increase or add the same for an elevation decrease from the station value. If the barometer cannot be adjusted to agree within 2.5 mm (0.1 in.) Hg of the reference barometric pressure, it should be returned to the manufacturer.

1.1.8 Graduated Cylinder and/or Triple Beam Balance - A graduated cylinder or triple beam balance may be used to measure the water condensed in the impingers during sampling. Additionally,

the graduated cylinder may be used to measure the water initially placed in the first and second impingers. In either case, the required accuracy is 1 ml or 1 g; therefore, the cylinder must have subdivisions ≤ 2 ml, and the triple beam balance is usually capable of weighing to the nearest 0.5 g.

1.1.9 Stack Gas Temperature Sensor - A thermocouple, thermometer, or equivalent, for measuring the stack gas temperature within $\pm 1^\circ\text{C}$ (2°F) is required when the gas stream is suspected of being saturated or containing water droplets. This accuracy should be in the range of about 10° to 82°C (50° to 180°F). Upon receipt check the specifications and calibrate as described in Section 3.3.2.

Table 1.1 ACTIVITY MATRIX FOR PROCUREMENT AND
ACCEPTANCE OF EQUIPMENT

Apparatus and supplies	Acceptance limits	Frequency and method of measurements	Action if requirements are not met
Sampling probe liner	Specified material of construction; equipped with heating system capable of maintaining $120^{\circ} \pm 14^{\circ}\text{C}$ ($248^{\circ} \pm 25^{\circ}\text{F}$)	Visually check, and run heating system	Repair, return to supplier, or reject
Differential pressure gauge (manometer)	Meet criteria (Method 2, Sec 3.1.2); agree within 5% of gauge-oil manometer	Check against gauge-oil manometer at a minimum of 3 points: 0.64(0.025); 12.7 (0.5); 25.4(1.0) mm (in.) H_2O	Repair or return to supplier
Vacuum gauge	Range 0-760 mm (0-30 in.) ± 2.5 mm (0.1 in.) Hg at 380 mm (15 in.) Hg	Check against a mercury U-tube manometer upon receipt	Adjust or return to supplier
Vacuum pump	Leak free and capable of maintaining a flgw rate of 0.02-0.03 m^3/min (0.66-1.0 ft^3/min) for pump inlet vacuum of 380 mm (15 in.) Hg	Check upon receipt for leaks and capacity	Repair or return to supplier
Orifice meter	$\Delta\text{H@}$ of 46.74 ± 6.35 mm (1.84 ± 0.25 in.) H_2O ; not mandatory	Upon receipt, visually check for damage, and calibrate against wet test meter	Repair if possible; otherwise return to supplier
Impingers	Standard stock glass; pressure drop across impingers not excessive (Subsec 1.1.6)	Visually check upon receipt; check pressure drop (Subsec 1.1.6)	Return to supplier

(continued)

Table 1.1 (continued)

Apparatus and supplies	Acceptance limits	Frequency and method of measurements	Action if requirements are not met
Dry gas meter	Capable of measuring total volume within $\pm 2\%$ at a flow rate of $0.02 \text{ m}^3/\text{min}$ ($0.75 \text{ ft}^3/\text{min}$)	Check for damage upon receipt; calibrate against wet test meter (Sec 3.3.2)	Reject if damaged, behaves erratically, or cannot be properly adjusted
Thermometers	Should read within $\pm 1^\circ\text{C}$ of true value in the range of 0°C to 25°C for impinger thermometer, and $\pm 3^\circ\text{C}$ of true value in the range of 0° to 90°C for dry gas meter thermometers	Check upon receipt for dents or bent stem; calibrate against mercury-in-glass thermometer (Sec 3.3.2)	Reject if unable to calibrate
Barometer	Capable of measuring atmospheric pressure within $\pm 2.5 \text{ mm}$ (0.1 in.) Hg	Check against a mercury-in-glass barometer or equivalent; calibrate (Sec 3.1.2)	Determine correction factor or reject if difference is more than $\pm 2.5 \text{ mm}$ (0.1 in.) Hg
Graduated cylinder	Glass, Class-A, 250 ml, subdivisions $\leq 2 \text{ ml}$	Upon receipt, check stock number, cracks, breaks, and manufacturer flaws	Replace or return to supplier
Trip balance	500-g capacity; capable of measuring within $\pm 0.5 \text{ g}$	Check with standard weights upon receipt	As above
Stack gas temperature sensor	Within $\pm 1^\circ\text{C}$ (2°F) in range of 10° to 82°C (50° to 180°F)	Upon receipt check specifications; then calibrate (Sec 3.3.2)	As above

2.0 CALIBRATION OF APPARATUS

Calibration of the apparatus is one of the most important functions in maintaining data quality. The detailed calibration procedures included in this section are designed for the equipment specified by Method 4 and described in the previous section. A laboratory log book of all calibrations must be maintained. Table 2.1 at the end of this section summarizes the quality assurance activities for calibration.

2.1 Metering System

2.1.1 Wet Test Meter - Wet test meters are calibrated by the manufacturer to an accuracy of $\pm 0.5\%$. The calibration of the wet test meter must be checked initially upon receipt and yearly thereafter. A wet test meter with a capacity of $3.4 \text{ m}^3/\text{h}$ ($120 \text{ ft}^3/\text{h}$) will be necessary to calibrate the dry gas meter. For large wet test meters ($> 3\ell/\text{rev}$), there is no convenient method to check the calibration. For this reason, several methods are suggested, and other methods may be approved by the administrator. The initial calibration may be checked by any of the following methods:

1. Certification from the manufacturer that the wet test meter is within $\pm 1\%$ of true value at the wet test meter discharge, so that only a leak check of the system is then required.

2. Calibration by any primary air or liquid displacement method that displaces at least one complete revolution of the wet test meter.

3. Comparison against a smaller wet test meter that has previously been calibrated against a primary air or liquid displacement method, as described in Section 3.5.2.

4. Comparison against a dry gas meter that has previously been calibrated against a primary air or liquid displacement method.

The calibration of the test meter should be checked annually. The calibration check can be made by the same method as that of the original calibration, with the exception that the comparison method need not be recalibrated if the calibration check is within $\pm 1\%$ of the true value. When this agreement is not obtained, then the comparison method or wet test meter must be recalibrated against a primary air or liquid displacement method.

2.1.2 Sample Meter System - The sample meter system--consisting of the pump, vacuum gauge, valves, orifice meter, and dry gas meter--is initially calibrated by stringent laboratory methods before it is used in the field. After the initial acceptance, the calibration is rechecked after each field test series. This recheck is designed to provide the tester with a method that can be used more often and with less effort to ensure that the calibration has not changed. When the quick check indicates that the calibration factor has changed, the tester must again use the complete laboratory procedure to obtain the new calibration factor. After recalibration, the metered sample volume must be multiplied by either the initial or the recalibrated calibration factor that yields the lowest gas volume for each test run.

Before initial calibration of the metering system, a leak check should be conducted. The meter system should be leak free. Both positive (pressure) and negative (vacuum) leak checks should be performed. Following is a pressure leak-check procedure that will check the metering system from the quick disconnect inlet to the orifice outlet and will check the orifice-inclined manometer for leaks:

1. Disconnect the orifice meter line from the downstream orifice pressure tap (the one closest to the exhaust of the orifice), and plug this tap.
2. Vent the negative side of the inclined manometer to the atmosphere. If the inclined manometer is equipped with a three-way valve, this step can be performed by merely turning the

three-way valve that is on the negative side of the orifice-inclined manometer to the vent position.

3. Place a one-hole rubber stopper with a tube through its one hole in the exit of the orifice, and connect a piece of rubber or plastic tubing to the tube, as shown in Figure 2.1.

4. Open the positive side of the orifice-inclined manometer to the "reading" position. If the inclined manometer is equipped with a three-way valve, this will be the line position.

5. Plug the inlet to the vacuum pump. If a quick disconnect with a leak-free check valve is used on the control module, the inlet will not have to be plugged.

6. Open the main valve and the bypass valve.

7. Blow into the tubing connected to the end of the orifice until a pressure of 127 to 178 mm (5 to 7 in.) H₂O has built up in the system.

8. Plug or crimp the tubing to maintain this pressure.

9. Observe the pressure reading for a 1-min period. No noticeable movement in the manometer fluid level should occur. If the meter box has a leak, a bubbling-type leak-check solution may aid in locating the leak(s).

After the metering system is determined to be leak free by the positive leak-check procedure, the vacuum system to and including the pump should be checked by plugging the air inlet to the meter box. If a quick disconnect with a leak-free stopper system is presently on the meter box, then the inlet will not have to be plugged. Turn the pump on, pull a vacuum within 75 mm (3 in.) Hg of absolute zero, and observe the dry gas meter. If the leakage exceeds 1.5×10^{-4} m³/min (0.005 ft³/min), the leak(s) must be found and minimized until the above specifications are satisfied.

Leak checking the meter system before initial calibration is not mandatory, but is recommended.

Note: For metering systems having diaphragm pumps, the normal leak-check procedure described above will not detect

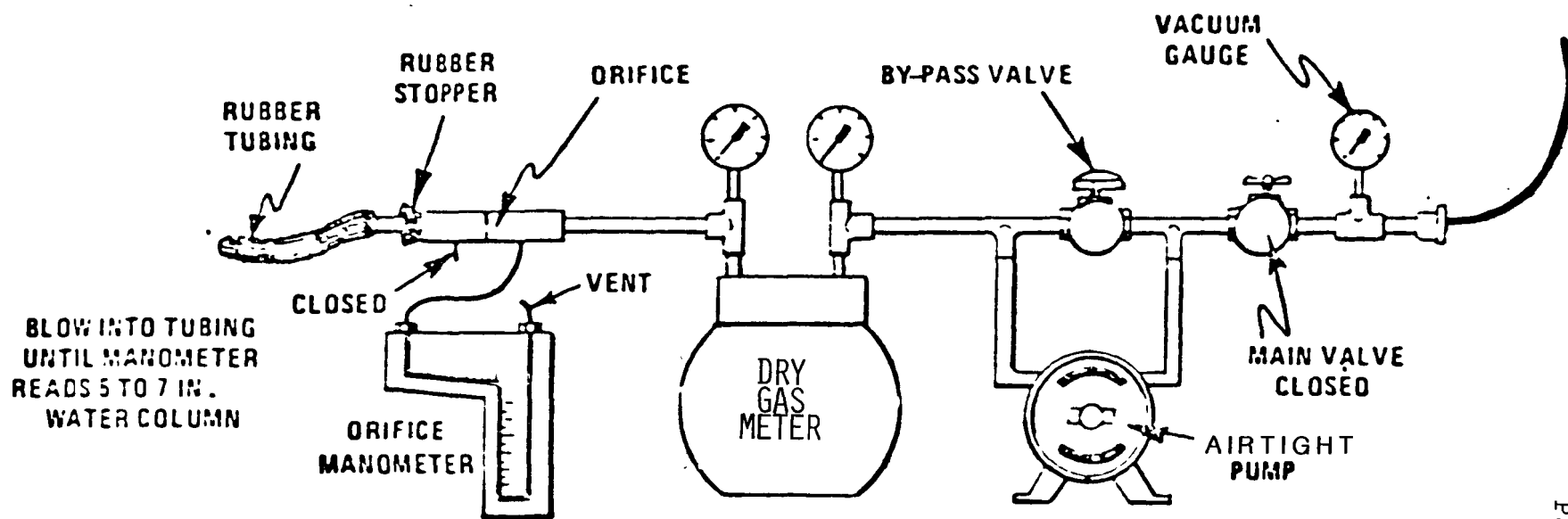


Figure 2.1 Positive leak check of metering system.

leakages within the pump. For these cases, the following leak-check procedure is suggested: make a 10-min calibration run at $0.00057 \text{ m}^3/\text{min}$ ($0.02 \text{ ft}^3/\text{min}$); at the end of the run, take the difference of the measured wet test meter and dry gas meter volumes; divide the difference by 10 to get the leak rate. The leak rate should not exceed $0.00057 \text{ m}^3/\text{min}$ ($0.02 \text{ ft}^3/\text{min}$).

Initial calibration - The dry gas meter and orifice meter can be calibrated simultaneously and should be calibrated when first purchased and any time the posttest check yields a Y outside the range of the calibration factor $Y \pm 0.05Y$. A calibrated wet test meter (properly sized, with $\pm 1\%$ accuracy) should be used to calibrate the dry gas meter and the orifice meter.

The dry gas meter and the orifice meter should be calibrated in the following manner:

1. Before its initial use in the field, leak check the metering system, as described in Subsection 2.1.2. Leaks, if present, must be eliminated before proceeding.

2. Assemble the apparatus, as shown in Figure 2.2, with the wet test meter replacing the probe and impingers--that is, with the outlet of the wet test meter connected to a needle valve that is connected to the inlet side of the meter box.

3. Run the pump for 15 min with the orifice meter differential (ΔH) set at 12.7 mm (0.5 in.) H_2O to allow the pump to warm up and to permit the interior surface of the wet test meter to be wetted.

4. Adjust the needle valve so that the vacuum gauge on the meter box will read between 50 and 100 mm (2 to 4 in.) Hg during calibration.

5. Collect the information required in the forms provided (Figure 2.3A or 2.3B). Sample volumes, as shown, should be used.

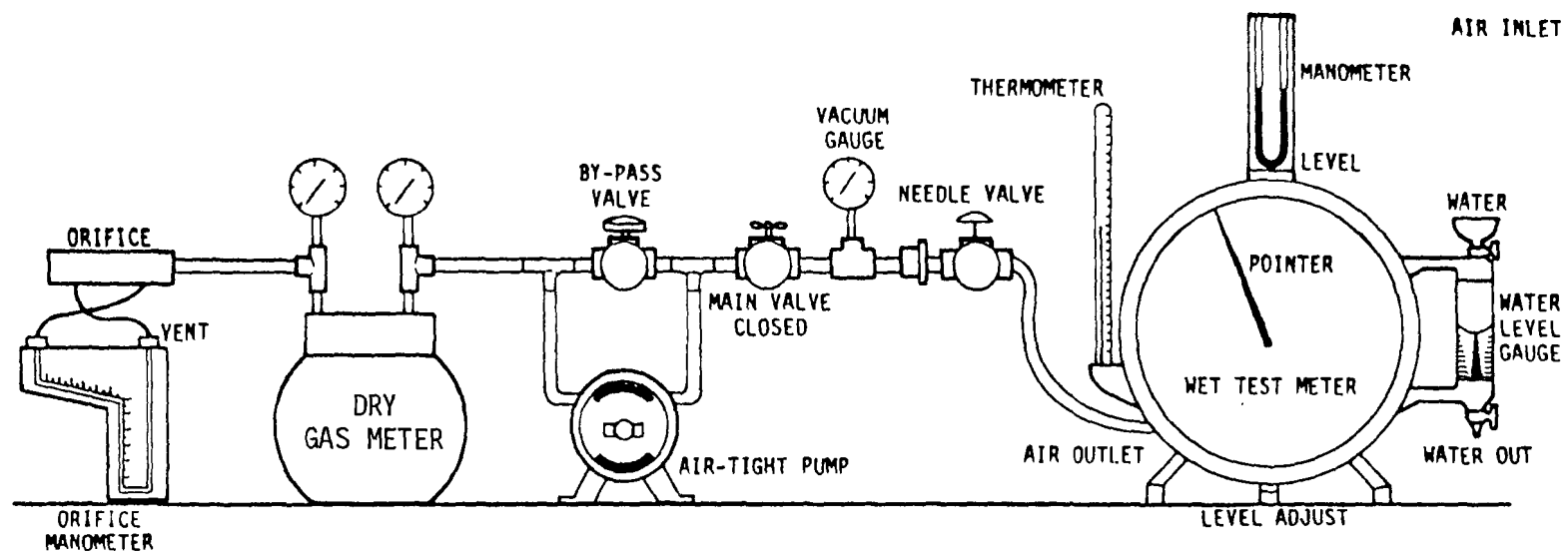


Figure 2.2 Sample meter system calibration setup.

Date 8/10/79

Meter box number FM-2

Barometric pressure, $P_b = 29.00$ in. Hg Calibrated by WGD

Orifice manometer setting (ΔH), in. H_2O	Gas volume		Temperature				Time (θ), min	Y_i	$\Delta H@_i$, in. H_2O
	Wet test meter (V_w), ft ³	Dry gas meter (V_d), ft ³	Wet test meter (t_w), °F	Dry gas meter					
				Inlet (t_{di}), °F	Outlet (t_{do}), °F	Avg ^a (t_d), °F			
0.5	5	883.548 878.519	65 65	69 66	64 63	66	10 ^{49/60}	1.995	1.34
1.0	5								
1.5	10								
2.0	10								
3.0	10								
4.0	10								
Avg									

ΔH , in. H_2O	$\frac{\Delta H}{13.6}$	$Y_i = \frac{V_w P_b (t_d + 460)}{V_d (P_b + \frac{\Delta H}{13.6}) (t + 460)}$	$\Delta H@_i = \frac{0.0317 \Delta H}{P_b (t_d + 460)} \left[\frac{(t_w + 460) \theta}{V_w} \right]^2$
0.5	0.0368	$\frac{5(29.00)(526)}{(5.029)(29.04)(525)}$	$\frac{0.317(0.5)}{29.00(526)} \left[\frac{(525)(10.82)}{5} \right]^2$
1.0	0.0737		
1.5	0.110		
2.0	0.147		
3.0	0.221		
4.0	0.294		

^a If there is only one thermometer on the dry gas meter, record the temperature under t_d .

Figure 2.3A Dry gas meter calibration data form (English units).
(front side)

Nomenclature:

V_w = Gas volume passing through the wet test meter, ft^3 .

V_d = Gas volume passing through the dry gas meter, ft^3 .

t_w = Temperature of the gas in the wet test meter, $^{\circ}\text{F}$.

t_{d_i} = Temperature of the inlet gas of the dry gas meter, $^{\circ}\text{F}$.

t_{d_o} = Temperature of the outlet gas of the dry gas meter, $^{\circ}\text{F}$.

t_d = Average temperature of the gas in the dry gas meter, obtained by the average t_{d_i} and t_{d_o} , $^{\circ}\text{F}$.

ΔH = Pressure differential across orifice, in. H_2O .

Y_i = Ratio of accuracy of wet test meter to dry gas meter for each run; tolerance $Y_i = Y \pm 0.02Y$.

Y = Average ratio of accuracy of wet test meter to dry gas meter for all six runs; tolerance $Y = Y \pm 0.01Y$.

$\Delta H@_i$ = Orifice pressure differential at each flow rate that gives $0.75 \text{ ft}^3/\text{min}$ of air at standard conditions for each calibration run, in. H_2O ; tolerance = $\Delta H@ \pm 0.15$ (recommended).

$\Delta H@$ = Average orifice pressure differential that gives $0.75 \text{ ft}^3/\text{min}$ of air at standard conditions for all six runs, in. H_2O ; tolerance = 1.84 ± 0.25 (recommended).

θ = Time for each calibration run, min.

P_b = Barometric pressure, in. Hg.

Figure 2.3A. Dry gas meter calibration data (English units). (backside)

Date 8/10/79

Meter box number FM-2

Barometric pressure, $P_b =$ 736 mm Hg

Calibrated by WGD

Orifice manometer setting (ΔH), mm H ₂ O	Gas volume		Temperature				Time (θ), min	Y_i	$\Delta H@_i$, mm H ₂ O
	Wet test meter (V_w), m ³	Dry gas meter (V_d), m ³	Wet test meter (t_w), °C	Dry gas meter					
				Inlet (t_{d_i}), °C	Outlet (t_{d_o}), °C	Avg ^a (t_d), °C			
10	0.15	25.0320 24.8800	18 18	20 19	18 17	18	19 10.60	.986	23
25	0.15								
40	0.30								
50	0.30								
75	0.30								
100	0.30								
Avg									

ΔH , mm H_2O	$\frac{\Delta H}{13.6}$	$Y_i = \frac{V_w P_b (t_d + 273)}{V_d (P_d + \frac{\Delta H}{13.6}) (t_w + 273)}$	$\Delta H@_i = \frac{0.00117 \Delta H}{P_b (t_d + 273)} \left[\frac{(t_w + 273) \theta}{V_w} \right]^2$
10	0.7	$\frac{(0.15)(736)(291)}{(0.152)(737)(291)}$	$\frac{(0.00117)(10)}{(736)(291)} \left[\frac{(291)(10.60)}{0.152} \right]^2$
25	1.8		
40	2.94		
50	3.68		
75	5.51		
100	7.35		

^a If there is only one thermometer on the dry gas meter, record the temperature under t_d .

Figure 2.3B Dry gas meter calibration data form (metric units).
(front side)

Nomenclature:

V_w = Gas volume passing through the wet test meter, m^3 .

V_d = Gas volume passing through the dry gas meter, m^3 .

t_w = Temperature of the gas in the wet test meter, $^{\circ}C$.

t_{d_i} = Temperature of the inlet gas of the dry gas meter, $^{\circ}C$.

t_{d_o} = Temperature of the outlet gas of the dry gas meter, $^{\circ}C$.

t_d = Average temperature of the gas in the dry gas meter, obtained by the average of t_{d_i} and t_{d_o} , $^{\circ}C$.

ΔH = Pressure differential across orifice, mm H_2O .

Y_i = Ratio of accuracy of wet test meter to dry gas meter for each run; tolerance $Y_i = Y \pm 0.02Y$.

Y = Average ratio of accuracy of wet test meter to dry gas meter for all six runs; tolerance $Y = Y \pm 0.01Y$.

$\Delta H@_i$ = Orifice pressure differential at each flow rate that gives $0.021 m^3$ of air at standard conditions for each calibration run, mm H_2O ; tolerance $\Delta H@_i = \Delta H@ \pm 3.8$ mm H_2O (recommended).

$\Delta H@$ = Average orifice pressure differential that gives $0.021 m^3$ of air at standard conditions for all six runs, mm H_2O ; tolerance $\Delta H@ = 46.74 \pm 6.3$ mm H_2O (recommended).

θ = Time of each calibration run, min.

P_b = Barometric pressure, mm Hg.

Figure 2.3B. Dry gas meter calibration data (metric units). (backside)

6. Calculate Y_i for each of the six runs, using the equation in Figure 2.3A or B under the Y_i column, and record the results on the form in the space provided.

7. Calculate the average Y for the six runs using the following equation:

$$Y = \frac{Y_1 + Y_2 + Y_3 + Y_4 + Y_5 + Y_6}{6} .$$

Record the average on Figure 2.3A or B in the space provided.

8. The dry gas meter should be cleaned, adjusted, and recalibrated, or rejected if one or more values of Y fall outside the interval $Y \pm 0.02Y$. Otherwise, the average Y (calibration factor) is acceptable and will be used for future checks and subsequent test runs.

9. Calculate $\Delta H@_i$ for each of the six runs using the equation in Figure 2.3A or B under the $\Delta H@_i$ column, and record on the form in the space provided.

10. Calculate the average $\Delta H@$ for the six runs using the following equation:

$$\Delta H@ = \frac{\Delta H@_1 + \Delta H@_2 + \Delta H@_3 + \Delta H@_4 + \Delta H@_5 + \Delta H@_6}{6} .$$

Record the average on Figure 2.3A or B in the space provided.

11. Adjust the orifice meter or reject it if $\Delta H@_i$ varies by more than ± 3.9 mm (0.15 in.) H_2O over the range of 10 to 100 mm (0.4 to 4.0 in.) H_2O . Otherwise, the average $\Delta H@$ is acceptable and will be used for subsequent test runs.

Posttest calibration check - After each field test series, conduct a calibration check of the metering system, as in Subsection 2.1.2, except for the following variations:

1. Three calibration runs at a single intermediate orifice meter setting may be used with the vacuum set at the maximum value reached during the test series. The single intermediate

orifice meter setting should be based on the previous field test. A valve must be inserted between the wet test meter and the inlet of the metering system to adjust the vacuum.

2. If a temperature-compensating dry gas meter was used, the calibration temperature for the dry gas meter must be within $\pm 6^{\circ}\text{C}$ (10.8°F) of the average meter temperature during the test series.

3. Use Figure 2.4A or 2.4B, and record the required information.

If the calibration factor Y deviates 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 Y deviates by $>5\%$, recalibrate the metering system (as in Subsection 2.1.2), and use whichever meter coefficient (initial or recalibrated) that yields the lowest gas volume for each test run.

Alternate procedures--for example, using the orifice meter coefficients--may be used, subject to the approval of the administrator.

2.2 Temperature Gauges

2.2.1 Impinger Thermometer - The thermometer used to measure the temperature of the gas stream exiting the impinger train should initially be compared with a mercury-in-glass thermometer which meets ASTM E-1 No. 63C or 63F specifications. The procedure is as follows:

1. Place both the reference thermometer and the test thermometer in an ice bath. Compare readings after they both stabilize.

2. Remove the thermometers from the bath and allow both to come to room temperature. Again, compare readings after they both stabilize.

3. Accept the test thermometer if its reading agrees within $\pm 1^{\circ}\text{C}$ (2°F) of the reference thermometer reading at both temperatures. If the difference is greater than $\pm 1^{\circ}\text{C}$ (2°F),

Test number AB1-3 Date 9/13/79 Meter box number FM-7 Plant Acme Power Plant
 Barometric pressure, $P_b = 28.72$ in. Hg Dry gas meter number FM-7 Pretest Y 0.986

Orifice manometer setting, (ΔH), in. H ₂ O	Gas volume		Temperature				Time (θ), min	Vacuum setting, in. Hg	Y_i	Y_i
	Wet test meter (V_w), ft ³	Dry gas meter (V_d), ft ³	Wet test meter (t_w), °F	Dry gas meter						$V_w P_b (t_d + 460)$
				Inlet (t_{d_i}), °F	Outlet (t_{d_o}), °F	Average ^a (t_d), °F				$V_d \left(P_b + \frac{\Delta H}{13.6} \right) (t_w + 460)$
1.41	10	886.544 876.321	72	83	75	79	13.35	3	0.987	$\frac{10628.72(79+460)}{10.223(28.72+\frac{17}{13.6}(72+460))}$
	10									
	10									
										Y =

^a If there is only one thermometer on the dry gas meter, record the temperature under t_d
 where

V_w = Gas volume passing through the wet test meter, ft³.

V_d = Gas volume passing through the dry gas meter, ft³.

t_w = Temperature of the gas in the wet test meter, °F.

t_{d_i} = Temperature of the inlet gas of the dry gas meter, °F.

t_{d_o} = Temperature of the outlet gas of the dry gas meter, °F.

t_d = Average temperature of the gas in the dry gas meter, obtained by the average of t_{d_i} and t_{d_o} , °F.

ΔH = Pressure differential across orifice, in. H₂O.

Y_i = Ratio of accuracy of wet test meter to dry gas meter for each run.

Y = Average ratio of accuracy of wet test meter to dry gas meter for all three runs;
 tolerance = pretest Y $\pm 0.05Y$.

P_b = Barometric pressure, in. Hg.

θ = Time of calibration run, min.

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

Test number AB1-3 Date 9/13/79 Meter box number FM-7 Plant Acme Power Plant
 Barometric pressure, P_b = 730 mm Hg Dry gas meter number FM-7 Pretest Y 0.993

Orifice manometer setting, (ΔH), mm H ₂ O	Gas volume		Temperature				Time (θ), min	Vacuum setting, mm Hg	Y_i	Y_i	Y_i
	Wet test meter (V_w), m ³	Dry gas meter (V_d), m ³	Wet test meter (t_w), °C	Dry gas meter							$V_w P_b (t_d + 273)$
				Inlet (t_{d_i}), °C	Outlet (t_{d_o}), °C	Average ^a (t_d), °C					$V_d P_b + \frac{\Delta H}{13.6} t_w + 273$
36	.3	26.1742 25.8730	21	23.5	21.5	22.5	10.5	75	0.990	$\frac{36 \times 730 \times (21.5 + 273)}{0.3012 (730 + \frac{36}{13.6} \times 21.5 + 273)}$	
	.3										
	.3										
Y =											

^a If there is only one thermometer on the dry gas meter, record the temperature under t_d

where

V_w = Gas volume passing through the wet test meter, m³.

V_d = Gas volume passing through the dry gas meter, m³.

t_w = Temperature of the gas in the wet test meter, °C.

t_{d_i} = Temperature of the inlet gas of the dry gas meter, °C.

t_{d_o} = Temperature of the outlet gas of the dry gas meter, °C.

t_d = Average temperature of the gas in the dry gas meter, obtained by the average of t_{d_i} and t_{d_o} , °C.

ΔH = Pressure differential across orifice, mm H₂O.

Y_i = Ratio of accuracy of wet test meter to dry gas meter for each run.

Y = Average ratio of accuracy of wet test meter to dry gas meter for all three runs;
 tolerance = pretest Y \pm 0.05Y.

P_b = Barometric pressure, mm Hg.

θ = Time of calibration run, min.

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

the thermometer should be adjusted and recalibrated until the criteria are met, or it should be rejected.

4. Prior to each field trip compare the room temperature with the meter thermometer and the mercury-in-glass thermometer. If the readings are not within $\pm 2^{\circ}\text{C}$ (4°F), the meter thermometer should be replaced or recalibrated.

2.2.2 Dry Gas Thermometers - The thermometers used to measure the metered gas sample temperature should initially be compared with a mercury-in-glass thermometer as above, using a similar procedure.

1. Place the reference and the test thermometers in a hot water bath maintained at 40° to 50°C (104° to 122°F). Compare the readings after both stabilize.

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

3. Accept the test thermometer if its reading agrees within 3°C (5.4°F) of the reference thermometer reading at both temperatures. If not, either the thermometer should be adjusted and recalibrated or a temperature correction factor should be marked on the thermometer where it is readily visible to the operator. When the factor is used, it must be noted on the pretest sampling check form (Figure 2.5) and in the calibration log.

4. Compare the temperatures prior to each field trip at room temperature with the thermometer as part of the meter system. If the readings or corrected values are not within $\pm 6^{\circ}\text{C}$ (10.8°F) of the mercury-in-glass thermometer value, the meter thermometer should be replaced or recalibrated.

2.3 Barometer

The field barometer should be adjusted initially and before each test series to agree within ± 2.5 mm (0.1 in.) Hg of the mercury-in-glass barometer or with the pressure reported by a nearby National Weather Service Station. Correction for elevation difference between the station and the sampling point should be applied at a rate of -2.5 mm Hg/30 m (0.1 in. Hg/100 ft). Record results on the pretest sampling check form (Figure 2.1).

Date January 12, 1980 Calibrated by B. C. Blagun
Meter box number FM-1 $\Delta H@$ 1.41

Dry Gas Meter*

Pretest calibration factor 0.986 (within 2% of the average factor for each calibration run)

Impinger Thermometer

Was a pretest temperature correction used? yes ☒ no
If yes, temperature correction _____ (within 2°C (4°F) of reference value)

Dry Gas Meter Thermometer

Was a pretest temperature correction made? yes ☒ no
If yes, temperature correction _____ (within 6°C (10.8°F) of reference value)

Barometer

Was the pretest field barometer reading correct? ☒ yes ☐ no

Stack Gas Temperature Sensor (if required)*

Was a temperature sensor required for moisture determination purposes? yes ☒ no

Was a pretest temperature correction used? yes ☒ no
If yes, temperature correction _____ (within $\pm 1^\circ\text{C}$ over the entire range)

Did the temperature sensor agree with the reference thermometer (within $\pm 1^\circ\text{C}$ (2°F) over the range of 10° to 82°C (50° to 180°F))? ☒ yes ☐ no

*Most significant items/parameters to be checked.

Figure 2.5 Pretest sampling checks.

2.4 Trip Balance

The trip balance should be calibrated initially by using Class-S standard weights and should be within ± 0.5 g of the standard weight. Adjust or return the balance to the manufacturer if limits are not met.

2.5 Stack Gas Temperature Sensor

The stack gas temperature must be accurately determined when the stack is suspected of being saturated or having water droplets. Therefore proper calibration of the stack gas temperature sensor is important for this method. Upon receipt, the sensor should be calibrated over the entire range. An ASTM E-1 No. 3C or 3F thermometer should be used as the reference temperature. The initial and, as required, recalibration procedure is as follows:

1. Place both the temperature sensor and the reference thermometer in water or in a controlled-temperature atmosphere.
2. Record both temperatures after each has stabilized for 30 s. Increase the temperature in increments of about 6°C (10°F), taking readings over the entire range (10 - 82°C (50 - 180°F)).
3. Both values should agree within $\pm 1^{\circ}\text{C}$ (2°F). If not, the temperature sensor should be adjusted if possible. However, if the values are off by a constant factor over the entire range, a correction factor may be used.

After each field use, the temperature sensor calibration should be checked. The procedure for the check is as follows:

1. Check the temperature sensor with the reference thermometer at a temperature within $\pm 5^{\circ}\text{C}$ (10°F) of the average stack temperature. If the values agree within $\pm 2^{\circ}\text{C}$ (4°F), then the pretest calibration is acceptable.
2. When the above agreement is not met, the temperature sensor should be recalibrated at a temperature within $\pm 2^{\circ}\text{C}$ (4°F) of the average stack temperature, and a correction factor should be determined with the reference thermometer. The difference

between the temperature sensor and the reference thermometer should be used to correct the average stack temperature for calculation purposes. Also, a complete recalibration of the temperature sensor is suggested.

Table 2.1 ACTIVITY MATRIX FOR EQUIPMENT CALIBRATION REQUIREMENTS

Apparatus	Acceptance limits	Frequency and method of measurements	Action if requirements are not met
Wet test meter	Capacity of at least $3.4 \text{ m}^3/\text{h}$ ($120 \text{ ft}^3/\text{h}$) and accuracy within $\pm 1\%$	Calibrate initially and then yearly by the liquid displacement technique; see Subsec 2.1.1	Adjust until specifications are met, or return to manufacturer
Dry gas meter	$Y_i = Y \pm 0.02Y$ at a flow rate of $0.02\text{--}0.03 \text{ m}^3/\text{min}$ ($0.66\text{--}1 \text{ ft}^3/\text{min}$)	Calibrate vs. wet test meter initially to agree, and when the posttest check is not within $Y \pm 0.05Y$	Repair or replace, and then recalibrate
Thermometers	Impinger thermometer $\pm 1^\circ\text{C}$ (2°F); dry gas meter thermometer $\pm 3^\circ\text{C}$ (5.4°F) over range	Calibrate each initially as a separate component against a mercury-in-glass thermometer; before each field trip, compare each as part of the train with the mercury-in-glass thermometer	Adjust, determine a constant correction factor, or reject
Barometer	$\pm 2.5 \text{ mm}$ (0.1 in.) Hg of the mercury-in-glass barometer	Calibrate initially using mercury-in-glass barometer; check before and after each field test	Adjust to agree with certified barometer
Stack gas temperature sensor for moisture determination	Pretest calibration $\pm 1^\circ\text{C}$ (2°F) over range; posttest check $\pm 2^\circ\text{C}$ (4°F)	Calibrate initially over the range with an ASTM reference thermometer; after each field test, make a single-point calibration check	Adjust to agree with reference thermometer; use a constant correction factor, or reject; posttest data corrected for calculation purposes

3.0 PRESAMPLING OPERATIONS

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

3.1 Apparatus Check and Calibration

A pretest check will have to be made on most of the sampling apparatus. Figure 3.1 should be used as a pretest operations and packing list. An inquiry must be made as to whether the stack gas is saturated or has water droplets.

3.1.1 Sampling Train - The specifications of the Method 4 sampling train used by the EPA are given in Figure 1.1. Commercial models of this system are available. Each individual or fabricated train must be in compliance with the specifications of the Reference Method, Section 3.3.10.

3.1.2 Probe - Clean the probe internally by brushing first with tap water, then with deionized distilled water, and finally with acetone; allow it to dry in the air. In extreme cases, the probe liner can be cleaned with stronger reagents. In either case, the objective is to leave the probe liner free from contaminants. The probe's heating system should be checked to see that it is operating properly. The probe should be sealed at the inlet or tip and checked for leaks at a vacuum of 380 mm (15 in.) Hg, and the probe must be leak free under these conditions.

3.1.3 Impinger and Glass Connections - All glassware should be cleaned first with detergent and thoroughly rinsed with tap water and then with deionized distilled water. All glassware should be visually inspected for cracks or breakage and then repaired or discarded if defective.

3.1.4 Pump - The vacuum pump should be serviced as recommended by the manufacturer, or every 3 mo, or upon erratic behavior (nonuniform or insufficient pumping action). Check oiler jars, if used, every 10 tests.

Apparatus check	Acceptable		Quantity required	Ready		Packed and loaded	
	Yes	No		Yes	No	Yes	No
<u>Probe type</u>							
Borosilicate glass <input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>		3	<input checked="" type="checkbox"/>		<input checked="" type="checkbox"/>	
Quartz glass _____							
Other _____							
Heater and leak checked* <input checked="" type="checkbox"/>							
<u>Filter</u>							
In-stack <input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>		1 Box	<input checked="" type="checkbox"/>		<input checked="" type="checkbox"/>	
Out-stack <input type="checkbox"/>							
Glass wool _____							
Other _____							
<u>Condenser</u>							
Impingers <input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>		5 GS 10 MOD	<input checked="" type="checkbox"/>		<input checked="" type="checkbox"/>	
Other _____							
<u>Cooling System</u>							
Ice bath <input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>		3	<input checked="" type="checkbox"/>		<input checked="" type="checkbox"/>	
Other _____							
<u>Metering System</u>							
Vacuum gauge <input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>		2	<input checked="" type="checkbox"/>		<input checked="" type="checkbox"/>	
Checked* <input checked="" type="checkbox"/>							
Pump <input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>		2	<input checked="" type="checkbox"/>		<input checked="" type="checkbox"/>	
Leak checked* <input checked="" type="checkbox"/>							
Thermometers <input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>		2 (0-200°F)			<input checked="" type="checkbox"/>	
Calibrated* <input checked="" type="checkbox"/>							
Dry gas meter <input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>		2	<input checked="" type="checkbox"/>		<input checked="" type="checkbox"/>	
Calibrated* <input checked="" type="checkbox"/>							
Other _____							

*Most significant items/parameters to be checked.

Figure 3.1 Pretest preparation checklist. (continued)

Figure 3.1 (continued)

Apparatus check	Acceptable		Quantity required	Ready		Packed and loaded	
	Yes	No		Yes	No	Yes	No
<u>Barometer</u>							
Mercury <u>✓</u>	✓		1	✓		✓	
Aneroid <u> </u>							
Other <u> </u>							
Calibrated* <u>✓</u>							
<u>Quantitative Instrument</u>							
Graduated cylinder <u>✓</u>	✓		3	✓		✓	
Trip balance <u>✓</u>	✓		2	✓		✓	
Calibrated* <u>YES</u>							
<u>Stack Temperature Sensor*</u>							
Type <u>THERMOCOUPLE</u>	✓		2	✓		✓	
Calibrated <u>YES</u>							

*Most significant items/parameters to be checked.

3.1.5 Dry Gas Meter - A dry gas meter calibration check should be made using the procedure in Section 3.3.2.

3.1.6 Silica Gel - Either dry the used silica gel at 175°C (350°F) or use fresh silica gel and weigh several 200- to 300-g portions in airtight containers to the nearest 0.5 g. Record the total weight (silica gel plus container) on each container.

3.1.7 Thermometers - The thermometers should be compared to the mercury-in-glass reference thermometer at ambient temperature (Subsection 2.2.1 of Section 3.3.2).

3.1.8 Barometer - The field barometer should be compared with the mercury-in-glass barometer or the weather station reading prior to each field trip (Section 3.3.2).

3.1.9 Stack Gas Temperature Sensor - A specially calibrated temperature sensor is required if the stack gas is saturated or has water droplets present. The sensor should be calibrated against a reference thermometer (Section 3.3.2).

3.1.10 Water - It is recommended, but not required, that 100 ml of deionized distilled water conforming to ASTM D1193-74 type 3 be used in each of the first two impingers.

3.2 Equipment Packing

The accessibility, condition, and functioning of measurement devices in the field depend on careful packing and on the care of movement on site. Equipment should be packed to withstand severe treatment during shipping and field handling operations. One major consideration in shipping cases is the construction materials. The following containers are suggested, but are not mandatory.

3.2.1 Probe - Seal the inlet and outlet of the probe and then wrap with polyethylene or other suitable material to protect the probe from breakage. An ideal container is a wooden case (or equivalent) lined with foam material and with separate compartments to hold individual probes. The case should have handles or eye-hooks that can withstand hoisting and that will be rigid enough to prevent bending or twisting during shipping and handling.

3.2.2 Impingers, Connectors, and Assorted Glassware - All impingers and glassware should be packed in rigid containers and protected by polyethylene packing material or other suitable material. Individual compartments for glassware will help to organize and protect each piece and simplify inventorying.

3.2.3 Volumetric Glassware - A sturdy case lined with foam material can contain drying tubes and assorted volumetric glassware.

3.2.4 Meter Box - The meter box--which contains the manometers, orifice meter, vacuum gauge, pump, dry gas meter, and thermometers--should be packed in a shipping container unless its housing is sufficient to protect components during travel. Pump oil sump and oiler jars should be drained to prevent fouling of the components during shipment. Additional pump oil should be packed if oil is required. It is advisable to carry a spare meter box in case of failure.

3.2.5 Wash Bottles and Storage Containers - Storage containers and miscellaneous glassware should be packed in a rigid foam-lined container.

Table 3.1 ACTIVITY MATRIX FOR PRESAMPLING PREPARATIONS

Apparatus	Acceptance limits	Frequency and method of measurements	Action if requirements are not met
Probe	<p>1. Probe liner free of contaminants and constructed of borosilicate glass, quartz, or equivalent; metal liners must be approved by administrator</p> <p>2. Probe leak free at 380 mm (15 in.) Hg</p> <p>3. Probe that prevents moisture condensation</p>	<p>1. Clean probe internally by brushing using tap water, then deionized distilled water, and finally acetone; air dry before test</p> <p>2. Visually check before test</p> <p>3. Check heating system initially and when moisture cannot be prevented during testing</p>	<p>1. Repeat cleaning procedure, and reassemble</p> <p>2. Replace</p> <p>3. Repair or replace</p>
Impingers, filter holders, and glass containers	Clean and free of breaks, cracks, leaks, etc.	Clean with detergent and tap water, then deionized distilled water	Repair or discard
Pump	Sampling rate of about 0.02-.03 m ³ /min (0.66-1 ft ³ /min) up to 380 mm (15 in.) Hg vacuum at pump inlet	Service every 3 mo or upon erratic behavior; check oiler jars every 10 tests	Repair or return to manufacturer
Dry gas meter	Readings within $\pm 2\%$ average calibration factor; clean	Calibrate according to Sec 3.3.2 check for excess oil	As above
Thermometers	Readings within $\pm 2^{\circ}\text{C}$ (4°F) of mercury-in-glass thermometer	Compare with mercury-in-glass thermometer at room temperature prior to each field test	Replace or recalibrate
Barometer	Readings within 2.5 mm (0.1 in.) Hg	Compare with mercury-in-glass barometer or value reported by nearby National Weather Station corrected for elevation prior to each field test	As above

(continued)

Table 3.1 (continued)

Apparatus	Acceptance limits	Frequency and method of measurements	Action if requirements are not met
Stack gas temperature sensor for moisture determination	$\pm 1^{\circ}\text{C}$ (2°F) over range of 10° to 80°C (50° to 180°F)	Compare against ASTM reference thermometer	As above
Water	Deionized distilled; ASTM-D1193-74 type 3	Run blank evaporations prior to field use to eliminate high solids (only required if impinger contents to be analyzed)	Redistill or replace
Silica gel	Indicating type, size 6 to 16 mesh; dry used gel at 175°C (350°F) for at least 2 h; weigh 200 g portion to nearest 0.5 g; record the weight	Prior to each field test, observe drying time if appropriate; check weighings	Repeat procedure
<u>Package Equipment for Shipment</u>			
Probe	Packed in rigid container and protected by polyethylene foam	Prior to each shipment, check packing of equipment	Repack
Impingers, containers, and assorted glassware	Packed in rigid container and protected by polyethylene foam	As above	As above
Meter box	Meter box case and/or additional material to protect train components; pack spare meter box	As above	As above

4.0 ON-SITE MEASUREMENTS

The on-site activities include transporting the equipment to the test site, unpacking and assembling the equipment, making duct measurements, determining whether the stack gas is saturated or has water droplets, charging the impingers, obtaining a sample, and recording data. Table 4.1 at the end of this section summarizes the on-site quality assurance activities and Figure 4.1 is an on-site measurement checklist. Blank data forms are in Section 3.3.12 for the convenience of the Handbook user.

4.1 Handling Equipment

The most efficient means of transporting or moving the equipment from ground level to the sampling site should be decided during the preliminary site visit or through prior correspondence to minimize damage to the test equipment or injury to test personnel. A "laboratory" area should be designated for assembling the sampling train, placing the filter in the filter holder, charging the impingers, recovering the sample, and documenting the results; this area should be clean and should be free of excessive drafts.

4.2 Sampling

The on-site sampling includes addition of the water and silica gel to the impingers; setup of the sampling train; connection to the electrical service; preparation of the probe (leak check of entire sampling train and addition of particulate filter); insertion of the probe into stack; sealing of the port; check of the probe temperature; and sampling and recording the data (Figure 4.2). A final leak check of the train is mandatory after sampling.

4.2.1 Preliminary Measurements and Setup - The sampling site should be selected in accordance with Method 1. If this is impossible due to duct configuration or other reasons, the site should be approved by the administrator. A 115 V, 30-A

Procedure used: Reference ✓ Approximate _____

Reference Method

Conducted simultaneously with pollutant emission test? yes

Impingers properly placed?* yes

Impinger content: 1st 100 ml H₂O 2nd 100 ml H₂O 3rd empty

4th 200g Silica gel Modifications _____

Cooling System: Crushed ice ✓ Other _____

Sampling time per point 5 min

Probe heater (if applicable) on? yes Temp 250°F

Crushed ice in ice bath? yes

Leak check? (optional) yes Leakage rate 0.0

Sampling rate constant (within 10%)*? yes

All data properly recorded?* yes

Posttest leak check?* (mandatory) yes

Leakage rate* 0.0

Analysis - Impinger Content

Method: Volumetric ✓ Gravimetric _____

Measurement of volume of water condensed:

Graduated cylinder yes Other _____

Measurement of silica gel: Balance ✓ Other _____

Color of silica gel? blue Condition very little moisture

All analytical data properly recorded? yes

*Most significant items/parameters to be checked.

Figure 4.1 On-site measurement checklist

Plant Acme Power Plant Probe material Glass
 Location Boiler No. 1 Outlet Sample box number RG-3
 Operator MB Meter box number FM-2
 Date 8/10/79 Meter ΔH 1.41
 Run number APP-1 Meter cal. (Y) 1.016
 Ambient temperature 68°F Final leak rate 0.00
 Barometric pressure 29.00 Vacuum during leak check 2.0
 Probe length 8 ft Thermometer number BE-5
 Static pressure -10.0 in H₂O

	Impinger volume, ml	Silica gel weight, g
Final	271	215.0
Initial	200	203.5

Traverse point number	Sampling time (θ), min	Stack temperature, $^{\circ}\text{C}$ ($^{\circ}\text{F}$)	Pressure differential across orifice meter (ΔH), mm (in.) H ₂ O	Meter reading gas sample volume, m ³ (ft ³)	ΔV_m , * m ³ (ft ³)	Gas sample temperature at dry gas meter		Temperature of gas leaving condenser or last impinger, $^{\circ}\text{C}$ ($^{\circ}\text{F}$)
						Inlet ($T_{m_{in}}$) $^{\circ}\text{C}$ ($^{\circ}\text{F}$)	Outlet ($T_{m_{out}}$) $^{\circ}\text{C}$ ($^{\circ}\text{F}$)	
Start	0	129	—	517.321	—	—	—	—
1	5	133	1.0	519.95	2.63	68	68	68
2	10	136	1.0	522.59	2.64	72	69	65
3	15	137	1.0	525.21	2.62	76	70	65
4	20	137	1.0	527.85	2.64	78	71	66
5	25	137	1.0	530.49	2.64	80	72	66
6	30	138	1.0	533.10	2.61	84	73	65
7	35	138	1.0	535.73	2.63	86	75	65
8	40	137	1.0	538.36	2.63	88	75	66
9	45	137	1.0	541.00	2.64	90	76	67
10	50	135	1.0	543.62	2.62	93	78	67
11	55	130	1.0	546.25	2.63	95	79	68
12	60	129	1.0	548.86	2.61	96	80	68
Total	60							
Average		134.8	1.0		2.628		78.8	

* Acceptable $\Delta V_m = 0.9 < \frac{V_{\text{final}} - V_{\text{initial}}}{\text{number of points}} < 1.1$ 2.37 to 2.89.

Figure 4.2 Method 4 field and sample recovery data form.

electrical supply is necessary to operate the standard sampling train. A minimum of eight traverse points should be used for rectangular stacks having equivalent diameters <0.61 m (<24 in.), and a minimum of 12 should be used for all other stacks unless otherwise specified by the administrator. Record all data on the traverse point location form shown in Section 3.0 (introduction to this volume). These measurements will be used to locate the sampling probe during preliminary measurements and actual sampling.

Select a suitable probe liner and probe length so that all traverse points can be sampled. For large stacks, consider sampling from opposite sides of the stack to reduce the length of the probe.

Select a total sampling time so that a minimum gas volume of 0.60 m^3 (21 sft^3) can be collected at a constant rate of $\leq 0.021 \text{ m}^3/\text{min}$ ($0.75 \text{ ft}^3/\text{m}$). The rate can be limited by selecting a pressure drop (ΔH) which is $< \Delta H_0$ for the orifice meter.

Note: If moisture saturated or droplet-laden gas streams are suspected, two calculations of the moisture content of the stack gas should be made--one using a value based on the saturated conditions (Equation 4-1) and another using the results of the impinger analysis. The lower of these two B_{ws} values should be considered correct.

To determine the moisture content in moisture saturated or droplet-laden gas streams, attach a temperature sensor capable of measuring $\pm 1^\circ\text{C}$ (2°F) to the probe; measure the stack gas temperature at each traverse point during the traverse; measure the absolute stack pressure. Determine the moisture percentage, either by:

1. Using a psychrometric chart and making appropriate corrections if stack pressure is different from that of the chart, or
2. Using saturation vapor pressure (S.V.P.) Tables 6.1A and 6.1B of Section 3.3.6 and Equation 4-1.

$$B_{ws} = \frac{S.V.P.}{P_{bar} + \frac{P_{static}}{13.6}} \quad \text{Equation 4-1}$$

where

B_{ws} = water vapor in the gas stream, proportion by volume

S.V.P. = saturated vapor pressure of water at average stack temperature, mm (in.) Hg

P_{bar} = barometric pressure, mm (in.) Hg, and

P_{static} = static pressure of the stack, mm (in.) H_2O .

If the psychrometric chart or the saturation vapor pressure tables are not applicable (based on evaluation of the process), alternate methods approved by the administrator should be used.

The stack gas can be checked for saturation with wet and dry bulb thermometers. When the stack is saturated, the wet and dry bulb temperatures are the same. This will not, however, check for the presence of water droplets.

4.2.2 Condenser Preparation - Place known volumes of water in the first and second impingers; generally, 100 ml in each impinger is adequate. Immerse the tips of the impinger tubes at least 13.0 mm (0.5 in.) in the water. The third impinger should be left dry to trap any entrained water droplets. Place a known amount of silica gel in the fourth impinger; generally, 200 g is sufficient. Record the amount of water and silica gel placed in the impingers. If the stack temperature is high $>400^{\circ}C$ ($752^{\circ}F$), a lower sampling rate may be necessary to maintain the temperature leaving the fourth impinger at $\leq 20^{\circ}C$ ($\leq 68^{\circ}F$).

Alternatively, each impinger and its contents can be weighed to the nearest 0.5 g. Record these weights on the analytical data form (Figure 4.3) for determining the amount of water condensed.

4.2.3 Sampling Train Assembly - Assemble the sampling train as shown in Figure 1.1, and perform the following:

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

Plant ACME Power Plant
Date 8-10-79
Run number APP-1

	Volume of liquid water collected	
	Impinger volume, ml	Silica gel weight, g
Final	271	215.0
Initial	200	203.5
Liquid collected	71	11.5
Total volume collected		g* 825ml

* Convert weight of water to volume by dividing total weight increase by density of water (1 g/ml):

$$\frac{\text{Increase, g}}{1 \text{ g/ml}} = \text{water volume, ml.}$$

Figure 4.3 Method 4 analytical data form.

2. Leak check the sampling train just prior to use by disconnecting the probe from the first impinger or (if applicable, from the filter holder); plug the inlet to the first impinger (or filter holder); and pull a 380 mm (15 in.) Hg vacuum. If the leakage rate is >4% of the average sampling rate or if it is $\geq 0.00057 \text{ m}^3/\text{min}$ ($0.02 \text{ ft}^3/\text{m}$), whichever is less, it is unacceptable. This leak check is recommended but not mandatory.

3. Place a loosely packed filter of glass wool in the end of the probe if an external heated filter is not used, and connect the probe to the sampling train.

4. Attach a stack temperature sensor on the probe when required.

4.2.4 Sampling Train Operation (Constant Rate) - Sampling is performed at a constant rate of approximately $0.02 \text{ m}^3/\text{min}$ ($0.75 \text{ ft}^3/\text{m}$) or less during the entire period as follows:

1. Record the initial dry gas meter readings, barometric pressures, and other data as indicated in Figure 4.2.

2. Position the tip of the probe at the first sampling point, and turn on the pump.

3. Adjust the sample flow to the predetermined constant rate of $0.021 \text{ m}^3/\text{min}$ ($0.75 \text{ ft}^3/\text{m}$) or less.

4. Take other readings required by Figure 4.2 at least once at each sample point during each time increment.

5. Record the dry gas meter readings at the end of each time increment.

6. Record the stack gas temperature at each point when the stack gas is saturated or has water droplets.

7. The static pressure of the stack must also be determined when the moisture content is to be calculated using the partial pressure method.

8. Repeat steps 3 through 5 for each sampling point.

9. Turn off the pump, remove probe from the stack, and record the final readings after each traverse.

10. Leak check (as described in Subsection 4.2.3) after the last traverse, and record all leakage rates. This leak check is mandatory.

11. Cap the impingers with serum caps (or equivalent) and transport to the sample cleanup area if the train passes the leak check. If it does not, either reject the test results or correct the sample volume (see Section 3.4.6).

12. Check the sampling rate and the sample volume (ΔV_m) for each point. The volume for each point should be within $\pm 10\%$ of the average sample volume for all points. If all are within the limit, then the sample run is acceptable; otherwise, reject the results and either repeat the test run or consult the administrator.

4.3 Sample Recovery

Measure the volume of the condensed moisture to the nearest 1 ml. Determine the increase in weight of the silica gel (or gel plus impinger) to the nearest 0.5 g. Record these data on the data form shown in Figure 4.3 or on a similar form.

4.4 Sample Logistics, Data Collection, and Equipment Packing

Follow the above procedures until the required number of runs are completed. At the completion of the test:

1. Be sure that all data recorded during the field test are duplicated by using carbon paper or by using data forms and a laboratory notebook. Mail one set of data to the base laboratory, or give it to another team member or the agency, and have the other handcarried.

2. Examine all sampling equipment for damage and for proper packing for shipment. Label all shipping containers properly to prevent sample or equipment loss.

Table 4.1 ACTIVITY MATRIX FOR ON-SITE MEASUREMENT CHECKS

Apparatus	Acceptance limits	Frequency and method of measurements	Action if requirements are not met
Condenser, addition of water and silica gel to system	100 ml of distilled water in first two impingers; approximately 200 g of silica gel in fourth impinger	Either use graduated cylinder to measure water or weigh each impinger and its contents to nearest 0.5 g	Correct the additions
Assembling sampling train	<ol style="list-style-type: none"> 1. Assembled to specifications in Fig 1.1 2. Leak rate $<4\%$ or $0.00057 \text{ m}^3/\text{min}$ ($0.02 \text{ ft}^3/\text{min}$), whichever is less 	<ol style="list-style-type: none"> 1. Assemble before each sample run 2. Leak check before sampling by plugging the nozzle or inlet to first impinger and pulling a vacuum of 380 mm (15 in.) Hg 	<ol style="list-style-type: none"> 1. Reassemble 2. Correct leak
Sampling	<ol style="list-style-type: none"> 1. Sampling volume for each point within $\pm 10\%$ of average sample volume for all points 2. Minimum total sample gas volume of 0.60 sm^3 (21 sft^3) at a constant sampling rate $<0.021 \text{ m}^3/\text{min}$ ($0.75 \text{ ft}^3/\text{min}$) 3. Minimum number and location of points specified by Method 1 	<ol style="list-style-type: none"> 1. Calculate for each test run 2. Make a quick calculation before testing; do an exact calculation after traverse 3. Check before the first test run by measuring duct and using Method 1 	<ol style="list-style-type: none"> 1. Repeat test run 2. As above 3. Repeat the procedure to comply with specifications of Method 1

(continued)

Table 4.1 (continued)

Apparatus	Acceptance limits	Frequency and method of measurements	Action if requirements are not met
Sampling (cont.)	4. Leakage rate <4% of the average sampling volume or $<0.00057 \text{ m}^3/\text{min}$ ($0.02 \text{ ft}^3/\text{min}$), whichever is less	4. Leak check after each test run or before equipment replacement during test at the maximum vacuum during the test (mandatory)	4. Correct the sample volume, or repeat the sample run
Sample recovery	Volume of moisture condensed to nearest 1 ml; weight increase of silica gel to nearest 0.5 g	Use volumetric/gravimetric measurement	Repeat the measurement
Sample logistics, data collection, and packing of equipment	1. All data recorded correctly 2. All equipment examined for damage and labeled for shipment 3. All sample containers and blanks properly labeled and packaged	1. After completion of each test and before packing 2. As above 3. Visually check upon completion of each sample	1. Complete the data 2. Repeat the sampling if damage occurred during test 3. Correct when possible

5.0 POSTSAMPLING OPERATIONS

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

Posttest checks will have to be made on most of the sampling apparatus. The checks will include three calibration runs at a single orifice meter setting; cleaning; and/or routine maintenance. The cleaning and maintenance are discussed in APTD-0576². Figure 5.1 should be used to record the posttest checks.

5.1.1 Metering System - The metering system has two components that must be checked--the dry gas meter and the dry gas meter thermometer(s).

The dry gas meter thermometer(s) should be compared with the ASTM mercury-in-glass thermometer at room temperature. If the two readings agree within 6°C (10.8°F), they are acceptable; if not, the thermometer must be recalibrated according to Section 3.3.2 after the posttest check of the dry gas meter. For calculations, use the dry gas meter thermometer readings (field or recalibration values) that would give the higher temperatures--that is, if the field readings are higher, no correction is necessary, but if the recalibration value is higher, add the difference in the two readings to the average dry gas meter temperature reading.

The dry gas meter must be posttested (Section 3.3.2). The metering system should not have any of the leaks that were corrected prior to the posttest check. If the dry gas meter calibration factor (Y) does not deviate by >5% from the initial calibration factor, the dry gas meter volumes obtained during the test series are acceptable. If Y deviates by >5%, recalibrate the metering system (Section 3.3.2).

Date 1/12/80 Calibrated by B. C. Blagum
Meter box number EM-1

Dry Gas Meter

Pretest calibration factor Y 0.986 (must be within $\pm 2\%$)*
Posttest checks, Y_1 0.987 Y_2 _____ (must be within $\pm 5\%$ of
pretest)
Recalibration required? _____ yes ☒ no
If yes, recalibration factor Y _____ (must be within $\pm 2\%$)*
Lower calibration factor, Y 0.986 for calculations (pretest
or posttest)*

Dry Gas Thermometer

Was a pretest meter temperature correction used? _____ yes ☒ no
If yes, temperature correction _____ (within $\pm 3^\circ\text{C}$ (5.4°F)
over range)*
Post test comparison with mercury-in-glass thermometer O.K.
(within $\pm 6^\circ\text{C}$ (10.8°F) at room temperature)
Recalibration required? _____ yes ☒ no
Recalibration temperature correction, if used _____ (within
 $\pm 3^\circ\text{C}$ (5.4°F) over range)*
If yes; no correction is necessary for calculations when meter
thermometer temperature is higher.
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 +2.5 mm (0.1 in.) Hg
Was recalibration required? _____ yes ☒ no
If yes; no correction is necessary for calculations when the
field barometer has the lower reading
If the mercury-in-glass reading is lower, then subtract the dif-
ference from the field data readings for the calculation

Stack Gas Temperature Sensor (if required)

Average stack temperature 135 $^\circ\text{C}$ ($^\circ\text{F}$)
Posttest comparison 135 [within $\pm 2^\circ\text{C}$ (4°F)]*
Was recalibration required? _____ yes ☒ no

*Most significant items/parameters to be checked.

Figure 5.1 Posttest equipment checks.

For the calculations, use the calibration factor (initial or recalibration) that yields the lower gas volume for each test run.

5.1.2 Barometer - The field barometer should be compared to the mercury-in-glass barometer. If the readings agree within ± 5 mm (0.2 in.) Hg, the field readings are acceptable; if not, use the lesser calibration value for the calculations. If the field barometer reads lower than the mercury-in-glass barometer, the field data are acceptable. If the mercury-in-glass barometer gives the lower reading, use the difference in the two readings (the adjusted barometric value) in the calculations.

5.1.3 Stack Gas Temperature Sensor - The stack gas temperature sensor should be compared with an ASTM mercury-in-glass reference thermometer. Place both the stack sensor and reference thermometer in an atmosphere (air or water) that is within $\pm 5^{\circ}\text{C}$ (10°F) of the average stack temperature. If both values agree within $\pm 2^{\circ}\text{C}$ (4°F) then the pretest calibration is acceptable. If not, then calculate the moisture content using both the pretest calibration and the posttest corrected values. If either or both calculated values are greater than the measured moisture, then either or both may be eliminated from any final emissions calculations.

Table 5.1 ACTIVITY MATRIX FOR POSTTEST OPERATIONS

Apparatus	Acceptance limits	Frequency and method of measurements	Action if requirements are not met
Dry gas meter	Within $\pm 5\%$ of the initial calibration factor	Make three runs at a single, intermediate orifice setting and at highest vacuum occurring during test (Sec 3.3.2)	Recalibrate; use calibration factor that gives lesser sample volume
Dry gas meter thermometer	Within $\pm 6^{\circ}\text{C}$ (10.8°F) at room temperature	Compare with ASTM mercury-in-glass thermometer after each field test	Recalibrate; use higher temperature for calculations
Barometer	Within ± 5 mm (0.2 in.) Hg at ambient pressure	Compare with mercury-in-glass barometer after each field test	Recalibrate; use lower barometric values for calculations
Stack temperature sensor	Within $\pm 2^{\circ}\text{C}$ (4°F) of the reference check temperature	After each run, compare with reference temperature	Recalibrate; perform calculations with and without temperature correction

6.0 CALCULATIONS

Calculation errors due to mathematical mistakes can be a large part of total system error. Therefore, each set of calculations should be repeated or spot-checked by a team member other than the one who performed them originally. If a difference greater than a typical roundoff error is detected, the calculations should be checked step by step until the source of error is found and corrected. A computer program can be advantageous in reducing calculation errors. If a standardized computer program is used, the original data entry should be checked; if differences are observed, a new computer run should be made. Table 6.2 at the end of this section summarizes the quality assurance activities for calculations.

Carryout calculations, retaining at least one significant digit beyond that of the acquired data. Roundoff after final calculations to two significant digits for each run or sample in accordance with the ASTM 380-76 procedures. Record the results on Figure 6.1A, 6.1B, or 6.1C.

6.1 Nomenclature

The terms defined and listed alphabetically herein are to be used in calculating dry gas and water vapor volumes and moisture contents, and in verifying constant sampling rate.

B_{ws}	= Water vapor in the gas stream, proportion by volume
ΔH	= Average pressure differential across the orifice meter, mm (in.) H_2O
$\Delta H@_i$	= Measurement of pressure differential across the orifice meter, mm (in.) H_2O
L_a	= Maximum acceptable leakage rate for either a pretest leak check or a leak check ₃ following a component change; equal to 0.00057 m ³ /min (0.01995 ft ³ /min)
M_w	= Molecular weight of water, 18.0 g/g-mole (18.0 lb/lb-mole)

P_{bar}	= Barometric pressure, mm (in.) Hg
P_m	= Absolute pressure at the dry gas meter (for this method, same as barometric pressure), mm (in.) Hg
P_s	= Absolute stack pressure, mm (in.) Hg
P_{static}	= Static pressure of the stack, mm (in.) H_2O
P_{std}	= Standard absolute pressure, 760 mm (29.92 in.) Hg
ρ_w	= Density of water, 0.9982 g/ml (0.002201 lb/ml)
R	= Ideal gas constant, 0.06236 (mm Hg) (m^3)/(g-mole) (K) for metric units and 21.85 (in. Hg) (ft^3)/(lb-mole) ($^{\circ}\text{R}$) for English units
S.V.P.	= Saturated vapor pressure of water at average stack temperature, mm (in.) Hg
T_m	= Absolute average dry gas meter temperature, K ($^{\circ}\text{R}$)
T_{std}	= Standard absolute temperature, 298K (528 $^{\circ}\text{R}$)
V_f	= Final volume of condenser water, ml
V_i	= Initial volume of condenser water, ml
V_m	= Volume of gas sample measured by dry gas meter, dcm (dcf)
ΔV_m	= Incremental volume ₃ measured by dry gas meter at each traverse point, dm^3 (dcf)
$V_{m(\text{std})}$	= Volume of gas sample measured by the dry gas meter, corrected to standard conditions, dsm^3 (dscf)
v_s	= Stack gas velocity, calculated by Method 2, using data from Method 5, m/s (ft/s)
$V_{\text{wc}(\text{std})}$	= Volume of condensed water vapor, corrected to standard conditions, sm^3 (scf)
$V_{\text{wsg}(\text{std})}$	= Volume of water vapor collected in silica gel, corrected to standard conditions, sm^3 (scf)
W_f	= Final weight of silica gel or silica gel plus impinger, g
W_i	= Initial weight of silica gel or silica gel plus impinger, g
Y	= Dry gas meter calibration factor

6.2 Condensed Water Vapor Volume

$$V_{wc(std)} = \frac{(V_f - V_i) \rho_w RT_{std}}{P_{std} M_w} = K_1 (V_f - V_i) \quad \text{Equation 6-1}$$

where

$$K_1 = 0.001333 \text{ m}^3/\text{ml} \text{ for metric units, or} \\
= 0.04707 \text{ ft}^3/\text{ml} \text{ for English units.}$$

6.3 Water Vapor Volume Collected in Silica Gel

$$V_{wsg(std)} = \frac{(W_f - W_i) RT_{std}}{P_{std} M_w} = K_2 (W_f - W_i) \quad \text{Equation 6-2}$$

where

$$K_2 = 0.001335 \text{ m}^3/\text{g} \text{ for metric units, or} \\
= 0.04715 \text{ ft}^3/\text{g} \text{ for English units.}$$

6.4 Dry Gas Volume, Corrected to Standard Conditions

Correct the sample volume measured by the dry gas meter to standard conditions (20°C and 760 mm Hg or 68°F and 29.92 in. Hg) by using Equation 6-3.

$$V_{m(std)} = V_m Y \frac{T_{std}}{T_m} \frac{P_m}{P_{std}} = \frac{K_3 V_m Y P_m}{T_m} \quad \text{Equation 6-3}$$

where

$$K_3 = 0.3858 \text{ K/mm Hg} \text{ for metric units, or} \\
= 17.64 \text{ } ^\circ\text{R/in. Hg} \text{ for English units.}$$

Note: If the leak rate observed during any mandatory leak checks exceeds the specified acceptable rate (L_a), either the value of V_m in Equation 6-3 may be corrected (as described in Section 3.4.6 of Method 5) or the test run may be invalidated.

VOLUME OF WATER VAPOR CONDENSED IN IMPINGERS

$$V_f = 271 \text{ ml}, V_i = 200 \text{ ml}$$

$$V_{wc(std)} = 0.04707 (V_f - V_i) = 0.334 \text{ ft}^3 \quad \text{Equation 6-1}$$

VOLUME OF WATER VAPOR COLLECTED IN SILICA GEL

$$W_f = 215 \text{ g}, W_i = 203 \text{ g}$$

$$V_{wsg(std)} = 0.04715 (W_f - W_i) = 0.542 \text{ ft}^3 \quad \text{Equation 6-2}$$

SAMPLE VOLUME

$$V_m = 31.54 \text{ ft}^3, T_m = 53.2^\circ \text{R}, P_m = 29.00 \text{ in. Hg}$$

$$Y = 1.016,$$

$$V_{m(std)} = 17.64 \frac{V_m Y P_m}{T_m} = 30.425 \text{ ft}^3 \quad \text{Equation 6-3}$$

MOISTURE CONTENT

$$V_{wc(std)} = 0.334 \text{ ft}^3, V_{wsg(std)} = 0.542 \text{ ft}^3,$$

$$V_{m(std)} = 30.425 \text{ ft}^3$$

$$B_{ws} = \frac{V_{wc(std)} + V_{wsg(std)}}{V_{wc(std)} + V_{wsg(std)} + V_{m(std)}} = 0.113 \quad \text{Equation 6-4}$$

Figure 6.1A Moisture content calculation form (English units).

VOLUME OF WATER VAPOR CONDENSED IN IMPINGERS

$$V_f = 271 \text{ ml}, V_i = 200 \text{ ml}$$

$$V_{wc(std)} = 0.001333 (V_f - V_i) = 0.0946 \text{ m}^3 \quad \text{Equation 6-1}$$

VOLUME OF WATER VAPOR COLLECTED IN SILICA GEL

$$W_f = 215 \text{ g}, W_i = 203 \text{ g}$$

$$V_{wsg(std)} = 0.001335 (W_f - W_i) = 0.0154 \text{ m}^3 \quad \text{Equation 6-2}$$

SAMPLE VOLUME

$$V_m = 0.8924 \text{ m}^3, T_m = 299.0 \text{ }^\circ\text{K}, P_m = 736.6 \text{ mm Hg}$$

$$Y = 1.016,$$

$$V_{m(std)} = 0.3858 \frac{V_m Y P_m}{T_m} = 0.8569 \text{ m}^3 \quad \text{Equation 6-3}$$

MOISTURE CONTENT

$$V_{wc(std)} = 0.0946 \text{ m}^3, V_{wsg(std)} = 0.0154 \text{ m}^3,$$

$$V_{m(std)} = 0.8569 \text{ m}^3$$

$$B_{ws} = \frac{V_{wc(std)} + V_{wsg(std)}}{V_{wc(std)} + V_{wsg(std)} + V_{m(std)}} = 0.114 \quad \text{Equation 6-4}$$

Figure 6.1B. Moisture content calculation form (metric units).

MOISTURE CONTENT

$$t_s \text{ avg} = 121.6. ^\circ\text{F}, 49.83 ^\circ\text{C}$$

$$P_{\text{bar}} = 29.00 \text{ in. Hg}, 736.6 \text{ mm Hg}$$

$$P_{\text{static}} = -1.50 \text{ in. H}_2\text{O}, -3.81 \text{ mm H}_2\text{O}$$

$$\text{S.V.P.} = 3.60 \text{ in. Hg}, 92.0 \text{ mm Hg}$$

$$B_{\text{ws}} = \frac{\text{S.V.P.}}{P_{\text{bar}} + \frac{P_{\text{static}}}{13.6}} = 0.125$$

Figure 6.1C Moisture content calculation form using saturation vapor pressure (English and metric units).

6.5 Moisture Content

$$B_{\text{ws}} = \frac{V_{\text{wc(std)}} + V_{\text{wsg(std)}}}{V_{\text{wc(std)}} + V_{\text{wsg(std)}} + V_{\text{m(std)}}} \quad \text{Equation 6-4}$$

Note: In moisture saturated or droplet-laden gas streams, two calculations of the moisture content of the stack gas should be made--one using a value based on the saturated conditions (Equation 6-5) and another using the results of the impinger analysis. The lower of these two B_{ws} values should be considered correct.

To determine the moisture content in moisture saturated or droplet-laden gas streams, attach a temperature sensor capable of measuring $\pm 1^\circ\text{C}$ (2°F) to the probe; measure the stack gas temperature at each traverse point during the traverse; measure the absolute stack pressure. Determine the moisture percentage, either by:

1. Using a psychrometric chart and making appropriate corrections if stack pressure is different from that of the chart, or
2. Using saturation vapor pressure Tables 6.1A and 6.1B and Equation 6-5.

$$B_{ws} = \frac{\text{S.V.P.}}{P_{\text{bar}} + \frac{P_{\text{static}}}{13.6}} \quad \text{Equation 6-5}$$

If the psychrometric chart or the saturation vapor pressure tables are not applicable (based on evaluation of the process), alternate methods approved by the administrator should be used.

6.6 Constant Sampling Rate Verification

For each sample point, determine the ΔV_m and calculate the average. If the value for any sample point differs from the average by >10%, reject the results and repeat the run.

Table 6.1A VAPOR PRESSURE OF WATER AT SATURATION (°F), in. Hg

Temp °F	0	1	2	3	4	5	6	7	8	9
50	.3626	.3764	.3906	.4052	.4203	.4359	.4520	.4586	.4858	.5035
60	.5218	.5407	.5601	.5802	.6009	.6222	.6442	.6669	.6903	.7144
70	.7392	.7648	.7912	.8183	.8462	.8750	.9046	.9352	.9666	.9989
80	1.032	1.066	1.102	1.138	1.175	1.213	1.253	1.293	1.335	1.378
90	1.422	1.467	1.513	1.561	1.610	1.660	1.712	1.765	1.819	1.875
100	1.932	1.992	2.052	2.114	2.178	2.243	2.310	2.379	2.449	2.921
110	2.596	2.672	2.749	2.829	2.911	2.995	3.081	3.169	3.259	3.351
120	3.446	3.543	3.642	3.744	3.848	3.954	4.063	4.174	4.289	4.406
130	4.525	4.647	4.772	4.900	5.031	5.165	5.302	5.442	5.585	5.732
140	5.881	6.034	6.190	6.380	6.513	6.680	6.850	7.024	7.202	7.384
150	7.569	7.759	7.952	8.150	8.351	8.557	8.767	8.981	9.200	9.424
160	9.652	9.885	10.12	10.36	10.61	10.86	11.12	11.38	11.65	11.92
170	12.20	12.48	12.77	13.07	13.37	13.67	13.98	14.30	14.62	14.96
180	15.29	15.63	15.98	16.34	16.70	17.07	17.44	17.82	18.21	18.61

Table 6.1B VAPOR PRESSURE OF WATER AT SATURATION (°C), mm Hg

Temp °C	0	1	2	3	4	5	6	7	8	9
10	9.20	9.92	10.67	11.07	11.65	12.79	13.73	14.74	15.26	16.36
20	17.50	18.77	20.1	20.78	22.23	23.80	25.15	27.09	27.98	29.85
30	31.83	33.91	36.12	37.26	39.65	42.16	44.83	47.63	49.07	52.12
40	55.32	58.67	62.20	64.03	67.87	71.86	76.07	80.49	82.78	87.53
50	92.51	97.74	103.20	106.02	111.91	118.03	124.46	131.19	134.67	141.86
60	149.38	157.23	165.43	169.67	178.41	187.55	197.08	207.01	212.12	222.68
70	233.68	245.16	257.05	263.14	275.84	289.05	302.77	316.99	324.36	339.60
80	355.09	371.35	388.37							

Table 6.2 ACTIVITY MATRIX FOR CALCULATION CHECKS

Characteristics	Acceptance limits	Frequency and method of measurement	Action if requirements are not met
Analytical data form	All data and calculations are shown	Visual check	Complete missing data values
Calculations	Difference between check and original calculations should not exceed roundoff error	Repeat all calculations starting with raw data for hand calculations; check all raw data input for computer calculations and hand calculate one sample per test	Indicate errors on analytical data form, Fig 4.2

7.0 MAINTENANCE

Normal use of emission testing equipment subjects it to corrosive gases, temperature extremes, vibrations, and shocks. Keeping the equipment in good operating order over an extended period of time requires routine maintenance and knowledge of the equipment. Maintenance of the entire sampling train should be performed either quarterly or after 1000 ft³ of operation, whichever occurs sooner. Maintenance procedures are summarized in Table 7.1 at the end of this section. The following procedures are recommended, but not required, to increase the reliability of the equipment.

7.1 Pumps

Several types of pumps are used in commercial sampling trains. Two of the most common types are the fiber vane pump with in-line oiler and the diaphragm pump. The fiber vane pump requires a periodic check of the oil and the oiler jar. The used oil (usually low nondetergent or machine weight) should be about the same translucent color as the unused or spare oil. When the fiber vane pump starts to run erratically or when the head is removed each year, the fiber vanes should be changed.

The diaphragm pump requires little maintenance. If the diaphragm pump leaks or runs erratically, it is normally due to a bad diaphragm or malfunctions in the valves; these parts are easily replaced and should be cleaned annually by complete disassembly of the train.

7.2 Dry Gas Meters

The dry gas meter should be checked for excess oil and component corrosion by removing the top plate every 3 mo. The meter should be disassembled and all components cleaned and checked more often if the dials show erratic rotation, or if the meter will not calibrate properly.

7.3 Inclined Manometer

The fluid should be changed when it is discolored or contains visible matter and when it is disassembled yearly. No

other routine maintenance is required since the inclined manometer is checked during the leak checks of both the pitot tube and the entire meter box.

7.4 Sampling Train

All remaining sample train components should be visually checked every 3 mo, and they should be completely disassembled and cleaned or replaced yearly. Many of the items, such as quick disconnects, should be replaced when damaged rather than after they are periodically checked. Normally, the best maintenance procedure is to replace the entire unit--for example, a meter box, sample box, or umbilical cord.

Table 7.1 ACTIVITY MATRIX FOR EQUIPMENT MAINTENANCE CHECKS

Apparatus	Acceptance limits	Frequency and method of measurements	Action if requirements are not met
Routine main-tenance	No erratic behavior	Routine maintenance quarterly; disassemble and clean yearly	Replace parts as needed
Fiber vane pump	Leak free and required flow	Periodic check of oil jar; remove head, and change fiber vanes	Replace as needed
Diaphragm pump	Leak free valves functioning properly with required flow	Clean valves during yearly disassembly	Replace when leaking or when running erratically
Dry gas meter	No excess oil, corrosion, or erratic rotation of the dial	Check every 3 mo for excess oil or corrosion by removing top plate; check valves and diaphragm when meter dial runs erratically or when meter will not calibrate	Replace parts as needed, or replace meter
Inclined manometer	No discoloration or visible matter in the fluid	Check periodically; change fluid during yearly disassembly	Replace parts as needed
Sampling train	No damage	Visually check every 3 mo; completely disassemble and clean or replace yearly	If failure noted, use another entire control console, sample box, or umbilical cord

8.0 AUDITING PROCEDURE

An audit is an independent assessment of data quality. Independence is achieved by using apparatus and standards that are different from those used by the regular field crew. Routine quality assurance checks by a field team are necessary for obtaining 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 activities for the auditing.

Based on the results of the collaborative tests of Method 4, a performance audit of data processing and a systems audit are recommended. These two audits are described in the Subsections 8.1 and 8.2.

8.1 Performance Audit of Data Processing

Performance audits are conducted by the auditor to quantitatively evaluate the quality of the data produced by the total measurement system (sample collection, sample analysis, and data processing). Due to the limited sizes of most emission-testing companies, it is recommended that these audits be performed by the responsible control agency once during every enforcement source test, regardless of whether the tests are conducted by agency or private company personnel. A source test for enforcement comprises a series of runs at one source.

Calculation errors are prevalent in Method 4. Data processing errors can be determined by auditing the data recorded on the field and the laboratory forms. The original and the check calculations should agree. If not, all of the data and calculations should be checked. The calculation errors should be clearly explained to the source-test team to prevent or minimize reoccurrence. The data processing errors may also be determined by requesting that copies of data sets compiled in the field and copies of manual data reductions (or computer printouts if used) be forwarded to the evaluator for audit.

8.2 Systems Audit

A systems audit is an on-site qualitative inspection and review of the quality assurance method used by the test team for

the total measurement system (sample collection, sample analysis, data processing, etc.). Initially, a systems audit specified by a quality assurance coordinator should be conducted for each enforcement source test, which by definition comprises three runs at one source. After the team gains experience with the method, the frequency of audit may be reduced--for example, once for every four tests.

The functions of the auditor are summarized by the following:

1. Observe procedures and techniques of the field team during sample collection.
2. Check/verify the records of apparatus calibration.
3. Record the results of the audit and forward them with comments on source team management to the quality assurance coordinator so that any needed corrective actions may be implemented.

The auditor should observe the field team's overall performance of the source test. Specific operations to observe should include (but not be limited to):

1. Setting up and leak testing the sampling train.
2. Constant rate sampling check of the sampling train.
3. Final leak check of train.
4. Sample recovery.

Figure 8.1 is a suggested checklist to be used by the auditor for developing a list of important techniques/steps to observe.

Yes	No	Operation
		<u>Presampling preparation</u>
_____	_____	1. Knowledge of process conditions
_____	_____	2. Calibration of pertinent equipment prior to each field test; in particular, the dry gas meter should be checked before each test
		<u>On-site measurements</u>
_____	_____	3. Leak testing of sample train after sample run
_____	_____	4. Addition of water and silica gel to impingers, and correct location of impingers
_____	_____	5. Constant sampling rate and not exceeding specified rate
_____	_____	6. Measurement of condensed water to within specified limits
_____	_____	7. Record of pertinent process condition during sample collection
_____	_____	8. Probe maintained at given temperature
		<u>Postsampling</u>
_____	_____	9. Calculation procedure/check
_____	_____	10. Calibration checks
COMMENTS		

Figure 8.1 Method 4 checklist to be used by auditors.

Table 8.1 ACTIVITY MATRIX FOR AUDITING PROCEDURES

Audit	Acceptance limits	Frequency of method of measurement	Action if requirements are not met
Data processing errors	Original and check calculations should agree	Once during every enforcement source test, do independent calculations starting with recorded data	Check and correct all data for the source test
Systems audit--observance of technique	Operation/technique described in this section of the Handbook	Once during every enforcement test until experience gained, then every fourth test; observe techniques; use audit checklist, Fig 8.1	Explain to team the deviations from recommended techniques; note the deviations on Fig 8.1

9.0 RECOMMENDED STANDARDS FOR ESTABLISHING TRACEABILITY

To achieve data of desired quality, two considerations are necessary: (1) the measurement process must be in a state of statistical control, and (2) the systematic errors, when combined with the random variations (errors of measurement), must result in an acceptable level of uncertainty. To ensure good data, it is necessary to perform quality control checks and independent audits of the measurement process; and to use materials, instruments, and procedures which can be traced to a standard of reference.

The working calibration standards should be traceable to primary or higher level standards such as those for the dry gas meter. The dry gas meter should be calibrated against a wet test meter which has been verified by an independent liquid displacement meter.

10.0 REFERENCE METHOD

METHOD 4—DETERMINATION OF MOISTURE IN STACK GASES

1. Principle and Applicability.

1.1 Principle. A gas sample is extracted proportionally from the source and moisture is removed from the gas stream, condensed, and determined either volumetrically or gravimetrically.

1.2 Applicability. This method is applicable for the determination of moisture in stack gas.

Two methods are given. One is a reference method for the accurate determination of moisture content as needed to calculate emission data. The other is an approximation method for moisture content to be subsequently used for setting isokinetic sampling rates. For this latter purpose, the tester may use any alternate means for approximating the moisture content, e.g. drying tubes, wet bulb-dry bulb technique, condensation techniques, stoichiometric calculations, previous experience, etc. However, the actual isokinetic rate maintained during a pollutant sampling run and the moisture content used to calculate emission data will not be based on the results of the approximation method (see exception in note below), but will be determined from the data of the reference method, which is normally conducted simultaneously with a pollutant measurement run.

NOTE.—Any of the approximation methods which are shown to the satisfaction of the Administration of yielding results to within 1% H₂O of the reference method results may be used in lieu of the reference method.

These methods are not applicable to gas streams that contain liquid droplets. For these cases, assume that the gas stream is saturated. Determine the average stack gas temperature using gauges described in Method 2 and by traversing according to Method 1. Then obtain the moisture percentage by (1) using a psychometric chart and making appropriate corrections, if stack pressure is different from that of the chart,

for absolute pressure or (2) by using saturation vapor pressure tables.

2. Reference Method.

The procedure for determining moisture content described in Method 5 is acceptable as a reference method.

2.1 Apparatus. A schematic of the sampling train used in this reference method is shown in Figure 4-1. All components shall be maintained and calibrated according to the procedure outlined in Method 5.

2.1.1 Probe—Stainless steel or glass tubing, sufficiently heated to prevent water condensation and equipped with a filter (either in-stack or heated out-stack) to remove particulate matter.

2.1.2 Condenser—Any system that cools the sample gas stream and allows measurement of the water condensed and moisture leaving the condenser, each to within 1 ml or 1 g. Acceptable means are to measure the condensed water either gravimetrically or volumetrically and to measure the moisture leaving the condenser by (1) monitoring the temperature and pressure at the exit of the condenser and using Dalton's law or (2) by passing the sample gas stream through a tared silica gel trap with exit gases kept below 20° C (68° F) and determining the weight gain.

2.1.3 Cooling system—Ice bath container and crushed ice, or equivalent, to aid in condensing moisture.

2.1.4 Drying tube—Tube packed with 6-16 mesh indicating-type silica gel, or equivalent, to dry the sample gas and protect the pump and dry gas meter. This may be an integral part of the condenser system, in which case the tube shall be immersed in the ice bath and a thermometer placed at the outlet for monitoring purposes. If approach (1) of section 2.1.2 is used to measure the moisture leaving the condenser, the temperature and pressure must be monitored before the silica gel tube.

2.1.5 Metering system—Vacuum gauge, leak-free pump, thermometers capable of measuring temperature to within 3° C (5.4° F), dry gas meter with ± 2 percent accuracy, and related equipment, or other metering systems approved by the Administrator, as required to maintain a proportional sampling rate and to determine sample gas volume.

2.1.6 Barometer—Mercury, aneroid, or other barometers 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 weather bureau 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 the 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.

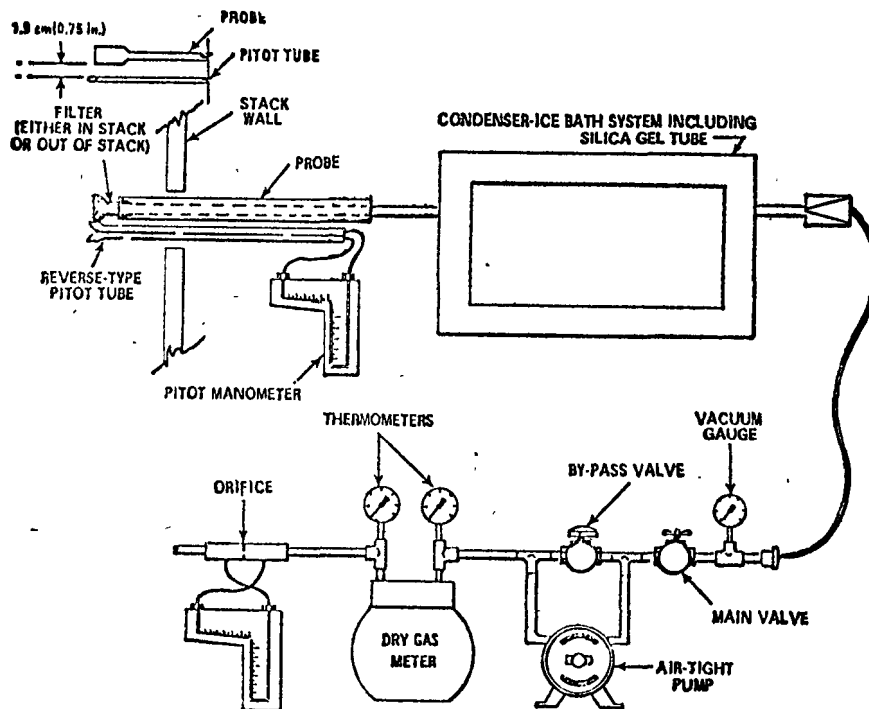


Figure 4-1. Moisture sampling train-reference method.

PLANT _____

LOCATION _____

OPERATOR _____

DATE _____

RUN NO. _____

AMBIENT TEMPERATURE _____

BAROMETRIC PRESSURE _____

PROBE LENGTH m(ft) _____

SCHEMATIC OF STACK CROSS SECTION

TRAVERSE POINT NUMBER	SAMPLING TIME (t), min.	STACK TEMPERATURE °C (°F)	VELOCITY HEAD (ΔP_s) $\frac{\rho V^2}{2}$	PRESSURE DIFFERENTIAL ACROSS ORIFICE METER (ΔH_o) $\frac{K \rho Q^2}{8 g C_d A_o^3}$	GAS SAMPLE VOLUME m^3 (ft ³)	GAS SAMPLE TEMPERATURE AT DRY GAS METER		TEMPERATURE OF GAS LEAVING CONDENSER OR LAST WIPPER °C (°F)
						INLET (Tm _{in}) °C (°F)	OUTLET (Tm _{out}) °C (°F)	
TOTAL						Avg.	Avg.	
AVERAGE						Avg.		

Figure 4-2. Field moisture determination-reference method.

	IMPINGER VOLUME, ml	SILICA GEL WEIGHT, g
FINAL		
INITIAL		
DIFFERENCE		

Figure 4-3. Analytical data-reference method.

2.1.7 Pitot tube—Type S, or equivalent, attached to probe to allow constant monitoring of the stack gas velocity so that the sampling flow rate can be regulated proportional to the stack gas velocity. The tips of the probe and pitot tube shall be adjacent to each other and the free space between them shall be about 1.9 cm (0.75 in.). When used with this method, the pitot tube need not be calibrated.

2.1.8 Differential pressure gauge—Inclined manometer capable of measuring velocity head to within 10 percent of the minimum measured value or ± 0.013 mm (0.0005 in.), in whichever is greater. Below a differential pressure of 1.3 mm (0.05 in.) water gauge, micromanometers with sensitivities of 0.013 mm (0.0005 in.) should be used. However, micromanometers are not easily adaptable to field conditions and are not easy to use with the pulsating flow. Thus, methods or other devices acceptable to the Administrator may be used when conditions warrant.

2.1.9 Temperature gauge—Thermocouple, liquid filled bulb thermometer, bimetallic thermometer, mercury-in-glass thermometer, or other gauges that are capable of measuring temperature to within 1.5 percent of the minimum absolute stack temperature.

2.1.10 Graduated cylinder and/or balance—To measure condensed water and moisture caught in the silica gel to within 1 ml or 1 g. Graduated cylinders shall have subdivisions no greater than 2 ml. Most laboratory balances are capable of weighing to the nearest 0.5 g or less. These balances are suitable for use here.

2.1.11 Temperature and pressure gauges—If Dalton's law is used to monitor temperature and pressure at condenser outlet. The temperature gauge shall have an accuracy of 1°C (2°F). The pressure gauge shall be capable of measuring pressure to within 2.5 mm Hg (0.1 in. Hg).

2.1.12 Silica gel—If used to measure moisture leaving condenser, indicating type, 6-16 mesh. If previously used, dry at 175°C (350°F) for 2 hours. New silica gel may be used as received.

2.2 Procedure. The procedure below is written for a condenser system incorporating silica gel and gravimetric analysis to measure the moisture leaving the condenser and volumetric analysis to measure the condensed moisture.

2.2.1 Select the sampling site and minimum number of sampling points according to Method 1 or as specified by the Administrator. Determine the range of velocity head using Method 2 for the purpose of making proportional sampling rate calculations.

Select a suitable velocity head to correspond to about $0.014\text{ m}^3/\text{min}$ (0.5 cfm). Select a suitable probe and probe length such that all traverse points can be sampled. Consider sampling from opposite sides (four total sampling ports) for large stacks to enable use of shorter probe lengths. Mark probe with heat resistant tape or by some other method to denote the proper distance into the stack or duct for each sampling point. Weigh and record weight of silica gel to the nearest 0.5 g.

2.2.2 Select a suitable total sampling time of no less than 1 hour such that a minimum total gas sample volume of 0.6 m^3 (20 ft³) at standard conditions will be collected and the sampling time per traverse point is not less than 2 min., or some greater time interval as specified by the Administrator.

2.2.3 Set up the sampling train as shown in Figure 4-1. Turn on the probe heating system to about 120°C (248°F) so as to prevent water condensation and allow time for temperature to stabilize. Place crushed ice in the ice bath container. Leak check the train by plugging the probe inlet and pulling a 380 mm Hg (15 in. Hg) vacuum. A leakage rate in excess of 4 percent of the average sampling rate or $0.00057\text{ m}^3/\text{min}$ (0.02 cfm), whichever is less, is unacceptable.

2.2.4 During the sampling run, maintain a sampling rate within 20 percent, or as specified by the Administrator, of constant proportionality. For each run, record the data required on the example data sheet shown in Figure 4-2. Be sure to record the initial dry gas meter reading. Record the dry gas meter reading at the beginning and end of each sampling time increment, when changes in flow rates are made, and when sampling is halted. Take other data point readings at each sample point at least once during each time increment.

2.2.5 To begin sampling position the probe tip at the first traverse point. Immediately start the pump and adjust the flow to proportional conditions. Traverse the cross section. Add more ice and, if necessary, salt to maintain a temperature of less than 20°C (68°F) at the silica gel outlet to avoid excessive moisture losses.

2.2.6 After collecting the sample, measure the volume increase of the liquid to the nearest 1 ml. Determine the increase in weight of the silica gel tube to the nearest 0.5 g. Record the information (see example, data sheet, Figure 4-3) and calculate the moisture percentage.

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

2.3.1 Nomenclature.

B_v = Proportion by volume
 M_w = Molecular weight of water, 18 g/g-mole (18 lb/lb-mole)
 P_m = Absolute pressure (for this method, same as barometric pressure) at the dry gas meter, mm Hg (in. Hg)
 P_{std} = Standard absolute pressure, 760 mm Hg (29.92 in. Hg)
 R = Ideal gas constant, 0.06236 (mm Hg)(m³)/(g-mole)(°K) for metric units and 21.83 (in. Hg)(ft³)/(lb-mole)(°R) for English units
 T_m = Absolute temperature at meter, °K (°R)
 T_{std} = Absolute temperature, 293° K (528° R)
 V_m = Dry gas volume measured by meter, dcm (dcf)
 $V_{m(std)}$ = Dry gas volume measured by the dry gas meter, corrected to standard conditions, dscm (dscf)
 $V_{wv(std)}$ = Volume of water vapor condensed corrected to standard conditions, m³ (ft³)
 $V_{wsc(std)}$ = Volume of water vapor collected in silica gel corrected to standard conditions, m³ (ft³)
 V_f = Final volume of condenser contents, ml
 V_i = Initial volume, if any, of condenser contents, ml
 W_f = Final weight of condenser contents, g
 W_i = Initial weight of condenser contents, g
 ρ_w = Density of water, 1 g/ml (0.00220 lb/ml)

2.3.2 Volume of water vapor condensed.

$$V_{wv(std)} = \frac{(V_f - V_i) \rho_w R T_{std}}{P_{std} M_w} = K \frac{V_m P_m}{T_m} \quad \text{Equation 4-3}$$

$$= K(V_f - V_i) \quad \text{Equation 4-1}$$

where:

$$K = 0.00134 \text{ m}^3/\text{ml} \text{ for metric units}$$

$$= 0.0472 \text{ ft}^3/\text{ml} \text{ for English units}$$

2.3.3 Volume of water vapor collected in silica gel.

$$V_{wsc(std)} = \frac{(W_f - W_i) R T_{std}}{P_{std} M_w} = K(W_f - W_i) \quad \text{Equation 4-2}$$

where:

$$K = 0.00134 \text{ m}^3/\text{g} \text{ for metric units}$$

$$= 0.0472 \text{ ft}^3/\text{g} \text{ for English units}$$

2.3.4 Gas volume.

$$V_{m(std)} = V_m \frac{(P_m)(T_{std})}{(P_{std})(T_m)}$$

where:
 $K = 0.3855 \text{ °K/mm Hg for metric units}$
 $= 17.65 \text{ °R/in. Hg for English units}$

2.3.5 Moisture Content:

$$B_w = \frac{V_{wv} + V_{wsc}}{V_{wv} + V_{wsc} + V_m}$$

Equation 4-4

2.3.6 Proportional sampling constant—For each time increment, calculate

$$V_m / \sqrt{\Delta P}$$

Calculate the average. If the value for any time increment falls beyond 20 percent of the average, reject the results and do run over.

3. Approximation Method.

The approximation method described below is presented only as a suggested method.

3.1 Apparatus.

3.1.1 Probe—Stainless steel or glass tubing sufficiently heated to prevent water condensation and equipped with a filter (either in-stack or heated out-stack) to remove particulate matter.

3.1.2 Impingers—Two midget impingers, each with 30 ml capacity, or equivalent.

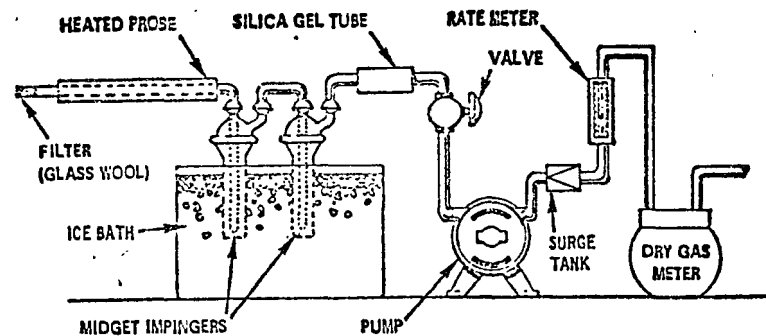


Figure 4-4. Moisture-sampling train.

LOCATION _____ COMMENTS _____
 TEST _____
 DATE _____
 OPERATOR _____
 BAROMETRIC PRESSURE _____

CLOCK TIME	GAS VOLUME THROUGH METER, (V _m), m ³ (ft ³)	RATE METER SETTING m ³ /min. (ft ³ /min.)	METER TEMPERATURE, °C (°F)

Figure 4-5. Field moisture determination.

3.1.3 Ice bath—Container and ice, to aid in condensing moisture in impingers.

3.1.4 Drying tube—Tube packed with 6-16 mesh indicating-type silica gel, or equivalent, to dry the sample gas and to protect the meter and pump.

3.1.5 Valve—Needle valve, to regulate sample gas flow rate.

3.1.6 Pump—Leak-free, diaphragm type, or equivalent, to pull gas through the train.

3.1.7 Volume meter—Dry gas meter, sufficiently accurate to measure the sample volume within 2 percent, and calibrated over the range of flow rates and conditions actually used during sampling.

3.1.8 Rate meter—Rotameter, to measure the flow range from 0 to 3 lpm (0 to 0.11 cfm).

3.1.9 Graduated cylinder—25 ml.

3.1.10 Barometer—Mercury, aneroid, or other barometers 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 weather bureau 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 decreases.

3.1.11 Vacuum gauge—At least 760 mm Hg (30 in. Hg) gauge, to be used for the sampling leak check.

3.2 Procedure.

3.2.1 Place exactly 5 ml distilled water in each impinger. Assemble the apparatus without the probe as shown in Figure 4-4. Leak check by placing a vacuum gauge at the inlet to the first impinger and drawing a vacuum of at least 250 mm Hg (10 in. Hg), plugging the outlet of the rotameter, and then turning off the pump. The vacuum shall remain constant for a least one minute. Carefully release the vacuum gauge before releasing the rotameter end.

3.2.2 Connect the probe and sample at a constant rate of 2 lpm (0.071 cfm). Continue sampling until the dry gas meter registers about 30 liters (1.1 ft³) or until visible liquid droplets are carried over from the first impinger to the second. Record temperature, pressure, and dry gas meter readings as required by Figure 4-5.

3.2.3 After collecting the sample, combine the contents of the two impingers and measure volume to the nearest 0.5 ml.

3.3 Calculations. The calculation method presented is designed to estimate the moisture in the stack gas and therefore other data, which are only necessary for accurate moisture determinations, are not collected. The following equations adequately estimate the moisture content for the purpose of determining isokinetic sampling rate settings.

3.3.1 Nomenclature.

B_{wm} = Approximate water vapor in the gas stream leaving the impinger, 0.025 proportion by volume

B_w = Water vapor in the gas stream, proportion by volume

M_w = Molecular weight of water, 18 g/g-mole (18 lb/lb-mole)

P_m = Absolute pressure (for this method, same as barometric pressure) at the dry gas meter

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

P = Ideal gas constant, 0.06236 (mm Hg)(m³)/(g-mole)(°K) for metric units and 21.83 (in. Hg)(ft³)/(lb-mole)(°R) for English units

T_m = Absolute temperature at meter, °K (°R)

T_{std} = Standard absolute temperature, 293° K (528° R)

V_f = Final volume of impinger contents, ml

V_i = Initial volume of impinger contents, ml

V_m = Dry gas volume measured by dry gas meter, dcm (def)

$V_{m(std)}$ = Dry gas volume measured by dry gas meter, corrected to standard conditions, dscm (dscf)

$V_{w(std)}$ = Volume of water vapor condensed, corrected to standard conditions, m³ (ft³)

ρ_w = Density of water, 1 g/ml (0.00220 lb/ml)

3.3.2 Volume of water vapor collected.

$$V_{wv} = \frac{(V_f - V_i) \sigma_w R T_{std}}{P_{std} M_w}$$

$$= K(V_f - V_i) \quad \text{Equation 4-5}$$

Where:

$K = 0.00134 \text{ m}^3/\text{ml}$ for metric units

$= 0.0472 \text{ ft}^3/\text{ml}$ for English units

3.3.3 Gas volume.

$$V_{m(std)} = V_m \left(\frac{P_m}{P_{std}} \right) \left(\frac{T_{std}}{T_m} \right)$$

$$= K \frac{V_m P_m}{T_m}$$

where:

$K = 0.3855 \text{ °K/mm Hg}$ for metric units

$= 17.65 \text{ °R/in. Hg}$ for English units

3.3.4 Approximate moisture content.

$$B_{wm} = \frac{V_{wv}}{V_{wv} + V_{m(std)}} + B_w = \frac{V_{wv}}{V_{wv} + V_{m(std)}} + (0.025)$$

Equation 4-7

4. Calibration.

4.1 Use methods and equipment as specified in Methods 2 and 5 and APTD-0576 to calibrate dry gas meter, barometer, and thermometers.

5. References.

5.1 Air Pollution Engineering Manual, Danielson, J. A. (ed.), U.S. DHEW, PHS, National Center for Air Pollution Control, Cincinnati, Ohio, PHS Publication No. 999-AP-40, 1967.

5.2 Devorkin, Howard, et al., Air Pollution Source Testing Manual, Air Pollution Control District, Los Angeles, Calif., November 1963.

5.3 Methods for Determination of Velocity, Volume, Dust and Mist Content of Gases, Western Precipitation Division of Joy Manufacturing Co., Los Angeles, Calif., Bulletin WP-50, 1968.

11.0 REFERENCES

1. Martin, R. W. Construction Details of Isokinetic Source Sampling Equipment. APTD-0581. Air Pollution Control Office, EPA, Research Triangle Park, N.C., 1971.
2. Rom, J. J. Maintenance, Calibration, and Operation of Isokinetic Source Sampling Equipment. APTD-0576. Office of Air Programs, EPA, Research Triangle Park, N.C., 1972.
3. Midgett, M. R. The EPA Program for the Standardization of Stationary Source Emission Test Methodology--A Review. EPA-600/4-76-044. Environmental Monitoring and Support Laboratory, EPA, Research Triangle Park, N.C., 1976.

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 M4-1.2 indicates that the form is Figure 1.2 in Section 3.3.1 of the Method 4 Handbook. Future revisions of these forms, if any, can be documented by 1.2A, 1.2B, etc. Eight of the blank forms listed below are included in this section. Four are in the Method Highlights Section, as shown by the MH following the form number.

<u>Form</u>	<u>Title</u>
1.2	Procurement Log
2.3A & B	Meter Box Calibration Data and Calculation Form (English and Metric units)
2.4A & B	Posttest Meter Calibration Data Form (English and Metric units)
2.5 (MH)	Pretest Sampling Checks
3.1 (MH)	Pretest Preparation Checklist
4.1 (MH)	On-Site Measurement Checklist
4.2	Method 4 Field and Sample Recovery Data Form
4.3	Method 4 Analytical Data Form
5.1 (MH)	Posttest Equipment Checks
6.1A & B	Moisture Content Calculation Form (English and Metric units)
6.1.C	Moisture Content Calculation Form (English and Metric units)
8.1	Method 4 Checklist To Be Used By Auditors

PROCUREMENT LOG								
Item description	Quantity	Purchase order number	Vendor	Date		Cost	Dispo- sition	Comments
				Ordered	Received			

METER BOX CALIBRATION DATA AND CALCULATION FORM

(English units)

Date _____

Meter box number _____

Barometric pressure, P_b = _____ in. Hg Calibrated by _____

Orifice manometer setting (ΔH), in. H ₂ O	Gas volume		Temperature				Time (θ), min	Y _i	$\Delta H@_i$ in. H ₂ O
	Wet test meter (V _w), ft ³	Dry gas meter (V _d), ft ³	Wet test meter (t _w), °F	Dry gas meter					
				Inlet (t _{d_i}), °F	Outlet (t _{d_o}), °F	Avg ^a (t _d), °F			
0.5	5								
1.0	5								
1.5	10								
2.0	10								
3.0	10								
4.0	10								
Avg									

ΔH , in. H_2O	$\frac{\Delta H}{13.6}$	$Y_i = \frac{V_w P_b (t_d + 460)}{V_d (P_b + \frac{\Delta H}{13.6}) (t + 460)}$	$\Delta H@_i = \frac{0.0317 \Delta H}{P_b (t_d + 460)} \left[\frac{(t_w + 460) \Theta}{V_w} \right]^2$
0.5	0.0368		
1.0	0.0737		
1.5	0.110		
2.0	0.147		
3.0	0.221		
4.0	0.294		

^a If there is only one thermometer on the dry gas meter, record the temperature under t_d .

METER BOX CALIBRATION DATA AND CALCULATION FORM (English units)

Nomenclature:

V_w = Gas volume passing through the wet test meter, ft^3 .

V_d = Gas volume passing through the dry gas meter, ft^3 .

t_w = Temperature of the gas in the wet test meter, $^{\circ}\text{F}$.

t_{d_i} = Temperature of the inlet gas of the dry gas meter, $^{\circ}\text{F}$.

t_{d_o} = Temperature of the outlet gas of the dry gas meter, $^{\circ}\text{F}$.

t_d = Average temperature of the gas in the dry gas meter, obtained by the average t_{d_i} and t_{d_o} , $^{\circ}\text{F}$.

ΔH = Pressure differential across orifice, in. H_2O .

Y_i = Ratio of accuracy of wet test meter to dry gas meter for each run; tolerance $Y_i = Y \pm 0.02Y$.

Y = Average ratio of accuracy of wet test meter to dry gas meter for all six runs; tolerance $Y = Y \pm 0.01Y$.

$\Delta H@_i$ = Orifice pressure differential at each flow rate that gives $0.75 \text{ ft}^3/\text{min}$ of air at standard conditions for each calibration run, in. H_2O ; tolerance = $\Delta H@ \pm 0.15$ (recommended).

$\Delta H@$ = Average orifice pressure differential that gives $0.75 \text{ ft}^3/\text{min}$ of air at standard conditions for all six runs, in. H_2O ; tolerance = 1.84 ± 0.25 (recommended).

θ = Time for each calibration run, min.

P_b = Barometric pressure, in. Hg.

METER BOX CALIBRATION DATA AND CALCULATION FORM

(Metric units)

Date _____

Meter box number _____

Barometric pressure, P_b = _____ mm Hg Calibrated by _____

Orifice manometer setting (ΔH), mm H ₂ O	Gas volume		Temperature			Time (θ), min	Y _i	$\Delta H@_i$, mm H ₂ O
	Wet test meter (V _w), m ³	Dry gas meter (V _d), m ³	Wet test meter (t _w), °C	Dry gas meter				
				Inlet (t _{d_i}), °C	Outlet (t _{d_o}), °C			
10	0.15							
25	0.15							
40	0.30							
50	0.30							
75	0.30							
100	0.30							
						Avg		

ΔH , mm H_2O	$\frac{\Delta H}{13.6}$	$Y_i = \frac{V_w P_b (t_d + 273)}{V_d (P_d + \frac{\Delta H}{13.6}) (t_w + 273)}$	$\Delta H@_i = \frac{0.00117 \Delta H}{P_b (t_d + 273)} \left[\frac{(t_w + 273) \Theta}{V_w} \right]^2$
10	0.7		
25	1.8		
40	2.94		
50	3.68		
75	5.51		
100	7.35		

^a If there is only one thermometer on the dry gas meter, record the temperature under t_d .

METER BOX CALIBRATION DATA AND CALCULATION FORM (metric units)

Nomenclature:

V_w = Gas volume passing through the wet test meter, m^3 .

V_d = Gas volume passing through the dry gas meter, m^3 .

t_w = Temperature of the gas in the wet test meter, $^{\circ}C$.

t_{d_i} = Temperature of the inlet gas of the dry gas meter, $^{\circ}C$.

t_{d_o} = Temperature of the outlet gas of the dry gas meter, $^{\circ}C$.

t_d = Average temperature of the gas in the dry gas meter, obtained by the average of t_{d_i} and t_{d_o} , $^{\circ}C$.

ΔH = Pressure differential across orifice, mm H_2O .

Y_i = Ratio of accuracy of wet test meter to dry gas meter for each run; tolerance $Y_i = Y \pm 0.02Y$.

Y = Average ratio of accuracy of wet test meter to dry gas meter for all six runs; tolerance $Y = Y \pm 0.01Y$.

$\Delta H@_i$ = Orifice pressure differential at each flow rate that gives $0.021 m^3$ of air at standard conditions for each calibration run, mm H_2O ; tolerance $\Delta H@_i = \Delta H@ \pm 3.8$ mm H_2O (recommended).

$\Delta H@$ = Average orifice pressure differential that gives $0.021 m^3$ of air at standard conditions for all six runs, mm H_2O ; tolerance $\Delta H@ = 46.74 \pm 6.3$ mm H_2O (recommended).

θ = Time of each calibration run, min.

P_b = Barometric pressure, mm Hg.

POSTTEST DRY GAS METER CALIBRATION DATA FORM (English units)

Test number _____ Date _____ Meter box number _____ Plant _____

Barometric pressure, P_b = _____ in. Hg Dry gas meter number _____ Pretest Y _____

Orifice manometer setting, (ΔH), in. H ₂ O	Gas volume		Temperature				Time (θ), min	Vacuum setting, in. Hg	Y _i	$\frac{V_w P_b (t_d + 460)}{V_d \left(P_b + \frac{\Delta H}{13.6} \right) (t_w + 460)}$
	Wet test meter (V _w), ft ³	Dry gas meter (V _d), ft ³	Wet test meter (t _w), °F	Dry gas meter						
				Inlet (t _{d_i}), °F	Outlet (t _{d_o}), °F	Average _a (t _d), °F				
	10									
	10									
	10									
										Y =

^a If there is only one thermometer on the dry gas meter, record the temperature under t_d

where

V_w = Gas volume passing through the wet test meter, ft^3 .

V_d = Gas volume passing through the dry gas meter, ft^3 .

t_w = Temperature of the gas in the wet test meter, $^{\circ}F$.

t_{d_i} = Temperature of the inlet gas of the dry gas meter, $^{\circ}F$.

t_{d_o} = Temperature of the outlet gas of the dry gas meter, $^{\circ}F$.

t_d = Average temperature of the gas in the dry gas meter, obtained by the average of t_{d_i} and t_{d_o} , $^{\circ}F$.

ΔH = Pressure differential across orifice, in. H_2O .

Y_i = Ratio of accuracy of wet test meter to dry gas meter for each run.

Y = Average ratio of accuracy of wet test meter to dry gas meter for all three runs;
tolerance = pretest Y $\pm 0.05Y$.

P_b = Barometric pressure, in. Hg.

θ = Time of calibration run, min.

POSTTEST METER CALIBRATION DATA FORM (Metric units)

Test number _____ Date _____ Meter box number _____ Plant _____

Barometric pressure, P_b = _____ mm Hg Dry gas meter number _____ Pretest Y _____

Orifice manometer setting, (ΔH), mm H ₂ O	Gas volume		Temperature				Time (Θ), min	Vacuum setting, mm Hg	Y_i	$\frac{V_w P_b (t_d + 273)}{V_d \left(P_b + \frac{\Delta H}{13.6} \right) (t_w + 273)}$
	Wet test meter (V_w), m ³	Dry gas meter (V_d), m ³	Wet test meter (t_w), °C	Dry gas meter						
				Inlet (t_{d_i}), °C	Outlet (t_{d_o}), °C	Average ^a (t_d), °C				
	10									
	10									
	10									
										Y =

^a If there is only one thermometer on the dry gas meter, record the temperature under t_d

where

V_w = Gas volume passing through the wet test meter, m³.

V_d = Gas volume passing through the dry gas meter, m³.

t_w = Temperature of the gas in the wet test meter, °C.

t_{d_i} = Temperature of the inlet gas of the dry gas meter, °C.

t_{d_o} = Temperature of the outlet gas of the dry gas meter, °C.

t_d = Average temperature of the gas in the dry gas meter, obtained by the average of t_{d_i} and t_{d_o} , °C.

ΔH = Pressure differential across orifice, mm H₂O.

Y_i = Ratio of accuracy of wet test meter to dry gas meter for each run.

Y = Average ratio of accuracy of wet test meter to dry gas meter for all three runs;
tolerance = pretest Y \pm 0.05Y.

P_b = Barometric pressure, mm Hg.

θ = Time of calibration run, min.

METHOD 4 FIELD AND SAMPLE RECOVERY DATA FORM

Plant _____	Probe material _____
Location _____	Sample box number _____
Operator _____	Meter box number _____
Date _____	Meter ΔH @ _____
Run number _____	Meter cal. (Y) _____
Ambient temperature _____	Final leak rate _____
Barometric pressure _____	Vacuum during leak check _____
Probe length m(ft) _____	Thermometer number _____
	Static pressure _____

	Impinger volume, ml	Silica gel weight, g
Final		
Initial		

[illegible]

Total

Average

* Acceptable $\Delta V_m = 0.9 < \frac{V_{\text{final}} - V_{\text{initial}}}{\text{number of points}} < 1.1$ _____ to _____.

METHOD 4 ANALYTICAL DATA FORM

Plant _____

Date _____

Run number _____

	Volume of liquid water collected		
	Impinger volume, ml	Silica gel weight, g	
Final			
Initial			
Liquid collected			
Total volume collected		g*	ml

* Convert weight of water to volume by dividing total weight increase by density of water (1 g/ml):

$$\frac{\text{Increase, g}}{1 \text{ g/ml}} = \text{water volume, ml.}$$

MOISTURE CONTENT CALCULATION FORM
(English units)

VOLUME OF WATER VAPOR CONDENSED IN IMPINGERS

$$V_f = \text{---} \cdot \text{ml}, V_i = \text{---} \cdot \text{ml}$$

$$V_{wc(std)} = 0.04707 (V_f - V_i) = \text{---} \cdot \text{---} \text{ ft}^3 \quad \text{Equation 6-1}$$

VOLUME OF WATER VAPOR COLLECTED IN SILICA GEL

$$W_f = \text{---} \cdot \text{g}, W_i = \text{---} \cdot \text{g}$$

$$V_{wsg(std)} = 0.04715 (W_f - W_i) = \text{---} \cdot \text{---} \text{ ft}^3 \quad \text{Equation 6-2}$$

SAMPLE VOLUME

$$V_m = \text{---} \cdot \text{---} \text{ ft}^3, T_m = \text{---} \cdot \text{---} ^\circ\text{R}, P_m = \text{---} \cdot \text{---} \text{ in. Hg}$$

$$Y = \text{---} \cdot \text{---}$$

$$V_{m(std)} = 17.64 \frac{V_m Y P_m}{T_m} = \text{---} \cdot \text{---} \text{ ft}^3 \quad \text{Equation 6-3}$$

MOISTURE CONTENT

$$V_{wc(std)} = \text{---} \cdot \text{---} \text{ ft}^3, V_{wsg(std)} = \text{---} \cdot \text{---} \text{ ft}^3,$$

$$V_{m(std)} = \text{---} \cdot \text{---} \text{ ft}^3$$

$$B_{ws} = \frac{V_{wc(std)} + V_{wsg(std)}}{V_{wc(std)} + V_{wsg(std)} + V_{m(std)}} = \text{---} \cdot \text{---} \quad \text{Equation 6-4}$$

MOISTURE CONTENT CALCULATION FORM
(Metric units)

VOLUME OF WATER VAPOR CONDENSED IN IMPINGERS

$$V_f = \text{---} \cdot \text{ml}, V_i = \text{---} \cdot \text{ml}$$

$$V_{wc(std)} = 0.001333 (V_f - V_i) = \text{---} \cdot \text{---} \text{ m}^3 \quad \text{Equation 6-1}$$

VOLUME OF WATER VAPOR COLLECTED IN SILICA GEL

$$W_f = \text{---} \cdot \text{g}, W_i = \text{---} \cdot \text{g}$$

$$V_{wsg(std)} = 0.001335 (W_f - W_i) = \text{---} \cdot \text{---} \text{ m}^3 \quad \text{Equation 6-2}$$

SAMPLE VOLUME

$$V_m = \text{---} \cdot \text{---} \text{ m}^3, T_m = \text{---} \cdot \text{---} ^\circ\text{K}, P_m = \text{---} \cdot \text{---} \text{ mm Hg}$$

$$Y = \text{---} \cdot \text{---} ,$$

$$V_{m(std)} = 0.3858 \frac{V_m Y P_m}{T_m} = \text{---} \cdot \text{---} \text{ m}^3 \quad \text{Equation 6-3}$$

MOISTURE CONTENT

$$V_{wc(std)} = \text{---} \cdot \text{---} \text{ m}^3, V_{wsg(std)} = \text{---} \cdot \text{---} \text{ m}^3,$$

$$V_{m(std)} = \text{---} \cdot \text{---} \text{ m}^3$$

$$B_{ws} = \frac{V_{wc(std)} + V_{wsg(std)}}{V_{wc(std)} + V_{wsg(std)} + V_{m(std)}} = \text{---} \cdot \text{---} \quad \text{Equation 6-4}$$

MOISTURE CONTENT CALCULATION FORM
(English and metric units)

MOISTURE CONTENT

t_s avg = _ _ _ . _ °F, _ _ . _ _ °C

P_{bar} = _ _ . _ _ in. Hg, _ _ _ . _ mm Hg

P_{static} = _ _ . _ _ in. H_2O , _ _ . _ _ mm H_2O

S.V.P. = _ . _ _ in. Hg, _ _ . _ mm Hg

$$B_{ws} = \frac{S.V.P}{P_{\text{bar}} + \frac{P_{\text{static}}}{13.6}} = 0 . _ _ _$$

METHOD 4 CHECKLIST TO BE USED BY AUDITORS

Yes	No	Operation
		<u>Presampling preparation</u>
_____	_____	1. Knowledge of process conditions
_____	_____	2. Calibration of pertinent equipment prior to each field test; in particular, the dry gas meter should be checked before each test
		<u>On-site measurements</u>
_____	_____	3. Leak testing of sample train after sample run
_____	_____	4. Addition of water and silica gel to impingers, and correct location of impingers
_____	_____	5. Constant sampling rate and not exceeding specified rate
_____	_____	6. Measurement of condensed water to within specified limits
_____	_____	7. Record of pertinent process condition during sample collection
_____	_____	8. Probe maintained at given temperature
		<u>Postsampling</u>
_____	_____	9. Calculation procedure/check
_____	_____	10. Calibration checks
COMMENTS		

Section 3.4

METHOD 5--DETERMINATION OF PARTICULATE EMISSIONS
FROM STATIONARY SOURCES

OUTLINE

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SUMMARY

This method, when used in conjunction with Methods 1, 2, 3, and 4, is applicable for the determination of particulate emissions from stationary sources.

A gas sample is extracted isokinetically from the stack. Particulate matter is collected on an out-of-stack, glass fiber filter, maintained at $120^{\circ} \pm 14^{\circ}\text{C}$ ($248^{\circ} \pm 25^{\circ}\text{F}$) or at a temperature specified by an applicable subpart of the standards or approved by the administrator. The mass of particulate matter, which includes any material that condenses at or above the specified filter temperature, is measured gravimetrically after removal of uncombined water.

The Method Description which follows is based on the Reference Method that was promulgated on August 18, 1977. Results of an initial collaborative test program indicated the need for more specific quality controls and a better defined Reference Method, which resulted in the expansion and revisions incorporated in the August 18, 1977 promulgation. As a result, competence of the tester becomes the primary factor affecting the precision of Method 5. Results of the most recent collaborative test program, conducted with competent test teams, showed a within-laboratory deviation (standard deviation percent of mean value) of 10.4% and a between laboratory deviation of 12.1%.²

The main documents used in preparing the description and in detailing calibration and maintenance procedures are references 1, 3, and 4 (Section 3.4.11). Data forms are provided in Section 3.4.12 for the convenience of the Handbook users.

METHOD HIGHLIGHTS

EPA Method 5, collectively with EPA Methods 1, 2, 3, and 4 comprise the most widely used system for evaluating emissions from stationary sources. Consequently, many of the special problems and procedures common to several related methods are discussed in depth in this section of the Handbook. As opposed to some methods, the most significant errors associated with this test method occur during the sample collection and recovery phase instead of in the analysis phase. Therefore, this method requires competent personnel adhering to the procedures. Competence can be determined, most accurately, through observation and evaluation by a qualified observer on site.

The blank data forms at the end of this section may be removed from the Handbook and used in the pretest, test, and posttest operations. Each form has a subtitle (e.g., Method 5, Figure 3.1) to assist the user in finding a similar filled-in form in the method description (e.g., in Section 3.4.3). On the blank and filled-in forms, the items/parameters that can cause the most significant errors are designated with an asterisk.

1. Procurement of Equipment

Section 3.4.1 (Procurement of Apparatus and Supplies) gives the specifications, criteria and design features for equipment and materials required for performing Method 5 tests. Special design criteria have been established for the pitot tube, probe, nozzle, and temperature sensor assembly.

These criteria specify the necessary spacing requirements for the various components of the assembly to prevent aerodynamic interferences that could cause large errors in velocity pressure measurement. Seamless, corrosion resistant metal probe liners have also been made optional, subject to the approval of the administrator.

Section 3.4.1 is designed as a guide for the procurement and initial check of equipment and supplies. The activity matrix (Table 1.1) at the end of Section 3.4.1 can be used as a quick reference; it follows the same order as the written description in the main text.

2. Pretest Preparation

Section 3.4.2 (Calibration of Apparatus) provides a step-by-step description of the required calibration procedures for components of the Method 5 sampling train. Data forms have been developed to record the data and to provide a calibration record. Careful attention should be given to the steps in each procedure, since most procedures have not been previously written and referenced in the Federal Register. The calibration section can be removed and compiled, along with calibration sections from all other methods, into a separate quality assurance Reference Manual for use by calibration personnel. A pretest checklist (Figure 3.1) or a similar form should be used to summarize calibration data.

Section 3.4.3 (Presampling Operations) provides the tester with a guide for supplies and equipment preparation for field tests. The pretest preparation form (Figure 3.2) can be used as an equipment checkout and packing list. (Due to the length of this figure, the blank data forms are in Section 3.4.12.) This form was designed to provide the user with a single form that can include any combination of Methods 1 through 8 for the same field trip. The method for packing and the description of packing containers should help protect the equipment, but are not required. Filter holders and impingers may be loaded and charged in the base laboratory. If this is done, seal the inlet and outlet of the filter holder, the impingers containing water, and the impinger containing silica gel.

3. On-site Measurements

Section 3.4.4 (On-site Measurements) contains a step-by-step procedure for performing sampling and sample recovery. Several

on-site measurement requirements have been added which will significantly improve the accuracy and precision of the method. These added requirements include:

1. Make a corresponding change in the sampling rate when velocity pressure at each sampling point changes by >20%,
2. Leak check the sampling train at the conclusion of the sampling run and prior to each component change during a sample run,
3. Leak check the pitot tube at the conclusion of the sampling run, and
4. Have one traverse diameter in a plane containing the greatest expected concentration variation.

The on-site measurement checklist (Figure 4.5) is provided to assist the tester with a quick method of checking requirements.

4. Posttest Operations

Section 3.4.5 (Postsampling Operations) gives the posttest equipment check procedures and a step-by-step analytical procedure. Figure 5.1, or a similar form, should be used to summarize the posttest calibration checks and should be included in the emission test report.

The posttest operation forms (Figures 5.5 and 5.6) will provide laboratory personnel with a summary of analytical procedures used to determine the sample rinse and filter weights. This analytical procedure description can be removed from the main text and compiled, along with analytical procedures for other methods, into a separate quality assurance analytical reference manual for laboratory personnel. The use of blank filters as control samples is required to provide an independent check on the state of control of the samples. Procedures are also given for data corrections when equipment calibration factors change.

Section 3.4.6 (Calculations) provides the tester with the required equations, nomenclature, and suggested number of significant digits. It is suggested that a programmable calculator be used, if available, to reduce the chances of calculation error.

Section 3.4.7 (Maintenance) supplies the tester with a guide for a routine maintenance program. The program is not a requirement, but is suggested for the reduction of equipment malfunctions.

5. Auditing Procedures

Section 3.4.8 (Auditing Procedures) contains a description of necessary activities for conducting performance and system audits. The performance audit is a check on calculation errors, and therefore is not needed for the analytical phase since it consists of only a gravimetric determination. Together, a performance audit of data processing and a systems audit of on-site measurements should provide the independent assessment of data quality needed to allow the collaborative test results to be used in the final data evaluation.

Section 3.4.9 (Recommended Standards for Establishing Traceability) recommends the primary standards to which the sample collection and analysis should be traceable.

6. References

Sections 3.4.10 and 3.4.11 (References) provides the reader with the Reference Method and an extensive list of all the references used in the compilation of this section of the Handbook along with numerous additional sources.

PRETEST SAMPLING CHECKS
(Method 5, Figure 3.1)

Date _____ Calibrated by _____
Meter box number _____ $\Delta H@$ _____

Dry Gas Meter*

Pretest calibration factor, Y _____ (within $\pm 2\%$ of the
average factor for each calibration run)

Impinger Thermometer

Was a pretest temperature correction used? _____ yes _____ no
If yes, temperature correction _____ (within $\pm 3^\circ\text{C}$ (5.4°F)
over range)

Dry Gas Meter Thermometers

Was a pretest temperature correction made? _____ yes _____ no
If yes, temperature correction _____ (within $\pm 3^\circ\text{C}$ (5.4°F) over
range)

Stack Temperature Sensor*

Was a stack temperature sensor calibrated against a reference
thermometer? _____ yes _____ no
If yes, give temperature range with which the readings agreed
within $\pm 1.5\%$ of the reference values _____ to _____ K ($^\circ\text{R}$)

Barometer

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

Nozzle*

Was the nozzle calibrated to the nearest 0.025 mm (0.001 in.)?
_____ yes _____ no

*Most significant items/parameters to be checked.

ON-SITE MEASUREMENTS CHECKLIST
(Method 5, Figure 4.5)

Sampling Train Schematic Drawing

Apparatus

Probe nozzle: stainless steel _____ glass _____
Button-hook _____ elbow _____ size _____
Clean? _____
Probe liner: borosilicate _____ quartz _____ other _____
Clean? _____
Heating system* _____
Checked? _____
Pitot tube: Type S _____ other _____
Properly attached to probe?* _____
Modifications _____
Pitot tube coefficient _____
Differential pressure gauge: two inclined manometers _____
other _____ sensitivity _____
Filter holder: borosilicate glass _____ glass frit _____
filter support _____ silicone gasket _____ other _____
Clean? _____
Condenser: number of impingers _____
Clean? _____
Contents: 1st _____ 2nd _____ 3rd _____ 4th _____
Cooling system _____
Proper connections? _____
Modifications _____
Barometer: mercury _____ aneroid _____ other _____
Gas density determination: temperature sensor type _____
pressure gauge _____
temperature sensor properly attached to probe?* _____

Procedure

Recent calibration: pitot tubes* _____
meter box* _____ thermometers/thermocouples* _____
Filters checked visually for irregularities?* _____
Filters properly labeled?* _____
Sampling site properly selected? _____
Nozzle size properly selected?* _____

(continued)

(continued)

Selection of sampling time? _____
All openings to sampling train plugged to prevent pretest contamination? _____
Impingers properly assembled? _____
Filter properly centered? _____
Pitot tube lines checked for plugging or leaks?* _____
Meter box leveled? _____ Periodically? _____
Manometers zeroed? _____
 $\Delta H@$ from most recent calibration _____
Nomograph set up properly? _____
Care taken to avoid scraping nipple or stack wall?* _____
Effective seal around probe when in-stack? _____
Probe moved at proper time? _____
Nozzle and pitot tube parallel to stack wall at all times?* _____
Filter changed during run? _____
Any particulate lost? _____
Data forms complete and data properly recorded?* _____
Nomograph setting changed when stack temp changed significantly? _____
Velocity pressure and orifice pressure readings recorded accurately?* _____
Posttest leak check performed?* _____ (mandatory)
Leakage rate _____ @ in. Hg _____
Orsat analysis _____ from stack _____ integrated _____
Fyrite combustion analysis _____ sample location _____
Bag system leakchecked?* _____
If data forms cannot be copied, record:
approximate stack temp _____ volume metered _____
% isokinetic calculated at end of each run _____

SAMPLE RECOVERY

Brushes: nylon bristle _____ other _____
Clean? _____
Wash bottles: glass _____
Clean? _____
Storage containers: borosilicate glass _____ other _____
Clean? _____ Leakfree? _____
Petri dishes: glass _____ polyethylene _____ other _____
Clean? _____
Graduated cylinder/or balance: subdivisions ≤ 2 ml?* _____
other _____
Balance: type _____
Plastic storage containers: airtight? _____
Clean? _____
Probe allowed to cool sufficiently? _____
Cap placed over nozzle tip to prevent loss of particulate?* _____

(continued)

(continued)

During sampling train disassembly, are all openings capped? _____
Clean-up area description: _____
Clean? _____ Protected from wind? _____
Filters: glass fiber _____ type _____
Silica gel: type (6 to 16 mesh)? new? _____ used? _____
Color? _____ Condition? _____
Filter handling: tweezers used? _____
surgical gloves? _____ other _____
Any particulate spilled? * _____
Water distilled? _____
Stopcock grease: acetone-insoluble? _____
heat-stable silicone? _____ other _____
Probe handling: acetone rinse _____
distilled water rinse _____
Particulate recovery from: probe nozzle _____
probe fitting _____ probe liner _____
front half of filter holder _____
Blank: acetone _____ distilled water _____
Any visible particles on filter holder inside probe? * _____
All jars adequately labeled? _____ Sealed tightly? _____
Liquid level marked on jars? * _____
Locked up? _____
Acetone reagent: <0.001% residue? _____
glass bottles _____ (required)
acetone blanks? _____

*Most significant items/parameters to be checked.

POSTTEST CALIBRATION CHECKS
(Method 5, Figure 5.1)

Plant _____ Calibrated by _____

Meter box number _____ Date _____

Dry Gas Meter

Pretest calibration factor, Y _____ (within $\pm 2\%$)

Posttest check, Y* _____ (within $\pm 5\%$ of pretest)

Recalibration required? _____ yes _____ no

If yes, recalibration factor, Y _____ (within $\pm 2\%$)

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

Dry Gas Meter Thermometers

Was a pretest temperature correction used? _____ yes _____ no
If yes, temperature correction _____ ($\pm 3^\circ\text{C}$ (5.4°F) over range)

Posttest comparison with mercury-in-glass thermometer?* (within $\pm 6^\circ\text{C}$ (10.8°F) at ambient temperature)

Recalibration required? _____ yes _____ no

Recalibration temperature correction? _____ ($\pm 3^\circ\text{C}$ (5.4°F) over range)*

If yes, no correction necessary for calculations if meter thermometer temperature is higher; if calibration temperature is higher, add correction to average meter temperature for calculations

Stack Temperature Sensor

Was a pretest temperature correction used? _____ yes _____ no
If yes, temperature correction _____ $^\circ\text{C}$ ($^\circ\text{F}$) (within $\pm 1.5\%$ of readings in K ($^\circ\text{R}$) over range)

Average stack temperature of compliance test, T_s _____ K ($^\circ\text{R}$)

Temperature of reference thermometer or solution for recalibration _____ K ($^\circ\text{R}$)* (within $\pm 10\%$ of T_s)

Temperature of stack thermometer for recalibration _____ K ($^\circ\text{R}$)

Difference between reference and stack thermometer temperatures, ΔT_s _____ K ($^\circ\text{R}$)

Do values agree within $\pm 1.5\%$?* _____ yes _____ no

If yes, no correction necessary for calculations

If no, calculations must be done twice--once with the recorded values and once with the average stack temperature corrected to correspond to the reference temperature differential (ΔT_s); both final result values must be reported since there is no way to determine which is correct

(continued)

(continued)

Barometer

Was the pretest field barometer reading correct? ____ yes ____ no

Posttest comparison?* _____ mm (in.) Hg (± 2.5 mm (0.1 in.) Hg)

Was calibration required? _____ yes _____ no

If yes, no correction necessary for calculations when the field barometer has a lower reading; if the mercury-in-glass reading is lower, subtract the difference from the field data readings for the calculation

*Most significant items/parameters to be checked.

PROCEDURE FOR WEIGHING FILTERS
BEFORE AND AFTER SAMPLING
(Method 5, Figure 5.5)

Status

- _____ 1. Label the filter and/or the petri dish--both with the same label number; label the filter on top and bottom; check each filter visually against the light for irregularities, flaws, and pinhole leaks
- _____ 2. Check the desiccator; be sure the lid is sealed tightly and the anhydrous calcium sulfate is dry; if not dry, heat the desiccant in the oven for 2 h at 180°-200°C (350° - 400°F), and let cool in the balance room before putting it back into the desiccator
- _____ 3. Take off the lid of the filter container and desiccate the filter for 24 h; during desiccation, be sure that filters are widely spread, and not overlapping
- _____ 4. Adjust the analytical balance to zero, and check the accuracy with a 0.500-g Class-S weights (within ± 0.5 mg); use tweezers to carefully place the filter on the pan of the balance, and weigh it to the nearest 0.1 mg. The time of weighing should not be > 2 min, and the relative humidity should be $< 50\%$

Very important: Desiccator should be tightly covered immediately after removing the filter to be weighed; never leave the desiccator open while weighing a sample because samples in the desiccator will be exposed to moisture in the room, which will cause gains in their weights
- _____ 5. Put the filter back into the petri dish without the lid, desiccate for ≥ 6 h and reweigh the filter; the two recorded weights should agree to ± 0.5 mg; if not, desiccate for another 6 h and reweigh until weight is constant within ± 0.5 mg; keep the tare weight of the filter in file for future use
- _____ 6. Be sure the filters that arrived from the field are handled and analyzed whenever possible by the same person who started the project--the person who tared the filters before sampling; use the same balance

(continued)

(continued)

- _____ 7. Perform step #2, and then uncover the filter container and visually examine the filter to see if it is torn; write down all observations that you think will help justify the final data
- _____ 8. Desiccate the filter for 24 h, and weigh it to the nearest 0.1 mg; record the weight then desiccate again for 6 h, and reweigh; the difference between the two recorded weights should be within ± 0.5 mg; the balance should be zeroed and checked with a 0.500-g Class-S weight, and the relative humidity must be $< 50\%$
- _____ 9. Continue the processes of desiccating and weighing until consistent data are obtained; however, after the third trial, if no satisfactory data are obtained, confer with the supervisor

Notes

- 1. When weighing the filter and sample, be sure to use a clean brush and to add all particulates or pieces of the filter that might be left in the container
- 2. Be sure to use tweezers to handle the filters; never hold them directly with your hand
- 3. Write down the date and time each time a filter is weighed

PROCEDURE FOR ANALYSIS OF ACETONE RINSE SAMPLES
(Method 5, Figure 5.6)

Status

I. Preparing Containers for Shipment

- _____ 1. Select the appropriate size and number of bottles to be shipped to the field; include extra bottles
- _____ 2. Clean the bottles and caps thoroughly with soap detergent, rinse with tap water, and then rinse at least twice with deionized distilled water
- _____ 3. Rinse the clean bottles with acetone to get rid of most of the water; remember that one batch of acetone could be used for more than one container
- _____ 4. Check the containers and the caps individually after they are dry to be sure no detergent or other contaminant is present; tightly cap all containers

II. Handling and Analysis of Acetone Rinse Samples

Important: Blanks and samples should have identical analytical treatments; never handle with bare hands any analysis glassware once tared; always use tongs or disposable gloves

- _____ 1. Log the samples received from the field, and check each container for leakage; if the sample volume level is marked on the container, check to see if the sample still matches the level, if not, write a note of that
- _____ 2. Use a dry, clean glass funnel to transfer the acetone rinse into the dry, clean 250-ml graduated cylinder
- _____ 3. Record the volume of the sample to the nearest 1.0 ml, and transfer it into a dry, clean, tared (to the nearest 0.1 mg) 250- or 300-ml beaker, depending on the volume of the sample; add 50 ml to the recorded sample volume to account for the acetone rinse of all containers

(continued)

(continued)

Status

- _____ 4. Rinse the container with two 25-ml portions of acetone (reagent grade); cap the container, and shake very gently; transfer the acetone rinse into the graduated cylinder to rinse it, and then pour the rinse through the funnel into the beaker that contains the sample; thus, the container, the graduated cylinder, and the funnel have been rinsed
- _____ 5. Repeat steps 3 and 4 for each sample
- _____ 6. Let the samples and blanks dry at room temperature in a dust-free environment or under a watchglass
- _____ 7. Weigh a clean, empty dry beaker, and place it in the same atmosphere where the samples are drying to find out if there was any particulate collected on the samples from the surroundings while drying (not mandatory)
- _____ 8. Transfer the totally evaporated samples and blanks along with the empty beaker into a tightly sealed desiccator that contains dry anhydrous calcium sulfate (CaSO_4)
- _____ 9. Desiccate for 24 h
- _____ 10. Zero the balances and check the accuracy with a 100-g Class-S standard weight prior to weighing; the reading should be 100 g \pm 0.5 mg, and the relative humidity in the balance room should be \leq 50%
- _____ 11. Weigh the samples, blanks, and empty beaker to the nearest 0.1 mg

It is very important to:

- a. Keep the desiccator tightly closed while weighing
- b. Remove the samples to be weighed from the desiccator one at a time, weigh each, and put each immediately back into the desiccator
- c. Keep the weighing time \leq 2 min

(continued)

(continued)

Status

- d. Be sure that both sides of the balance are closed when weighing
- e. Turn all balance knobs to zero after the weighings
- _____ 12. Record the weights of the samples, blanks, and empty beaker; record the date and time, each time a sample is weighed
- _____ 13. Desiccate the samples, blanks, and empty beaker for >6 h; data on the first and second weighings should agree within ± 0.5 mg; if not, desiccate again for 6 h and reweigh until consistent data are obtained; after the third trial, consult the supervisor
- _____ 14. If there is >2 mg change in the weight of the empty beaker, note it on the analytical data form
- _____ 15. Calculate the data recorded on the data forms (Figures 5.3 and 5.4) provided for this analysis

1.0 PROCUREMENT OF APPARATUS AND SUPPLIES

A schematic of the sampling train used in Method 5 is shown in Figure 1.1. Commercial models of this train are available. For those who want to build their own, construction details are in APTD-0581³; allowable modifications are described in the following sections.

The operating, maintenance, and calibrating procedures for the sampling train are in APTD-0576⁴. Since correct usage is important in obtaining valid results, all users are advised to read this document and adopt its procedures unless alternatives are outlined herein.

In this section, applicable specifications, criteria, and/or design features are given to aid in the selection of equipment which assures good quality data collection. Procedures and limits (where applicable) for acceptance checks are given.

During the procurement of equipment and supplies, it is suggested that a procurement log (Figure 1.2) 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, and a blank copy of the log is in Section 3.4.12 for the convenience of the handbook user. If calibration is required as part of the acceptance check, the data are to be recorded in a calibration log. Table 1.1 at the end of this section is a summary of the quality assurance activities for the procurement and acceptance of apparatus and supplies.

1.1 Sampling Apparatus

1.1.1 Probe Liner - The sampling probe should be constructed of borosilicate (Pyrex) or quartz glass tubing with an outside diameter (OD) of about 16 mm (0.625 in.), encased in a stainless steel sheath with an OD of 25.4 mm (1.0 in.). Whenever practical, every effort should be made to use the borosilicate or quartz glass liners; alternatively, metal seamless liners of 316

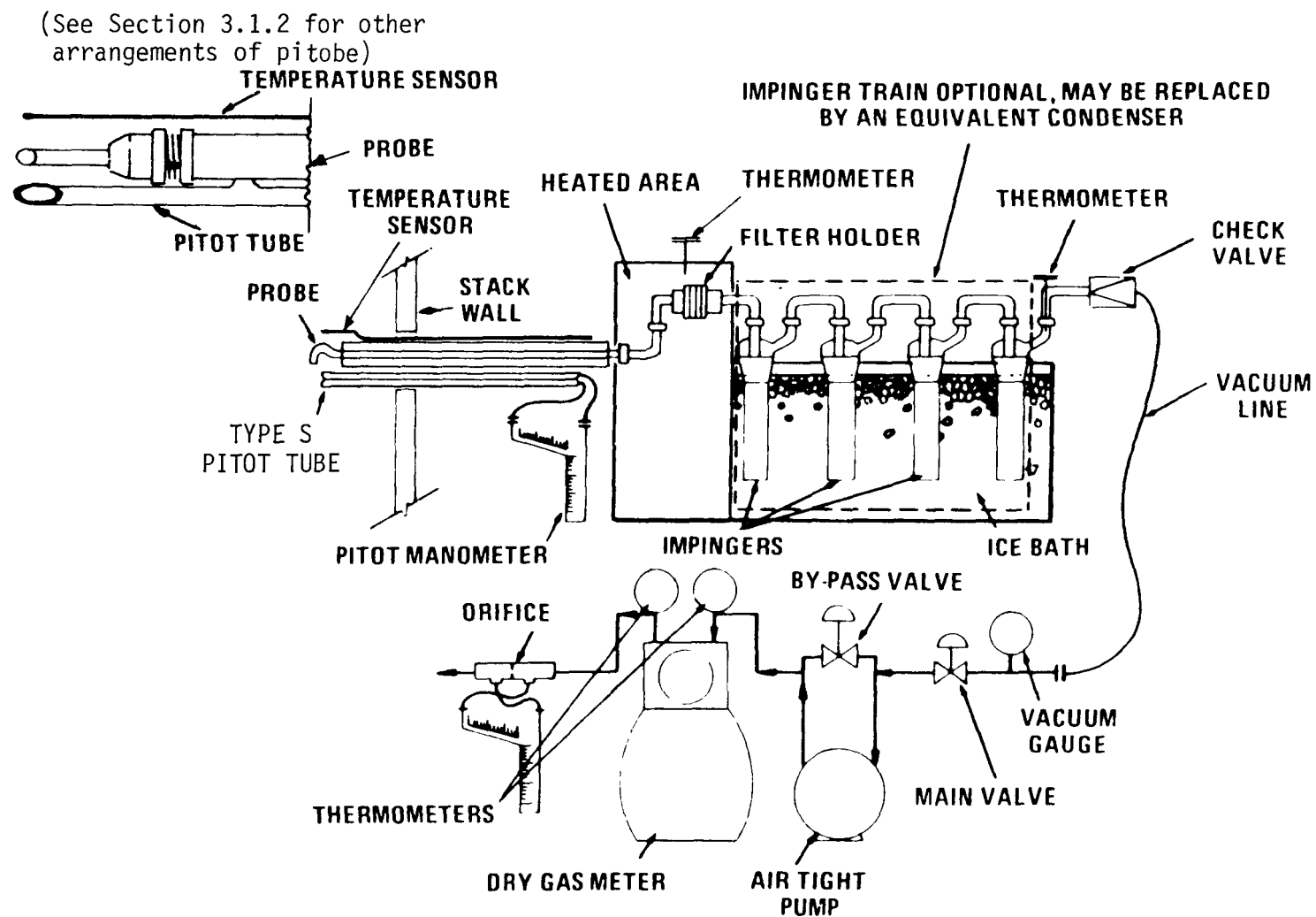


Figure 1.1 Schematic of Method 5 sampling train.

Item description	Quantity	Purchase order number	Vendor	Date		Cost	Disposition	Comments
				Ordered	Received			
Meter Console	1	26549	West Co.	7/14/79	8/29/79	24.50	In service	

Figure 1.2 Example of a procurement log.

stainless steel, Incoloy 825, or other corrosion resistant metals may be used if approved by the administrator.

A heating system is required which will maintain an exit gas temperature of $120^{\circ} \pm 14^{\circ}\text{C}$ ($248^{\circ} \pm 25^{\circ}\text{F}$) during sampling. Other temperatures may be specified by a subpart of the regulations and must be approved by the administrator for a particular application. Since the actual probe outlet temperature is not usually monitored during sampling, probes constructed in accordance to APTD-0581³ and utilizing the calibration procedures in APTD-0576⁴ will be acceptable.

Either borosilicate or quartz glass liners may be used for stack temperatures up to about 480°C (900°F), but quartz glass liners must be used from 480° to 900°C (900° to 1650°F). Either type of liner may be used at higher temperatures for short times periods, with administrator approval. However, the absolute upper limits--the softening temperatures of 820°C (1508°F) and 1500°C (2732°F)--for borosilicate and quartz respectively must be observed.

Upon receiving a new probe, the user should visually check it for specifications: that is, is it the length and composition ordered? The probe should be visually checked for breaks or cracks, and it should be checked for leaks on a sampling train (Figure 1.1). This includes a proper nozzle to probe connection with a Viton-O-ring Teflon ferrales or asbestos string. The probe heating system should be checked as follows:

1. Connect the probe with a nozzle attached to the inlet of the pump.
2. Electrically connect and turn on the probe heater for 2 or 3 min. The probe should become warm to the touch.
3. Start the pump and adjust the needle valve until a flow rate of about $0.02 \text{ m}^3/\text{min}$ ($0.75 \text{ ft}^3/\text{min}$) is achieved.
4. Be sure the probe remains warm to the touch and the heater is capable of maintaining the exit air temperature at a minimum of 100°C (212°F). If it cannot, the probe should be repaired, returned to the supplier, or rejected.

1.1.2 Probe Nozzle - The probe nozzle should be designed with a sharp, tapered leading edge and constructed of either seamless 316 stainless steel tubing or glass, formed in a button-hook or elbow configuration. The tapered angle should be $\leq 30^\circ$, with the taper on the outside to preserve a constant inside diameter (ID).

A range of nozzle ID's--for example, 0.32 to 1.27 cm (0.125 to 0.5 in.)--in increments of 0.16 cm (0.0625 in.) should be available for isokinetic sampling. Larger nozzle sizes may be required if high volume sampling trains are used or if very low flows are encountered.

Upon receipt of the nozzle from the manufacturer, the user should inspect it for roundness and for damage to the tapered edge such as nicks, dents, and burrs. The diameter should be checked with a micrometer; calibration procedures are described in Section 3.4.2. A slight variation from exact sizes should be expected due to machining tolerances. Each nozzle should be engraved with an identification number for inventory and calibration purposes.

1.1.3 Pitot Tube - The pitot tube, preferably of Type S design, should meet the requirements of Method 2, Section 3.1.2. The pitot tube is attached to the probe as shown in Figure 1.1. The proper pitot tube-sampling nozzle configuration for prevention of aerodynamic interference is shown in Figures 2.6 and 2.7 of Method 2, Section 3.1.2.

The pitot tube should be visually inspected for both vertical and horizontal tip alignments. If the tube is purchased as an integral part of a probe assembly, the dimensional clearances should be checked using Figures 2.6 and 2.7. Repair or return any pitot tube which does not meet specifications. Calibration procedure for a pitot tube is covered in Section 3.4.2.

1.1.4 Differential Pressure Gauge - The differential pressure gauge should be an inclined manometer or the equivalent as specified in Method 2, Section 3.1.2. Two gauges are required. One is utilized to monitor the stack velocity pressure, and the other to measure the orifice pressure differential.

Initially, check the gauge against a gauge-oil manometer at a minimum of three points: 0.64 mm (0.025 in.); 12.7 mm (0.5 in.); and 25.4 mm (1.0 in.) H₂O. The gauge should read within 5% of the gauge-oil manometer at each test point. Repair or return to the supplier any gauge which does not meet these requirements.

1.1.5 Filter Holder - A filter holder of borosilicate glass with a glass or stainless steel mesh frit filter support and a silicone rubber gasket is required by the Reference Method. Other gasket materials (e.g., Teflon or Viton) may be used if approved by the administrator. The holder design must provide a positive seal against leakage from the outside or around the filter. The holder should be durable, easy to load, and leak free in normal applications. It is positioned immediately following the probe, with the filter placed toward the flow.

1.1.6 Filter Heating System - Any heating system may be used which is capable of maintaining the filter holder at 120° ±14°C (248° ±25°F) during sampling. Other temperatures may be specified by a subpart of the regulations or approved by the administrator for a particular application. A gauge capable of measuring temperatures to within 3°C (5.4°F) should be provided to monitor the temperature around the filter during sampling.

Before sampling, the heating system and the temperature monitoring device should be checked. It is desirable that the heating element be easily replaceable in case of a malfunction during sampling.

1.1.7 Condenser - Four impingers should be connected in series with leak-free ground-glass fittings or any similar noncontaminating fittings. The first, third, and fourth impingers must be the Greenburg-Smith design modified by replacing the inserts with a glass tube that has an unobstructed 13-mm (0.5-in.) ID and that extends to within 13 mm (0.5 in.) of the flask bottom. The second impinger must be a Greenburg-Smith with the standard tip and plate. Modifications--for example, using flexible connections between impingers, using materials other than glass, or

using a flexible vacuum hose to connect the filter holder to the condenser--may be used if approved by the administrator. The fourth impinger outlet connection must allow insertion of a thermometer capable of measuring $\pm 1^{\circ}\text{C}$ (1.8°F) of true value in the range of 0° to 25°C (32° to 77°F).

Alternatively, any system that cools the gas stream and allows measurement of the condensed water and the water vapor leaving the condenser, each to within 1 ml or 1 g, may be used with approval from the administrator.

Upon receipt of a standard Greenburg-Smith impinger, the user should fill the inner tube with water. If the water does not drain through the orifice in 6 to 8 s or less, the impinger tip should be replaced or enlarged to prevent an excessive pressure drop in the sampling system. Each impinger should be checked visually for damage--breaks, cracks, or manufacturing flaws such as poorly shaped connections.

1.1.8 Metering System - The metering system should consist of a vacuum gauge, a vacuum pump, thermometers capable of measuring $\pm 3^{\circ}\text{C}$ (5.4°F) of true value in the range of 0 to 90°C (32° to 194°F), a dry gas meter with 2% accuracy at the required sampling rate; and related equipment as shown in Figure 1.1. Other metering systems capable of maintaining sampling rates within 10% of isokinetic and determining sample volumes to within 2% may be used if approved by the administrator. Sampling trains with metering systems designed for sampling rates higher than that described in APTD-0581³ and APTD-0576⁴ may be used if the above specifications can be met.

When the metering system is used with a pitot tube, the system should permit verification of an isokinetic sampling rate through the use of a nomograph or by calculation.

Upon receipt or after construction of the equipment, the user should perform both positive and negative pressure leak checks before beginning the system calibration procedure

described in Subsection 2.1 of Section 3.4.2. Any leakage requires repair or replacement of the malfunctioning item.

1.1.9 Barometer - A mercury, aneroid, or other barometer capable of measuring atmospheric pressure to within ± 2.5 mm (0.1 in.) Hg is required.

A preliminary check of a new barometer should be made against a mercury-in-glass barometer or the equivalent. In lieu of this, the absolute barometric pressure may be obtained from a nearby weather service station and adjusted for elevation difference between the station and the sampling point. Either subtract 2.5 mm Hg/30 m (0.1 in. Hg/100 ft) from the station value for an elevation increase or add the same for an elevation decrease. If the barometer cannot be adjusted to agree within 2.5 mm (0.1 in.) Hg of the reference barometric pressure, it should be returned to the manufacturer or rejected.

1.1.10 Gas Density Determination Equipment - A temperature sensor and a pressure gauge as described in Method 2 (Section 3.1.2) are required. Additionally, a gas analyzer as described by Method 3 may be required.

It is preferable that the temperature sensor be permanently attached to either the probe or the pitot tube. In either case, it is recommended that a fixed configuration (Figure 1.1) be maintained. Alternatively, the sensor may be attached just prior to field use as described in Section 3.4.2.

1.2 Sample Recovery Apparatus

1.2.1 Probe Liner and Nozzle Brushes - Nylon bristle brushes with stainless steel wire handles are recommended. The probe brush must be at least as long as the probe. A separate, smaller, and very flexible brush should be used for the nozzle.

1.2.2 Wash Bottles - Two 500-ml wash bottles are recommended for probe and glassware rinsing. Glass bottles are preferred, but polyethylene is acceptable; however, if polyethylene is used, it is recommended that it not be used for acetone storage for longer than a month.

1.2.3 Sample Storage Containers - Recommended are 500- or 1000-ml chemically resistant, borosilicate glass bottles for storage of acetone rinses. The bottles must have leak-proof screw caps with leak-proof, rubber-backed Teflon cap liners, or they must be constructed to preclude leakage and to resist chemical attack. Wide-mouthed bottles are easiest to use, but narrow mouth bottles are less prone to leakage. As an alternative to glass, polyethylene bottles may be used, but storage times should be minimized.

Prior to field use, the cap seals and the bottle cap seating surfaces should be inspected for chips, cuts, cracks, and manufacturing deformities which would allow leakage.

1.2.4 Petri Dishes - Glass or polyethylene petri dishes are recommended for storage and for transportation of the filter and collected sample.

1.2.5 Graduated Cylinder and/or Triple Beam Balance - Either a graduated cylinder or a triple beam balance may be used to measure the water condensed in the impingers during sampling. Additionally, the graduated cylinder may be used to measure water initially placed in the first and second impingers. In either case, the required accuracy is 1 ml or 1 g; therefore, the cylinder must have subdivisions ≤ 2 ml. Most triple beam balances are capable of weighing to the nearest 0.1 g.

1.2.6 Plastic Storage Containers - Several airtight plastic containers are required for storage of silica gel.

1.2.7 Funnel and Rubber Policeman - A funnel and rubber policeman are needed to transfer the used silica gel from the impinger to a storage container unless silica gel is weighed in the field after the test. A Teflon policeman is helpful for recovery of the filter.

1.3 Analytical Equipment

1.3.1 Glassware - Borosilicate glass dishes should be used to facilitate filter weighing. A 250-ml glass beaker is required for evaporation of the acetone rinse.

1.3.2 Balances - Two balances are required. One should be analytical grade and capable of weighing the filter and the sample beaker to within ± 0.1 mg. The other should be as described in Subsection 1.2.5.

1.4 Reagents and Other Supplies

All reagents should meet specifications established by the Committee on Analytical Reagents of the American Chemical Society (ACS). If reagents that meet these specifications are not available or if other specifications are not given, use the best grade available.

1.4.1 Sampling -

Filters - Glass fiber filters without organic binders must be used. The filters must exhibit at least 99.95% collection efficiency of a 0.3- μ dioctyl phthalate smoke particle, in accordance with ASTM standard method D2986 -71. Manufacturer's quality control test data are sufficient for validation of efficiency.

Silica Gel - Use indicating type 6-16 mesh. If previously used, dry at 175°C (347°F) for at least 2 h before reuse. New silica gel may be used as received.

Water - When material collected by the impingers is to be analyzed, distilled water must be used. A water blank should be analyzed before field use to prevent false high values on test samples. For standard particulate sampling, distilled water is recommended, but not required.

Crushed Ice - Enough crushed ice is needed to maintain the exit temperature of the silica gel impinger or condenser at $< 20^{\circ}\text{C}$ (68°F) throughout the test period.

Stopcock Grease - An acetone insoluble, heat stable, silicone grease must be used when the sealing of ground-glass connections is required. This is not necessary if screw-on connectors with Teflon sleeves are used.

1.4.2 Sample Recovery - Reagent ACS grade acetone with $\leq 0.001\%$ residue in glass bottles must be used. Acetone supplied in metal

containers is unacceptable due to the prevalently high residue levels. An acetone blank should be run prior to field use, and the acetone must be rejected if blank residue weight is $>0.001\%$ of the total acetone weight.

1.4.3 Sample Analysis -

Acetone - Same as Subsection 1.4.2.

Desiccant - An indicating type anhydrous calcium sulfate is required. Other types of desiccants may be used if approved by the administrator.

Table 1.1 ACTIVITY MATRIX FOR PROCUREMENT OF APPARATUS
AND SUPPLIES

Apparatus	Acceptance limits	Frequency and method of measurements	Action if requirements are not met
<u>Sampling</u>			
Probe liner	Specified material of construction; equipped with heating system capable of maintaining $120^{\circ} \pm 14^{\circ}\text{C}$ ($248^{\circ} \pm 25^{\circ}\text{F}$) at the exit	Visually check and run the heating system	Repair, return to supplier, or reject
Probe nozzle	Stainless steel (316) with sharp, tapered angle $\leq 30^{\circ}$; difference in measured diameters ≤ 0.1 mm (0.004 in.); no nicks, dents, or corrosion (Subsec 1.1.2)	Visually check before each test; use a micrometer to measure ID before field use after each repair	Reshape and sharpen, return to the supplier, or reject
Pitot tube	Type S (Sec 3.1.2); attached to probe with impact (high pressure) opening plane even with or above nozzle entry plane	Calibrated according to Sec 3.1.2	Repair or return to supplier
Differential pressure gauge (manometer)	Meets criteria (Sec 3.1.2); agree within 5% of gauge-oil manometer	Check against a gauge-oil manometer at a minimum of 3 points: 0.64(0.025); 12.7 (0.5); 25.4(1.0) mm (in.) H_2O	Repair or return to supplier
Vacuum gauge	0-760 mm (0-30 in.) Hg range, ± 25 mm (1 in.) at 380 mm (15 in.) Hg	Check against mercury U-tube manometer upon receipt	Adjust or return to supplier
Vacuum pump	Leak free; capable of maintaining a flow rate of 0.02-0.03 m^3/min (0.66 to 1.1 ft^3/min) for pump inlet vacuum of 380 mm (15 in.) Hg	Check upon receipt for leaks and capacity	Repair or return to supplier

(continued)

Table 1.1 (continued)

Apparatus	Acceptance limits	Frequency and method of measurements	Action if requirements are not met
Orifice meter	ΔH_Q of 46.74 ± 6.35 mm (1.84 ± 0.25 in.) H_2O at $68^\circ F$ (not mandatory)	Upon receipt, visually check for damage and calibrate against wet test meter	Repair if possible otherwise return to supplier
Impingers	Standard stock glass; pressure drop not excessive (Subsec 1.1.7)	Visually check upon receipt; check pressure drop (Subsec 1.1.6)	Return to supplier
Filter holder	Leak free; borosilicate glass	Visually check before use	As above
Dry gas meter	Capable of measuring volume within $\pm 2\%$ at a flow rate of $0.02 \text{ m}^3/\text{min}$ ($0.75 \text{ ft}^3/\text{min}$)	Check for damage upon receipt and calibrate (Sec 3.4.2) against wet test meter	Reject if damaged, behaves erratically, or cannot be properly adjusted
Thermometers	$\pm 1^\circ C$ ($2^\circ F$) of true value in the range of 0° to $25^\circ C$ (32° to $77^\circ F$) for impinger thermometer and $\pm 3^\circ C$ ($5.4^\circ F$) of true value in the range of $0^\circ C$ to $90^\circ C$ (32° to $194^\circ F$) for dry gas meter thermometers	Check upon receipt for dents or bent stem, and calibrate (Sec 3.4.2) against mercury-in-glass thermometer	Reject if unable to calibrate
Barometer	Capable of measuring atmospheric pressure within ± 2.5 mm (0.1 in.) Hg	Check against a mercury-in-glass barometer or equivalent; calibrate (Sec 3.1.2)	Determine correction factor, or reject if difference more than ± 2.5 mm (0.1 in.) Hg
<u>Sample Recovery</u>			
Probe liner and nozzle	Nylon bristles with stainless steel stem; as long as the probe; properly sized and shaped	Visually check for damage upon receipt	Replace or return to supplier
Wash bottles	Two; polyethylene or glass; 500 ml	Visually check for damage upon receipt	Replace or return to supplier

(continued)

Table 1.1 (continued)

Apparatus	Acceptance limits	Frequency and method of measurements	Action if requirements are not met
Storage container	Polyethylene or glass; 500 or 1000 ml	Visually check for damage upon receipt	Replace or return to supplier
Graduated cylinder	Glass and class A; 250 ml with subdivisions ≤ 2 ml	Upon receipt, check for stock number, cracks, breaks, and manufacturer flaws	Replace or return to supplier
Funnel	Glass suitable for use with sample bottles	Visually check for damage upon receipt	Replace or return to supplier
Rubber policeman	Properly sized	Visually check for damage upon receipt	Replace or return to supplier
Petri dishes	Glass or polyethylene; sized to fit the glass fiber filters	Visually check for damage upon receipt	Replace or return to supplier
Balance	Capable of measuring silica gel to ± 0.5 g	Check with standard weights upon receipt and before each use	Replace or return to manufacturer
Beakers and weighing dishes	Glass	Upon receipt, check for stock number, cracks, breaks, and manufacturing flaws	Replace or return to manufacturer
Triple beam balance	500-g capacity; capable of measuring within ± 1 g	Check with standard weights upon receipt and before each use	Replace or return to manufacturer
Analytical balance	Capable of measuring to ± 0.1 mg	As above	As above
Filters	Glass fiber without organic binder; 99.95% collection efficiency for 0.3μ dioctyl phthalate smoke particles	Manufacturer's guarantee that filters were tested according to ASTM D2986-71; observe under light for defects	Return to supplier

(continued)

Table 1.1 (continued)

Apparatus	Acceptance limits	Frequency and method of measurements	Action if requirements are not met
<u>Reagents</u>			
Silica gel	Indicating type 6-16 mesh	Upon receipt, check label for grade or certification	Return to supplier
Distilled water	Meets ASTM D1193-74; type 3 (only when impinger particulate catch included)	Check each lot, or specify type when ordering	Replace or return to manufacturer
Stopcock grease	Acetone insoluble, heat stable silicone grease	Upon receipt, check label for grade or certification	Replace or return to manufacturer
Acetone	ACS grade; <0.001% residue in glass bottles	Upon receipt, verify residue by evaporating a blank sample	Replace or return to supplier
Desiccant	Indicating type anhydrous calcium sulfate	Upon receipt, check for grade and certification	Replace or return to supplier

2.0 CALIBRATION OF APPARATUS

Calibration of apparatus is one of the most important functions in maintaining data quality. The detailed calibration procedures included in this section are designed for the equipment specified by Method 5 and described in the previous section. A laboratory log book of all calibrations must be maintained. Table 2.1 at the end of this section summarizes the quality assurance activities for calibration.

2.1 Metering System

2.1.1 Wet Test Meter - Wet test meters are calibrated by the manufacturer to an accuracy of $\pm 0.5\%$. The calibration of the wet test meter must be checked initially upon receipt and yearly thereafter. A wet test meter with a capacity of $3.4 \text{ m}^3/\text{h}$ ($120 \text{ ft}^3/\text{h}$) will be needed to calibrate the dry gas meter. For large wet test meters ($>3\ell/\text{rev}$), there is no convenient method for checking the calibration; for this reason, several methods are suggested, and other methods may be approved by the administrator. The initial calibration may be checked by any of the following methods:

1. Certification from the manufacturer that the wet test meter is within $\pm 1\%$ of true value at the wet test meter discharge, so that only a leak check of the system is then required.

2. Calibration by any primary air or liquid displacement method that displaces at least one complete revolution of the wet test meter.

3. Comparison against a smaller wet test meter that has previously been calibrated against a primary air or liquid displacement method, as described in Section 3.5.2.

4. Comparison against a dry gas meter that has previously been calibrated against a primary air or liquid displacement method.

The calibration of the test meter should be checked annually. The calibration check can be made by the same method as that of the original calibration; however, the comparison method need not be recalibrated if the calibration check is within $\pm 1\%$ of the true value. When this agreement is not obtained, the comparison method or wet test meter must be recalibrated against a primary air or liquid displacement method.

2.1.2 Sample Meter System - The sample meter system--consisting of the pump, vacuum gauge, valves, orifice meter, and dry gas meter--should be initially calibrated by stringent laboratory methods before it is used in the field. After the initial acceptance, the calibration should be rechecked after each field test series. This recheck is designed to provide the tester with a method that can be used more often and with less effort to ensure that the calibration has not changed. When the quick check indicates that the calibration factor has changed, the tester must again use the complete laboratory procedure to obtain the new calibration factor. After recalibration, the metered sample volume must be multiplied by either the initial or the recalibrated calibration factor--that is, the one that yields the lower gas volume for each test run.

Before initial calibration of the metering system, a leak check should be conducted. The meter system should be leak free. Both positive (pressure) and negative (vacuum) leak checks should be performed. Following is a pressure leak-check procedure that will check the metering system from the quick disconnect inlet to the orifice outlet and will check the orifice-inclined manometer:

1. Disconnect the orifice meter line from the downstream orifice pressure tap (the one closest to the exhaust of the orifice), and plug this tap (Figure 2.1).

2. Vent the negative side of the inclined manometer to the atmosphere. If the inclined manometer is equipped with a

three-way valve, this step can be performed by merely turning the three-way valve that is on the negative side of the orifice-inclined manometer to the vent position.

3. Place a one-hole rubber stopper with a tube through its hole in the exit of the orifice, and connect a piece of rubber or plastic tubing to the tube, as shown in Figure 2.1.

4. Open the positive side of the orifice-inclined manometer to the "reading" position; if the inclined manometer is equipped with a three-way valve, this will be the line position.

5. Plug the inlet to the vacuum pump. If a quick disconnect with a leak-free check valve is used on the control module, the inlet will not have to be plugged.

6. Open the main valve and the bypass valve.

7. Blow into the tubing connected to the end of the orifice until a pressure of 127 to 178 mm (5 to 7 in.) H_2O has built up in the system.

8. Plug or crimp the tubing to maintain this pressure.

9. Observe the pressure reading for a 1-min period. No noticeable movement in the manometer fluid level should occur. If the meter box has a leak, a bubbling-type leak-check solution may aid in locating the leak(s).

After the metering system is determined to be leak free by the positive leak-check procedure, the vacuum system to and including the pump should be checked by plugging the air inlet to the meter box. If a quick disconnect with a leak-free stopper system is presently on the meter box, the inlet will not have to be plugged. Turn the pump on, pull a vacuum within 7.5 cm (3 in.) Hg of absolute zero, and observe the dry gas meter. If the leakage exceeds $0.00015 \text{ m}^3/\text{min}$ ($0.005 \text{ ft}^3/\text{min}$), the leak(s) must be found and minimized until the above specifications are satisfied.

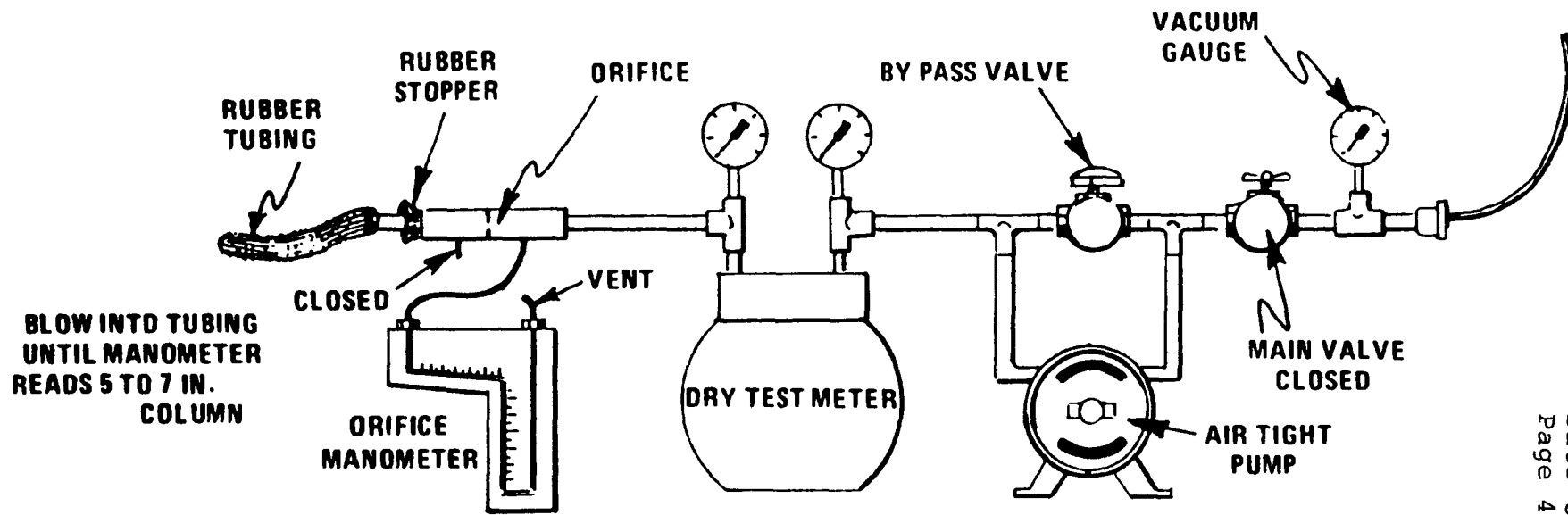


Figure 2.1 Positive leak check of metering system.

Leak checking the meter system before initial calibration is not mandatory, but is recommended.

Note: For metering systems having diaphragm pumps, the normal leak-check procedure described above will not detect leakages within the pump. For these cases, the following leak-check procedure is suggested: make a 10-min calibration run at $0.00057 \text{ m}^3/\text{min}$ ($0.02 \text{ ft}^3/\text{min}$); at the end of the run, take the difference between the measured wet test meter and the dry gas meter volumes; divide the difference by 10, to get the leak rate. The leak rate should not exceed $0.00057 \text{ m}^3/\text{min}$ ($0.02 \text{ ft}^3/\text{min}$).

Initial calibration - The dry gas meter and the orifice meter can be calibrated simultaneously and should be calibrated when first purchased and any time the posttest check yields a Y outside the range of the calibration factor $Y \pm 0.05Y$. A calibrated wet test meter (properly sized, with $\pm 1\%$ accuracy) should be used to calibrate the dry gas meter and the orifice meter.

The dry gas meter and the orifice meter should be calibrated in the following manner:

1. Before its initial use in the field, leak check the metering system. Leaks, if present, must be eliminated before proceeding.

2. Assemble the apparatus, as shown in Figure 2.2, with the wet test meter replacing the probe and impingers--that is, with the outlet of the wet test meter connected to a needle valve that is connected to the inlet side of the meter box.

3. Run the pump for 15 min with the orifice meter differential (ΔH) set at 12.7 mm (0.5 in.) H_2O to allow the pump to warm up and to permit the interior surface of the wet test meter to be wetted.

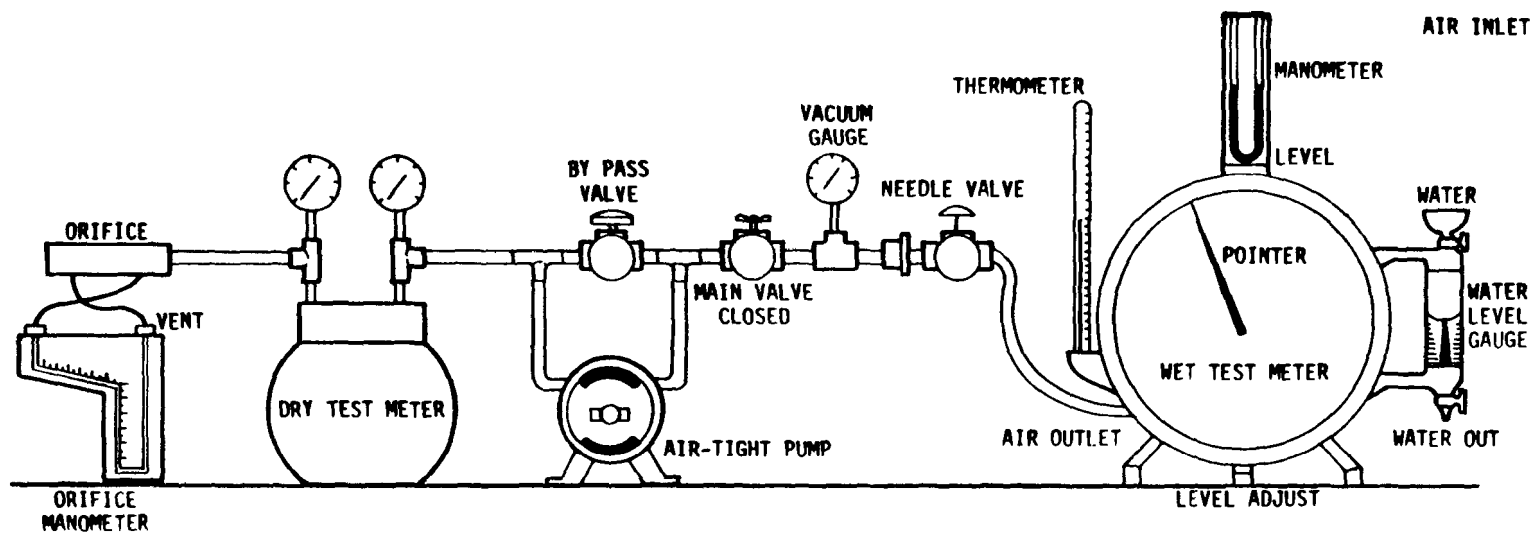


Figure 2.2 Sample meter system calibration setup.

4. Adjust the needle valve so that the vacuum gauge on the meter box is between 50 and 100 mm (2 to 4 in.) Hg during calibration.

5. Collect the information required in the forms provided (Figure 2.3A or 2.3B). Sample volumes, as shown, should be used.

6. Calculate Y_i for each of the six runs, using the equation in Figure 2.3A or 2.3B under the Y_i column, and record the results on the form in the space provided.

7. Calculate the average Y (calibration factor) for the six runs using the following equation:

$$Y = \frac{Y_1 + Y_2 + Y_3 + Y_4 + Y_5 + Y_6}{6} .$$

Record the average on Figure 2.3A or 2.3B in the space provided.

8. Clean, adjust, and recalibrate, or reject the dry gas meter if one or more values of Y fall outside the interval $Y \pm 0.02Y$. Otherwise, the average Y is acceptable and should be used for future checks and subsequent test runs.

9. Calculate $\Delta H@_i$ for each of the six runs using the equation in Figure 2.3A or 2.3B under the $\Delta H@_i$ column, and record on the form in the space provided.

10. Calculate the average $\Delta H@$ for the six runs using the following equation:

$$\Delta H@ = \frac{\Delta H@_1 + \Delta H@_2 + \Delta H@_3 + \Delta H@_4 + \Delta H@_5 + \Delta H@_6}{6} .$$

Record the average on Figure 2.3A or 2.3B in the space provided.

11. Adjust the orifice meter or reject it if $\Delta H@_i$ varies by more than ± 3.9 mm (0.15 in.) H_2O over the range of 10 to 100 mm (0.4 to 4.0 in.) H_2O . Otherwise, the average $\Delta H@$ is acceptable and should be used for subsequent test runs.

Date 7/31/79

Meter box number FM-2

Barometric pressure, $P_b = 29.64$ in. Hg Calibrated by MEB

Orifice manometer setting (ΔH), in. H_2O	Gas volume		Temperatures				Time (θ), min	Y_i	$\Delta H@_i$, in. H_2O
	Wet test meter (V_w), ft ³	Dry gas meter (V_d), ft ³	Wet test meter (t_w), °F	Dry gas meter					
				Inlet (t_{d_i}), °F	Outlet (t_{d_o}), °F	Avg ^a (t_d), °F			
0.5	5	130.000 135.140	71.5 71.5	91 98	82 85	87	12 47/60	1.004	1.79
1.0	5								
1.5	10								
2.0	10								
3.0	10								
4.0	10								
Avg									

ΔH , in. H_2O	$\frac{\Delta H}{13.6}$	$Y_i = \frac{V_w P_b (t_d + 460)}{V_d (P_b + \frac{\Delta H}{13.6}) (t_w + 460)}$	$\Delta H@_i = \frac{0.0317 \Delta H}{P_b (t_d + 460)} \left[\frac{(t_w + 460) \theta}{V_w} \right]^2$
0.5	0.0368	$\frac{5(29.64)(549)}{5.14(29.67)(531.5)}$	$\frac{(0.0317)(0.5)}{(29.64)(549)} \left[\frac{(531.5)(12.78)}{5} \right]^2$
1.0	0.0737		
1.5	0.110		
2.0	0.147		
3.0	0.221		
4.0	0.294		

^a If there is only one thermometer on the dry gas meter, record the temperature under t_d .

Figure 2.3A Dry gas meter calibration data (English units).
(front side)

Nomenclature:

V_w = Gas volume passing through the wet test meter, ft^3 .

V_d = Gas volume passing through the dry gas meter, ft^3 .

t_w = Temperature of the gas in the wet test meter, $^{\circ}\text{F}$.

t_{d_i} = Temperature of the inlet gas of the dry gas meter, $^{\circ}\text{F}$.

t_{d_o} = Temperature of the outlet gas of the dry gas meter, $^{\circ}\text{F}$.

t_d = Average temperature of the gas in the dry gas meter, obtained by the average t_{d_i} and t_{d_o} , $^{\circ}\text{F}$.

ΔH = Pressure differential across orifice, in. H_2O .

Y_i = Ratio of accuracy of wet test meter to dry gas meter for each run. Tolerance $Y_i = Y \pm 0.02 Y$.

Y = Average ratio of accuracy of wet test meter to dry gas meter for all six runs.
Tolerance $Y = Y \pm 0.01 Y$.

$\Delta H@_i$ = Orifice pressure differential at each flow rate that gives $0.75 \text{ ft}^3/\text{min}$ of air at standard conditions for each calibration run, in. H_2O . Tolerance = $\Delta H@ \pm 0.15$ (recommended).

$\Delta H@$ = Average orifice pressure differential that gives $0.75 \text{ ft}^3/\text{min}$ of air at standard conditions for all six runs, in. H_2O . Tolerance = 1.84 ± 0.25 (recommended).

θ = Time for each calibration run, min.

P_b = Barometric pressure, in. Hg.

Figure 2.3A. Dry gas meter calibration data (English units). (backside)

Date 7/31/79

Meter box number FM-2

Barometric pressure, $P_b =$ 736 mm Hg Calibrated by MEB

Orifice manometer setting (ΔH), mm H ₂ O	Gas volume		Temperatures				Time (θ), min	Y _i	$\Delta H@_i$, mm H ₂ O
	Wet test meter (V _w), m ³	Dry gas meter (V _d), m ³	Wet test meter (t _w), °C	Dry gas meter					
				Inlet (t _{d_i}), °C	Outlet (t _{d_o}), °C	Avg ^a (t _d), °C			
10	0.15	25.0320 24.8800	18 18	20 19	18 17	18	10 ¹⁹ / ₂₀	.986	23
25	0.15								
40	0.30								
50	0.30								
75	0.30								
100	0.30								
Avg									

ΔH , mm H_2O	$\frac{\Delta H}{13.6}$	$Y_i = \frac{V_w P_b (t_d + 273)}{V_d (P_d + \frac{\Delta H}{13.6}) (t_w + 273)}$	$\Delta H@_i = \frac{0.00117 \Delta H}{P_b (t_d + 273)} \left[\frac{(t_w + 273) \theta}{V_w} \right]^2$
10	0.7	$\frac{(0.15)(736)(291)}{(0.152)(737)(291)}$	$\frac{0.00117(10)}{(736)(29)} \left[\frac{(291)(10.9)}{0.152} \right]^2$
25	1.8		
40	2.94		
50	3.68		
75	5.51		
100	7.35		

^a If there is only one thermometer on the dry gas meter, record the temperature under t_d .

Figure 2.3B Dry gas meter calibration data (metric units).
(front side)

Nomenclature:

V_w = Gas volume passing through the wet test meter, m^3 .

V_d = Gas volume passing through the dry gas meter, m^3 .

t_w = Temperature of the gas in the wet test meter, $^{\circ}C$.

t_{d_i} = Temperature of the inlet gas of the dry gas meter, $^{\circ}C$.

t_{d_o} = Temperature of the outlet gas of the dry gas meter, $^{\circ}C$.

t_d = Average temperature of the gas in the dry gas meter, obtained by the average of t_{d_i} and t_{d_o} , $^{\circ}C$.

ΔH = Pressure differential across orifice, mm H_2O .

Y_i = Ratio of accuracy of wet test meter to dry gas meter for each run. Tolerance $Y_i = Y \pm 0.02 Y$.

Y = Average ratio of accuracy of wet test meter to dry gas meter for all six runs.
Tolerance $Y = Y \pm 0.01 Y$.

$\Delta H@_i$ = Orifice pressure differential at each flow rate that gives $0.021 m^3$ of air at standard conditions for each calibration run, mm H_2O . Tolerance $\Delta H@_i = \Delta H@ \pm 3.8$ mm H_2O (recommended).

$\Delta H@$ = Average orifice pressure differential that gives $0.021 m^3$ of air at standard conditions for all six runs, mm H_2O . Tolerance $\Delta H@ = 46.74 \pm 6.3$ mm H_2O (recommended).

θ = Time of each calibration run, min.

P_b = Barometric pressure, mm Hg.

Figure 2.3B Dry gas meter calibration data (metric units). (backside)

Posttest calibration check - After each field test series, conduct a calibration check of the metering system, except for the following variations:

1. Three calibration runs at a single intermediate orifice meter setting may be used with the vacuum set at the maximum value reached during the test series. The single intermediate orifice meter setting should be based on the previous field test. A valve must be inserted between the wet test meter and the inlet of the metering system to adjust the vacuum.

2. If a temperature-compensating dry gas meter was used, the calibration temperature for the dry gas meter must be within $\pm 6^{\circ}\text{C}$ (10.8°F) of the average meter temperature during the test series.

3. Use Figure 2.4A or 2.4B, and record the required information.

If the calibration factor Y deviates by $<5\%$ from the initial calibration factor Y, then the dry gas meter volumes obtained during the test series are acceptable. If Y deviates by $>5\%$, recalibrate the metering system, and use whichever meter coefficient (initial or recalibrated) that yields the lowest gas volume for each test run.

Alternate procedures (e.g., using the orifice meter coefficients) may be used, subject to the approval of the administrator.

2.2 Temperature Gauges

2.2.1 Impinger Thermometer

- The thermometer used to measure temperature of the gas leaving the impinger train should initially be compared with a mercury-in-glass thermometer which meets ASTM E-1 No. 63C or 63F specifications. The procedure is as follows:

1. Place both the reference thermometer and the test thermometer in an ice bath. Compare readings after they stabilize.

Test numbers AB1-3 Date 9/13/79 Meter box number FM-7 Plant Acme Power Plant
 Barometric pressure, P_b = 28.72 in. Hg Dry gas meter number FM-7 Pretest Y 0.986

Orifice manometer setting, (ΔH), in. H ₂ O	Gas volume		Temperature				Time (θ), min	Vacuum setting, in. Hg	Y_i	Y_i
	Wet test meter (V_w), ft ³	Dry gas meter (V_d), ft ³	Wet test meter (t_w), °F	Dry gas meter						$V_w P_b (t_d + 460)$
				Inlet (t_{d_i}), °F	Outlet (t_{d_o}), °F	Average ^a (t_d), °F				$V_d P_b + \frac{\Delta H}{13.6} t_w + 460$
1.41	10	886.544 876.321	72	83	75	79	13.35	3	0.987	$\frac{10(28.72)(79+460)}{10(28.72 + \frac{1.41}{13.6})(72+460)}$
	10									
	10									
										Y =

^a If there is only one thermometer on the dry gas meter, record the temperature under t_d .

V_w = Gas volume passing through the wet test meter, ft³.

V_d = Gas volume passing through the dry gas meter, ft³.

t_w = Temperature of the gas in the wet test meter, °F.

t_{d_i} = Temperature of the inlet gas of the dry gas meter, °F.

t_{d_o} = Temperature of the outlet gas of the dry gas meter, °F.

t_d = Average temperature of the gas in the dry gas meter, obtained by the average of t_{d_i} and t_{d_o} , °F.

ΔH = Pressure differential across orifice, in H₂O.

Y_i = Ratio of accuracy of wet test meter to dry gas meter for each run.

Y = Average ratio of accuracy of wet test meter to dry gas meter for all three runs;
 tolerance = pretest Y \pm 0.05Y

P_b = Barometric pressure, in. Hg.

θ = Time of calibration run, min.

Figure 2.4A Posttest dry gas meter calibration form (English units).

Test numbers AB1-3 Date 9/13/79 Meter box number FM-7 Plant Acme Power Plant
 Barometric pressure, P_b = 730 mm Hg Dry gas meter number FM-7 Pretest Y 0.993

Orifice manometer setting, (ΔH), mm H ₂ O	Gas volume		Temperature				Time (θ), min	Vacuum setting, mm Hg	Y_i	Y_i	$\frac{V_w P_b (t_d + 273)}{V_d P_b + \frac{\Delta H}{13.6} t_w + 273}$
	Wet test meter (V_w), m ³	Dry gas meter (V_d), m ³	Wet test meter (t_w), °C	Dry gas meter							
				Inlet (t_{d_i}), °C	Outlet (t_{d_o}), °C	Average ^a (t_d), °C					
36	0.30	26.1742 19.8730	21	23.5	21.5	22.5	13.50	75	0.990		$\frac{0.30(730)(21.5+273)}{0.30(730+\frac{75}{13.6})(21+23)}$
	0.30										
	0.30										
											Y =

^a If there is only one thermometer on the dry gas meter, record the temperature under t_d .

V_w = Gas volume passing through the wet test meter, m³.

V_d = Gas volume passing through the dry gas meter, m³.

t_w = Temperature of the gas in the wet test meter, °C.

t_{d_i} = Temperature of the inlet gas of the dry gas meter, °C.

t_{d_o} = Temperature of the outlet gas of the dry gas meter, °C.

t_d = Average temperature of the gas in the dry gas meter, obtained by the average of t_{d_i} and t_{d_o} , °C.

ΔH = Pressure differential across orifice, in H₂O.

Y_i = Ratio of accuracy of wet test meter to dry gas meter for each run.

Y = Average ratio of accuracy of wet test meter to dry gas meter for all three runs;
 tolerance = pretest Y \pm 0.05Y

P_b = Barometric pressure, in. Hg.

θ = Time of calibration run, min.

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

2. Remove the thermometers from the bath and allow both to come to room temperature. Again, compare readings after they stabilize.

3. Accept the test thermometer if its reading agrees within 1°C (2°F) of the reference thermometer reading at both temperatures. If the difference is greater than $\pm 1^{\circ}\text{C}$ (2°F), the thermometer should be adjusted and recalibrated until the criteria are met, or it should be rejected.

2.2.2 Dry Gas Thermometers - The thermometers used to measure the metered gas sample temperature should initially be compared with a mercury-in-glass thermometer as above, using a similar procedure.

1. Place the dial type or 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 thermometers stabilize.

3. Accept the dial type or equivalent thermometer if the values agree within 3°C (5.4°F) at both points 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 pretest sampling check form (Figure 3.1).

4. Prior to each field trip, compare the temperature reading of the mercury-in-glass thermometer at room temperature with that of the meter system thermometer. The values or corrected values should be within $\pm 6^{\circ}\text{C}$ (10.8°F) of one another, or the meter thermometer should be replaced or recalibrated. Record any temperature correction factors on Figure 3.1 or on a similar form.

2.2.3 Stack Temperature Sensor - The stack temperature sensor should be calibrated upon receipt or checked before field use. Each sensor should be uniquely marked for identification. The calibration should be performed at three points and then extrapolated over the range of temperatures anticipated during actual

sampling. For the three point calibration, a reference ASTM mercury-in-glass thermometer should be used.

The following procedure is recommended for calibrating stack temperature sensors (thermocouples and thermometers) for field use.

1. For the ice point calibration, form a slush from crushed ice and liquid water (preferably deionized, distilled) in an insulated vessel such as a Dewar flask.

Taking care that they do not touch the sides of the flask, insert the stack temperature sensor into the slush to a depth of at least 2 in. Wait 1 min to achieve thermal equilibrium, and record the readout on the potentiometer. Obtain three readings taken in 1-min intervals. Note: Longer times may be required to attain thermal equilibrium with thick-sheathed thermocouples.

2. Fill a large Pyrex beaker with water to a depth ≥ 4 in. Place several boiling chips in the water, and bring the water to a full boil using a hot plate as the heat source. Insert the stack temperature sensor(s) in the boiling water to a depth of at least 2 in., taking care not to touch the sides or bottom of the beaker.

Alongside the sensor(s), an ASTM reference thermometer should be placed. If the entire length of the mercury shaft in the thermometer cannot be immersed, a temperature correction will be required to give the correct reference temperature.

After 3 min, both instruments will attain thermal equilibrium. Simultaneously record temperatures from the ASTM reference thermometer and the stack temperature sensor three times at 1-min intervals.

3. For thermocouple, repeat Step 2 with a liquid that has a boiling point (such as cooking oil) in the 150° - 250°C (300° - 500°F) range. Record all data on Figure 2.5. For thermometers, other than thermocouples, repeat Step 2 with a liquid that boils at the maximum temperature that the thermometer is to be used, or

Date 9-12-78 Thermocouple number TC-46
Ambient temperature 21 °C Barometric pressure 29.67 in. Hg
Calibrator TC Reference: mercury-in-glass ASTM 3C
other _____

Reference point number	Source ^a (specify)	Reference thermometer temperature, °C	Thermocouple potentiometer temperature, °C	Temperature difference, ^b %
0°	ICE WATER	1°C	1°C	—
100°	BOILING WATER	101.5°C	101°C	0.1%
—	BOILING COOKING OIL	205.5°C	203°C	0.5%

^aType of calibration system used.

$$^b \left[\frac{(\text{ref temp, } ^\circ\text{C} + 273) - (\text{test thermom temp, } ^\circ\text{C} + 273)}{\text{ref temp, } ^\circ\text{C} + 273} \right] 100 \leq 1.5\%.$$

Figure 2.5 Stack temperature sensor calibration data form.

place the stack thermometer and reference thermometer in a furnace or other device to reach the required temperature. Note: If the thermometer is to be used at temperatures higher than the reference thermometers will record, the stack thermometer may be calibrated with a thermocouple previously calibrated with the above procedure.

4. If the absolute values of the reference thermometer and thermocouple(s) agree within $\pm 1.5\%$ at each of the three calibration points, plot the data on linear graph paper and draw the best-fit line to the three points or calculate the constants of the linear equation using the least-square method. The data may be extrapolated above and below the calibration points and cover the entire manufacturer's suggested range for the thermocouple. For the portion of the plot or equation that agrees within 1.5% of the absolute reference temperature, no correction need be made. For all other portions that do not agree within $\pm 1.5\%$ use the plot or equation to correct the data.

If the absolute values of the reference thermometer and stack temperature sensor (other than the thermocouple) agree within $\pm 1.5\%$ at each of the three points, the thermometer may be used over the range of calibration points for testing without applying any correction factor. The data cannot be extrapolated outside the calibration points.

2.3 Probe Heater

The probe heating system should be calibrated prior to field use according to the procedure outlined in APTD-0576.⁴ Probes constructed according to APTD-0581³ need not be calibrated if the curves of APTD-0576⁴ are used.

2.4 Barometer

The field barometer should be adjusted initially and before each test series to agree within ± 2.5 mm (0.1 in.) Hg of the mercury-in-glass barometer or with the station pressure value reported by a nearby National Weather Service station and corrected for elevation. The correction for elevation difference

between the station and the sampling point should be applied at a rate of -2.4 mm Hg/30 m (-0.1 in. Hg/100 ft). Record the results on the pretest sampling check form (Figure 3.1 of Section 3.4.3).

2.5 Probe Nozzle

Probe nozzles should be calibrated before initial use in the field. Using a micrometer, measure the ID of the nozzle to the nearest 0.025 mm (0.001 in.). Make three measurements using different diameters each time, and obtain the average. The difference between the high and the low numbers should not exceed 0.1 mm (0.004 in.). When nozzles become nicked, dented, or corroded, they should be reshaped, sharpened, and recalibrated before use. Each nozzle should be permanently and uniquely identified. Figure 2.6 is an example of a nozzle calibration data form.

2.6 Pitot Tube

The Type S pitot tube assembly should be calibrated using the procedure outlined in Section 3.1.2 of Method 2.

2.7 Trip Balance

The trip balance should be calibrated initially by using Class-S standard weights and should be within ± 0.5 g of the standard weight. Adjust or return the balance to the manufacturer if limits are not met.

2.8 Analytical Balance

The analytical balance should initially be checked with Class-S weights, and the data should be recorded on an analytical balance calibration log or on a similar form. The balances should be adjusted to agree within ± 2 mg of the Class-S weight, or it should be adjusted or returned to manufacturer.

Nozzle identification number	Nozzle Diameter ^a			$\Delta D,$ ^b mm (in.)	D_{avg} ^c
	$D_1,$ mm (in.)	$D_2,$ mm (in.)	$D_3,$ mm (in.)		
37	0.251	0.252	0.253	0.002	0.252

$a_{D_{1,2,3}}$ = three different nozzles diameter (in.); each diameter must be within (0.025 in. to 0.1 in.)

b ΔD = maximum difference between any two diameters, mm (in.),
 $\Delta D \leq (0.10 \text{ mm}) 0.004 \text{ in.}$

^c D_{avg} = average of D_1 , D_2 , and D_3 .

Figure 2.6 Nozzle calibration data form.

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 $>3.4 \text{ m}^3/\text{h}$ ($120 \text{ ft}^3/\text{h}$); 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	$Y_i = Y \pm 0.02 Y$	Calibrate vs wet test meter initially, and when posttest check exceeds $Y \pm 0.05 Y$	Repair, or replace and then recalibrate
Thermometers	Impinger thermometer $\pm 1^\circ\text{C}$ (2°F); dry gas meter thermometer $\pm 3^\circ\text{C}$ (5.4°F) over range; stack temperature sensor $\pm 1.5\%$ of absolute temperature	Calibrate each initially as a separate component against a mercury-in-glass thermometer; then before each field trip compare each as part of the train with the mercury-in-glass thermometer	Adjust; determine a constant correction factor; or reject
Probe heating system	Capable of maintaining $120^\circ \pm 14^\circ\text{C}$ ($248^\circ \pm 25^\circ\text{F}$) at a flow rate of 20 l/min ($0.71 \text{ ft}^3/\text{min}$)	Calibrate component initially by APTD-0576; if constructed by APTD-0581, or use published calibration curves	Repair, or replace and then reverify the calibration
Barometer	$\pm 2.5 \text{ mm}$ (0.1 in.) Hg of mercury-in-glass barometer	Calibrate initially vs mercury-in-glass barometer; check before and after each field test	Adjust to agree with a certified barometer
Probe nozzle	Average of three ID measurements of nozzle; difference between high and low $\leq 0.1 \text{ mm}$ (0.004 in.)	Use a micrometer to measure to nearest 0.025 mm (0.001 in.)	Recalibrate, reshape, and sharpen when nozzle becomes nicked, dented, or corroded

(continued)

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Table 2.1 (continued)

Apparatus	Acceptance limits	Frequency and method of measurement	Action if requirements are not met
Analytical balance	± 1 mg of Class-S weights	Check with Class-S weights upon receipt	Adjust or repair

3.0 PRESAMPLING OPERATIONS

The quality assurance activities for presampling operations 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

A pretest check will have to be made on most of the sampling apparatus. Figure 3.1 should be used to record the pretest calibration checks. Figure 3.2 or a similar form is recommended to aid the tester in preparing an equipment checklist, status form, and packing list for Methods 1 through 8, Method 17, and particle sizing.

3.1.1 Sampling Train - A schematic of the EPA Method 5 sampling train is Figure 1.1. Commercial models of this system are available. Each train must be in compliance with the specifications of the Reference Method, Section 3.4.10.

3.1.2 Probe and Nozzle - Clean the probe and the nozzle internally by brushing first with tap water, then with deionized distilled water, and finally with acetone; allow both to dry in the air. In extreme cases, the probe liner can be cleaned with stronger reagents. In either case, the objective is to leave the probe liner free from contaminants. The probe's heating system should be checked to see that it is operating properly. The probe should be sealed at the inlet or tip and checked for leaks at a vacuum of 380 mm (15 in.) Hg, and the probe must be leak free under these conditions.

3.1.3 Impingers, Filter Holder, and Glass Connectors - All glassware should be cleaned first with detergent and tap water and then with deionized distilled water. All glassware should be visually inspected for cracks or breakage and then repaired or discarded if defective.

3.1.4 Pump - The vacuum pump should be serviced as recommended by the manufacturer, or every 3 mo, or upon erratic behavior

Date 9/11/79 Calibrated by MEB
Meter box number FB-1 $\Delta H@$ 1.87

Dry Gas Meter*

Pretest calibration factor Y 1.013 (within $\pm 2\%$ of the average factor for each calibration run).

Impinger Thermometer

Was a pretest temperature correction used? yes ☒ no
If yes, temperature correction _____ (within $\pm 3^\circ\text{C}$ (5.4°F) over range)

Dry Gas Meter Thermometers

Was a pretest temperature correction made? yes ☒ no
If yes, temperature correction _____ (within $\pm 3^\circ\text{C}$ (5.4°F) over range)

Stack Temperature Sensor*

Was a stack temperature sensor calibrated against a reference thermometer? ☒ yes _____ no
If yes, give temperature range with which the readings agreed within $\pm 1.5\%$ of the reference values _____ to _____ K ($^\circ\text{R}$)

Barometer

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

Nozzle*

Was the nozzle calibrated to the nearest 0.025 mm (0.001 in.)?
☒ yes _____ no

*Most significant items/parameters to be checked.

Figure 3.1 Pretest sampling checks.

Client _____ PN _____ Transport vehicle _____
Project manager _____ Presurveyed by _____
Date needed by _____ Loaded by _____

1. General Pretest Checklist

	Quantity	Ready	Loaded
Asbestos wrapping material, roll			
Auxiliary parts box			
Balance, triple beam and weights			
Bucket			
Calibration Data			
Camera			
Certificate of insurance			
Clamps			
Carpenter			
C-Clamps			
Hose			
Cleanup box			
Clipboards			
Clocks			
Condenser, coil type			
Containers			
Size			
Type			
Conveyor stands			
High			
Low			

Figure 3.2 General pretest preparation form.

(continued)

Figure 3.2 (continued)

	Quantity	Ready	Loaded
Data forms			
Detector tubes			
Type			
Range			
Electrical equipment			
Adapters, multioutlet			
Extension cords (length)			
Lights			
Filter holder			
Glass, 3 in. glass frit			
Glass, 3 in. s.s. frit			
Gelman, 47 mm			
Alundum thimble			
Impactor (type)			
Fire extinguisher			
First-aid kit			
Fuses for meter box			
Glassware sets			
EPA-5 w/cyclone			
EPA-5 w/cyclone bypass			
EPA-5 hotbox only			
EPA-6 SO ₂			
EPA-8 sulfuric acid mist			
EPA-13A fluoride			
EPA-13B fluoride			
Other			

(continued)

Figure 3.2 (continued)

	Quantity	Ready	Loaded
Gloves			
Work			
Asbestos			
Heaters			
Catalytic			
Electric			
Hoist			
Hotplate			
Ice chest			
Ladder			
Manometers			
Inclined/micro/magnehelix			
0-0.25 in. H ₂ O			
0-1.00 in. H ₂ O			
0-2.00 in. H ₂ O			
0-3.00 in. H ₂ O			
U-tube			
0-16 in. H ₂ O			
0-36 in. H ₂ O			
0-36 in. Hg			
Meter boxes (calibrated and checked)			
Meter, dry gas with thermometers			
Toolbox with standard accessories			
Moisture tubes			
Nomographs			
NO _x sampling apparatus			
Probe			
Length			
Type			

(continued)

Figure 3.2 (continued)

			Quantity	Ready	Loaded
Manifold kit with attachments					
2-l flask w/stoppers					
0-36 in. Hg manometer					
0-27 in Hg vacuum pump					
Variac for probe heat					
25 ft extension cord					
Orsat gas sampling apparatus					
Probe (length)					
Sample line					
Condenser					
Pump assembly					
Bags					
Orsat analyzer w/squeeze bulb					
small					
large					
Nitrogen cylinder w/valve					
Fyrite sampler w/squeeze bulb					
Orsat and Fyrite reagents					
CO ₂					
O ₂					
CO					
Probes (except NO _x)	Total length	Gasket			
Stainless steel					
2 ft					
3 ft					
4 ft					
5 ft					

(continued)

Figure 3.2 (continued)

	Quantity	Ready	Loaded
6 ft			
8 ft			
10 ft			
14 ft			
Glass tube			
2 ft			
3 ft			
4 ft			
5 ft			
6 ft			
8 ft			
10 ft			
14 ft			
Method 17 and impactor			
"Nozzles" w/caps			
1/8 in.			
3/16 in.			
1/4 in.			
5/16 in.			
3/8 in.			
7/16 in.			
1/2 in.			

(continued)

Figure 3.2 (continued)

		Quantity	Ready	Loaded
Nozzle calipers				
Pipe wrench (large)				
Pitot tube type	Effective length			
	2 ft			
	3 ft			
	4 ft			
	5 ft			
	6 ft			
	8 ft			
	10 ft			
	14 ft			
Potentiometer				
-160° to 2450°F				
-150° to 1800°F				
Pulley				
Radios (2-way)				
Rags				
Reagents				
Acetone, gal				
H_2O (distilled), gal				
Methylene chloride, gal				
H_2O_2 (30%) pint				
Isopropyl alcohol (80%) gal				
H_2SO_4 (concentrated)				
Silica gel, lbs				
jars @ 200 g				

(continued)

Figure 3.2 (continued)

	Quantity	Ready	Loaded
Ropes			
Size			
Safety equipment			
Glasses			
Goggles			
Hardhats			
Respirators			
Harness			
Earplugs			
Sample boxes			
EPA 5 - hotbox only			
EPA 5 - particulate			
EPA 6 - SO ₂			
EPA 8 - sulfuric acid mist			
EPA 13A - fluoride			
EPA 13B - fluoride			
Other			
Sample box hook and straps			
Impinger-umbilical cord connector			
Standard			
Hotbox only			
Sample port cover			
Sample containers			
Glass jars, petri dishes, etc.			
Sample shipping boxes			
Screwjacks			
Tape			
Duct			
Electrical			
High temp glass			

(continued)

Figure 3.2 (continued)

		Quantity	Ready	Loaded
Tape measures				
0-8 ft				
0-100 ft				
Tarps				
Test literature				
Thermocouple	Effective length			
	2 ft			
	3 ft			
	4 ft			
	5 ft			
	6 ft			
	8 ft			
	10 ft			
	14 ft			
Thermometer, dial type, long stem				
50°-450°F				
150°-750°F				
200°-1000°F				
Tie cord (spool)				
Toolbox (additional to standard)				
Circular saw				
Drill and bits				
Jigsaw				
Hacksaw				
Handsaw				
Handtools				

(continued)

Figure 3.2 (continued)

			Quantity	Ready	Loaded
Traverse board					
Type	Length				
Tubing	Size	Length			
Polyethylene					
Tygon					
Teflon					
Stainless steel					
Copper					
Other					
Umbilical cord	Length				
Standard					

(continued)

Figure 3.2 (continued)

	Quantity	Ready	Loaded
Hotbox			
Method 17 and impactor			
Variacs			
Warming cords			
Weather gear			
Jumpsuits			
Rainsuits			
Boots			
Ski masks			
Wood assortment			

2. Source Test Analytical Cleanup Checklist

	Quantity	
	Standard	Additional
Ballpoint pens,	6	
Barometer, calibrated	1	
Beakers, 250 ml		
Brush, balance	1	
Nozzle	1	
Probe 6 ft	1	
10 ft	1	
16 ft	1	

(continued)

Figure 3.2 (continued)

	Quantity	
	Standard	Additional
Caps		
Nozzle		
Probe, screw type	2	
Serum	6	
Clamps		
Hose	2	
Pinch no. 12	1 box-12	
Pinch no. 28	1 box-12	
Tubing	1	
Cleanup rack	1	
Filter holders, standard	2	
Hotbox	1	
SO ₂	0	
Filter media		
G.F. 47 mm		
G.F. 3 in.	20	
Paper, 3 in. Whatman		
Impactor		
Thimbles		
Funnels, standard	2	
Silica gel	2	
Polyethylene	1	
Glass wool	1 jar	
Graduated cylinders,		
25 ml	1	
50 ml	1	
100 ml	1	
250 ml	2	
500 ml	1	

(continued)

Figure 3.2 (continued)

	Quantity	
	Standard	Additional
Guth bottles		
Acetone	1	
Spare	1	
Water	1	
Kimwipes	2 boxes	
Knife		
Labels	10	
Marking pens (sharp, water resistant)	1	
Parafilm, box	1	
Pipe cleaners	6	
Rubberbands	10	
Pencils		
Grease	4	
Regular	6	
Petri dishes, 3 in.	4-5	
Pipette bulbs		
Pipettes, 5 ml		
10 ml		
25 ml		
Policemen, Teflon	1	
Scissors	1	
Screwdriver		
Phillips	1	
Regular	1	
Stopcock grease, tube	1	
Tape		
Duct	1	
High temp	1	
Label		

(continued)

Figure 3.2 (continued)

	Quantity	
	Standard	Additional
Tape measure, 8 ft	1	
Thermometer, mercury, 6 in. pocket	1	
Thimble gaskets		
Filter		
Holder		
Tubing		
Rubber, assorted sizes, 3 ft	Assorted	
Tygon, assorted sizes, 3 ft	Assorted	
Tweezers	2	
Wrenches		
Adjustable	2	
Pipe		

(nonuniform or insufficient pumping action). Check oiler jars, if used, every 10 tests.

3.1.5 Dry Gas Meter - A dry gas meter calibration check should be made using the procedure in Section 3.4.2.

3.1.6 Silica Gel - Either dry the used silica gel at 175°C (350°F) or use fresh silica gel and weigh several 200- to 300-g portions in airtight containers to the nearest 0.5 g. Record the total weight (silica gel plus container) for each container. The silica gel does not have to be weighed if the moisture content is not to be determined.

3.1.7 Thermometers - The thermometers should be compared to the mercury-in-glass reference thermometer at ambient temperature.

3.1.8 Barometer - The field barometer should be compared with the mercury-in-glass barometer or the weather station reading, after making an elevation correction, prior to each field trip.

3.2 Reagents and Equipment

3.2.1 Sampling

Filters - Check the filters visually against light for irregularities, flaws, and pinhole leaks. Either label the filters on the backside near the edge using numbering machine ink, or label the petri dishes and keep the filters in their respective dishes except during actual sampling and weighing.

Dessicate the filters at 20° ±5.6°C (68° ±10°F) and at ambient pressure for at least 24 h, and then weigh at 6-h intervals until weight changes of <0.5 mg from the previous weighings are achieved. During each weighing, the filter must not be exposed to the laboratory atmosphere for >2 min or to a relative humidity of >50%. An alternative procedure is oven drying the filters at 105°C (220°F) for 2 to 3 h followed by desiccation for 2 h and by weighing to a constant weight, as described above. A 0.5-g Class-S standard weight (Class-S weight within 1 g of the filter weight) should be placed on the analytical balance prior to each series of weighings. Either the balance should agree within ±0.5 mg of the Class-S weight(s)

or the balance should be corrected. A data form should be kept with the balance at all times for recording the dates and acceptabilities of the balance checks. Record the final weight to the nearest 0.1 mg.

Water - 100 ml of deionized distilled water is needed for each of the first two impingers.

Ice - Crushed ice is needed to keep the gas that exits into the last impinger below 21°C (70°F).

Stopcock grease - Silicone grease that is acetone insoluble and heat stable may be used sparingly at each connection point of the sampling train to prevent gas leaks. This is not necessary if screw-on connectors with Teflon (or similar) sleeves are used.

Acetone recovery - Acetone will be required on site for rinsing the probe and the glassware that is upstream from the filter holder. Deionized distilled water will be required if the impinger solutions are to be recovered for analysis.

3.3 Equipment Packing

The accessibility, condition, and functioning of measurement devices in the field depend on careful packing and on the careful movement on site. Equipment should be packed to withstand severe treatment during shipping and field handling operations. One major consideration in shipping cases is the construction materials. The following containers are suggested, but are not mandatory.

3.3.1 Probe - Seal the inlet and outlet of the probe to protect the probe from breakage. Then pack the probe inside the container lined with polyethylene or other suitable material. An ideal container is a wooden case (or the equivalent) lined with foam material with separate compartments to hold the individual probes. The case should have handles or eye-hooks that can withstand hoisting and that will be rigid enough to prevent bending or twisting during shipping and handling.

3.3.2 Impingers, Connectors, and Assorted Glassware - All impingers and glassware should be packed in rigid containers and protected by polyethylene or other suitable material.

Individual compartments for glassware will help to organize and protect each piece.

3.3.3 Volumetric Glassware - A sturdy case lined with foam material can contain drying tubes and assorted volumetric glassware.

3.3.4 Meter Box - The meter box--which contains the manometers, orifice meter, vacuum gauge, pump, dry gas meter, and thermometers--should be packed in a shipping container unless its housing is sufficient to protect components during travel. Additional pump oil should be packed if oil is required. It is advisable to carry a spare meter box in case of failure.

3.3.5 Wash Bottles and Storage Containers - Storage containers and miscellaneous glassware should be packed in a rigid foam-lined container.

Table 3.1 ACTIVITY MATRIX FOR PRESAMPLING OPERATIONS

Apparatus	Acceptance limits	Frequency and method of measurements	Action if requirements are not met
Probe	<p>1. Probe liner free of contaminants and constructed of borosilicate glass, quartz, or equivalent; metal liner must be approved by administrator</p> <p>2. Probe leak free at 380 mm (15 in.) Hg</p> <p>3. Probe heating system prevents moisture condensation</p>	<p>1. Clean probe internally by brushing with tap water, deionized distilled water, and acetone; air dry before test</p> <p>2. Visually check before test</p> <p>3. Check heating system initially and when moisture cannot be prevented during testing (Sec 3.4.1)</p>	<p>1. Repeat cleaning and assembly procedures</p> <p>2. Replace</p> <p>3. Repair or replace</p>
Impingers, filter holders, and glass containers	Clean and free of breaks, cracks, leaks, etc.	Clean with detergent, tap water, and deionized distilled water	Repair or discard
Pump	Sampling rate of 0.02-0.03 m ³ /min (0.66 to 1.0 ft ³ /min) up to 380 mm (15 in.) Hg at pump inlet	Service every 3 mo or upon erratic behavior; check oiler jars every 10 tests	Repair or return to manufacturer
Dry gas meter	Clean and readings within $\pm 2\%$ of average calibration factor	Calibrate according to Sec 3.4.2; check for excess oil	As above
<u>Reagents and Equipment</u>			
Sampling filters	Free of irregularities, flaws, pinhole leaks; desiccate 24 h at 20 ^o $\pm 5.6^{\circ}\text{C}$ (68 ^o $\pm 10^{\circ}\text{F}$), or oven dry at 105 ^o (220 ^o F) 2 to 3 h; constant weight ± 0.1 mg	Visually check prior to testing; weigh on balance to 0.1 mg prior to field use	Replace

(continued)

Table 3.1 (continued)

Apparatus	Acceptance limits	Frequency and method of measurements	Action if requirements are not met
Water	Deionized distilled conforming to ASTM-D1193-74, Type 3	Run blank evaporations prior to field use to eliminate high solids (only required if impinger contents to be analyzed)	Redistill or replace
Stopcock grease	Acetone insoluble, heat stable silicone grease	Check label data upon receipt	Replace
Sample recovery acetone	Reagent grade, $\leq 0.001\%$ residue, in glass bottles	Run blank evaporations upon receipt	Replace or return to supplier
<u>Packing Equipment for Shipment</u>			
Probe	Rigid container protected by polyethylene foam	Prior to each shipment	Repack
Impingers, containers, and assorted glassware	Rigid container protected by polyethylene foam	As above	As above
Pump	Sturdy case lined with polyethylene foam material if not part of meter box	As above	As above
Meter box	Meter box case and/or additional material to protect train components; pack spare meter box	As above	As above
Wash bottles and storage containers	Rigid foam-lined container	As above	As above

4.0 ON-SITE MEASUREMENTS

The on-site activities include transporting equipment to the test site, unpacking and assembling the equipment, making duct measurements, performing the velocity traverse, determining molecular weights and stack gas moisture contents, sampling for particulates, and recording the data. Table 4.1 at the end of this section summarizes the quality assurance activities for on-site activities. Blank data forms are in Section 3.4.12 for the convenience of the Handbook user.

4.1 Handling of Equipment

The most efficient means of transporting or moving the equipment from ground level to the sampling site should be decided during the preliminary site visit (or prior correspondence). Care should be exercised to prevent damage to the test equipment or injury to test personnel during the moving phase. A "laboratory" area should be designated for assembling the sampling train, placing the filter in the filter holder, charging the impingers, recovering the sample, and documenting the results; this area should be clean and free of excessive drafts.

4.2 Sampling

The on-site sampling includes preliminary measurements and setup, placing the filter in the filter holder, setting up the sampling train, preparing the probe, checking for leaks along the entire train, inserting the probe into the stack, sealing the port, checking the temperature of the probe, sampling at designated points, and recording the data. A final leak check must always be performed upon completion of the sampling.

4.2.1 Preliminary Measurements and Setup - The sampling site should be selected in accordance with Method 1. If this is impossible due to duct configuration or other reasons, the site should be approved by the administrator. A 115-V, 30-A electrical supply is necessary to operate the standard sampling train.

Either measure the stack and determine the minimum number of traverse points by Method 1, or check the traverse points determined during the preliminary site visit (Section 3.0). Record all data on the traverse point location form shown in Method 1. These measurements will be used to locate the pitot tube and the sampling probe during preliminary measurements and actual sampling.

4.2.2 Stack Parameters - Check the sampling site for cyclonic or nonparallel flow as described in Method 1 (Section 3.0). The sampling site must be acceptable before a valid sample can be taken. Determine the stack pressure, temperature, and the range of velocity heads encountered (Method 2). Determine the moisture content using the approximation Method 4 or its alternatives for the purpose of setting the isokinetic sampling rate. If the particular source has been tested before or if a good estimate of the moisture is available, this should be sufficient. The Reference Method (Section 3.4.10) uses the condensate collected during sampling to determine the moisture content used in final calculations. If the stack is saturated with moisture or has water droplets, the moisture content must also be determined by partial pressure with the use of a more accurate stack gas temperature sensor (Method 4).

Determine the dry molecular weight of the stack gas, as required in Method 2. If an integrated gas sample is required, follow Method 3 procedures and take the gas sample simultaneously with and for the same total length of time as the particulate run. The sampling and the analytical data forms for molecular weight determinations are in Method 3.

Using the stack parameters obtained by these preliminary measurements, the user can set up the nomograph as outlined in APTD-0576.⁴ An example nomograph data form is Figure 4.1.

Select a nozzle size based on the range of velocity heads, so that it is not necessary to change the size to maintain isokinetic sampling rates during the run. Install the selected nozzle

Plant Pollution Free Inc.
Date 7-12-77
Sampling location Boiler outlet

Calibrated pressure differential across orifice, in. H ₂ O	$\Delta H_{@}$	1.91
Average meter temperature (ambient + 20°F), °F	$t_{m_{avg}}$	80
Percent moisture in gas stream by volume, %	B_{wo}	0.06
Barometric pressure at meter, in. Hg	P_m	29.48
Static pressure in stack, in. Hg ($P_m \pm 0.073 \times$ stack gauge pressure, in. H ₂ O)	P_s	-0.01
Ratio of static pressure to meter pressure	P_s/P_m	1
Average stack temperature, °F	$t_{s_{avg}}$	540
Average velocity head, in. H ₂ O	Δp_{avg}	0.1
Maximum velocity head, in. H ₂ O	Δp_{max}	0.3
C factor		1.0
Calculated nozzle diameter, in.		0.385
Actual nozzle diameter, in.		0.375
Reference Δp , in. H ₂ O		.148

Figure 4.1 Nomograph data form (English units).

using a Vitron A O-ring when either glass or stainless steel liners are used. The tester may opt to install the nozzle on a stainless steel liner by a leak-free mechanical connection (see APTD-0576 for details⁴). Other connecting systems such as Teflon ferrules may be used. Mark the probe with heat resistant tape or by some other acceptable method to denote the proper distance into the stack or duct for each sampling point.

Select a total sampling time greater than or equal to the minimum total sampling time specified in the test procedures for the specific industry so that:

1. The sampling time per point is ≥ 2 min (greater time interval may be specified by the administrator).

2. The sample volume corrected to standard conditions exceeds the required minimum total gas sample volume.

The latter can be based on an approximate average sampling rate. It is recommended that the number of minutes sampled at each point be either an integer or an integer plus one-half minute to avoid timekeeping errors. In some circumstances (e.g., batch cycles), it may be necessary to sample for shorter times at the traverse points and to obtain smaller gas sample volumes. In these cases, the administrator's approval must be obtained first.

4.2.3 Sampling Train Preparation - During preparation of the sampling train, keep all openings where contamination can occur covered until just prior to assembly or until sampling commences.

Place 100 ml of distilled water (a graduated cylinder may be used) in each of the first two impingers; leave the third impinger empty; and place ≥ 200 -300 g of preweighed silica gel in the fourth impinger. Record the weight of the silica gel and the container on the appropriate data form. Place the empty container in a safe place for use later in the sample recovery. If moisture content is to be determined by impinger analysis, weigh each of the first three impingers to the nearest 0.5 g, and record these weights.

Using a tweezer or clean disposable surgical gloves, place a filter in the filter holder. Be sure that the filter is properly centered and that the gasket is properly placed to prevent the sample gas stream from circumventing the filter. Check the filter for tears after the assembly is completed.

4.2.4 Sampling Train Assemblage - Assemble the train as shown in Figure 1.1, using (if necessary) a very light coat of silicone grease only on the outside of all ground-glass joints to avoid contamination. Place crushed ice and water around the impingers.

If not already an integral part of the probe assembly, a temperature sensor should be attached to the metal sheath of the sampling probe so that the sensor extends beyond the probe tip and does not touch any metal. Its position should be about 1.9 to 2.54 cm (0.75 to 1 in.) from the pitot tube and the nozzle to avoid interference with the gas flow. Alternative arrangements are shown in Method 2.

4.2.5 Sampling Train Leak Checks - Leak checks are necessary to assure that the sample has not been biased low by dilution air. The Reference Method (Section 3.4.10) specifies that leak checks be performed at certain times as discussed below.

Pretest - A pretest leak check is recommended, but not required. If the tester opts to conduct the pretest leak check, the following procedure should be used:

After the sampling train has been assembled, set the filter heating system at the desired operating temperature. Allow time for the temperature to stabilize. If a Vitron A O-ring or other leak-free gasket is used in connecting the probe nozzle to the probe liner, leak check the train at the sampling site by plugging the nozzle and pulling a 380 mm (15 in.) Hg vacuum.

Note: A lower vacuum may be used if it is not exceeded during the test.

If an asbestos string is used for the probe gasket, do not connect the probe to the train during the leak check. Instead, leak check the train by first plugging the inlet to the filter

holder and pulling a 380 mm (15 in.) Hg vacuum (see previous note). Then connect the probe to the train and leak check at about 25 mm (1 in.) Hg vacuum; alternatively, the probe may be leak checked with the rest of the sampling train in one step at a 380 mm (15 in.) Hg vacuum. Leakage rates $>4\%$ of the average sampling rate or $0.00057 \text{ m}^3/\text{min}$ ($0.02 \text{ ft}^3/\text{min}$), whichever is less, are unacceptable.

The following leak-check instructions for the sampling train are taken from APTD-0581³ and APTD-0576.⁴ Start the pump with the bypass valve fully open and the coarse adjust valve closed. Open the coarse adjust valve and then slowly close the bypass valve until the desired vacuum is reached. Do not reverse the direction of the bypass valve; this will cause distilled water to back up from the impingers into the filter holder. If the desired vacuum is exceeded, either leak check at this higher vacuum or end the leak check as described below and start over.

When the leak check is complete, first slowly remove the plug from the inlet to the probe or the filter holder and then close the coarse adjust valve and immediately turn off the vacuum pump. (This prevents the water in the impingers from being forced back into the filter holder and prevents the silica gel from being forced back into the third impinger.) Visually check to be sure water did not contact the filter and that the filter has no tears before beginning the test.

During the Sampling - If a component (e.g., filter assembly or impinger) change is necessary during the sampling run, a leak check should be conducted before the change. The leak check should be done according to the procedure outlined above, except that it should be at a vacuum equal to or greater than the maximum value recorded up to that point in the test. If the leakage rate is $\leq 0.00057 \text{ m}^3/\text{min}$ ($0.02 \text{ ft}^3/\text{min}$) or 4% of the average sampling rate (whichever is less), the results are acceptable, and no correction need be applied to the total volume of dry gas metered. If, however, a higher leakage rate is obtained, the

tester either should record the leakage rate and plan to correct the sample volume as shown in Section 6.3(b) of the Reference Method (Section 3.4.10), or should void the sampling run. Note: Be sure to record the dry gas meter reading before and after each leak check performed during and after each test run so that the sample volume can be corrected.

Posttest - A leak check is mandatory at the conclusion of each sampling run. The leak check should be in accordance with the procedures in this section and at a vacuum equal to or greater than the maximum value reached during the sampling run. If the leakage rate is $\leq 0.00057 \text{ m}^3/\text{min}$ ($0.02 \text{ ft}^3/\text{min}$) or 4% of the average sampling rate (whichever is less), the results are acceptable, and no correction need be applied to the total volume of dry gas metered. If, however, a higher leakage rate is obtained, the tester either should record the leakage rate and correct the sample volume as shown in Section 6.3(a) or 6.3(b) of the Reference Method (Section 3.4.10), or should void the sample run. Note: Be sure to record the dry gas meter reading before and after performing the leak check so that the sample volume can be corrected.

4.2.6 Sampling Train Operation - Just prior to sampling, clean the portholes to minimize the chance of sampling deposited material. Verify that the probe and the filter heating systems are up to the desired temperatures and that the pitot tube and the nozzle are located properly. Follow the procedure below for sampling.

1. Record the initial dry gas meter readings, barometric pressure, and other data as indicated in Figure 4.2.

2. Position the tip of the probe at the first sampling point with the nozzle tip pointing directly into the gas stream. When in position, block off the open area around the probe and the porthole to prevent flow disturbances and unrepresentative dilution of the gas stream.

Plant ACME POWER PLANT Meter calibration (Y) 1.013 Sheet 1 of 1
 City MEGAWATT, OH Pitot tube (C) 0.84 Nozzle identification number 31
 Location UNIT 5, OUTLET Probe length 10 FT Nozzle diameter 0.3080 mm (in.)
 Operator M. READEE Probe liner material 5. STEEL Thermometer number CF56
 Date 2-31-78 Probe heater setting 0.7 Final leak rate 0.001 m³/min (cfm)
 Run number APP-1 Ambient temperature 40 Vacuum during leak check 3.0 mm (in.) Hg
 Stack diam, ~~mm~~ (in.) 102 Barometric pressure (P_b) 29.23 mm (in.) Hg
 Sample box number A Assumed moisture 8% Filter number 100217
 Meter box number FB-1 Static pressure (P_a) -0.6 mm (in.) H₂O Remarks _____
 Meter ΔH@ 1.87 C Factor 0.96 _____
 Reference ΔP 0.295 mm (in.) H₂O _____

Traverse point number	Sampling time, (θ), min	Clock time, (24 h)	Vacuum, mm (in.) Hg	Stack temperature (T), °C (°F)	Velocity head (ΔP _s), mm (in.) H ₂ O	Pressure differential across orifice meter (ΔH), mm (in.) H ₂ O	Gas sample volume (V), m ³ (ft ³)	Gas sample temperature at dry gas meter		Temperature of gas leaving condenser or last impinger, °C (°F)	Filter temp, °C (°F)
								Inlet, °C (°F)	Outlet, °C (°F)		
START	0	1332	—	—	—	—	181.733	—	—	—	—
N-1	5		1.0	309	0.37	2.3	185.792	45	46	47	280
2	10		1.0	312	0.35	2.2	189.784	53	46	48	250
3	15		2.0	314	0.36	2.25	193.773	58	47	48	250
4	20		2.0	311	0.36	2.25	197.835	60	48	49	260
5	25		2.5	315	0.40	2.5	202.058	61	49	50	270
6	30	1402	2.0	313	0.39	2.4	206.189	61	50	50	270
E-1	35	1420	2.5	311	0.43	2.7	211.184	62	50	51	
2	40		2.5	314	0.43	2.7	214.848	62	51	51	
3	45		2.5	313	0.40	2.5	219.085	61	51	51	
4	50		2.5	313	0.35	2.2	223.142	61	51	50	
5	55		2.5	312	0.29	1.8	226.793	62	50	51	
6	60	1445	2.0	311	0.28	1.7	230.380	62	51	52	
	Total 60		Max 2.5	Avg 312.3			Total 48.647	Avg 59	Avg 49	Max 52	

Figure 4.2 Particulate field data form.

3. Turn on the pump and immediately adjust the sample flow to attain isokinetic conditions. Nomographs, calculator programs, and routines are available to aid in the rapid determination of the orifice pressure drop corresponding to the isokinetic sampling rate. If the nomograph is designed as shown in APTD-0576,⁴ it can be used only with an Type S pitot tube which has a C_p coefficient of 0.85 ± 0.02 and when the stack gas dry molecular weight (M_s) is 29 ± 4 . If C_p and M_s are outside these ranges, do not use the nomograph without compensating for the differences. Recalibrate isokinetic rate or reset nomograph if the absolute stack temperature (T_s) changes more than 10%.

4. Take other readings required by Figure 4.2 at least once at each sampling point during each time increment.

5. Record the dry gas meter readings at the end of each time increment.

6. Repeat steps 3 through 5 for each sampling point.

7. Turn off the pump, remove the probe from the stack, and record the final readings after each traverse.

8. Conduct the mandatory posttest leak check (Subsection 4.2.5) at the conclusion of the last traverse. Record any leakage rate. Also, leak check the pitot lines (Method 2, Section 2.1); the lines must pass this leak check to validate the velocity pressure data.

9. Disconnect the probe, and then cap the nozzle and the end of the probe with polyethylene or equivalent caps.

During the test run, a sampling rate of $\pm 10\%$ of the isokinetic rate must be maintained unless otherwise specified by the administrator. The sampling rate must be adjusted at any sampling point if a 20% variation in velocity pressure occurs.

Periodically during the test, observe the connecting glassware--from the probe, through the filter, to the first impinger--for water condensation. If any is evident, adjust the probe and/or filter heater setting upward until the condensation is eliminated; add ice around the impingers to maintain the silica gel exit temperature at 20°C (68°F).

The manometer level and zero should also be checked periodically during each traverse. Vibrations and temperature fluctuations can cause the manometer zero to shift.

4.3 Sample Recovery

The Reference Method (Section 3.4.10) requires that the sample be recovered from the probe, from all glassware preceding the filter, from the front half of the filter holder, and from the filter in an area sheltered from wind and dust to prevent contamination of the sample. The capped-off impinger box and the capped sampling probe can be transported to the cleanup area without risk of losing or contaminating the sample.

4.3.1 Filter - Initially take three unused filters for each field test series and label them as filter blanks. (These three should have been tared when the sample filters were tared, since they are used as the control samples for the check on the analytical balance.) The filter used for the sample run should be recovered. Using a pair of tweezers and/or clean disposable surgical type gloves, carefully remove the filter from the filter holder, and place it in its designated petri dish. Any filter fibers or particulates which adhere to the filter gasket should be removed with a nylon bristle brush or a sharp blade and placed in the container, which should then be closed, sealed, and labeled.

4.3.2 Probe and Connecting Glassware - Initially, put a minimum of 200 ml of the acetone used for sample recovery in a sample bottle, mark the liquid level, seal, and label the bottle (Figure 4.3). Then enter the bottle number on the sample recovery and integrity form (Figure 4.4). A single sample bottle is usually adequate for the collection of all the rinses; it should be labeled and recorded in the same manner as the blank sample.

Clean the outside of the probe, the pitot tube, and the nozzle to prevent particulates from being brushed into the sample bottle. Carefully remove the probe nozzle, and rinse the

Plant <u>Acme Power Plant</u>	City <u>Greentown, Wisconsin</u>	Remarks: 	
Site <u>Boiler outlet</u>	Sample type <u>Acetone Rinse</u>		
Date <u>7-28-78</u>	Run number <u>APP-1</u>		
Front rinse <input checked="" 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 <u>Acetone</u>	Level marked <u>yes</u>		
Volume: Initial <u>100 ml</u>	Final <u>100 ml</u>		
Clean up by <u>T. Clark</u>			

Figure 4.3. Example of a sample label.

inside surface (using a nylon bristle brush and several acetone rinses) into the sample bottle until no particles are visible in the rinse. Clean the swagelok fitting by the same procedure.

The following probe rinsing procedure should be performed by two people to preclude sample loss.

1. Rinse the probe liner by tilting and rotating the probe while squirting acetone into the upper (or nozzle) end to assure complete wetting of the inside surface.

2. Allow the acetone to drain into the sample bottle using a funnel to prevent spillage.

3. Hold the probe in an inclined position and squirt acetone into the upper end while pushing the probe brush through the liner with a twisting motion, and catch the drainage in the sample bottle. Repeat the brushing procedure three or more times (six or more when metal probe liners are used) until no particles are visible in the drainage or until a visual inspection of the liner reveals none remaining inside.

4. Rinse the liner once more.

Plant ACME POWER PLANT Sample date 7-28-79
Sample location BOILER 1 OUTLET Run number APP-1
Sample recovery person T. CLARK Recovery date 7-28-79
Filter(s) number 23007

MOISTURE

<u>Impingers</u>		<u>Silica gel</u>	
Final volume (wt)	<u>225</u> ml (g)	Final wt	<u>210</u> g _____ g
Initial volume (wt)	<u>200</u> ml (g)	Initial wt	<u>200</u> g _____ g
Net volume (wt)	<u>75</u> ml (g)	Net wt	<u>10</u> g _____ g
Total moisture	<u>85</u> g		
Color of silica gel	<u>1/4 spent</u>		
Description of impinger water	<u>Slightly cloudy</u>		

RECOVERED SAMPLE

Blank filter container number 23000 Sealed? YES
 Filter container number 23007C Sealed? YES
 Description of particulate on filter Light grey

Acetone rinse container number 22007 Liquid level marked? YES
Acetone blank container number 22000 Liquid level marked? YES
Samples stored and locked? YES
Remarks _____

Date of laboratory custody 7-29-79
Laboratory personnel taking custody T. WAGNER
Remarks

Figure 4.4 Sample recovery and integrity data form.

5. Rinse the brush to collect any particulates which may be retained within the bristles.

6. Wipe all the connecting joints clean of silicone grease, and clean the inside of the front half of the filter holder by rubbing the surface with a nylon bristle brush and rinsing it with acetone. Repeat the procedure at least three times or until no particles are evident in the rinse.

7. Make a final rinse of the filter holder and brush.

8. Clean any connecting glassware which precedes the filter holder, using step 6.

After all the rinsings have been collected, tighten the lid on the sample bottle securely. As a precaution in case of leakage, mark the acetone level on the bottle, and note it on the sample recovery form (Figure 4.4).

4.3.3 Impinger Water - Make a notation on the sample recovery form (Figure 4.4) of any color or film in the impinger water. Determine the liquid quantity in the impingers either by measuring the volume to the nearest 1 ml with a graduated cylinder or by weighing it to the nearest 0.5 g with a balance. Record the data appropriately on the same sample recovery form. If a different type of condenser is used, determine the liquid catch gravimetrically or volumetrically employing a suitable procedure.

After determining the liquid gain, discard the water unless it is to be further analyzed. In this case, follow the sample recovery procedures recommended by the control agency requiring the analysis.

4.3.4 Silica Gel - Note the color of the indicating silica gel to determine whether it has been completely spent, and make a notation of its condition on Figure 4.4.

1. Transfer the silica gel from the fourth impinger to its original container using a funnel and a rubber policeman, and seal the container. It is not necessary to remove the small amount of dust particles that may adhere to the impinger wall; since the weight gain is used for moisture calculations, do not use water or other liquids to transfer the silica gel.

2. Determine the final weight gain to the nearest 0.5 g, if a balance is available.

4.4 Sample Logistics (Data) and Packing of Equipment

Follow the above procedures until the required number of runs are completed. Log all data on the sample recovery form (Figure 4.4). If the probe and glassware (impinger, filter holder, and connectors) are to be used in the next test, rinse all with distilled deionized water and then acetone. The following are recommended after the test.

1. Check all sample containers for proper labeling (time, date, and location of tests, number of tests, and any other pertinent data). Be sure a blank has been taken and labeled.

2. Record all data taken during the field test in duplicate by using either carbon paper or data forms and a field laboratory notebook. Avoid the use of water soluble pens. One set of data should be mailed to the base laboratory, given to another team member, or given to the agency; the other set should be handcarried. Duplication can prevent costly embarrassing mistakes.

3. Examine all sample and blank containers and sampling equipment for damage and for proper packing for shipment to the base laboratory. Label all shipping containers to prevent loss of samples or equipment.

4. A quick check of sampling and sample recovery procedures can be made using the on-site checklist, Figure 4.5.

Apparatus

Probe nozzle: stainless steel ☒ glass ☐
Button-hook ☒ elbow ☐ size ☐
Clean? ☐
Probe liner: borosilicate ☒ quartz ☐ other ☐
Clean? ☐
Heating system* ☐
Checked? ☐
Pitot tube: Type S ☒ other ☐
Properly attached to probe?* ☐
Modifications ☐
Pitot tube coefficient ☐
Differential pressure gauge: two inclined manometers ☒
other ☐ sensitivity 0.01 - 0 to 1
Filter holder: borosilicate glass ☒ glass frit ☒
filter support ☐ silicone gasket ☐ other ☐
Clean? ☒
Condenser: number of impingers std.
Clean? ☒
Contents: 1st 100 ml H₂O 2nd 100 ml H₂O 3rd ☐ 4th Silica gel
Cooling system ice / water
Proper connections? ☒
Modifications N/A
Barometer: mercury ☐ aneroid ☒ other ☐
Gas density determination: temperature sensor type thermocouple
pressure gauge 20 in. - U-tube manometer
temperature sensor properly attached to probe?* ☒

Procedure

Recent calibration: pitot tubes* ☒ dimensional check
meter box* ☒ thermometers/thermocouples* ☒
Filters checked visually for irregularities?* yes
Filters properly labeled?* yes
Sampling site properly selected? yes
Nozzle size properly selected?* yes
Selection of sampling time? yes
All openings to sampling train plugged to prevent pretest contamination? yes
Impingers properly assembled? yes
Filter properly centered? yes
Pitot tube lines checked for plugging or leaks?* yes
Meter box leveled? yes Periodically? yes
Manometers zeroed? yes

Figure 4.5 On-site measurements.

(continued)

Figure 4.5 (continued)

$\Delta H@$ from most recent calibration 1.90
Nomograph setup properly? Yes
Care taken to avoid scraping nipple or stack wall?* Yes
Effective seal around probe when in-stack? Yes
Probe moved at proper time? Yes
Nozzle and pitot tube parallel to stack wall at all times?* Yes
Filter changed during run? No
Any particulate lost? No
Data forms complete and data properly recorded?* Yes
Nomograph setting changed when stack temp changed significantly?
Yes
Velocity pressure and orifice pressure readings recorded
accurately?* Yes
Posttest leak check performed?* Yes (mandatory)
Leakage rate 0.01 @ in. Hg 15 in.
Orsat analysis Yes from stack integrated ✓
Fyrite combustion analysis sample location
Bag system leakchecked?* Yes
If data forms cannot be copied, record:
approximate stack temp 317°F volume metered 81 ft³
% isokinetic calculated at end of each run 99%

SAMPLE RECOVERY

Brushes: nylon bristle Yes other _____
Clean? Yes
Wash bottles: glass Yes
Clean? Yes
Storage containers: borosilicate glass Yes other _____
Clean? Yes Leakfree? Yes
Petri dishes: glass Yes polyethylene _____ other _____
Clean? Yes
Graduated cylinder/or balance: subdivisions <2 ml?* Yes
other _____
Balance: type triple beam
Plastic storage containers: airtight? Yes
Clean? Yes
Probe allowed to cool sufficiently? Yes (25 min)
Cap placed over nozzle tip to prevent loss of particulate?* _____
Yes
During sampling train disassembly, are all openings capped? Yes
Clean-up area description: Power Plant Lab
Clean? Yes Protected from wind? Yes
Filters: glass fiber Yes type 1106 BH
Silica gel: type (6 to 16 mesh)? new? Yes used? _____
Color? blue Condition? good

(continued)

Figure 4.5 (continued)

Filter handling: tweezers used? Yes
surgical gloves? _____ other _____
Any particulate spilled?* No
Water distilled? Yes
Stopcock grease: acetone-insoluble? Yes
heat-stable silicone? _____ other _____
Probe handling: acetone rinse Yes
distilled water rinse _____
Particulate recovery from: probe nozzle Yes
probe fitting _____ probe liner Yes
front half of filter holder Yes
Blank: acetone Yes distilled water Yes
Any visible particles on filter holder inside probe?:* No
All jars adequately labeled? Yes Sealed tightly? Yes
Liquid level marked on jars?* Yes
Locked up? Yes
Acetone reagent: <0.001% residue? will be checked at lab during analysis.
glass bottles Yes (required)
acetone blanks? Yes

*Most significant items/parameters to be checked.

Table 4.1 ACTIVITY MATRIX FOR ON-SITE MEASUREMENT CHECKS

Apparatus	Acceptance limits	Frequency and method of measurements	Action if requirements are not met
<u>Sampling</u>			
Filter	Centered in holder; no breaks, damage, or contamination during loading	Use tweezers or surgical gloves to load	Discard filter, and reload
Condenser (addition of reagents)	100 ml of distilled water in first two impingers; 200-300 g of silica gel in fourth impinger	Use graduated cylinder to add water, or weigh each impinger and its contents to the nearest 0.5 g	Reassemble system
Assembling sampling train	1. Assembly specifications in Fig 1.1 2. Leak rate $<4\%$ or $0.00057 \text{ m}^3/\text{min}$ ($0.02 \text{ ft}^3/\text{min}$), whichever is less	1. Before each sampling run 2. Leak check before sampling by plugging the nozzle or inlet to first impinger and by pulling a vacuum of 380 mm (15 in.) Hg	1. Reassemble 2. Correct the leak
Sampling (isokinetically)	1. Within $\pm 10\%$ of isokinetic condition 2. Standard checked for minimum sampling time and volume; sampling time/point $>2 \text{ min}$ 3. Minimum number of points specified by Method 1 4. Leakage rate $<0.00057 \text{ m}^3/\text{min}$ ($0.02 \text{ ft}^3/\text{min}$) or 4% of the average sampling volume, whichever is less	1. Calculate for each sample run 2. Make a quick calculation before test, and exact calculation after 3. Check before the first test run by measuring duct and using Method 1 4. Leak check after each test run or before equipment replacement during test at the maximum vacuum during the test (mandatory)	1. Repeat the test run 2. As above 3. Repeat the procedure to comply with specifications of Method 1 4. Correct the sample volume, or repeat the sampling

(continued)

Table 4.1 (continued)

Apparatus	Acceptance limits	Frequency and method of measurements	Action if requirements are not met
Sample recovery	Noncontaminated sample	Transfer sample to labeled polyethylene containers after each test run; mark level of solution in the container	Repeat the sampling
Sample logistics, data collection, and packing of equipment	<ol style="list-style-type: none"> 1. All data recorded correctly 2. All equipment examined for damage and labeled for shipment 3. All sample containers and blanks properly labeled and packaged 	<ol style="list-style-type: none"> 1. After completion of each test and before packing 2. As above 3. Visually check upon completion of each sampling 	<ol style="list-style-type: none"> 1. Complete data 2. Repeat the sampling if damage occurred during the test 3. Correct when possible

5.0 POSTSAMPLING OPERATIONS

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

5.1 Apparatus Checks

Posttest checks will have to be made on most of the sampling apparatus. These checks will include three calibration runs at a single orifice meter setting; cleaning; and/or routine maintenance. Cleaning and maintenance are discussed in Section 3.4.7 and in APTD -0576.⁴ Figure 5.1 should be used to record the posttest checks.

5.1.1 Metering System - The metering system has two components that must be checked--the dry gas meter and the dry gas meter thermometer(s).

The dry gas meter thermometer(s) should be compared with the ASTM mercury-in-glass thermometer at room temperature. If the two readings agree within 6°C (10.8°F), they are acceptable; if not, the thermometer must be recalibrated according to Subsection 2.2 of Section 3.4.2 after the posttest check of the dry gas meter. For calculations, use the dry gas meter thermometer readings (field or recalibration values) that would give the higher temperatures. That is, if the field readings are higher, no correction is necessary, but if the recalibration value is higher, add the difference in the two readings to the average dry gas meter temperature reading.

The posttest check of the dry gas meter is described in Section 3.4.2. The metering system should not have any leaks that were corrected prior to the posttest check. If the dry gas meter calibration factor (Y) deviates by <5% from the initial calibration factor, the dry gas meter volumes obtained during the test series are acceptable. If Y deviates by >5%, recalibrate the metering system (Section 3.4.2). For the calculations, use the calibration factor (initial or recalibration) that yields the lower gas volume for each test run.

Plant Acme Power Plant Calibrated by M Brown
Meter box number FB-1 Date 7/31/79

Dry Gas Meter

Pretest calibration factor, Y 0.986 (within $\pm 2\%$)
Posttest check, Y* 0.987 (within $\pm 5\%$ of pretest)
Recalibration required? yes ☒ no ☐
If yes, recalibration factor, Y 0.986 (within $\pm 2\%$)
Lower calibration factor, Y 0.986 for calculations (pretest or posttest)

Dry Gas Meter Thermometers

Was a pretest temperature correction used? yes ☒ no ☐
If yes, temperature correction (within $\pm 3^{\circ}\text{C}$ (5.4°F) over range)
Posttest comparison with mercury-in-glass thermometer?* (within $\pm 6^{\circ}\text{C}$ (10.8°F) at ambient temperature)
Recalibration required? yes ☒ no ☐
Recalibration temperature correction? (within $\pm 3^{\circ}\text{C}$ (5.4°F) over range)*
If yes, no correction necessary for calculations if meter thermometer temperature is higher; if calibration temperature is higher, add correction to average meter temperature for calculations

Stack Temperature Sensor

Was a pretest temperature correction used? yes ☒ no ☐
If yes, temperature correction $^{\circ}\text{C}$ ($^{\circ}\text{F}$) (within $\pm 1.5\%$ of readings in K ($^{\circ}\text{R}$) over range)
Average stack temperature of compliance test, T_s 780 K ($^{\circ}\text{R}$)
Temperature of reference thermometer or solution for recalibration 528 K ($^{\circ}\text{R}$)* (within $\pm 10\%$ of T_s)
Temperature of stack thermometer for recalibration 528 K ($^{\circ}\text{R}$)
Difference between reference and stack thermometer temperatures, ΔT_s 0 K ($^{\circ}\text{R}$)
Do values agree within $\pm 1.5\%$?* yes ☒ no ☐
If yes, no correction necessary for calculations
If no, calculations must be done twice--once with the recorded values and once with the average stack temperature corrected to correspond to the reference temperature differential (ΔT_s) both final result values must be reported since there is no way to determine which is correct

Figure 5.1 Posttest calibration checks.

(continued)

Figure 5.1 (continued)

Barometer

Was the pretest field barometer reading correct? ☒ yes ☐ no

Posttest comparison?* 29.55 mm (in.) Hg (± 2.5 mm (0.1 in.) Hg)

Was calibration required? ☐ yes ☒ no

If yes, no correction necessary for calculations when the field barometer has a lower reading; if the mercury-in-glass reading is lower, subtract the difference from the field data readings for the calculation

*Most significant items/parameters to be checked.

5.1.2 Stack Temperature Sensors - The stack temperature sensor readings should be compared with the reference thermometer readings.

For thermocouple(s), compare the thermocouple and reference thermometer values at ambient temperature. If the values agree within $\pm 1.5\%$ of the absolute temperature, the calibration is considered valid. If the values do not agree within $\pm 1.5\%$, recalibrate the thermocouple as described in Section 3.4.2 to determine the difference (ΔT_s) at the average stack temperature (T_s). Note: This comparison may be done in the field immediately following the tests.

For thermometers, compare the reference thermometer (1) at ambient temperatures for average stack temperature below 100°C (212°F), (2) in boiling water for stack temperatures from 100°C to 200°C , and (3) in a boiling liquid with the boiling point above 200°C for stack temperature between 200°C to 405°C . For stack temperatures above 405°C compare the stack thermometer with a thermocouple at a temperature within $\pm 10\%$ of the average stack temperature. If the absolute values agree within $\pm 1.5\%$ the calibration is considered valid. If not, determine the error (ΔT_s) to correct the average stack temperature.

5.1.3 Barometer - The field barometer should be compared to the mercury-in-glass barometer. If the readings agree within ± 5 mm (0.2 in.) Hg, the field readings are acceptable; if not, use the lesser calibration value for the calculations. If the field barometer reads lower than the mercury-in-glass barometer, the field data are acceptable. If the mercury-in-glass barometer gives the lower reading, use the difference in the two readings (the adjusted barometric value) in the calculations.

5.2 Analysis (Base Laboratory)

The analytical procedures consist of evaporations and weighings. Although both types of procedures are relatively simple, it is essential that sample handling be minimized and be done carefully to avoid loss and contamination.

For these procedures, the term "constant weight" means either a difference between two consecutive weighings of ≤ 0.5 mg or 1% in the total weight less the tare weight (whichever is greater) with a minimum of 6 h of desiccation between weighings. Class-S standard weights should be used to check the balance before each series of weighings and these weights should be recorded on the analytical balance calibration form (Figure 5.2). The balance results should agree within ± 2 mg of the Class-S weights.

Acetone evaporations should be performed at ambient temperature and pressure. However, they may be performed at elevated temperatures with close supervision if the following precautions are observed:

1. Acetone is highly flammable and has a low flashpoint, 15°C (59°F); therefore, adequate ventilation is essential to prevent vapor concentration around the heat source.
2. The temperature must be below the boiling point of acetone, approximately 56°C (133°F), to prevent "bumping".
3. The acetone solution must be swirled occasionally to maintain an even temperature.

5.2.1 Filter - Leave the filter in the petri dish or transfer the filter and any loose particulate matter to a tared weighing dish and desiccate for a minimum of 24 h. Weigh the filter to a constant weight and record the results to the nearest 0.1 mg on the analytical data form, Figure 5.3.

Alternatively, the sample filter may be oven dried at 105°C (220°F) for 2 to 3 h, allowed to cool in a desiccator and then weighed to a constant weight. Treat the blank filter in the same manner as the sample filter. The average final weight of the blank filters should be within ± 5 mg of the initial tare weight or 2% of the sample weight, whichever is greater. If the above limit is not met, complete the analysis and calculation using the standard procedures and make a note in the test report of the nonagreement. The blank filter may be used in a later test, so

Figure 5.2 Analytical balance calibration form.

Plant ACME Power Plant Run number APP-1
Sample location Boiler 1 Outlet
Relative humidity 50%
Density of acetone (ρ_a) 0.7908 g/ml

Sample type	Sample identifiable	Liquid level marked and/or container sealed
Acetone rinse	yes	✓
filter(s)	yes	✓

Acetone rinse container number 22007
Acetone rinse volume (V_{aw}) 590 ml
Acetone blank residue concentration (C_a) 0.009 mg/g
 $W_a = C_a V_{aw} \rho_a = (0.009) (590) (0.7908) = 4.199$ mg
Date and time of wt 7-30-78 ; 9:00AM Gross wt 104900.5 mg
Date and time of wt 8-2-78 ; 9:15AM Gross wt 104900.5 mg
Average gross wt 104900.5 mg
Tare wt 104290.0 mg
Less acetone blank wt (W_a) 4.199 mg
Weight of particulate in acetone rinse (m_a) 606.381 mg
Filter(s) container number 23007C
Date and time of wt 7-30-78 ; 9:45AM Gross wt 539.0 mg
Date and time of wt 8-1-78 ; 10:15AM Gross wt 539.0 mg
Average gross wt 539.0 mg
Tare wt 419.4 mg
Weight of particulate on filter(s) (m_f) 119.6 mg
Weight of particulate in acetone rinse 606.381 mg
Total weight of particulate (m_n) 725.981 mg

Note: In no case should a blank residue >0.01 mg/g or 0.001% of the weight of acetone used be subtracted from the sample weight.

Remarks _____

Signature of analyst Cheryl Hoffman
Signature of reviewer Craig Caldwell

Figure 5.3 Sample analytical data form.

record the blank filter weight on the blank analysis form, Figure 5.4. To aid the reviewer or the analyst in the filter weighing procedures, the analytical steps are summarized in Figure 5.5.

5.2.2 Acetone Rinse and Acetone Blank - Initially, confirm that no leakage has occurred during transportation of the sample. If a noticeable amount of leakage has occurred, either void the sample or use methods approved by the administrator to correct the final results. Measure the contents in the container either volumetrically to the nearest 1 ml or gravimetrically to the nearest 0.5 g. Transfer the contents to a tared 250-ml beaker. Evaporate to dryness and then desiccate for a minimum of 24 h. Weigh to a constant weight and record the data to the nearest 0.1 mg on the analytical data form (Figure 5.3); record the data for the acetone blank on a separate form, (Figure 5.4). To aid the reviewer or the analyst in the acetone rinse weighing procedures, the analytical steps are summarized in Figure 5.6.

5.2.3 Silica Gel - If not completed in the field, weigh the used silica gel to the nearest 0.5 g, and record the data on the sample recovery form (Figure 4.4).

Plant ACME Power Plant
Sample location Boiler 1 Outlet
Relative humidity 50%
Liquid level marked and container sealed yes
Density of acetone (ρ_a) 0.7908 g/ml
Blank volume (V_a) 300 ml
Date and time of wt 7-30-78, 8:00 AM Gross wt 98382.5 mg
Date and time of wt 8-1-78, 8:00 AM Gross wt 98382.5 mg
Average gross wt 98382.5 mg
Tare wt 98380.365 mg
Weight of blank (m_{ab}) 2.135 mg

$$C_a = \frac{m_{ab}}{V_a \rho_a} = \frac{(2.135)}{(300)(0.7908)} = 0.009 \text{ mg/g}$$

Note: In no case should a blank residue greater than 0.01 mg/g (or 0.001% of the blank weight) be subtracted from the sample weight.

Filters Filter number 2300
Date and time of wt 7-30-78, 8:30 AM Gross wt 410.7 mg
Date and time of wt 8-1-78, 8:45 AM Gross wt 410.7 mg
Average gross wt 410.7 mg
Tare wt 410.7 mg
Difference wt 0.0 mg

Note: Average difference must be less than ± 5 mg or 2% of total sample weight whichever is greater.

Remarks _____

Signature of analyst Cheryl Hoffman

Signature of reviewer Graig Caldwell

Figure 5.4 Blank analytical data form.

Status

- | | |
|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| <div style="text-align: center;">✓</div> <hr style="width: 50px; margin: 0 auto;"/> | 1. Label the filter and/or the petri dish--both with the same label number; label the filter on top and bottom; check each filter visually against the light for irregularities, flaws, and pinhole leaks |
| <div style="text-align: center;">✓</div> <hr style="width: 50px; margin: 0 auto;"/> | 2. Check the desiccator; be sure the lid is sealed tightly and the anhydrous calcium sulfate is dry; if not dry, heat the desiccant in the oven for 2 h at 180-200°C (350°-400°F), and let cool in the balance room before putting it back into the desiccator |
| <div style="text-align: center;">✓</div> <hr style="width: 50px; margin: 0 auto;"/> | 3. Take off the lid of the filter container and desiccate the filter for 24 h; during desiccation, be sure that filters are widely spread, and not overlapping |
| <div style="text-align: center;">✓</div> <hr style="width: 50px; margin: 0 auto;"/> | 4. Adjust the analytical balance to zero, and check the accuracy with a 0.500-g Class-S weights (within ±0.5 mg); use tweezers to carefully place the filter on the pan of the balance, and weigh it to the nearest 0.1 mg. The time of weighing should not be >2 min, and the relative humidity should be <50% |
| <p><u>Very important:</u> Desiccator should be tightly covered immediately after removing the filter to be weighed; never leave the desiccator open while weighing a sample because samples in the desiccator will be exposed to moisture in the room, which will cause gains in their weights</p> | |
| <div style="text-align: center;">✓</div> <hr style="width: 50px; margin: 0 auto;"/> | 5. Put the filter back into the petri dish without the lid, desiccate for ≥6 h and reweigh the filter; the two recorded weights should agree to ±0.5 mg; if not, desiccate for another 6 h and reweigh until weight is constant within ±0.5 mg; keep the tare weight of the filter in file for future use |
| <div style="text-align: center;">✓</div> <hr style="width: 50px; margin: 0 auto;"/> | 6. Be sure the filters that arrived from the field are handled and analyzed whenever possible by the same person who started the project--the person who tared the filters before sampling; use the same balance |

Figure 5.5 Procedure for weighing filters before and after sampling.

(continued)

Figure 5.5 (continued)

- ✓ 7. Perform step #2, and then uncover the filter container and visually examine the filter to see if it is torn; write down all observations that you think will help justify the final data
- ✓ 8. Desiccate the filter for 24 h, and weigh it to the nearest 0.1 mg; record the weight then desiccate again for 6 h, and reweigh; the difference between the two recorded weights should be within ± 0.5 mg; the balance should be zeroed and checked with a 0.500-g Class-S weight, and the relative humidity must be $< 50\%$
- ✓ 9. Continue the processes of desiccating and weighing until consistent data are obtained; however, after the third trial, if no satisfactory data are obtained, confer with the supervisor

Notes

- 1. When weighing the filter and sample, be sure to use a clean brush and to add all particulates or pieces of the filter that might be left in the container
- 2. Be sure to use tweezers to handle the filters; never hold them directly with your hand
- 3. Write down the date and time each time a filter is weighed

Status

I. Preparing Containers for Shipment

- ✓ 1. Select the appropriate size and number of bottles to be shipped to the field; include extra bottles
- ✓ 2. Clean the bottles and caps thoroughly with soap detergent, rinse with tap water, and then rinse at least twice with deionized distilled water
- ✓ 3. Rinse the clean bottles with acetone to get rid of most of the water; remember that one batch of acetone could be used for more than one container
- ✓ 4. Check the containers and the caps individually after they are dry to be sure no detergent or other contaminant is present; tightly cap all containers

II. Handling and Analysis of Acetone Rinse Samples

Important: Blanks and samples should have identical analytical treatments; never handle with bare hands any analysis glassware once tared; always use tongs or disposable gloves

- ✓ 1. Log the samples received from the field, and check each container for leakage; if the sample volume level is marked on the container, check to see if the sample still matches the level, if not, write a note of that
- ✓ 2. Use a dry, clean glass funnel to transfer the acetone rinse into the dry, clean 250-ml graduated cylinder
- ✓ 3. Record the volume of the sample to the nearest 1.0 ml, and transfer it into a dry, clean, tared (to the nearest 0.1 mg) 250- or 300-ml beaker, depending on the volume of the sample; add 50 ml to the recorded sample volume to account for the acetone rinse of all containers

Figure 5.6 Procedure for analysis of acetone rinse samples.

(continued)

Figure 5.6 (continued)

Status

- | | |
|----------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| <u>✓</u> | 4. Rinse the container with two 25-ml portions of acetone (reagent grade); cap the container, and shake very gently; transfer the acetone rinse into the graduated cylinder to rinse it, and then pour the rinse through the funnel into the beaker that contains the sample; thus, the container, the graduated cylinder, and the funnel have been rinsed |
| <u>✓</u> | 5. Repeat steps 3 and 4 for each sample |
| <u>✓</u> | 6. Let the samples and blanks dry at room temperature in a dust-free environment or under a watchglass |
| <u>✓</u> | 7. Weigh a clean, empty dry beaker, and place it in the same atmosphere where the samples are drying to find out if there was any particulate collected on the samples from the surroundings while drying (not mandatory) |
| <u>✓</u> | 8. Transfer the totally evaporated samples and blanks along with the empty beaker into a tightly sealed desiccator that contains dry anhydrous calcium sulfate (CaSO_4) |
| <u>✓</u> | 9. Desiccate for 24 h |
| <u>✓</u> | 10. Zero the balances and check the accuracy with a 100-g Class-S standard weight prior to weighing; the reading should be 100 g \pm 0.5 mg, and the relative humidity in the balance room should be \leq 50% |
| <u>✓</u> | 11. Weigh the samples, blanks, and empty beaker to the nearest 0.1 mg |

It is very important to:

- a. Keep the desiccator tightly closed while weighing
- b. Remove the samples to be weighed from the desiccator one at a time, weigh each, and put each immediately back into the desiccator
- c. Keep the weighing time \leq 2 min
- d. Be sure that both sides of the balance are closed when weighing

(continued)

Figure 5.6 (continued)

Status

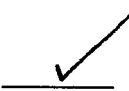
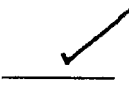
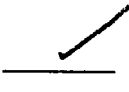
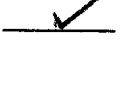

-  e. Turn all balance knobs to zero after the weighings
-  12. Record the weights of the samples, blanks, and empty beaker; record the date and time, each time a sample is weighed
-  13. Desiccate the samples, blanks, and empty beaker for >6 h; data on the first and second weightings should agree within ± 0.5 mg; if not, desiccate again for 6 h and reweigh until consistent data are obtained; after the third trial, consult the supervisor
-  14. If there is >2 mg change in the weight of the empty beaker, note it on the analytical data form
-  15. Calculate the data recorded on the data form (Figures 5.3 and 5.4) provided for this analysis

Table 5.1 ACTIVITY MATRIX FOR POSTSAMPLING OPERATIONS

Apparatus	Acceptance limits	Frequency and method of measurements	Action if requirements are not met
<u>Sampling</u>			
Dry gas meter	Within $\pm 5\%$ of calibration factor	Make three runs at a single, intermediate orifice setting and at highest vacuum occurring during test (Sec 3.4.2)	Recalibrate and use calibration factor that gives lesser sample volume
Meter thermometer	Within $\pm 6^\circ\text{C}$ (10.8°F) at ambient pressure	Compare with ASTM mercury-in-glass thermometer after each field test	Recalibrate and use higher temperature for calculations
Barometer	Within ± 5 mm (0.2 in.) Hg at ambient pressure	Compare with mercury-in-glass barometer after each field test	Recalibrate and use lower barometric values for calculations
Stack temperature	Within $\pm 1.5\%$ of the reference check temperature ($^{\circ}\text{R}$)	After each run, compare with reference temperature	Recalibrate and calculate with and without temperature correction

6.0 CALCULATIONS

Calculation errors due to mathematical mistakes can be a large part of total system error. Therefore, each set of calculations should be repeated or spot checked by a team member other than the one who performed them originally. If a difference greater than a typical roundoff error is detected, the calculations should be checked step by step until the source of error is found and corrected. A computer program can be advantageous in reducing calculation errors. If a standardized computer program is used, the original data entry should 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.

Carry out calculations, retaining at least one significant digit figure beyond that of the acquired data. Roundoff after final calculations to two significant digits for each run or sample in accordance with the ASTM 380-76 procedures. Record the results on Figure 6.1A or 6.1B.

6.1 Nomenclature

The following terms defined and listed alphabetically herein are to be used in calculating dry gas and water vapor volumes, moisture contents, acetone residues, particulate weights and concentrations, and isokinetic variations for each test.

SAMPLE VOLUME (ENGLISH UNITS)

$$V_m = 48.647 \text{ ft}^3, T_m = 514.0^\circ\text{R}, P_{\text{bar}} = 29.23 \text{ in. Hg}$$

$$Y = 1.013, \Delta H = 2.31 \text{ in. H}_2\text{O}$$

$$V_{m(\text{std})} = 17.64 V_m Y \left(\frac{P_{\text{bar}} + (\Delta H/13.6)}{T_m} \right) = 49.722 \text{ ft}^3$$

Equation 6-1

PARTICULATE CONCENTRATION (ENGLISH UNITS)

$$m_n = 50.6 \text{ mg}$$

$$C_s = 2.205 \times 10^{-6} \left(\frac{m_n}{V_{m(\text{std})}} \right) = 0.022 \times 10^{-4} \text{ lb/dscf}$$

Equation 6-8

Figure 6.1A Particulate calculation form (English units).

SAMPLE VOLUME (METRIC UNITS)

$$V_m = 1.377 \text{ m}^3, T_m = 285.^\circ \text{K}, P_{\text{bar}} = 742. \text{ mm Hg}$$

$$Y = 1.013, \Delta H = -52. \text{ mm H}_2\text{O}$$

$$V_{m(\text{std})} = 0.3858 V_m Y \left(\frac{P_{\text{bar}} + (\Delta H/13.6)}{T_m} \right) = 1.402 \text{ m}^3 \quad \text{Equation 6-1}$$

PARTICULATE CONCENTRATION (METRIC UNITS)

$$m_n = -50.6 \text{ mg}$$

$$C_s = 1 \times 10^{-3} \left(\frac{m_n}{V_{m(\text{std})}} \right) = 0.036 \text{ g/dscm}$$

Equation 6-8

Figure 6.1B Particulate calculation form (metric units).

A_n	= Area of nozzle, cross-sectional, m^2 (ft^2)
B_{ws}	= Water vapor in the gas stream, proportion by volume
C_a	= Concentration of acetone blank residue, mg/g
C_s	= Concentration of stack gas particulates, dry basis corrected to standard conditions, g/dscm (lb/dscf)
ΔH	= Average pressure differential across orifice meter, mm (in.) H_2O
I	= Variation of sampling from isokinetic conditions, %
L_a	= Maximum acceptable leakage rate for either a pretest leak check or a leak check following a component change; equal to $0.00057 m^3/min$ ($0.02 ft^3/min$) or 4% of the average sampling rate, whichever is less
L_i	= Individual leakage rate observed during the leak check conducted prior to the "ith" component change ($i = 1, 2, 3, \dots n$), m^3/min (ft^3/min)
L_p	= Leakage rate observed during the posttest leak check, m^3/min (ft^3/min)
m_a	= Mass of acetone residue after evaporation corrected for blank ($m_a = m'_a - W_a$), mg
m'_a	= Mass of acetone residue after evaporation, mg
m_{ab}	= Mass of acetone blank residue after evaporation, mg
m_f	= Filter weight gain, mg
m_n	= Total amount of particulates collected, mg
M_w	= Molecular weight of water, 18.0 g/g-mole (18.0 lb/lb-mole)
P_{bar}	= Barometric pressure at sampling site, mm (in.) Hg
P_s	= Absolute stack pressure, mm (in.) Hg
P_{std}	= Standard absolute pressure, 760 mm (29.92 in.) Hg

ρ_a	= Density of acetone, mg/ml (see bottle label)
ρ_w	= Density of water, 0.9982 g/ml (0.0022 lb/ml)
T_m	= Absolute average dry gas meter temperature, K ($^{\circ}$ R)
T_s	= Absolute average stack gas temperature, K ($^{\circ}$ R)
T_{std}	= Standard absolute temperature, 293K (528 $^{\circ}$ R)
θ	= Total sampling time, min
θ_1	= Interval of sampling time from beginning of a run until first component change, min
θ_i	= Interval of sampling time between two suc- cessive component changes, beginning with first and second changes, min
θ_p	= Interval of sampling time from final (nth) component change until the end of the sampling run, min
V_a	= Volume of acetone blank, ml
V_{aw}	= Volume of acetone used in wash, ml
V_{ic}	= Total volumes of liquid and silica gel col- lected in impingers, ml
V_m	= Volume of gas sample measured by dry gas meter, dcm (dcf)
$V_{m(std)}$	= Volume of gas sample measured by the dry gas meter, corrected to standard conditions, dscm (dscf)
v_s	= Stack gas velocity, calculated by Method 2, using data from Method 5, m/s (ft/s)
$V_{w(std)}$	= Volume of water vapor in the gas sample, corrected to standard conditions, scm (scf)
W_a	= Weight of residue due to acetone blank, mg
Y	= Dry gas meter calibration factor
13.6	= Specific gravity of mercury (Hg)
60	= Seconds per minute (s/min)

100 = Conversion to percent, %

6.2 Dry Gas Volume, Corrected to Standard Conditions

Correct the sample volume measured by the dry gas meter to standard conditions 20°C (68°F) and 760 mm (29.92 in.) Hg by using Equation 6-1. The average dry gas meter temperature (T_m) and the average orifice pressure drop (ΔH) are obtained by averaging the field data (see Figure 4.1).

$$\begin{aligned} V_{m(std)} &= V_m Y \frac{T_{std}}{T_m} \left(\frac{P_{bar} + (\Delta H/13.6)}{P_{std}} \right) \\ &= K_1 V_m Y \left(\frac{P_{bar} + (\Delta H/13.6)}{T_m} \right) \end{aligned} \quad \text{Equation 6-1}$$

where

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

Note: If the leakage rate observed during any mandatory leak check exceeds the maximum acceptable rate (L_a), either the value of V_m in Equation 6-1 may be corrected by using Equation 6-1A or 6-1B, or the test may be invalidated.

1. If no component changes were made during the sampling run, replace V_m in Equation 6-1 with:

$$V_m - (L_p - L_a)\theta. \quad \text{Equation 6-1A}$$

2. If one or more component changes were made, replace V_m in Equation 6-1 with:

$$V_m - (L_1 - L_a)\theta_1 - \sum_{i=2}^n (L_i - L_a)\theta_i - (L_p - L_a)\theta_p \quad \text{Equation 6-1B}$$

Substitute for only those leakage rates L_i or L_p which exceed L_a .

6.3 Water Vapor Volume, Corrected to Standard Conditions

$$V_{w(std)} = V_{ic} \frac{\rho_w}{M_w} \frac{R T_{std}}{P_{std}} = K_2 V_{ic} \quad \text{Equation 6-2}$$

where

$$K_2 = 0.001333 \text{ m}^3/\text{ml} \text{ for metric units, or} \\
= 0.04707 \text{ ft}^3/\text{ml} \text{ for English units.}$$

6.4 Gas Stream Moisture Content

$$B_{ws} = \frac{V_{w(std)}}{V_{m(std)} + V_{w(std)}}. \quad \text{Equation 6-3}$$

Note: If liquid droplets are in the gas stream, assume the stream to be saturated and use a psychrometric chart or saturated vapor pressure table to approximate the mixture percentage.

6.5 Acetone Blank Concentration

$$C_a = \frac{m_{ab}}{V_a \rho_a}. \quad \text{Equation 6-4}$$

6.6 Acetone Wash Residue

$$W_a = C_a V_{aw} \rho_a. \quad \text{Equation 6-5}$$

Or combining Equations 6-4 and 6-5:

$$W_a = \frac{m_a V_{aw}}{V_a}. \quad \text{Equation 6-6}$$

6.7 Particulate Weight

Determine the total particulate catch from the sum of the weights (obtained from containers 1 and 2) less the acetone wash residue (see Section 3.4.5).

$$m_n = m_f + m_a \quad \text{Equation 6-7}$$

6.8 Particulate Concentration

$$C_s = 1 \times 10^{-3} \left(\frac{m_n}{V_{m(std)}} \right) (\text{metric, mg/m}^3), \quad \text{Equation 6-8A}$$

$$C_x = 2.205 \times 10^{-6} \left(\frac{m_n}{V_{m(std)}} \right) (\text{English, lb/ft}^3). \quad \text{Equation 6-8B}$$

For convenience, the following conversion factors are given.

Conversion Factors

<u>From</u>	<u>To</u>	<u>Multiply by</u>
scf	m ³	0.02832
g/ft ³	gr/ft ³	15.43
g/ft ³	lb/ft ³	2.205×10^{-6}
g/ft ³	g/m ³	35.31

6.9 Isokinetic Variation

6.9.1 Calculation of I from Raw Data

$$I = \frac{100 T_s \left[K_3 V_{ic} + \left(\frac{V_m}{T_m} \right) (P_{bar} + \Delta H/13.6) \right]}{60 \theta v_s P_s A_n} \quad \text{Equation 6-9}$$

where

$$K_3 = 0.003464 \text{ mm Hg-m}^3/\text{ml-K for metric units, or}$$

$$= 0.002676 \text{ in. Hg-ft}^3/\text{ml-}^\circ\text{R for English units.}$$

6.9.2 Calculation of I from Intermediate Values

$$I = \frac{100 T_s V_{m(std)} P_{std}}{60 \theta v_s P_s A_n T_{std} (1 - B_{ws})}$$

$$= K_4 \frac{T_s V_{m(std)}}{\theta v_s P_s A_n (1 - B_{ws})} \quad \text{Equation 6-10}$$

where

$$K_4 = 4.320 \text{ for metric units, or}$$

$$= 0.09450 \text{ for English units.}$$

6.9.3 Acceptable Results - If $90\% \leq I \leq 110\%$, the results are acceptable. If the results are low in comparison to the standard and if the I is beyond the acceptable range, the administrator may opt to accept the results; otherwise, reject them and repeat the test.

Table 6.1 ACTIVITY MATRIX FOR CALCULATIONS

Apparatus	Acceptance limits	Frequency and method of measurements	Action if requirements are not met
Analysis data form	All data and calculations given on the form	Visual check	Complete the missing data values
Calculations	Difference between checked and original calculations not in excess of roundoff error; at least one decimal figure beyond that of acquired data retained	Repeat all calculations starting with raw data for hand calculations and for one sample per test	Indicate errors in analysis data on Fig 6.1A or B
Isokinetic variation	$90\% < I < 110\%$; see Eqs 6.9 and 6.10 for calculation of I	For each run, calculate I	Repeat the test, and adjust flow rates to maintain I within $\pm 10\%$ variation

7.0 MAINTENANCE

Normal use of emission testing equipment subjects it to corrosive gases, temperature extremes, vibrations, and shocks. Keeping the equipment in good operating order over an extended period of time requires routine maintenance and knowledge of the equipment. Maintenance of the entire sampling train should be performed either quarterly or after 1000 ft³ of operation, whichever occurs sooner. Maintenance procedures are summarized in Table 7.1 at the end of this section. The following procedures are recommended, but not required, to increase the reliability of the equipment.

7.1 Pumps

Several types of pumps are used in commercial sampling trains. Two of the most common types are the fiber vane pump with in-line oiler and the diaphragm pump. The fiber vane pump requires a periodic check of the oil and the oiler jar. Used oil (usually nondetergent or machine weight) should be about the same translucent color as unused or spare oil. When the pump starts to run erratically or when the head is removed each year, the fiber vanes should be changed.

The diaphragm pump requires little maintenance. If the diaphragm pump leaks or runs erratically, it is normally due to a bad diaphragm or malfunctions in the valves; these parts are easily replaced and should be cleaned annually by complete disassembly of the train.

7.2 Dry Gas Meters

The dry gas meter should be checked for excess oil and component corrosion by removing the top plate every 3 mo. The meter should be disassembled and all components cleaned and checked more often if the dials show erratic rotation, or if the meter will not calibrate properly.

7.3 Inclined Manometer

The fluid should be changed when it is discolored or contains visible matter, and when it is disassembled yearly. No other routine maintenance is required since the inclined manometer is checked during the leak checks of both the pitot tube and the entire meter box.

7.4 Sampling Train

All remaining sample train components should be visually checked every 3 mo, and they should be completely disassembled and cleaned or replaced yearly. Many of the items, such as quick disconnects, should be replaced when damaged rather than after they are periodically checked. Normally, the best maintenance procedure is to replace the entire unit--for example, a meter box, sample box, or umbilical cord.

Table 7.1 ACTIVITY MATRIX FOR EQUIPMENT MAINTENANCE CHECKS

Apparatus	Acceptance limits	Frequency and method of measurements	Action if requirements are not met
Routine main-tenance	No erratic behavior	Routine maintenance quarterly; disassemble and clean yearly	Replace parts as needed
Fiber vane pump	Leak free; required flow	Periodic check of oil jar; remove head and change fiber vanes	Replace as needed
Diaphragm pump	Leak-free valves functioning properly; required flow	Clean valves during yearly disassembly	Replace when leaking or when running erratically
Dry gas meter	No excess oil, corrosion, or erratic dial rotation	Check every 3 mo for excess oil or corrosion by removing the top plate; check valves and diaphragm when meter dial runs erratically or when meter will not calibrate	Replace parts as needed, or replace meter
Inclined manometer	No discoloration of or visible matter in the fluid	Check periodically; change fluid during yearly disassembly	Replace parts as needed
Sample train	No damage or leaks	Visually check every 3 mo; completely disassemble and clean or replace yearly	If failure noted, use another entire control console, sample box, or umbilical cord
Nozzle	No dents, corrosion, or other damage	Visually check before and after each test run	Use another nozzle or clean, sharpen, and recalibrate

8.0 AUDITING PROCEDURE

An audit is an independent assessment of data quality. Independence is achieved by using apparatus and standards that are different from those used by the regular field crew. Routine quality assurance checks by a field team are necessary for obtaining 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 activities for the auditing.

Based on the results of collaborative tests of Method 5, two specific performance audits are recommended:

1. Audit of sampling train volumetric flow measuring device.
2. Audit of data processing.

In addition to these performance audits, it is suggested that a systems audit be conducted as specified by the quality assurance coordinator. 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 quantitative evaluations of 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.

8.1.1 Audit of Sampling Train Volumetric Flow Metering Device -

The audit procedure described in this subsection can be used to determine the accuracy of the flow metering device (dry gas meter) in a sampling train. The dry gas meter is audited using a calibrated critical flow orifice housed in a quick-connect coupling and the following procedure:

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

2. Turn the power to the meter box on and start the pump.
3. Completely open the coarse flow rate control valve and close the fine flow rate control valve to give a maximum vacuum reading. Caution: A vacuum reading of <425 mm (17 in.) Hg will result in flow rate errors.
4. Allow the orifice and source sampling meter box to warmup for 45 min with flow controls adjusted as described in step 3 before starting quality assurance runs. If the audit is made at the conclusion of the sample run, the warmup period is not necessary.
5. Make triplicate quality assurance runs. For each run, record the initial and the final dry gas meter volumes, the dry gas meter inlet and outlet temperatures, the internal orifice pressure drop (ΔH), the ambient temperature, and the barometric pressure. The duration of the run should be slightly >15 min. The following procedure is recommended and should be performed three times to provide the required triplicate quality assurance runs: 15 min after a run is started, watch the dry gas meter needle closely. As the needle reaches the zero (12 o'clock) position, stop the pump and stopwatch simultaneously. Record the dry gas meter volume and the time.
6. Calculate the corrected dry gas volume for each run using Equation 8.1. For each replicate, record the corrected dry gas volume in dry standard cubic meters, the sampling time in decimal minutes, the barometric pressure in millimeters of Hg; and the ambient temperature in degrees celcius.

$$V_{m(std)} = V_m Y \left(\frac{T_{std}}{T_m} \right) \left(\frac{P_{bar} + \frac{\Delta H}{13.6}}{P_{std}} \right) \quad \text{Equation 8-1}$$

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

where:

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

The agency/organization determines the percent accuracy, % A between the measured standard volume and the audit or known standard volume. The %A is a measure of the bias of the volume measurement in the sampling phase of Method 5. Calculate %A using Equation 8-2.

$$\% A = \frac{V_{\text{std}} (M) - V_{\text{std}} (A)}{V_{\text{std}} (A)} \times 100 \quad \text{Equation 8-2}$$

where

$V_{\text{std}} (M)$ = volume measured by the field crew corrected to standard conditions, m^3 , and

$V_{\text{std}} (A)$ = audit or known volume of the audit device corrected to standard conditions, m^3 .

The recommended control limit for the performance audit is the 90th percentile value for % A, based on the results of three audits (5/78, 10/78, and 3/79) performed by the Environmental Monitoring Systems Laboratory, USEPA. By definition, 90% of the laboratory participants in the audits obtained values of % A less than the values tabulated below. The control limit is initially expected to be exceeded by 10% of the laboratories to be audited, based on these three audits. The 90th percentile values are given below for each audit.

<u>Audit date</u>	<u>90th percentile for % A</u>
05-78	±10.7
10-78	± 9.1
03-79	± 9.6

Based on the results of these audits, the recommended 90th percentile control limit for the performance audit is ±10%. The results of the audit should be included in the emission test report.

Responsible control agencies can obtain a calibrated critical orifice (when available) prior to each enforcement source test, conduct the audit, and return the orifice and data form to EPA for evaluation. Orifices may be obtained from the Source Test Audit coordinator, Quality Assurance Division, Environmental Monitoring Systems Laboratory, USEPA, Research Triangle Park, North Carolina 27711. It is also suggested that organizations that conduct compliance tests participate in the EPA semiannual audit of volume meters.

8.1.2 Performance Audit of Data Processing

Calculation errors are prevalent in Method 5. Data processing errors can be determined by auditing the data recorded on the field and the laboratory forms. The original and the check calculations should agree; if not, all of the data and calculations should be checked. Calculation errors should be clearly explained to the source test team to prevent or minimize reoccurrence. The data processing errors may also be determined by requesting that copies of data sets compiled in the field and copies of manual data reductions (or computer printouts if used) be forwarded to the evaluator for audit.

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 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 in the following:

1. Observe the procedures and techniques of the field team during sample collection.

2. Check/verify the records of apparatus calibrations and the quality control charts used in the laboratory analysis.

3. Record the results of the audit and forward them with comments on source team management to the quality assurance coordinator so that any needed corrective actions may be implemented.

The auditor should observe the field team's overall performance of the source test. Specific operations to observe should include, but not be limited to:

1. Setting up and leak testing the sampling train.
2. Isokinetic sampling check of the sampling train.
3. Final leak check of train.
4. Sample recovery.

Figure 8.1 is a suggested checklist to be used by the auditor for developing a list of important techniques/steps to observe.

Yes	No	Comment	OPERATION
			Presampling Preparation
<u>✓</u>	<u>—</u>	<u>OK</u>	1. Knowledge of process conditions
<u>✓</u>	<u>—</u>	<u>—</u>	2. Calibration of pertinent equipment: in particular, the dry gas meter, orifice meter, and pitot tube
			On-Site Measurements
<u>✓</u>	<u>—</u>	<u>—</u>	3. Sample train assembly
<u>✓</u>	<u>—</u>	<u>—</u>	4. Pretest leak check of train
<u>—</u>	<u>—</u>	<u>OK</u>	5. Isokinetic sampling
<u>✓</u>	<u>—</u>	<u>—</u>	6. Posttest check
<u>✓</u>	<u>—</u>	<u>—</u>	7. Sample recovery and integrity
<u>—</u>	<u>—</u>	<u>*</u>	8. Recording of pertinent process information during sample collec- tion
			Postsampling
<u>—</u>	<u>—</u>	<u>OK</u>	9. Check of analytical balance
<u>✓</u>	<u>—</u>	<u>—</u>	10. Use of acceptable detection blanks in correcting field sample results
<u>—</u>	<u>—</u>	<u>OK</u>	11. Calculation procedure/check
General Comments			
* PROBE SHORTED OUT DURING RUN 3 - BUT SAMPLING WAS ALLOWED TO BE CONTINUED.			

Figure 8.1 Method 5 checklist to be used by auditors.

Table 8.1 ACTIVITY MATRIX FOR AUDITING PROCEDURES

Audit	Acceptance limits	Frequency and method of measurement	Action if requirements are not met
Volumetric sampling phase of Method 5	Measured pretest volume within $\pm 10\%$ of the audit volume	Once during every enforcement source test, measure reference volume, and compare with true volume	Review operating technique
Data processing errors	Original and check calculations agree	Once during each enforcement source test, perform independent calculations starting with the recorded data	Check and correct all data
Systems audit	Conducted method as described in this section of the Handbook	Once during each enforcement test until experience gained, then every fourth test, observe techniques; use audit checklist Fig 8.1	Explain to team the deviations from recommended techniques; note the deviations on Fig 8.1

9.0 RECOMMENDED STANDARDS FOR ESTABLISHING TRACEABILITY

To achieve data of desired quality, two considerations are necessary: (1) the measurement process must be in a state of statistical control, and (2) the systematic errors, when combined with the random variations (errors of measurement), must result in a suitably small uncertainty.

To ensure good data, it is necessary to perform quality control checks and independent audits of the measurement process; to document the data by quality control charts (as appropriate); and to use materials, instruments, and procedures which can be traced to a standard of reference.

The working calibration standards should be traceable to primary or higher level standards such as those listed below.

1. The dry gas meter should be calibrated against a wet test meter which has been verified by liquid displacement, as described in Section 3.4.2.
2. The analytical balance should be checked against Class-S weights that are traceable to NBS standards.

10.0 REFERENCE METHOD

METHOD 5—DETERMINATION OF PARTICULATE EMISSIONS FROM STATIONARY SOURCES

1. Principle and Applicability

1.1 Principle. Particulate matter is withdrawn isokinetically from the source and collected on a glass fiber filter maintained at a temperature in the range of $120 \pm 14^\circ \text{C}$ ($248 \pm 25^\circ \text{F}$) or such other temperature as specified by an applicable subpart of the standards or approved by the Administrator, U.S. Environmental Protection Agency, for a particular application. The particulate mass, which includes any material that condenses at or above the filtration temperature, is determined gravimetrically after removal of uncombined water.

1.2 Applicability. This method is applicable for the determination of particulate emissions from stationary sources.

2. Apparatus

2.1 Sampling Train. A schematic of the sampling train used in this method is shown in Figure 5-1. Complete construction details are given in APTD-0581 (Citation 2 in Section 7); commercial models of this train are also available. For changes from APTD-0581 and for allowable modifications of the train shown in Figure 5-1, see the following subsections.

The operating and maintenance procedures for the sampling train are described in APTD-0576 (Citation 3 in Section 7). Since correct usage is important in obtaining valid results, all users should read APTD-0576 and adopt the operating and maintenance procedures outlined in it, unless otherwise specified herein. The sampling train consists of the following components:

2.1.1 Probe Nozzle. Stainless steel (316) or glass with sharp, tapered leading edge. The angle of taper shall be $\leq 30^\circ$ and the taper shall be on the outside to preserve a constant internal diameter. The probe nozzle shall be of the button-hook or elbow design, unless otherwise specified by the Administrator. If made of stainless steel, the nozzle shall be constructed from seamless tubing; other materials of construction may be used, subject to the approval of the Administrator.

A range of nozzle sizes suitable for isokinetic sampling should be available, e.g., 0.32 to 1.27 cm ($1/8$ to $1/2$ in.) or larger if higher volume sampling trains are used—inside diameter (ID) nozzles in increments of 0.16 cm ($1/16$ in.). Each nozzle shall be calibrated according to the procedures outlined in Section 5.

2.1.2 Probe Liner. Borosilicate or quartz glass tubing with a heating system capable of maintaining a gas temperature at the exit and during sampling of $120 \pm 14^\circ \text{C}$ ($248 \pm 25^\circ \text{F}$), or such other temperature as specified by an applicable subpart of the standards or approved by the Administrator for a particular application. (The tester may opt to operate the equipment at a temperature lower than that specified.) Since the actual temperature at the outlet of the probe is not usually monitored during sampling, probes constructed according to APTD-0581 and utilizing the calibration curves of APTD-0576 (or calibrated according to the procedure outlined in APTD-0576) will be considered acceptable.

Either borosilicate or quartz glass probe liners may be used for stack temperatures up to about 480°C (900°F). Quartz liners shall be used for temperatures between 480 and 900°C (900 and $1,650^\circ \text{F}$). Both types of liners may be used at higher temperatures than specified for short periods of time, subject to the approval of the Administrator. The softening temperature for borosilicate is 820°C ($1,508^\circ \text{F}$), and for quartz it is $1,500^\circ \text{C}$ ($2,732^\circ \text{F}$).

Whenever practical, every effort should be made to use borosilicate or quartz glass probe liners. Alternatively, metal liners (e.g., 316 stainless steel, Incoloy 825, or other corrosion resistant metals) made of seamless tubing may be used, subject to the approval of the Administrator.

2.1.3 Pitot Tube. Type S, as described in Section 2.1 of Method 2, or other device approved by the Administrator. The pitot tube shall be attached to the probe (as shown in Figure 5-1) to allow constant monitoring of the stack gas velocity. The impact (high pressure) opening

² Mention of trade names or specific products does not constitute endorsement by the Environmental Protection Agency.

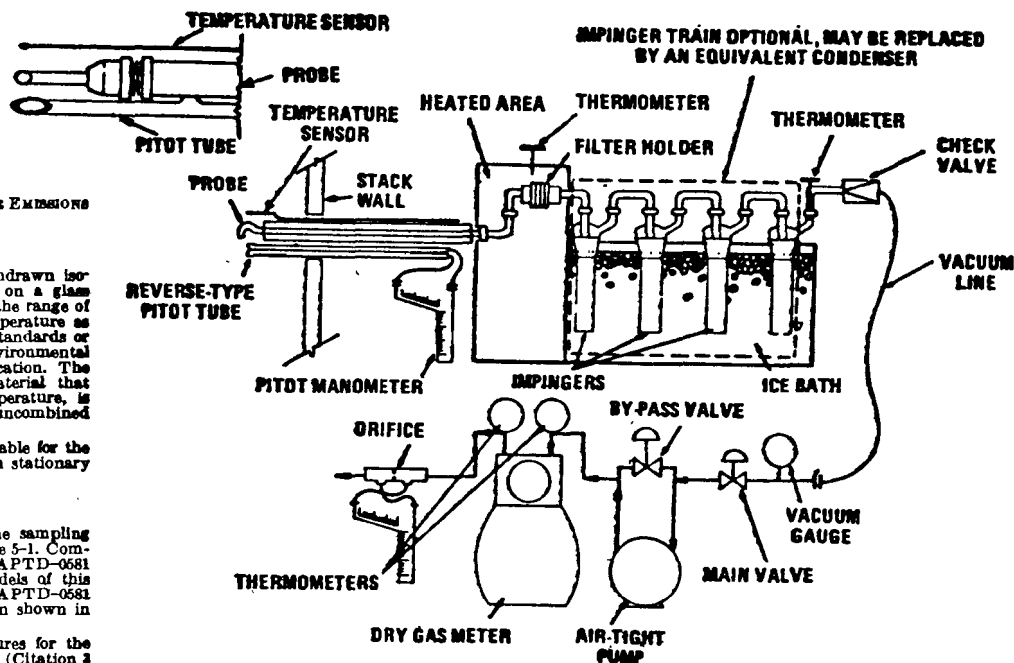


Figure 5-1. Particulate-sampling train.

plane of the pitot tube shall be even with or above the nozzle entry plane (see Method 2, Figure 2-6b) during sampling. The Type S pitot tube assembly shall have a known coefficient, determined as outlined in Section 4 of Method 2.

2.1.4 Differential Pressure Gauge. Inclined manometer or equivalent device (two), as described in Section 2.2 of Method 2. One manometer shall be used for velocity head (Δp) readings, and the other, for orifice differential pressure readings.

2.1.5 Filter Holder. Borosilicate glass, with a glass frit filter support and a silicone rubber gasket. Other materials of construction (e.g., stainless steel, Teflon, Viton) may be used, subject to approval of the Administrator. The holder design shall provide a positive seal against leakage from the outside or around the filter. The holder shall be attached immediately at the outlet of the probe (or cyclone, if used).

2.1.6 Filter Heating System. Any heating system capable of maintaining a temperature around the filter holder during sampling of $120 \pm 14^\circ \text{C}$ ($248 \pm 25^\circ \text{F}$), or such other temperature as specified by an applicable subpart of the standards or approved by the Administrator for a particular application. Alternatively, the tester may opt to operate the equipment at a temperature lower than that specified. A temperature gauge capable of measuring temperature to within 3°C (5.4°F) shall be installed so that the temperature around the filter holder can be regulated and monitored during sampling. Heating systems other than the one shown in APTD-0581 may be used.

2.1.7 Condenser. The following system shall be used to determine the stack gas moisture content: Four impingers connected in series with leak-free ground glass fittings or any similar leak-free non-contaminating fittings. The first, third, and fourth impingers shall be of the Greenburg-Smith design, modified by replacing the tip with 1.3 cm ($1/2$ in.) ID glass tube extending to about 1.3 cm ($1/2$ in.) from the bottom of the flask. The second impinger shall be of the Greenburg-Smith design with the standard tip. Modifications (e.g., using flexible connections between the impingers, using materials other than glass, or using flexible vacuum lines to connect the filter holder to the condenser) may be used, subject to the approval of the Administrator. The first and second impingers shall contain known quantities of water (Section 4.1.3), the third shall be empty, and the fourth shall contain a known weight of silica gel, or equivalent desiccant. A thermometer, capable of measuring temperature to within 1°C (2°F) shall be placed at the outlet of the fourth impinger for monitoring purposes.

Alternatively, any system that cools the sample gas stream and allows measurement of the water condensed and moisture leaving the condenser, such as within 1 ml or 1 g may be used, subject to the approval of the Administrator. Acceptable means are to measure the condensed water either gravimetrically or volumetrically and to measure the moisture leaving the condenser by:

(1) monitoring the temperature and pressure at the exit of the condenser and using Dalton's law of partial pressures; or (2) passing the sample gas stream through a tared silica gel (or equivalent desiccant) trap with exit gases kept below 20°C (68°F) and determining the weight gain.

If means other than silica gel are used to determine the amount of moisture leaving the condenser, it is recommended that silica gel (or equivalent) still be used between the condenser system and pump to prevent moisture condensation in the pump and metering devices and to avoid the need to make corrections for moisture in the metered volume.

NOTE.—If a determination of the particulate matter collected in the impingers is desired in addition to moisture content, the impinger system described above shall be used, without modification. Individual States or control agencies requiring this information shall be contacted as to the sample recovery and analysis of the impinger contents.

2.1.8 Metering System. Vacuum gauge, leak-free pump, thermometers capable of measuring temperature to within 3°C (5.4°F), dry gas meter capable of measuring volume to within 2 percent, and related equipment, as shown in Figure 5-1. Other metering systems capable of maintaining sampling rates within 10 percent of isokinetic and of determining sample volume to within 2 percent may be used, subject to the approval of the Administrator. When the metering system is used in conjunction with a pitot tube, the system shall enable checks of isokinetic rates.

Sampling trains utilizing metering systems designed for higher flow rates than that described in APTD-0581 or APTD-0576 may be used provided that the specifications of this method are met.

2.1.9 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.

2.1.10 Gas Density Determination Equipment. Temperature sensor and pressure gauge, as described in Sections 2.3 and 2.4 of Method 2, and gas analyzer, if necessary, as described in Method 3. The temperature sensor shall, preferably, be permanently attached to the pitot tube or sampling probe in a fixed configuration, such that the tip of the sensor extends beyond the leading edge of the probe sheath and does not touch any metal. Alternatively, the sensor may be attached just prior to use in the field. Note, however, that if the temperature sensor is attached in the field, the sensor must be placed in an interference-free arrangement with respect to the Type 8 pitot tube openings (see Method 2, Figure 2-7). As a second alternative, if a difference of not more than 1 percent in the average velocity measurement is to be introduced, the temperature gauge need not be attached to the probe or pitot tube. (This alternative is subject to the approval of the Administrator.)

2.2 Sample Recovery. The following items are needed:

2.2.1 Probe-Liner and Probe-Nozzle Brushes. Nylon bristle brushes with stainless steel wire handles. The probe brush shall have extensions (at least as long as the probe) of stainless steel, Nylon, Teflon, or similarly inert material. The brushes shall be properly sized and shaped to brush out the probe liner and nozzle.

2.2.2 Wash Bottles—Two. Glass wash bottles are recommended; polyethylene wash bottles may be used at the option of the tester. It is recommended that acetone not be stored in polyethylene bottles for longer than a month.

2.2.3 Glass Sample Storage Containers. Chemically resistant, borosilicate glass bottles, for acetone washes, 500 ml or 1000 ml. Screw cap liners shall either be rubber-backed Teflon or shall be constructed so as to be leak-free and resistant to chemical attack by acetone. (Narrow mouth glass bottles have been found to be less prone to leakage.) Alternatively, polyethylene bottles may be used.

2.2.4 Petri Dishes. For filter samples, glass or polyethylene, unless otherwise specified by the Administrator.

2.2.5 Graduated Cylinder and/or Balance. To measure condensed water to within 1 ml or 1 g. Graduated cylinders shall have subdivisions no greater than 2 ml. Most laboratory balances are capable of weighing to the nearest 0.5 g or less. Any of these balances is suitable for use here and in Section 2.3.4.

2.2.6 Plastic Storage Containers. Air-tight containers to store silica gel.

2.2.7 Funnel and Rubber Policeman. To aid in transfer of silica gel to container; not necessary if silica gel is weighed in the field.

2.2.8 Funnel. Glass or polyethylene, to aid in sample recovery.

2.3 Analysis. For analysis, the following equipment is needed:

2.3.1 Glass Weighing Dishes.

2.3.2 Desiccator.

2.3.3 Analytical Balance. To measure to within 0.1 mg.

2.3.4 Balance. To measure to within 0.5 g.

2.3.5 Beakers. 250 ml.

2.3.6 Hygrometer. To measure the relative humidity of the laboratory environment.

2.3.7 Temperature Gauge. To measure the temperature of the laboratory environment.

3. Reagents

3.1 Sampling. The reagents used in sampling are as follows:

3.1.1 Filters. Glass fiber filters, without organic binder, exhibiting at least 99.95 percent efficiency (≤ 0.05 percent penetration) on 0.3-micron dioctyl phthalate smoke particles. The filter efficiency test shall be conducted in accordance with ASTM standard method D 2906-71. Test data from the supplier's quality control program are sufficient for this purpose.

3.1.2 Silica Gel. Indicating type, 6 to 16 mesh. If previously used, dry at 175° C (350° F) for 2 hours. New silica gel may be used as received. Alternatively, other types of desiccants (equivalent or better) may be used, subject to the approval of the Administrator.

3.1.3 Water. When analysis of the material caught in the impingers is required, distilled water shall be used. Run blanks prior to field use to eliminate a high blank on test samples.

3.1.4 Crushed Ice.

3.1.5 Stopcock Grease. Acetone-insoluble, heat-stable silicone grease. This is not necessary if screw-on connectors with Teflon sleeves, or similar, are used. Alternatively, other types of stopcock grease may be used, subject to the approval of the Administrator.

3.2 Sample Recovery. Acetone—reagent grade, ≤ 0.001 percent residue, in glass bottles—is required. Acetone from metal containers generally has a high residue blank and should not be used. Sometimes, suppliers transfer acetone to glass bottles from metal containers; thus, acetone blanks shall be run prior to field use and only acetone with low blank values (≤ 0.001 percent) shall be used. In no case shall a blank value of greater than 0.001 percent of the weight of acetone used be subtracted from the sample weight.

3.3 Analysis. Two reagents are required for the analysis:

3.3.1 Acetone. Same as 3.2.

3.3.2 Desiccant. Anhydrous calcium sulfate, indicating type. Alternatively, other types of desiccants may be used, subject to the approval of the Administrator.

4. Procedure

4.1 Sampling. The complexity of this method is such that, in order to obtain reliable results, testers should be trained and experienced with the test procedures.

4.1.1 Pretest Preparation. All the components shall be maintained and calibrated according to the procedure described in APTD-0676, unless otherwise specified herein.

Weigh several 200 to 300 g portions of silica gel in air-tight containers to the nearest 0.5 g. Record the total weight of the silica gel plus container, on each container. As an alternative, the silica gel need not be preweighed, but may be weighed directly in its impinger or sampling holder just prior to train assembly.

Check filters visually against light for irregularities and flaws or pinhole leaks. Label filters of the proper diameter on the back side near the edge using numbering machine ink. As an alternative, label the shipping containers (glass or plastic petri dishes) and keep the filters in these containers at all times except during sampling and weighing.

Desiccate the filters at 20±5° C (68±10° F) and ambient pressure for at least 24 hours and weigh at intervals of at least 8 hours to a constant weight, i.e., ≤ 0.5 mg change from previous weighing; record results to the nearest 0.1 mg. During each weighing the filter must not be exposed to the laboratory atmosphere for a period greater than 2 minutes and a relative humidity above 50 percent. Alternatively (unless otherwise specified by the Administrator), the filters may be oven dried at 105° C (220° F) for 2 to 3 hours, desiccated for 2 hours, and weighed. Procedures other than those described, which account for relative humidity effects, may be used, subject to the approval of the Administrator.

4.1.2 Preliminary Determinations. Select the sampling site and the minimum number of sampling points according to Method 1 or as specified by the Administrator. Determine the stack pressure, temperature, and the range of velocity heads using Method 2; it is recommended that a leak-check of the pitot lines (see Method 2, Section 3.1) be performed. Determine the moisture content using Approximation Method 4 or its alternatives for the purpose of making isokinetic sampling rate settings. Determine the stack gas dry molecular weight, as described in Method 2, Section 3.6; if integrated Method 3 sampling is used for molecular weight determination, the integrated bag sample shall be taken simultaneously with, and for the same total length of time as, the particulate sample run.

Select a nozzle size based on the range of velocity heads, such that it is not necessary to change the nozzle size in order to maintain isokinetic sampling rates. During the run, do not change the nozzle size. Ensure that the proper differential pressure gauge is chosen for the range of velocity heads encountered (see Section 2.2 of Method 2).

Select a suitable probe liner and probe length such that all traverse points can be sampled. For large stacks, consider sampling from opposite sides of the stack to reduce the length of probe.

Select a total sampling time greater than or equal to the minimum total sampling time specified in the test procedures for the specific industry such that (1) the sampling time per point is not less than 2 min (or some greater time interval as specified by the Administrator), and (2) the sample volume taken (corrected to standard conditions) will exceed the required minimum total gas sample volume. The latter is based on an approximate average sampling rate.

It is recommended that the number of minutes sampled at each point be an integer or an integer plus one-half minute, in order to avoid timekeeping errors.

In some circumstances, e.g., batch cycles, it may be necessary to sample for shorter times at the traverse points and to obtain smaller gas sample volumes. In these cases, the Administrator's approval must first be obtained.

4.1.3 Preparation of Collection Train. During preparation and assembly of the sampling train, keep all openings where contamination can occur covered until just prior to assembly or until sampling is about to begin.

Place 100 ml of water in each of the first two impingers, leave the third impinger empty, and transfer approximately 200 to 300 g of preweighed silica gel from its container to the fourth impinger. More silica gel may be used, but care should be taken to ensure that it is not entrained and carried out from the impinger during sampling. Place the container in a clean place for later use in the sample recovery. Alternatively, the weight of the silica gel plus impinger may be determined to the nearest 0.5 g and recorded.

Using a tweezer or clean disposable surgical gloves, place a labeled (identified) and weighed filter in the filter holder. Be sure that the filter is properly centered and the gasket properly placed so as to prevent the sample gas stream from circumventing the filter. Check the filter for tears after assembly is completed.

When glass liners are used, install the selected nozzle using a Viton A O-ring when stack temperatures are less than 200° C (500° F) and an asbestos string gasket when temperatures are higher. See APTD-0676 for

details. Other connecting systems using either 316 stainless steel or Teflon ferrules may be used. When metal liners are used, install the nozzle as above or by a leak-free direct mechanical connection. Mark the probe with heat resistant tape or by some other method to denote the proper distance into the stack or duct for each sampling point.

Set up the train as in Figure 8-1, using (if necessary) a very light coat of silicone grease on all ground glass joints, greasing only the outer portion (see APTD-0676) to avoid possibility of contamination by the silicone grease. Subject to the approval of the Administrator, a glass cyclone may be used between the probe and filter holder when the total particulate catch is expected to exceed 100 mg or when water droplets are present in the stack gas.

Place crushed ice around the impingers.

4.1.4 Leak-Check Procedures

4.1.4.1 Pretest Leak-Check. A pretest leak-check is recommended, but not required. If the tester opts to conduct the pretest leak-check, the following procedure shall be used.

After the sampling train has been assembled, turn on and set the filter and probe heating systems at the desired operating temperatures. Allow time for the temperatures to stabilize. If a Viton A O-ring or other leak-free connection is used in assembling the probe nozzle to the probe liner, leak-check the train at the sampling site by plugging the nozzle and pulling a 380 mm Hg (15 in. Hg) vacuum.

Note.—A lower vacuum may be used, provided that it is not exceeded during the test. If an asbestos string is used, do not connect the probe to the train during the leak-check. Instead, leak-check the train by first plugging the inlet to the filter holder (cyclone, if applicable) and pulling a 380 mm Hg (15 in. Hg) vacuum (see Note immediately above). Then connect the probe to the train and leak-check at about 26 mm Hg (1 in. Hg) vacuum; alternatively, the probe may be leak-checked with the rest of the sampling train, in one step, at 380 mm Hg (15 in. Hg) vacuum. Leakage rates in excess of 4 percent of the average sampling rate or 0.00067 m³/min (0.02 cfm), whichever is less, are unacceptable.

The following leak-check instructions for the sampling train described in APTD-0676 and APTD-0681 may be helpful. Start the pump with bypass valve fully open and coarse adjust valve completely closed. Partially open the coarse adjust valve and slowly close the bypass valve until the desired vacuum is reached. Do not reverse direction of bypass valve; this will cause water to back up into the filter holder. If the desired vacuum is exceeded, either leak-check at this higher vacuum or end the leak check as shown below and start over.

When the leak-check is completed, first slowly remove the plug from the inlet to the probe, filter holder, or cyclone (if applicable) and immediately turn off the vacuum pump. This prevents the water in the impingers from being forced backward into the filter holder and silica gel from being entrained backward into the third impinger.

4.1.4.2 Leak-Checks During Sample Run. If, during the sampling run, a component (e.g., filter assembly or impinger) change becomes necessary, a leak-check shall be conducted immediately before the change is made. The leak-check shall be done according to the procedure outlined in Section 4.1.4.1 above, except that it shall be done at a vacuum equal to or greater than the maximum value recorded up to that point in the test. If the leakage rate is found to be no greater than 0.00057 m³/min (0.02 cfm) or 4 percent of the average sampling rate (whichever is less), the results are acceptable, and no correction will need to be applied to the total volume of dry gas metered; if, however, a higher leakage rate is obtained, the tester shall either record the leakage rate and plan to correct the sample volume as shown in Section 6.3 of this method, or shall void the sampling run.

Immediately after component changes, leak-checks are optional; if such leak-checks are done, the procedure outlined in Section 4.1.4.1 above shall be used.

4.1.4.3 Post-test Leak-Check. A leak-check is mandatory at the conclusion of each sampling run. The leak-check shall be done in accordance with the procedures outlined in Section 4.1.4.1, except that it shall be conducted at a vacuum equal to or greater than the maximum value reached during the sampling run. If the leakage rate is found to be no greater than 0.00057 m³/min (0.02 cfm) or 4 percent of the average sampling rate (whichever is less), the results are acceptable, and no correction need be applied to the total volume of dry gas metered. If, however, a higher leakage rate is obtained, the tester shall either record the leakage rate and correct the sample volume as shown in Section 6.3 of this method, or shall void the sampling run.

4.1.5 Particulate Train Operation. During the sampling run, maintain an isokinetic sampling rate (within 10 percent of true isokinetic unless otherwise specified by the Administrator) and a temperature around the filter of 120±14° C (248±25° F), or such other temperature as specified by an applicable subpart of the standards or approved by the Administrator.

For each run, record the data required on a data sheet such as the one shown in Figure 5-2. Be sure to record the initial dry gas meter reading. Record the dry gas meter readings at the beginning and end of each sampling time increment, when changes in flow rates are made, before and after each leak check, and when sampling is halted.

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ment of the isokinetic sampling rate without excessive computations. These nomographs are designed for use when the Type B pitot tube coefficient is 0.86 ± 0.02 , and the stack gas equivalent density (dry molecular weight) is equal to 29.4. APTD-0876 details the procedure for using the nomographs. If C_p and M_d are outside the above stated ranges do not use the nomographs unless appropriate steps (see Citation 7 in Section 7) are taken to compensate for the deviations.

AMBIENT TEMPERATURE _____
 BAROMETRIC PRESSURE _____
 ASSUMED MOISTURE, % _____
 PROBE LENGTH, m (ft) _____
 NOZZLE IDENTIFICATION NO. _____
 AVERAGE CALIBRATED NOZZLE DIAMETER, cm (in.) _____
 PROBE HEATER SETTING _____
 LEAK RATE, m³/min. (cfm) _____
 PROBE LINER MATERIAL _____
 STATIC PRESSURE, mm Hg (in. Hg) _____
 FILTER NO. _____

Figure 5-2. Particulate field data.

Container No. 2. Taking care to see that dust on the outside of the probe or other exterior surfaces does not get into the sample, quantitatively recover particulate matter or any condensate from the probe nozzle, probe

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fitting, probe liner, and front half of the filter holder by washing these components with acetone and placing the wash in a glass container. Distilled water may be used instead of acetone when approved by the Administrator and shall be used when specified by the Administrator; in these cases, save a water blank and follow the Administrator's directions on analysis. Perform the acetone rinses as follows:

Carefully remove the probe nozzle and clean the inside surface by rinsing with acetone from a wash bottle and brushing with a nylon bristle brush. Brush until the acetone rinse shows no visible particles, after which make a final rinse of the inside surface with acetone.

Brush and rinse the inside parts of the Swagelok fitting with acetone in a similar way until no visible particles remain.

Rinse the probe liner with acetone by tilting and rotating the probe while squirting acetone into its upper end so that all inside surfaces will be wetted with acetone. Let the acetone drain from the lower and into the sample container. A funnel (glass or polyethylene) may be used to aid in transferring liquid washes to the container. Follow the acetone rinse with a probe brush. Hold the probe in an inclined position, squirt acetone into the upper end as the probe brush is being pushed with a twisting action through the probe; hold a sample container underneath the lower end of the probe, and catch any acetone and particulate matter which is brushed from the probe. Run the brush through the probe three times or more until no visible particulate matter is carried out with the acetone or until none remains in the probe liner on visual inspection. With stainless steel or other metal probes, run the brush through in the above prescribed manner at least six times since metal probes have small crevices in which particulate matter can be entrapped. Rinse the brush with acetone, and quantitatively collect these washings in the sample container. After the brushing, make a final acetone rinse of the probe as described above.

It is recommended that two people be used to clean the probe to minimize sample losses. Between sampling runs, keep brushes clean and protected from contamination.

After ensuring that all joints have been wiped clean of silicone grease, clean the inside of the front half of the filter holder by rubbing the surfaces with a nylon bristle brush and rinsing with acetone. Rinse each surface three times or more if needed to remove visible particulate. Make a final rinse of the brush and filter holder. Carefully rinse out the glass cyclone, also (if applicable). After all acetone washings and particulate matter have been collected in the sample container, tighten the lid on the sample container so that acetone will not leak out when it is shipped to the laboratory. Mark the height of the fluid level to determine whether or not leakage occurred during transport. Label the container to clearly identify its contents.

Container No. 3. Note the color of the indicating silica gel to determine if it has been completely spent and make a notation of its condition. Transfer the silica gel from the fourth impinger to its original container and seal. A funnel may make it easier to pour the silica gel without spilling. A rubber policeman may be used as an aid in removing the silica gel from the impinger. It is not necessary to remove the small amount of dust particles that may adhere to the impinger wall and are difficult to remove. Since the gain in weight is to be used for moisture calculations, do not use any water or other liquids to transfer the silica gel. If a balance is available in the field, follow the procedure for container No. 3 in Section 4.3.

Impinger Water. Treat the impingers as follows: Make a notation of any color or film in the liquid catch. Measure the liquid which is in the first three impingers to within ± 1 ml by using a graduated cylinder or by weighing it to within ± 0.5 g by using a balance (if one is available). Record the volume or weight of liquid present. This information is required to calculate the moisture content of the effluent gas.

Discard the liquid after measuring and recording the volume or weight, unless analysis of the impinger catch is required (see Note, Section 2.1.7).

If a different type of condenser is used, measure the amount of moisture condensed either volumetrically or gravimetrically.

Whenever possible, containers should be shipped in such a way that they remain upright at all times.

4.3 Analysis. Record the data required on a sheet such as the one shown in Figure 5-3. Handle each sample container as follows:

Container No. 1. Leave the contents in the shipping container or transfer the filter and any loose particulate from the sample container to a tared glass weighing dish. Desiccate for 24 hours in a desiccator containing anhydrous calcium sulfate. Weigh to a constant weight and report the results to the nearest 0.1 mg. For purposes of this Section, 4.3, the term "constant weight" means a difference of no more than 0.5 mg or 1 percent of total weight less tare weight, whichever is greater, between two consecutive weighings, with no less than 6 hours of desiccation time between weighings.

Plant _____

Date _____

Run No. _____

Filter No. _____

Amount liquid lost during transport _____

Acetone blank volume, ml _____

Acetone wash volume, ml _____

Acetone blank concentration, mg/mg (equation 5-4) _____

Acetone wash blank, mg (equation 5-5) _____

CONTAINER NUMBER	WEIGHT OF PARTICULATE COLLECTED, mg		
	FINAL WEIGHT	TARE WEIGHT	WEIGHT GAIN
1			
2			
TOTAL			
Less acetone blank			
Weight of particulate matter			

	VOLUME OF LIQUID WATER COLLECTED	
	IMPINGER VOLUME, ml	SILICA GEL WEIGHT, g
FINAL		
INITIAL		
LIQUID COLLECTED		
TOTAL VOLUME COLLECTED		g ^a ml

CONVERT WEIGHT OF WATER TO VOLUME BY DIVIDING TOTAL WEIGHT INCREASE BY DENSITY OF WATER (1g/ml):

$$\frac{\text{INCREASE, g}}{1 \text{ g/ml}} = \text{VOLUME WATER, ml}$$

Figure 5-3. Analytical data.

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Alternatively, the sample may be oven dried at 105° C (220° F) for 2 to 3 hours, cooled in the desiccator, and weighed to a constant weight, unless otherwise specified by the Administrator. The tester may also opt to oven dry the sample at 105° C (220° F) for 2 to 3 hours, weigh the sample, and use this weight as a final weight.

Container No. 2. Note the level of liquid in the container and confirm on the analysis sheet whether or not leakage occurred during transport. If a noticeable amount of leakage has occurred, either void the sample or use methods, subject to the approval of the Administrator, to correct the final results. Measure the liquid in this container either volumetrically to ± 1 ml or gravimetrically to ± 0.5 g. Transfer the contents to a tared 250-ml beaker and evaporate to dryness at ambient temperature and pressure. Desiccate for 24 hours and weigh to a constant weight. Report the results to the nearest 0.1 mg.

Container No. 3. Weigh the spent silica gel (or silica gel plus impinger) to the nearest 0.5 g using a balance. This step may be conducted in the field.

"Acetone Blank" Container. Measure acetone in this container either volumetrically or gravimetrically. Transfer the acetone to a tared 250-ml beaker and evaporate to dryness at ambient temperature and pressure. Desiccate for 24 hours and weigh to a constant weight. Report the results to the nearest 0.1 mg.

NOTE.—At the option of the tester, the contents of Container No. 2 as well as the acetone blank container may be evaporated at temperatures higher than ambient. If evaporation is done at an elevated temperature, the temperature must be below the boiling point of the solvent; also, to prevent "bumping," the evaporation process must be closely supervised, and the contents of the beaker must be swirled occasionally to maintain an even temperature. Use extreme care, as acetone is highly flammable and has a low flash point.

5. Calibration

Maintain a laboratory log of all calibrations.

5.1 Probe Nozzle. Probe nozzles shall be calibrated before their initial use in the field. Using a micrometer, measure the inside diameter of the nozzle to the nearest

0.025 mm (0.001 in.). Make three separate measurements using different diameters each time, and obtain the average of the measurements. The difference between the high and low numbers shall not exceed 0.1 mm (0.004 in.). When nozzles become nicked, dented, or corroded, they shall be reshaped, sharpened, and recalibrated before use. Each nozzle shall be permanently and uniquely identified.

5.2 Pitot Tube. The Type S pitot tube assembly shall be calibrated according to the procedure outlined in Section 4 of Method 2.

5.3 Metering System. Before its initial use in the field, the metering system shall be calibrated according to the procedure outlined in APTD-0576. Instead of physically adjusting the dry gas meter dial readings to correspond to the wet test meter readings, calibration factors may be used to mathematically correct the gas meter dial readings to the proper values. Before calibrating the metering system, it is suggested that a leak-check be conducted. For metering systems having diaphragm pumps, the normal leak-check procedure will not detect leakages within the pump. For these cases the following leak-check procedure is suggested: make a 10-minute calibration run at 0.00057 m³/min (0.02 cfm); at the end of the run, take the difference of the measured wet test meter and dry gas meter volumes; divide the difference by 10, to get the leak rate. The leak rate should not exceed 0.00057 m³/min (0.02 cfm).

After each field use, the calibration of the metering system shall be checked by performing three calibration runs at a single, intermediate orifice setting (based on the previous field test), with the vacuum set at the maximum value reached during the test series. To adjust the vacuum, insert a valve between the wet test meter and the inlet of the metering system. Calculate the average value of the calibration factor. If the calibration has changed by more than 5 percent, recalibrate the meter over the full range of orifice settings, as outlined in APTD-0576.

Alternative procedures, e.g., using the orifice meter coefficients, may be used, subject to the approval of the Administrator.

NOTE.—If the dry gas meter coefficient values obtained before and after a test series differ by more than 5 percent, the test series shall either be voided, or calculations for the test series shall be performed using whichever meter coefficient value (i.e., before or after) gives the lower value of total sample volume.

5.4 Probe Heater Calibration. The probe heating system shall be calibrated before its initial use in the field according to the procedure outlined in APTD-0576. Probes constructed according to APTD-0581 need not be calibrated if the calibration curves in APTD-0576 are used.

5.5 Temperature Gauges. Use the procedure in Section 4.3 of Method 2 to calibrate in-stack temperature gauges. Dial thermometers, such as are used for the dry gas meter and condenser outlet, shall be calibrated against mercury-in-glass thermometers.

5.6 Leak Check of Metering System Shown in Figure 5-1. That portion of the sampling train from the pump to the orifice meter should be leak checked prior to initial use and after each shipment. Leakage after the pump will result in less volume being recorded than is actually sampled. The following procedure is suggested (see Figure 5-4): Close the main valve on the meter box. Insert a one-hole rubber stopper with rubber tubing attached into the orifice exhaust pipe. Disconnect and vent the low side of the orifice manometer. Close off the low side orifice tap. Pressurize the system to 13 to 18 cm (6 to 7 in.) water column by blowing into the rubber tubing. Pinch off the tubing and observe the manometer for one minute. A loss of pressure on the manometer indicates a leak in the meter box; leaks, if present, must be corrected.

5.7 Barometer. Calibrate against a mercury barometer.

6. Calculations

Carry out calculations, retaining at least one extra decimal figure beyond that of the acquired data. Round off figures after the final calculation. Other forms of the equations may be used as long as they give equivalent results.

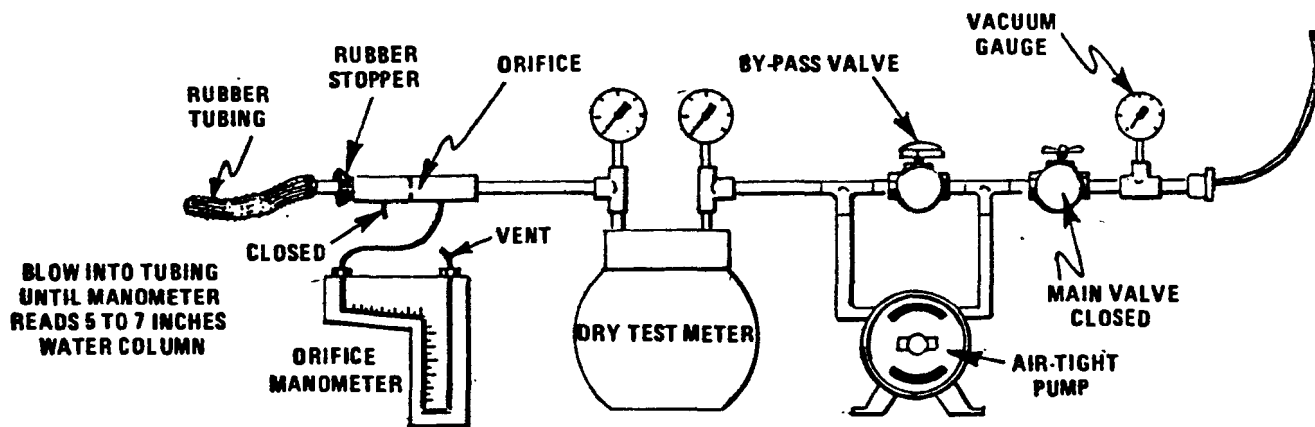


Figure 5-4. Leak check of meter box.

6.1 Nomenclature

- A_n = Cross-sectional area of nozzle, m² (ft²).
- B_m = Water vapor in the gas stream, proportion by volume.
- C_n = Acetone blank residue concentrations, mg/g.
- C_s = Concentration of particulate matter in stack gas, dry basis, corrected to standard conditions, g/dscm (g/dscf).
- I = Percent of isokinetic sampling.
- L_m = Maximum acceptable leakage rate for either a pretest leak check or for a leak check following a component change; equal to 0.00057 m³/min (0.02 cfm) or 4 percent of the average sampling rate, whichever is less.
- L_{i-1} = Individual leakage rate observed during the leak check conducted prior to the i^{th} component change ($i=1, 2, 3, \dots, n$), m³/min (cfm).
- L_n = Leakage rate observed during the post-test leak check, m³/min (cfm).
- m_s = Total amount of particulate matter collected, mg.
- M_w = Molecular weight of water, 18.0 g/g-mole (18.0 lb/lb-mole).
- m_a = Mass of residue of acetone after evaporation, mg.
- P_{bar} = Barometric pressure at the sampling site, mm Hg (in. Hg).
- P_s = Absolute stack gas pressure, mm Hg (in. Hg).
- P_{std} = Standard absolute pressure, 760 mm Hg (29.92 in. Hg).

- R = Ideal gas constant, 0.06236 mm Hg-m³/°K-g-mole (21.85 in. Hg-ft³/°R-lb-mole).
- T_m = Absolute average dry gas meter temperature (see Figure 5-2), °K (°R).
- T_s = Absolute average stack gas temperature (see Figure 5-2), °K (°R).
- T_{std} = Standard absolute temperature, 293° K (528° R).
- V_n = Volume of acetone blank, ml.
- V_w = Volume of acetone used in wash, ml.
- V_{L_i} = Total volume of liquid collected in impingers and silica gel (see Figure 5-3), ml.
- V_m = Volume of gas sample as measured by dry gas meter, dcm (dscf).
- $V_{m(i-1)}$ = Volume of gas sample measured by the dry gas meter, corrected to standard conditions, dcm (dscf).
- $V_{m(i-1)}$ = Volume of water vapor in the gas sample, corrected to standard conditions, scm (scf).
- V_s = Stack gas velocity, calculated by Method 2, Equation 2-9, using data obtained from Method 5, m/sec (ft/sec).
- W_w = Weight of residue in acetone wash, mg.
- Y = Dry gas meter calibration factor.
- ΔH = Average pressure differential across the orifice meter (see Figure 5-2), mm H₂O (in. H₂O).
- ρ_a = Density of acetone, mg/ml (see label on bottle).
- ρ_w = Density of water, 0.9982 g/ml (0.02201 lb/ml).
- t = Total sampling time, min.

- t_i = Sampling time interval, from the beginning of a run until the first component change, min.
- t_{i-1} = Sampling time interval, between two successive component changes, beginning with the interval between the first and second changes, min.
- t_n = Sampling time interval, from the final (n^{th}) component change until the end of the sampling run, min.
- 13.6 = Specific gravity of mercury.
- 60 = Sec/min.
- 100 = Conversion to percent.

6.2 Average dry gas meter temperature and average orifice pressure drop. See data sheet (Figure 5-2).

6.3 Dry Gas Volume. Correct the sample volume measured by the dry gas meter to standard conditions (30° C, 760 mm Hg or 68° F, 29.92 in. Hg) by using Equation 5-1.

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

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

Equation 5-1

where:
 $m_1 = 0.2854 \text{ }^\circ\text{K/mm Hg}$ for metric units
 $= 17.64 \text{ }^\circ\text{R/in. Hg}$ for English units

NOTE.—Equation 5-1 can be used as written unless the leakage rate observed during any of the mandatory leak checks (i.e., the post-test leak check or leak checks conducted prior to component changes) exceeds L_m . If L_p or L_s exceeds L_m , Equation 5-1 must be modified as follows:

(a) Case I. No component changes made during sampling run. In this case, replace V_m in Equation 5-1 with the expression:

$$V_m = (L_p - L_s)\theta$$

(b) Case II. One or more component changes made during the sampling run. In this case, replace V_m in Equation 5-1 by the expression:

$$\left[V_m - (L_1 - L_s)\theta_1 - \sum_{i=2}^n (L_i - L_s)\theta_i - (L_p - L_s)\theta_p \right]$$

and substitute only for those leakage rates (L_i or L_p) which exceed L_m .

6.4 Volume of water vapor.

Equation 5-2

$$V_{w(\text{std})} = V_{1s} \left(\frac{P_w}{P_{\text{std}}} \right) \left(\frac{RT_{\text{std}}}{P_{\text{std}}} \right) = K_3 V_{1s}$$

where:
 $K_3 = 0.001333 \text{ m}^3/\text{ml}$ for metric units
 $= 0.04707 \text{ ft}^3/\text{ml}$ for English units.

6.5 Moisture Content.

$$B_{ws} = \frac{V_{w(\text{std})}}{V_m(\text{std}) + V_{w(\text{std})}}$$

Equation 5-3

$$I = \frac{100 T_s [K_4 V_{1s} + (V_m/T_m) (P_{\text{bar}} + \Delta H/13.6)]}{60 \theta v_s P_s A_s}$$

Equation 5-2

where:
 $K_4 = 0.003454 \text{ mm Hg} \cdot \text{m}^3/\text{ml} \cdot \text{ }^\circ\text{K}$ for metric units.
 $= 0.002669 \text{ in. Hg} \cdot \text{ft}^3/\text{ml} \cdot \text{ }^\circ\text{R}$ for English units.

6.11.2 Calculation From Intermediate Values.

$$I = \frac{T_s V_m(\text{std}) P_{\text{std}} 100}{T_{\text{std}} v_s \theta A_s P_s 60 (1 - B_{ws})}$$

$$= K_4 \frac{T_s V_m(\text{std})}{P_s V_s A_s \theta (1 - B_{ws})}$$

Equation 5-8

where:
 $K_4 = 4.320$ for metric units
 $= 0.09450$ for English units.

6.12 Acceptable Results. If 90 percent $< I < 110$ percent, the results are acceptable. If the results are low in comparison to the standard and I is beyond the acceptable range, or if I is less than 90 percent, the Administrator may opt to accept the results. Use Citation 4 to make judgments. Otherwise, reject the results and repeat the test.

7. Bibliography

1. Addendum to Specifications for Incinerator Testing at Federal Facilities. PHS, NCAPC. Dec. 6, 1967.
2. Martin, Robert M. Construction Details of Isokinetic Source-Sampling Equipment. Environmental Protection Agency. Research Triangle Park, N.C. APTD-0681. April, 1971.
3. Rom, Jerome J. Maintenance, Calibration, and Operation of Isokinetic Source Sampling Equipment. Environmental Protection Agency. Research Triangle Park, N.C. APTD-0678. March, 1972.
4. Smith, W. S., R. T. Shigehara, and W. F. Todd. A Method of Interpreting Stack Sampling Data. Paper Presented at the 63d Annual Meeting of the Air Pollution Control Association, St. Louis, Mo. June 16-19, 1970.
5. Smith, W. S., et al. Stack Gas Sampling Improved and Simplified With New Equipment. APCA Paper No. 67-119. 1967.
6. Specifications for Incinerator Testing at Federal Facilities. PHS, NCAPC. 1967.
7. Shigehara, R. T. Adjustments in the EPA Nemo-graph for Different Pitot Tube Coefficients and Dry Molecular Weights. Stack Sampling News 2:4-11. October, 1974.

NOTE.—In saturated or water droplet-laden gas streams, two calculations of the moisture content of the stack gas shall be made, one from the impinger analysis (Equation 5-3), and a second from the assumption of saturated conditions. The lower of the two values of B_{ws} shall be considered correct. The procedure for determining the moisture content based upon assumption of saturated conditions is given in the Note of Section 1.3 of Method 4. For the purposes of this method, the average stack gas temperature from Figure 5-2 may be used to make this determination, provided that the accuracy of the in-stack temperature sensor is $\pm 1^\circ\text{C}$ (2°F).

6.6 Acetone Blank Concentration.

$$C_a = \frac{m_a}{V_a P_a}$$

Equation 5-4

6.7 Acetone Wash Blank.

$$W_a = C_a V_{aw} P_a$$

Equation 5-5

6.8 Total Particulate Weight. Determine the total particulate catch from the sum of the weights obtained from containers 1 and 2 less the acetone blank (see Figure 5-3). NOTE.—Refer to Section 4.1.5 to assist in calculation of results involving two or more filter assemblies or two or more sampling trains.

6.9 Particulate Concentration.

$$c_p = (0.001 \text{ g/mg}) (m_p/V_m(\text{std}))$$

Equation 5-6

6.10 Conversion Factors:

From	To	Multiply by
ccf	m ³	0.02832
g/ft ³	gr/ft ³	16.01
g/ft ³	lb/ft ³	2.205 × 10 ⁻³
g/ft ³	g/m ³	35.31

6.11 Isokinetic Variation.

6.11.1 Calculation From Raw Data.

8. Vellaro, R. F. A Survey of Commercially Available Instrumentation For the Measurement of Low-Range Gas Velocities. U.S. Environmental Protection Agency, Emission Measurement Branch, Research Triangle Park, N.C. November, 1976 (unpublished paper).

9. Annual Book of ASTM Standards. Part 26. Gaseous Fuels; Coal and Coke; Atmospheric Analysis. American Society for Testing and Materials. Philadelphia, Pa. 1974. pp. 617-622.

11.0 REFERENCES

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2. Hamil, H. F. and R. E. Thomas. Collaborative Study of Particulate Emissions Measurements by EPA Methods 2, 3, and 5 using Paired Particulate Sampling Trains. EPA-600/4-76-014. Environmental Protection Agency, Research Triangle Park, N.C., March 1976.
3. Martin, R. M. Construction Details of Isokinetic Source Sampling Equipment. Publication No. APTD-0581. Air Pollution Control Office, EPA, Research Triangle Park, N.C., 1971.
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5. Midgett, M. R. The EPA Program for the Standardization of Stationary Source Emission Test Methodology, A Review. EPA-600/4-76-044. Environmental Protection Agency, Research Triangle Park, N.C., August 1976.

Additional References

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Hanson, H. A. and D. P. Saari. Effective Sampling Techniques for Particulate Emissions from Typical Stationary Sources - Interim Report. Contract No. 68-02-1796, EPA-600/2-77-036. Fluidyne Engineering Corp., Minneapolis, Minnesota, February 1977.

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 the text section. For example, Form M5-1.2 indicates that the form is Figure 1.2 in Section 3.4.1 of the Method 5 Handbook. Future revisions of these forms, if any, can be documented by 1.2A, 1.2B, etc. Fourteen of the blank forms listed below are included in this section. Five are in the Method Highlights Section as shown by the MH following the form number and one is left blank in the text.

<u>Form</u>	<u>Title</u>
1.2	Procurement Log
2.3A & B	Dry Gas Meter Calibration Data Form (English and Metric units)
2.4A & B	Posttest Meter Calibration Data Form (English and Metric units)
2.5	Stack Temperature Sensor Calibration Data Form
2.6	Nozzle Calibration Data Form
3.1 (MH)	Pretest Sampling Checks
3.2 (Text)	General Pretest Checklist
4.1	Nomograph Data Form
4.2	Particulate Field Data Form
4.3	Sample Label
4.4	Sample Recovery and Integrity Data Form
4.5 (MH)	On-Site Measurement Checklist
5.1 (MH)	Posttest Calibration Checks
5.2	Analytical Balance Calibration Data Form

<u>Form</u>	<u>Title</u>
5.3	Sample Analytical Data Form
5.4	Blank Analytical Data Form
5.5 (MH)	Procedure for Weighing Filters Before and After Sampling
5.6 (MH)	Procedure for Analysis of Acetone Rinse Samples
6.1A & 6.1B	Particulate Calculation Data Form (English and Metric units)
8.1	Method 5 Checklist To Be Used by Auditors

PROCUREMENT LOG

Item description	Quantity	Purchase order number	Vendor	Date		Cost	Disposition	Comments
				Ordered	Received			

METER BOX CALIBRATION DATA AND CALCULATION FORM

(English units)

Date _____

Meter box number _____

Barometric pressure, P_b = _____ in. Hg Calibrated by _____

Orifice manometer setting (ΔH), in. H ₂ O	Gas volume		Temperatures				Time (θ), min	Y_i	$\Delta H@_i$ in. H ₂ O
	Wet test meter (V_w), ft ³	Dry gas meter (V_d), ft ³	Wet test meter (t_w), °F	Dry gas meter					
				Inlet (t_{di}), °F	Outlet (t_{do}), °F	Avg ^a (t_d), °F			
0.5	5								
1.0	5								
1.5	10								
2.0	10								
3.0	10								
4.0	10								
Avg									

ΔH , in. H_2O	$\frac{\Delta H}{13.6}$	$Y_i = \frac{V_w P_b (t_d + 460)}{V_d (P_b + \frac{\Delta H}{13.6}) (t_w + 460)}$	$\Delta H@_i = \frac{0.0317 \Delta H}{P_b (t_d + 460)} \left[\frac{(t_w + 460) \theta}{V_w} \right]^2$
0.5	0.0368		
1.0	0.0737		
1.5	0.110		
2.0	0.147		
3.0	0.221		
4.0	0.294		

^a If there is only one thermometer on the dry gas meter, record the temperature under t_d .

METER BOX CALIBRATION DATA AND CALCULATION FORM (English units)

Nomenclature:

V_w = Gas volume passing through the wet test meter, ft^3 .

V_d = Gas volume passing through the dry gas meter, ft^3 .

t_w = Temperature of the gas in the wet test meter, $^{\circ}\text{F}$.

t_{d_i} = Temperature of the inlet gas of the dry gas meter, $^{\circ}\text{F}$.

t_{d_o} = Temperature of the outlet gas of the dry gas meter, $^{\circ}\text{F}$.

t_d = Average temperature of the gas in the dry gas meter, obtained by the average t_{d_i} and t_{d_o} , $^{\circ}\text{F}$.

ΔH = Pressure differential across orifice, in. H_2O .

Y_i = Ratio of accuracy of wet test meter to dry gas meter for each run. Tolerance $Y_i = Y \pm 0.02 Y$.

Y = Average ratio of accuracy of wet test meter to dry gas meter for all six runs.
Tolerance $Y = Y \pm 0.01 Y$.

$\Delta H@_i$ = Orifice pressure differential at each flow rate that gives $0.75 \text{ ft}^3/\text{min}$ of air at standard conditions for each calibration run, in. H_2O . Tolerance = $\Delta H@ \pm 0.15$ (recommended).

$\Delta H@$ = Average orifice pressure differential that gives $0.75 \text{ ft}^3/\text{min}$ of air at standard conditions for all six runs, in. H_2O . Tolerance = 1.84 ± 0.25 (recommended).

θ = Time for each calibration run, min.

P_b = Barometric pressure, in. Hg.

METER BOX CALIBRATION DATA AND CALCULATION FORM

(Metric units)

Date _____

Meter box number _____

Barometric pressure, P_b = _____ mm Hg Calibrated by _____

Orifice manometer setting (ΔH), mm H ₂ O	Gas volume		Temperatures				Time (θ), min	Y_i	$\Delta H@_i$, mm H ₂ O
	Wet test meter (V_w), m ³	Dry gas meter (V_d), m ³	Wet test meter (t_w), °C	Dry gas meter					
				Inlet (t_{d_i}), °C	Outlet (t_{d_o}), °C	Avg ^a (t_d), °C			
10	0.15								
25	0.15								
40	0.30								
50	0.30								
75	0.30								
100	0.30								
							Avg		

ΔH , mm H ₂ O	$\frac{\Delta H}{13.6}$	$Y_i = \frac{V_w P_b (t_d + 273)}{V_d (P_d + \frac{\Delta H}{13.6}) (t_w + 273)}$	$\Delta H@_i = \frac{0.00117 \Delta H}{P_b (t_d + 273)} \left[\frac{(t_w + 273) \theta}{V_w} \right]^2$
10	0.7		
25	1.8		
40	2.94		
50	3.68		
75	5.51		
100	7.35		

^a If there is only one thermometer on the dry gas meter, record the temperature under t_d .

METER BOX CALIBRATION DATA AND CALCULATION FORM (metric units)

Nomenclature:

V_w = Gas volume passing through the wet test meter, m^3 .

V_d = Gas volume passing through the dry gas meter, m^3 .

t_w = Temperature of the gas in the wet test meter, $^{\circ}C$.

t_{d_i} = Temperature of the inlet gas of the dry gas meter, $^{\circ}C$.

t_{d_o} = Temperature of the outlet gas of the dry gas meter, $^{\circ}C$.

t_d = Average temperature of the gas in the dry gas meter, obtained by the average of t_{d_i} and t_{d_o} , $^{\circ}C$.

ΔH = Pressure differential across orifice, mm H_2O .

Y_i = Ratio of accuracy of wet test meter to dry gas meter for each run. Tolerance $Y_i = Y \pm 0.02 Y$.

Y = Average ratio of accuracy of wet test meter to dry gas meter for all six runs.
Tolerance $Y = Y \pm 0.01 Y$.

$\Delta H@_i$ = Orifice pressure differential at each flow rate that gives $0.021 m^3$ of air at standard conditions for each calibration run, mm H_2O . Tolerance $\Delta H@_i = \Delta H@ \pm 3.8 \text{ mm } H_2O$ (recommended).

$\Delta H@$ = Average orifice pressure differential that gives $0.021 m^3$ of air at standard conditions for all six runs, mm H_2O . Tolerance $\Delta H@ = 46.74 \pm 6.3 \text{ mm } H_2O$ (recommended).

θ = Time of each calibration run, min.

P_b = Barometric pressure, mm Hg.

POSTTEST DRY GAS METER CALIBRATION DATA FORM (English units)

Test numbers _____ Date _____ Meter box number _____ Plant _____

Barometric pressure, P_b = _____ in. Hg Dry gas meter number _____ Pretest Y _____

Orifice manometer setting, (ΔH), in. H ₂ O	Gas volume		Temperature				Time (Θ), min	Vacuum setting, in. Hg	Y _i	Y _i
	Wet test meter (V _w), ft ³	Dry gas meter (V _d), ft ³	Wet test meter (t _w), °F	Dry gas meter						$V_w P_b (t_d + 460)$
				Inlet (t _{d_i}), °F	Outlet (t _{d_o}), °F	Average ^a (t _d), °F				$V_d P_b + \frac{\Delta H}{13.6} t_w + 460$
	10									
	10									
	10									
										Y =

^a If there is only one thermometer on the dry gas meter, record the temperature under t_d .

V_w = Gas volume passing through the wet test meter, ft³.

V_d = Gas volume passing through the dry gas meter, ft³.

t_w = Temperature of the gas in the wet test meter, °F.

t_{d_i} = Temperature of the inlet gas of the dry gas meter, °F.

t_{d_o} = Temperature of the outlet gas of the dry gas meter, °F.

t_d = Average temperature of the gas in the dry gas meter, obtained by the average of t_{d_i} and t_{d_o} , °F.

ΔH = Pressure differential across orifice, in H₂O.

Y_i = Ratio of accuracy of wet test meter to dry gas meter for each run.

Y = Average ratio of accuracy of wet test meter to dry gas meter for all three runs;
tolerance = pretest Y \pm 0.05Y

P_b = Barometric pressure, in. Hg.

θ = Time of calibration run, min.

POSTTEST METER CALIBRATION DATA FORM (Metric units)

Test numbers _____ Date _____ Meter box number _____ Plant _____

Barometric pressure, P_b = _____ mm Hg Dry gas meter number _____ Pretest Y _____

Orifice manometer setting, (ΔH), mm H ₂ O	Gas volume		Temperature			Time (θ), min	Vacuum setting, mm Hg	Y _i	Y _i $\frac{V_w P_b (t_d + 273)}{V_d P_b + \frac{\Delta H}{13.6} t_w + 273}$
	Wet test meter (V _w), m ³	Dry gas meter (V _d), m ³	Wet test meter (t _w), °C	Dry gas meter					
				Inlet (t _d _i), °C	Outlet (t _d _o), °C				
	.3								
	.3								
	.3								

Y = _____

^a If there is only one thermometer on the dry gas meter, record the temperature under t_d .

where

V_w = Gas volume passing through the wet test meter, m^3 .

V_d = Gas volume passing through the dry gas meter, m^3 .

t_w = Temperature of the gas in the wet test meter, $^{\circ}C$.

t_{d_i} = Temperature of the inlet gas of the dry gas meter, $^{\circ}C$.

t_{d_o} = Temperature of the outlet gas of the dry gas meter, $^{\circ}C$.

t_d = Average temperature of the gas in the dry gas meter, obtained by the average of t_{d_i} and t_{d_o} , $^{\circ}C$.

ΔH = Pressure differential across orifice, mm H_2O .

Y_i = Ratio of accuracy of wet test meter to dry gas meter for each run.

Y = Average ratio of accuracy of wet test meter to dry gas meter for all three runs;
tolerance = pretest Y $\pm 0.05Y$

P_b = Barometric pressure, mm Hg.

Θ = Time of calibration run, min.

Date _____ Thermocouple number _____
Ambient temperature _____°C Barometric pressure _____ in. Hg
Calibrator _____ Reference: mercury-in-glass _____
other _____

Reference point number	Source ^a (specify)	Reference thermometer temperature, °C	Thermocouple potentiometer temperature, °C	Temperature difference, ^b %

$$b \left[\frac{(\text{ref temp, } ^\circ\text{C} + 273) - (\text{test thermom temp, } ^\circ\text{C} + 273)}{\text{ref temp, } ^\circ\text{C} + 273} \right] 100 \leq 1.5\%.$$

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NOZZLE CALIBRATION DATA FORM

Date _____ Calibrated by _____

Nozzle identification number	Nozzle Diameter ^a			$\Delta D'$ ^b mm (in.)	D_{avg} ^c
	D_1' mm (in.)	D_2' mm (in.)	D_3' mm (in.)		

where:

^aD_{1,2,3}, = three different nozzles diameters, mm (in.); each diameter must be within (0.025 mm) 0.001 in.

b ΔD = maximum difference between any two diameters, mm (in.),
 $\Delta D \leq (0.10 \text{ mm}) 0.004 \text{ in.}$

^c D_{avg} = average of D_1 , D_2 , and D_3 .

NOMOGRAPH DATA FORM (English units)

Plant _____

Date _____

Sampling location _____

Calibrated pressure differential across orifice, in. H ₂ O	$\Delta H_{@}$	
Average meter temperature (ambient + 20°F), °F	$t_{m\text{ avg}}$	
Percent moisture in gas stream by volume, %	B_{wo}	
Barometric pressure at meter, in. Hg	P_m	
Station pressure in stack, in. Hg ($P_m \pm 0.073 \times \text{stack gauge pressure, in. H}_2\text{O}$)	P_s	
Ratio of static pressure to meter pressure	P_s/P_m	
Average stack temperature, °F	$t_{s\text{ avg}}$	
Average velocity head, in. H ₂ O	Δp_{avg}	
Maximum velocity head, in. H ₂ O	Δp_{max}	
C factor		
Calculated nozzle diameter, in.		
Actual nozzle diameter, in.		
Reference Δp , in. H ₂ O		

PARTICULATE FIELD DATA FORM

Plant _____ Meter calibration (Y) _____ Sheet _____ of _____
City _____ Pitot tube (C) _____ Nozzle identification number _____
Location _____ Probe length P _____ Nozzle diameter _____ mm (in.)
Operator _____ Probe liner material _____ Thermometer number _____
Date _____ Probe heater setting _____ Final leak rate _____ m^3/min (cfm)
Run number _____ Ambient temperature _____ Vacuum during leak check _____
Stack diam, mm (in.) _____ Barometric pressure (P_b) _____ mm (in.) Hg
Assumed moisture _____ Filter number _____
Sample box number _____ Static pressure (P_a) _____ mm (in.) H_2O Remarks _____
Meter box number _____ C Factor _____
Meter $\Delta H@$ _____ Reference ΔP _____ mm (in.) H_2O

Traverse point number	Sampling time, (t), min	Clock time, (24 h)	Vacuum, mm (in.) Hg	Stack temperature (T), °C (°F)	Velocity head (ΔP_s), mm (in.) H_2O	Pressure differential across orifice meter (ΔH), mm (in.) H_2O	Gas sample volume (V), m^3 (ft ³)	Gas sample temperature at dry gas meter		Temperature of gas leaving condenser or last impinger, °C (°F)	Filter temp, °C (°F)
								Inlet, °C (°F)	Outlet, °C (°F)		
	Total		Max	Avg			Total	Avg	Avg	Max	

SAMPLE LABEL

Plant _____	City _____	Remarks: _____ _____ _____	
Site _____	Sample type _____		
Date _____	Run number _____		
Front rinse	Front filter		Front solution
Back rinse	Back filter		Back solution
Solution _____	Level marked _____		
Volume: Initial _____	Final _____		
Clean up by _____			

SAMPLE RECOVERY AND INTEGRITY DATA FORM

Plant _____ Sample date _____
 Sample location _____ Run number _____
 Sample recovery person _____ Recovery date _____
 Filter(s) number _____

MOISTURE

<u>Impingers</u>		<u>Silica gel</u>	
Final volume (wt)	_____ ml (g)	Final wt	_____ g _____ g
Initial volume (wt)	_____ ml (g)	Initial wt	_____ g _____ g
Net volume (wt)	_____ ml (g)	Net wt	_____ g _____ g
Total moisture _____ g			
Color of silica gel _____			
Description of impinger water _____			

RECOVERED SAMPLE

Blank filter container number _____ Sealed _____
 Filter container number _____ Sealed _____
 Description of particulate on filter _____

Acetone rinse container number _____	Liquid level marked? _____
Acetone blank container number _____	Liquid level marked? _____

Samples stored and locked _____
 Remarks _____

Date of laboratory custody _____
 Laboratory personnel taking custody _____
 Remarks _____

ANALYTICAL BALANCE CALIBRATION FORM

Balance name	Number

Classification of standard weights

[illegible]

SAMPLE ANALYTICAL DATA FORM

Plant _____ Run number _____

Sample location _____

Relative humidity _____

Density of acetone (ρ_a) _____ g/ml

Sample type	Sample identifiable	Liquid level marked and/or container sealed
Acetone rinse filter(s)		

Acetone rinse container number _____

Acetone rinse volume (V_{aw}) _____ ml

Acetone blank residue concentration (C_a) _____ mg/g

$W_a = C_a V_{aw} \rho_a = () () () =$ _____ mg

Date and time of wt _____ Gross wt _____ mg

Date and time of wt _____ Gross wt _____ mg

Average gross wt _____ mg

Tare wt _____ mg

Less acetone blank wt (W_a) _____ mg

Weight of particulate in acetone rinse (m_a) _____ mg

Filter(s) container number _____

Date and time of wt _____ Gross wt _____ mg

Date and time of wt _____ Gross wt _____ mg

Average gross wt _____ mg

Tare wt _____ mg

Weight of particulate on filter(s) (m_f) _____ mg

Weight of particulate in acetone rinse _____ mg

Total weight of particulate (m_n) _____ mg

Note: In no case should a blank residue >0.01 mg/g or 0.001% of the weight of acetone used be subtracted from the sample weight.

Remarks _____

Signature of analyst _____

Signature of reviewer _____

BLANK ANALYTICAL DATA FORM

Plant _____
 Sample location _____
 Relative humidity _____
 Liquid level marked and container sealed _____
 Density of acetone (ρ_a) _____ g/ml
 Blank volume (V_a) _____ ml
 Date and time of wt _____ Gross wt _____ mg
 Date and time of wt _____ Gross wt _____ mg
 Average gross wt _____ mg
 Tare wt _____ mg
 Weight of blank (m_{ab}) _____ mg

$$C_a = \frac{m_{ab}}{V_a \rho_a} = \frac{(\quad)}{(\quad)(\quad)} = \quad \text{mg/g}$$

Note: In no case should a blank residue greater than 0.01 mg/g (or 0.001% of the blank weight) be subtracted from the sample weight.

Filters _____ Filter number _____
 Date and time of wt _____ Gross wt _____ mg
 Date and time of wt _____ Gross wt _____ mg
 Average gross wt _____ mg
 Tare wt _____ mg
 Difference wt _____ mg

Note: Average difference must be less than ± 5 mg or 2% of total sample weight whichever is greater.

Remarks _____

Signature of analyst _____

Signature of reviewer _____

PARTICULATE CALCULATION FORM (English units)

SAMPLE VOLUME (ENGLISH UNITS)

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

$$Y = \text{---} \cdot \text{---}, \Delta H = \text{---} \cdot \text{---} \text{ in. H}_2\text{O}$$

$$V_{m(\text{std})} = 17.64 V_m Y \left(\frac{P_{\text{bar}} + (\Delta H/13.6)}{T_m} \right) = \text{---} \cdot \text{---} \text{ ft}^3$$

Equation 6-1

PARTICULATE CONCENTRATION (ENGLISH UNITS)

$$m_n = \text{---} \cdot \text{---} \text{ mg}$$

$$C_s = 2.205 \times 10^{-6} \left(\frac{m_n}{V_{m(\text{std})}} \right) = \text{---} \cdot \text{---} \times 10^{-4} \text{ lb/dscf}$$

Equation 6-8

PARTICULATE CALCULATION FORM (metric units)

SAMPLE VOLUME (METRIC UNITS)

$$V_m = _ . _ _ _ m^3, T_m = _ _ _ . ^\circ K, P_{bar} = _ _ _ . mm Hg$$

$$Y = _ . _ _ _, \Delta H = _ _ _ . mm H_2O$$

$$V_{m(std)} = 0.3858 V_m Y \left(\frac{P_{bar} + (\Delta H/13.6)}{T_m} \right) = _ . _ _ _ m^3 \quad \text{Equation 6-1}$$

PARTICULATE CONCENTRATION (METRIC UNITS)

$$m_n = _ _ _ _ . _ mg$$

$$C_s = 1 \times 10^{-3} \left(\frac{m_n}{V_{m(std)}} \right) = _ . _ _ _ g/dscm \quad \text{Equation 6-8}$$

METHOD 5 CHECKLIST TO BE USED BY AUDITORS

Yes	No	Comment	OPERATION
			Presampling Preparation
—	—	—	1. Knowledge of process conditions
—	—	—	2. Calibration of pertinent equipment: in particular, the dry gas meter, orifice meter, and pitot tube
			On-Site Measurements
—	—	—	3. Sample train assembly
—	—	—	4. Pretest leak check of train
—	—	—	5. Isokinetic sampling
—	—	—	6. Posttest check
—	—	—	7. Sample recovery and integrity
—	—	—	8. Recording of pertinent process information during sample collec- tion
			Postsampling
—	—	—	9. Check of analytical balance
—	—	—	10. Use of acceptable detection blanks in correcting field sample results
—	—	—	11. Calculation procedure/check
General Comments			

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 l/min for 20 min. Based on theoretical calculations, the upper concentration limit in a 20-l 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 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 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_2 reacting with the particulate matter.

The tester also has the option of determining the emissions of SO_2 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_2 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_2/m^3 (14, 70, and 130×10^{-6} lb SO_2/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 SO₂/m³ (17.6, 35.2, and 52.8 × 10⁻⁶ lb SO₂/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) (ΔH_0 , 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_2 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_2 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.

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°F) of reference values for calibration and within $\pm 2^\circ\text{C}$ (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 $\pm 3^\circ\text{C}$ (5.4°F) of reference values for calibration and within $\pm 6^\circ\text{C}$ (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.

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 ₂ O ₂ , 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_2O_2 _____

3rd: 15 ml of 3% H_2O_2 _____

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.

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 $\pm 2\%$ 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 $\pm 6^\circ\text{C}$ (10.8°F) of reference values
Recalibration required? _____ yes _____ no
Recalibration temperature correction if used _____ within $\pm 3^\circ\text{C}$ (5.4°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 ± 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.

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

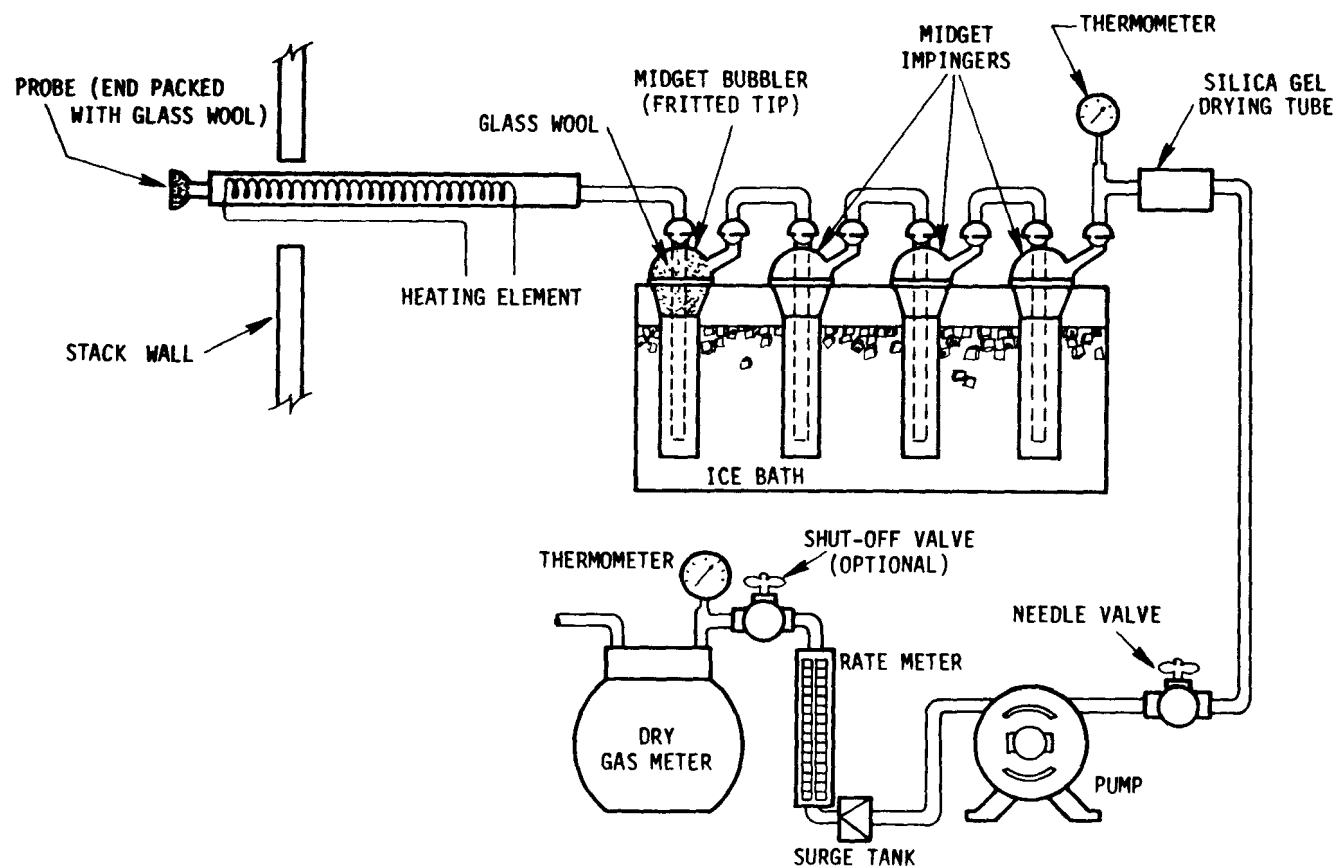


Figure 1.1. SO₂ sampling train.

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

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.

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_2 .

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

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 $\pm 2\%$ 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 $0.003 \text{ m}^3/\text{min}$ ($0.1 \text{ ft}^3/\text{min}$) with an accuracy of $\pm 1\%$; 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

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°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°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.) H_2O .

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.

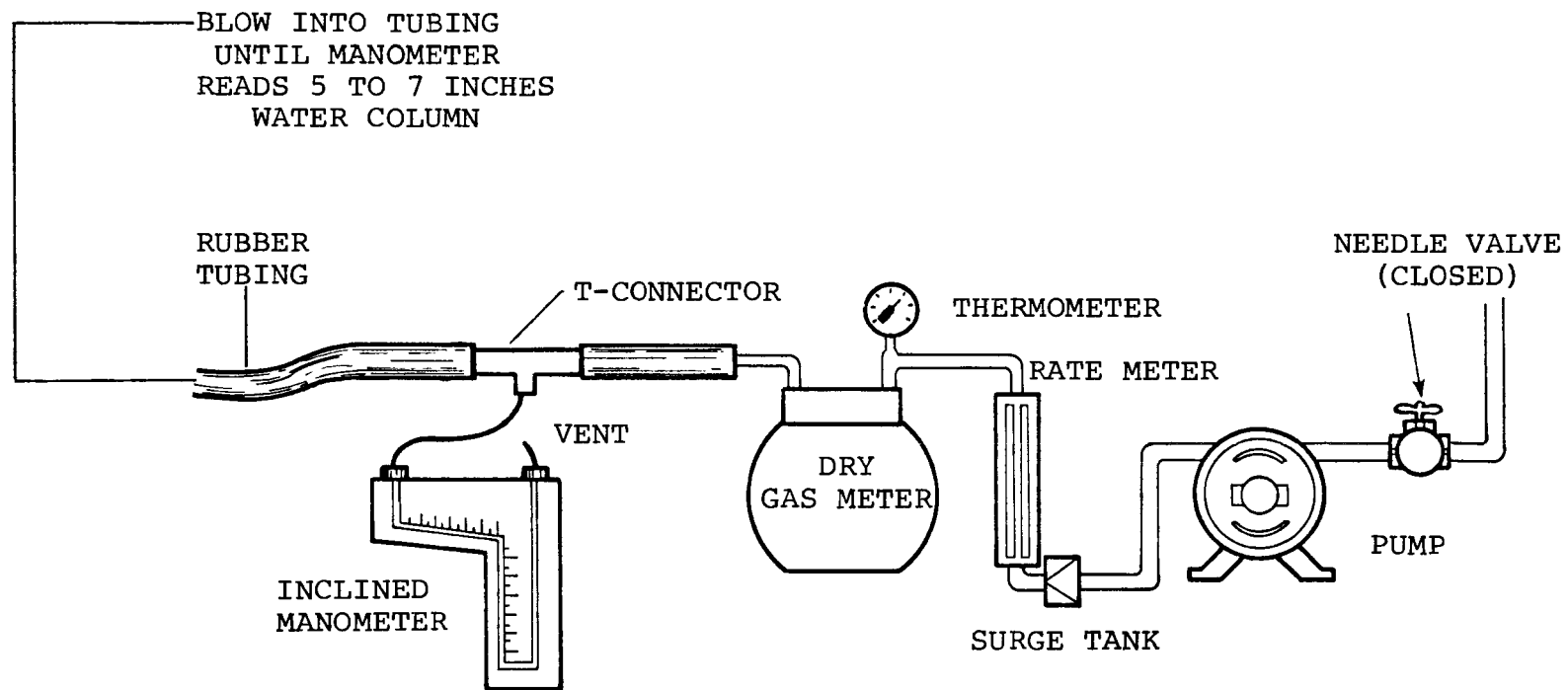


Figure 1.3. Meter box leak check.

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°F) of the true value when checked at two different ambient temperatures against a mercury-in-glass thermometer that conforms to ASTM E-1 No. 63C or 63F. The two ambient temperatures used to calibrate the thermometer must differ by a minimum of 10°C (18°F). Damaged thermometers that cannot be calibrated are to be rejected.

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 ± 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 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 H_2O blank at 352 nm on a spectrophotometer. If absorbance exceeds 0.1, reject the alcohol for use. Peroxides may be removed from isopropanol by redistilling or by passing through a column of activated alumina. After peroxides are removed, check for peroxide impurities using the same method as above. However, reagent grade isopropanol with suitably low peroxide levels may be obtained from commercial sources. Therefore, rejection of contaminated lots may be a more efficient procedure.

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.

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 H_2SO_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.

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 $\pm 2\%$ 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 $\pm 1\%$ at a flow rate of 1 l/min	Upon assembly, leak check all connections and check calibration by liquid displacement	As above
Rotameter	Within $\pm 5\%$ 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 $\pm 1^\circ\text{C}$ (2°F) of true value in the range of 0°C to 25°C (32° to 77°F) for impinger and $\pm 3^\circ\text{C}$ (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)

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 ± 2.5
Vacuum gauge	0 to 760 mm (0 to 29.92 in.) Hg range, ± 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_2O_2 , reagent grade or certified ACS	Upon receipt, check label for grade or certification	Replace or return to manufacturer
Potassium iodide solution	Potassium iodide, reagent grade or certified ACS	As above	As above
Thorin indicator	1-(o-arsonophenylazo)-2-naphthol-3,6-disulfonic acid disodium salt, reagent grade or certified ACS	As above	As above
Barium perchlorate solution	Barium perchlorate trihydrate ($Ba(ClO_4)_2 \cdot 3H_2O$), reagent grade or certified ACS	As above	As above
Sulfuric acid solution	Sulfuric acid, 0.0100N $\pm 0.0002N$	Have certified by manufacturer or standardize against 0.0100N NaOH that has been standardized against potassium acid phthalate (primary standard grade)	As above

2.0 CALIBRATION OF APPARATUS

Calibration of the apparatus is one of the most important functions in maintaining data quality. The detailed calibration procedures included in this section were designed for the equipment specified by Method 6 and described in the previous section. 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.

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- ℓ mark. Record the final volume on the wet test meter.

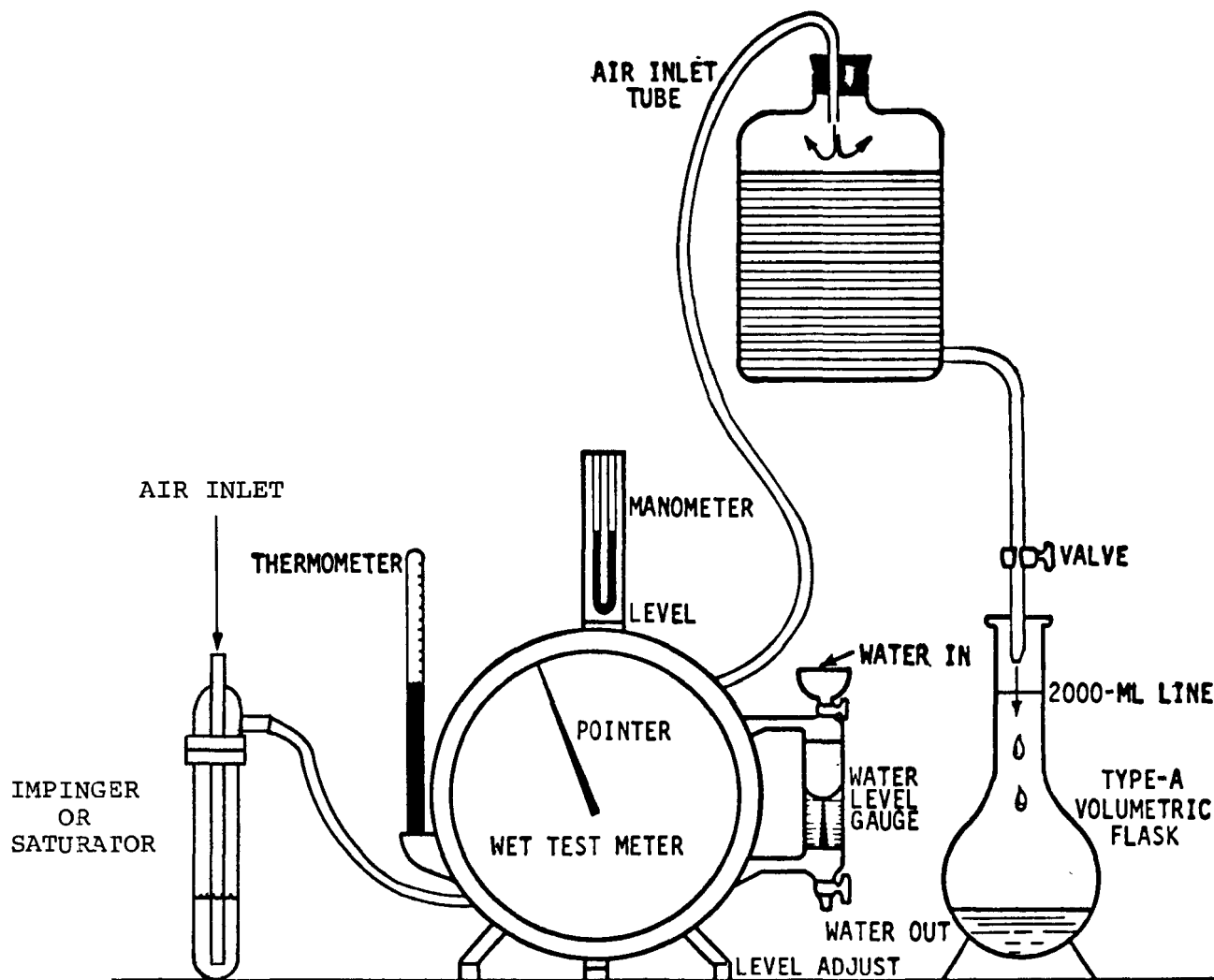


Figure 2.1. Calibration check apparatus for wet test meter.

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

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

Calculations:

^b $V_m = V_f - V_i$.

^c % 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.

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 cm³/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).

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

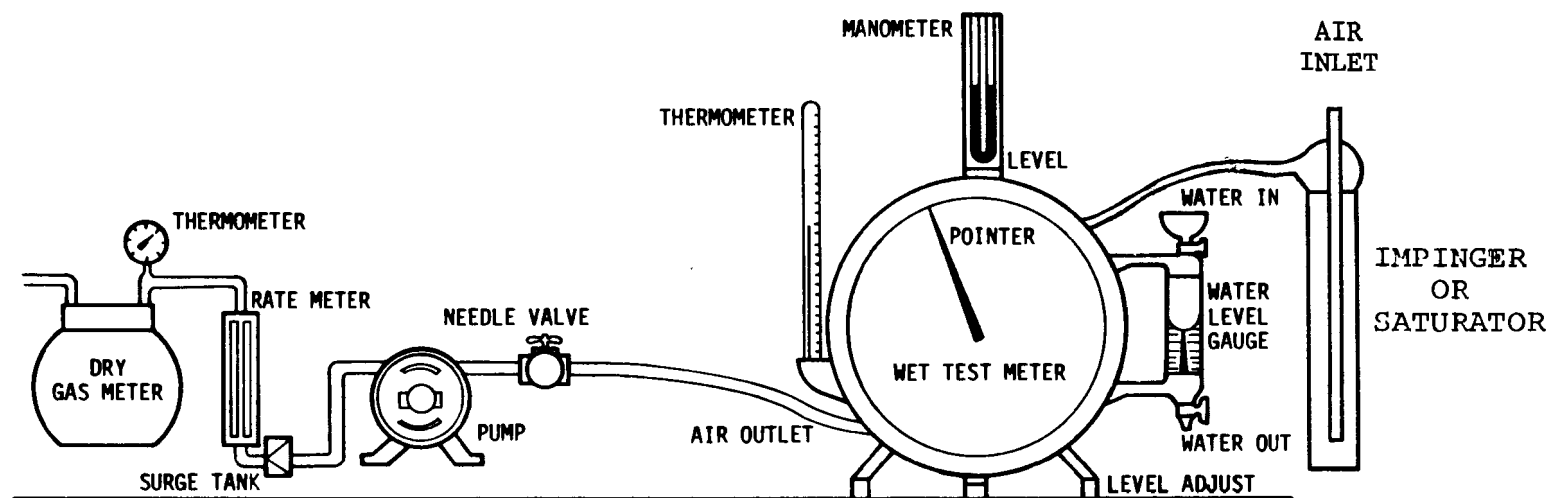


Figure 2.3. Sample meter system calibration setup.

Date 1/25/78 Calibrated by J. 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), ^a in. H ₂ O	Rota-meter setting (R_s), ft ³ /min	Wet test meter gas volume (V_w), ^b ft ³	Dry test meter gas volume (V_d), ^b ft ³		Wet test meter gas temp (t_w), °F	Inlet gas temp (t_{d_i}), °F	Dry test meter				(Y_{r_i}) , ^f
			Initial	Final			Outlet gas temp (t_{d_o}), °F	Average gas temp (t_d), ^c °F	Time of run (θ), ^d min	Average ratio (Y_i), ^e	
0.25	0.035	1.058	725.613	726.672	72	80	78	79	30	1.015	1.022
0.25	0.035	1.059	728.961	730.021	72	82	80	81	30	1.019	1.026
0.25	0.035	1.061	732.098	733.158	72	84	80	82	30	1.018	1.030

^a D_m expressed as negative number.

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

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

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

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

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

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

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

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

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), ^a mm H ₂ O	Rota-meter setting (R_s), ℓ/min	Wet test meter gas volume (V_w), ^b ℓ	Dry test meter gas volume (V_d), ^b ℓ		Wet test meter gas temp (t_w), °C	Inlet gas temp (t_{d_i}), °C	Dry test meter				(Y_{r_i}) , ^f
			Initial	Final			Outlet gas temp (t_{d_o}), °C	Average gas temp (t_d), ^c °C	Time of run (Θ), ^d min	Average ratio (Y_i), ^e	
5.4	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

^a D_m expressed as negative number.

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

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

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

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

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

^f 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.

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

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

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°F) at both points. If the difference is greater than $\pm 1^{\circ}\text{C}$ (2°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°F) of each other, replace or recalibrate the meter thermometer.

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

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 ± 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 ± 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).

Date 9/15/78 Calibrated by WGD
Meter box number FM-1 $\Delta H@$ 1.41

Dry Gas Meter*

Pretest calibration factor = 0.986 (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°F) of reference values for calibration and within $\pm 2^\circ\text{C}$ (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 $\pm 3^\circ\text{C}$ (5.4°F) of reference values for calibration and within $\pm 6^\circ\text{C}$ (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.

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	$Y_1 = Y \pm 0.02Y$ at a flow rate of about 1 l/min	Calibrate vs. wet test meter initially and when the posttest check is not within $Y \pm 0.05$	Repair and then recalibrate, or replace
Impinger thermometer	Within $\pm 1^\circ\text{C}$ (2°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 $\pm 3^\circ\text{C}$ (5.4°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 ± 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

3.0 PRESAMPLING OPERATIONS

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

3.1 Apparatus Check and Calibration

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

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

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

* Most significant items/parameters to be checked.

Figure 3.1. Pretest preparations.

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).

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 $\pm 2\%$ 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

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 (ft ³)	Sample flow rate setting, l/min (ft ³ /min)	Sample volume metered (ΔV_m), l (ft ³)	Percent deviation, ^a %	Dry gas meter temp, °C (°F)	Impinger temp, °C (°F)
0	1100	120.20	—	—	—	—	—
5	1105	125.30	1.0	5.1	2	27	19
10	1110	130.10	1.0	4.8	4	29	20
15	1115	135.20	1.0	5.1	2	30	20
20	1120	140.20	1.0	5.0	0	30	20
25	1130	145.20	1.0	5.0	0	30	20
Total 25		Total 2500		ΔV_{avg}^m 5.0	Avg dev 1.6	Avg 29	Max temp 20

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

Figure 4.1. Field sampling data form for SO₂.

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

rotameter (capacity of 0 to 40 cm³/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.) H₂O 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.

3. Adjust the sample flow to a constant rate of approximately 1.0 l/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 l corrected to standard conditions.) The total sample volume at meter conditions should be approximately 28 l (1 ft³). 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 midjet impinger with 15 ml of 3% H₂O₂. The tester may opt to use ambient air without purification.

9. Calculate the sampling rate during the purging of the sample. The sample volume (ΔV_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

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 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 H_2O_2 . Analysis of the isopropanol may be useful in detecting cleanup or sampling errors. Cap off the midget impinger section with the use of polyethylene or equivalent caps before transport to the cleanup area. 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% H_2O_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

Plant	<u>Acme Power Plant</u>	City	<u>Anywhere, USA</u>	Remarks
Site	<u>Boiler No. 3</u>	Sample type	<u>SO₂</u>	
Date	<u>8/10/77</u>	Run number	<u>50-1</u>	
Front rinse	<input type="checkbox"/>	Front filter	<input type="checkbox"/>	
Back rinse	<input type="checkbox"/>	Back filter	<input type="checkbox"/>	
Solution	<u>H₂O₂</u>	Level marked	<input checked="" type="checkbox"/>	
Volume: Initial	<u>30mL</u>	Final	<u>< 100 mL</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 Container checked for leaks. Sample volume < 100 mlSignature of field sample trustee Joe Smith

Laboratory Data Checks

Lab person with direct responsibility for recovered samples D. JonesDate recovered samples received 8/11/77Analyst 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.

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% H₂O₂ ✓
3rd: 15 ml of 3% H₂O₂ ✓
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_2O_2 to first two midget impingers	Prepare 3% H_2O_2 fresh daily; use pipette or graduated cylinder to add solutions	Reassemble collection system
Assembling the sampling train	<ol style="list-style-type: none"> 1. Assemble to specifications in Fig. 1.1 2. A leakage rate $\leq 2\%$ of the average sampling rate 	<ol style="list-style-type: none"> 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 	<ol style="list-style-type: none"> 1. Reassemble 2. Correct the leak
Sampling (constant rate)	<ol style="list-style-type: none"> 1. Within $\pm 10\%$ 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_2 from isopropanol 	<ol style="list-style-type: none"> 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 	<ol style="list-style-type: none"> 1. Repeat the sampling, or obtain acceptance from a representative of the Administrator 2. As above 3. As above 4. As above

(continued)

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	1. All data are recorded correctly	1. Visually check upon completion of each run and before packing	1. Complete the data form
	2. All equipment examined for damage and labeled for shipment	2. As above	2. Redo test if damage occurred during testing
	3. All sample containers properly labeled and packaged	3. Visually check upon completion of test	3. Correct when possible

5.0 POSTSAMPLING OPERATIONS

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

5.1 Apparatus Check

A posttest check--including a calibration check, the cleaning, and/or the performance of routine maintenance--should be made on most of the sampling apparatus. Cleaning and maintenance of the sampling apparatus are discussed in Section 3.5.7. Figure 5.1 should be used to record the posttest checks.

5.1.1 Metering System - The metering system has three components that must be checked: dry gas meter thermometer(s), dry gas meter, and rotameter.

The dry gas meter thermometer should be checked by comparison with the ASTM mercury-in-glass thermometer at room temperature. If the readings agree within 6°C (10.8°F), they are acceptable. When the readings are outside this limit, the thermometer must be recalibrated according to Section 2.5.2 after the posttest check of the dry gas meter. For calculations, the dry gas meter thermometer reading (field or recalibration) that would give the higher temperature is used. That is, if the field reading is higher, no correction of the data is necessary; if the recalibration value is higher, the difference in the two readings is added to the average dry gas meter temperature reading.

The posttest checks of the dry gas meter and rotameter are similar to the initial calibration, as described in Section 3.5.2, but they include the following exceptions:

1. The metering system should not have had any leaks corrected prior to the posttest check.
2. Three or more revolutions of the dry gas meter are sufficient.
3. Only two independent runs need be made. If the posttest dry gas meter calibration factor (Y) does not deviate by >5%

Meter Box Number JS-1

Dry Gas Meter*

Pretest calibration factor $Y = 1.01$
Posttest check $Y_1 = 1.011$ $Y_2 = 1.011$ ($\pm 5\%$ of pretest factor)*
Recalibration required? yes no
If yes, recalibration factor $Y =$ _____ (within $\pm 2\%$ of calibration factor for each calibration run)
Lower calibration factor, $Y =$ _____ for pretest or posttest calculations

Rotameter

Pretest calibration factor $Y_r = 1.03$
Posttest check $Y_r = 1.05$ (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
 -2°C within $\pm 6^\circ\text{C}$ (10.8°F) of reference values
Recalibration required? yes no
Recalibration temperature correction if used _____ within $\pm 3^\circ\text{C}$ (5.4°F) of reference values
If meter thermometer temperature is higher, no correction is 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 $+1.0$ mm (in.) Hg within ± 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.

Figure 5.1 Posttest sampling checks.

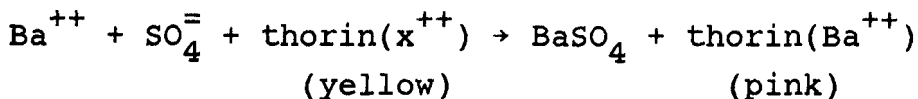
from the initial calibration factor, the dry gas meter volumes obtained during the test series are acceptable. If it deviates by >5% recalibrate the metering system as in Section 3.5.2, using the calibration factor (initial or recalibration) that yields the lower gas volume for each test run. The lesser calibration factor will give the lower gas volume.

The rotameter calibration factor (Y_r) can also be determined during the calibration of the dry gas meter. If Y_r does not deviate by >10% from the initial calibration factor, the rotameter operation is acceptable. If Y changes by >10%, the rotameter should be cleaned and recalibrated. No corrections need be made for any calculations.

5.1.2 Barometer - The field barometer readings are acceptable if they agree within ± 5 mm (0.2 in.) Hg when compared with those of the mercury-in-glass barometer. When the comparison is not within this range, the lesser calibration value should be used for the calculations. If the field barometer reads lower than the mercury-in-glass barometer, the field data are acceptable; but if the mercury-in-glass barometer gives the lower reading, the barometric value adjusted for the difference in the two readings should be used in the calculation.

5.2 Analysis (Base Laboratory)

Calibrations and standardizations are of the utmost importance to a precise and accurate analysis. The analysis is based on the insolubility of barium sulfate (BaSO_4) and on the formation of a colored complex between excess barium ions and the thorin indicator, 1-(o-arsonophenylazo)-2-naphthol-3,6-disulfonic acid, disodium salt. Aliquots from the impinger solution are analyzed by titration with barium perchlorate to the pink endpoint. The barium ions react preferentially with sulfate ions in solution to form a highly insoluble barium sulfate precipitate. When the barium has reacted with all of the sulfate ions, the excess barium then reacts with the thorin indicator to form a metallic salt of the indicator and to give a color change as shown in Equation 5-1.



Equation 5-1

Upon completion of each step of the standardization or of each sample analysis, the data should be entered on the proper data form. At the conclusion of the sample analysis, the data form should be reviewed and signed by the laboratory person with direct responsibility for the sample.

5.2.1 Reagents (Standardization and Analysis) - The following reagents are required for the analysis of the samples:

1. Water. Deionized distilled water that conforms to ASTM specification D1193-74, Type 3. At the option of the analyst, the KMnO_4 test for oxidizable organic matter may be omitted when high concentrations of organic matter are not expected. Note: The water must meet the ASTM specifications since sulfate ions and many other anions present in distilled water are not identified in the normal standardization of the acid by NaOH titration, which measures the hydrogen ion concentration rather than the sulfate ion concentration. This added sulfate concentration will result in an erroneous standardization of the barium perchlorate titration, which directly measures sulfate ion concentration and not hydrogen ion concentration. A check on the acceptability of the water is detailed in Subsection 5.2.4.

2. Isopropanol. 100%, ACS reagent grade. Check for peroxide impurities as described in Section 3.5.1.

3. Thorin indicator. Dissolve 0.20 \pm 0.002 g of 1-(o-arsonophenylazo)-2-naphthol-3,6-disulfonic acid, disodium salt, or the equivalent, in 100 ml of deionized distilled water. Measure the distilled water in the 100-ml graduated cylinder (Class A).

4. Sulfuric acid standard, 0.0100N. Either purchase manufacturer-guaranteed or standardize the H_2SO_4 to $\pm 0.002\text{N}$ against 0.0100N NaOH that has been standardized against potassium acid phthalate (primary standard grade) as described in Subsection 5.2.3. The 0.01N H_2SO_4 may be prepared in the following manner:

- a. Prepare 0.5N H_2SO_4 by adding approximately 1500 ml of 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 ($\text{Ba}(\text{ClO}_4)_2 \cdot 3\text{H}_2\text{O}$) in 200 ml of distilled water and dilute to 1 ℓ with isopropanol. Alternatively, 1.22 g of barium chloride dihydrate ($\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$) may be used instead of the perchlorate. Standardize, as in Subsection 5.2.4, 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.

3. Weigh to the nearest 0.1 mg, three 40-mg portions of the phthalate. Dissolve each portion in 100 ml of freshly boiled deionized distilled water in a 250-ml Erlenmeyer flask.

4. Add two drops of phenolphthalein indicator, and titrate the phthalate solutions with the NaOH solution. Observe titrations against a white background to facilitate detection of the pink endpoint. The endpoint is the first faint pink color that persists for at least 30 s.

5. Compare the endpoint colors of the other two titrations against the first. The normality is the average of the three values calculated using the following equation.

$$N_{\text{NaOH}} = \frac{\text{mg KHP}}{\text{ml titrant} \times 204.23}$$

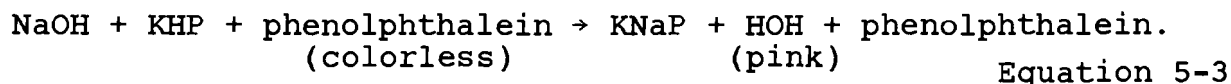
where

N_{NaOH} = calculated normality of sodium hydroxide,

mg KHP = weight of the phthalate, mg, and

ml titrant = volume of sodium hydroxide titrant, ml.

The chemical reaction for this standardization is shown in Equation 5-3. The sodium hydroxide is added to the potassium hydrogen phthalate and colorless phenolphthalein solution until there is an excess of diluted hydroxyl ions which causes the phenolphthalein solution to change to a pink color.



5.2.3 Standardization of Sulfuric Acid - To standardize sulfuric acid, proceed as follows:

1. Pipette 25 ml of the H_2SO_4 into each of three 250-ml Erlenmeyer flasks.

2. Add 25 ml of deionized distilled water to each.

3. Add two drops of phenolphthalein indicator, and titrate with the standardized NaOH solution to a persistent pink endpoint, using a white background.

4. Titrate a blank of 25 ml of 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:

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

where

$N_{H_2SO_4}$ = calculated normality of sulfuric acid,
ml NaOH_{acid} = volume of titrant used for H₂SO₄, ml,
ml NaOH_{blank} = volume of titrant used for blank, ml, and
 N_{NaOH} = normality of sodium hydroxide.

5.2.4 Standardization of Barium Perchlorate (0.0100N) - 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.

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 } 0.0102 N, avg
3 24.50 ml 0.01020 N }

Sample number	Sample identification number	Total sample volume (V_{soln}), ml	Sample aliquot volume (V_a) ^a , ml	Volume of titrant (V_t) ^b , ml		
				1st titration	2nd titration	Average
1	50-1	100	20	11.31	11.29	11.30
2						
3						
4						
5						
6						
Blank		N/A		0	0	$V_{tb} = 0$

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

^b $\frac{\text{1st titration}}{\text{2nd titration}} = 0.99 \text{ to } 1.01$ or $|\text{1st titration} - \text{2nd titration}| \leq 0.2 \text{ ml}$.

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
ml $\text{Ba}(\text{ClO}_4)_2$ = 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 H_2SO_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.

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 thorin indicator.

8. Initially, titrate the blank to a faint pink endpoint using the standardized barium perchlorate. The blank must contain <0.5 ml of titrant, or the 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, ^a ml			
		1st	2nd	3rd	Avg
1	0930	25.0	25.0		25.0

^a Two titrant volumes must agree within 0.2 ml.

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

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

(must agree within $\pm 5\%$, 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.

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_{soln_i}).
4. Put water in the sample storage container to the mark of the transferred sample, and measure the final volume (V_{soln_f}).

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.

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

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

where

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

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

V_{soln_i} = initial sample volume placed in storage container, ml, and

V_{soln_f} = final sample volume removed from storage container, ml.

6. Both the corrected and uncorrected values should be submitted in the test report to the Agency.

Proceed with the analysis as follows:

1. Transfer the contents of the sample bottle to a 100-ml volumetric flask (V_{soln}), and dilute to the mark with deionized distilled water.

2. Pipette a 20-ml aliquot (V_a) of this solution into a 250-ml Erlenmeyer flask, and add 80 ml of 100% 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.

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°F) at ambient temperature	Compare with ASTM mercury-in-glass thermometer after each field test	Recalibrate and use higher temperature value for calculations
Barometer	Within ± 5.0 mm (0.2 in.) Hg at ambient pressure	Compare with mercury-in-glass barometer after each field test	Recalibrate and use lower barometric value for calculations
<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	Titants 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 restandardize
Sample analysis	Titrant volumes differ by $\leq 1\%$ 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 titrations do not meet criterion

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.

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 K/mm Hg for metric units, or
= 17.64 $^{\circ}$ R/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^a

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

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

Equation 6-1

SO₂ Concentration

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

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

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

Equation 6-2

^a 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).

Sample Volume^a

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

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

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

Equation 6-1

SO₂ Concentration

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

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

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

Equation 6-2

^a 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).

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 ℓ (100 ft³) 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.

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 main-tenance	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

8.0 AUDITING PROCEDURE

An audit is an independent assessment of data quality. Independence is achieved if the individual(s) performing the audit and their standards and equipment are different from the regular field crew and their standards and equipment. Routine quality assurance checks by a field team are necessary in generation of good quality data, but they are not part of the auditing procedure. Table 8.1 at the end of this section summarizes the quality assurance functions for auditing.

Based on the results of collaborative tests^{2,3,4} of Method 6, two specific performance audits are recommended:

1. Audit of the analytical phase of Method 6.
2. Audit of data processing.

It is suggested that a systems audit be conducted as specified by the quality assurance coordinator, in addition to these performance audits. The two performance audits and the systems audit are described in detail in Subsections 8.1 and 8.2, respectively.

8.1 Performance Audits

Performance audits are made to 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. 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 actual analysis of the field samples which is required.

8.1.1 Pretest Audit of Analytical Phase Using Aqueous

Ammonium Sulfate (Optional) - The pretest audit described in this subsection 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 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.

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.

The testing laboratory should provide the agency/organization requesting the performance test with a notification of the intent to test 30 days prior to the enforcement source test. The testing laboratory should also request that the agency/organization provide the following performance audit samples: two samples at a low concentration (500 to 1000 mg SO₂/dscm of gas sampled or approximately 10 to 20 mg of ammonium sulfate per sample) and two samples at a high concentration (1500 to 2500 mg SO₂/dscm of gas sampled or about 30 to 50 mg of ammonium sulfate per sample). At least 10 days prior to the enforcement source test, the agency/organization should provide the four audit samples. The concentration of the two low and the two high audit samples should not be identical.

The testing laboratory will analyze one sample at the low concentration and one at the high concentration, and submit their results to the agency/organization prior to the enforcement source test. (Note: The analyst performing this optional audit must be the same analyst audited during the field sample analysis described in Subsection 8.1.2).

The agency/organization determines the percent accuracy, %A, between the measured SO₂ concentration and the audit or known values of concentration. The %A is a measure of the bias of the analytical phase of Method 6. Calculate %A using Equation 8-1.

$$\%A = \frac{C_{SO_2}(M) - C_{SO_2}(A)}{C_{SO_2}(A)} \times 100 \quad \text{Equation 8-1}$$

where

$C_{SO_2}(M)$ = concentration measured by the lab analyst
mg/ml, and

$C_{SO_2}(A)$ = audit or known concentration of the audit
sample, mg/ml.

The recommended control limit for the pretest audit is the 90th percentile value for %A based on the results of three audits (11/77, 5/78, and 10/78) performed by the Environmental Monitoring and Support Laboratory, USEPA, Research Triangle Park, North Carolina.^{13,14} By definition, 90% of the laboratory participants in the audit obtained values of %A less than the values tabulated below. The control limit is expected to be exceeded by 10% of the laboratories to be audited, based on these three audits. The 90th percentile values and the known audit concentrations are given below for each concentration range, 500 to 1000 mg SO₂/dscm and 1500 to 2500 mg SO₂/dscm.

500 to 1000 mg SO₂/dscm

<u>Audit date</u>	<u>Known audit concentration mg SO₂/dscm</u>	<u>90th percentile for %A, %</u>
5/78	686	4.1
10/78	572	6.4

1500 to 2500 mg SO₂/dscm

<u>Audit date</u>	<u>Known audit concentration mg SO₂/dscm</u>	<u>90th percentile for %A, %</u>
11/77	1411	6.6
11/77	2593	4.0
5/78	2479	4.5
5/78	1907	4.5
10/78	2555	4.9
10/78	1754	5.2

Based on the results of these audits, the recommended 90th percentile control limit for pretest audits is 7% for both concentration ranges.

If the results of the pretest audit exceed 7% the agency/organization should provide the correct results to the testing laboratory. After taking any necessary corrective action, the testing laboratory should then analyze the two remaining samples and report the results immediately to the agency/organization before the enforcement source test analysis.

8.1.2 Audit of Analytical Phase Using Aqueous Ammonium

Sulfate (Required) - The agency should provide 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 percent accuracy of the audit samples is determined using Equation 8-1. The results of the calculated %A should be included in the enforcement source test report as an assessment of accuracy of the analytical phase of Method 8 during the actual enforcement source test.

8.1.3 Audit of Data Processing - Calculation errors are prevalent in Method 8. Data-processing errors can be determined by auditing the data recorded on the field and laboratory forms. The original and audit (check) calculation should agree within roundoff; 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 occur 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--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 in the following:

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. Checking for constant rate sampling.
4. Purging the sampling train.

Figure 8.1 is a suggested checklist for the auditor.

Presampling Preparation

Yes	No	Comment	
<u> </u>	<u> </u>	<u>OK</u>	1. Knowledge of process conditions
<u>✓</u>	<u> </u>	<u> </u>	2. Calibration of pertinent equipment, in particular, the dry gas meter, prior to each field test

On-site Measurements

<u>✓</u>	<u> </u>	<u> </u>	3. Leak testing of sampling train after sample run
<u>✓</u>	<u> </u>	<u> </u>	4. Preparation and addition of absorbing solutions to impingers
<u> </u>	<u> </u>	<u>OK</u>	5. Constant rate sampling
<u>✓</u>	<u> </u>	<u> </u>	6. Purging of the sampling train and rinsing of the impingers and connecting tubes to recover the sample
<u>✓</u>	<u> </u>	<u> </u>	7. Recording of pertinent process conditions during sample collection
<u> </u>	<u> </u>	<u>*</u>	8. Maintaining the probe at a given temperature

Postsampling

<u>**</u>	<u> </u>	<u> </u>	9. Control sample analysis--accuracy and precision
<u> </u>	<u> </u>	<u>OK</u>	10. Sample aliquoting techniques
<u> </u>	<u> </u>	<u>OK</u>	11. Titration technique, particularly endpoint precision
<u>✓</u>	<u> </u>	<u> </u>	12. Use of detection blanks in correcting field sample results
<u> </u>	<u> </u>	<u>OK</u>	13. Calculation procedure/check
<u> </u>	<u> </u>	<u>OK</u>	14. Calibration checks
<u> </u>	<u> </u>	<u>OK</u>	15. Standardized barium perchlorate solution

General Comments

- * Probe shorted out during run 3 but sampling was allowed to be continued.
- ** First set of audit samples were acceptable.

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

Table 8.1 ACTIVITY MATRIX FOR AUDITING PROCEDURE

Audit	Acceptance limits	Frequency and method of measurement	Action if requirements are not met
Analytical phase using aqueous ammonium sulfate	Measured %A of the pretest audit sample should be less than the 90th percentile value, 7%	<u>Frequency:</u> Once during every enforcement source test <u>Method:</u> Measure reference samples and compare with true values	Review operating technique
Data-processing errors	The original and check calculations within round-off error	<u>Frequency:</u> Once during every enforcement source test <u>Method:</u> Independent calculations, starting with recorded data	Check and correct all data for the source test
Systems audit	Operation technique described in this section of the Handbook	<u>Frequency:</u> Once during every enforcement test until experience gained, then every fourth test <u>Method:</u> Observation of techniques, assisted by audit checklist, Fig. 8.1	Explain to team the deviations from recommended techniques; note on Fig. 8.1

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.

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-thorin 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_2/m^3 (2.12×10^{-2} lb/ft³). Although no upper limit has been established, tests have shown that concentrations as high as 80,000 mg/m³ of SO_2 can be collected efficiently in two midge impingers, each containing 15 milliliters of 3 percent hydrogen peroxide, at a rate of 10 lpm for 20 minutes. Based on theoretical calculations, the upper concentration limit in a 20-liter sample is about 93,300 mg/m³.

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_2 analysis. When samples are being taken from a gas stream with high concentrations of very fine metallic fumes (such as in inlets to control devices), 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 interferences by reacting with SO_2 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 8 in place of the midge impinger equipment of Method 6. However, the Method 8 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 rates and solution volumes defined in Method 6. The tester also has the option of determining SO_2 simultaneously with particulate matter and moisture determinations by (1) replacing the water in a Method 5 impinger system with 3 percent peroxide solution, or (2) by replacing the Method 5 water impinger system with a Method 8 isopropanol-filter-peroxide system. The analysis for SO_2 must be consistent with the procedure in Method 8.

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-mm inside diameter, with a heating system to prevent water condensation and a filter (either in-stack or heated out-stack) 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 30-ml midge impingers. The bubbler and midge impingers must be connected in series with leak-free glass connectors. Silicone 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 absorbers 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 run 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_2 .

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 (2°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 desiccants (equivalent or better) 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 2 percent of the selected flow rate of about 1000 cc/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 5°C (54°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 760 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 sizes.

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

2.3.3 Burettes. 5- and 50-ml sizes.

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 862 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 D1193-74, Type 3. At the option of the analyst, the KMnO_4 test for oxidizable organic matter may be omitted when high concentrations of organic matter are not expected to be present.

3.1.2 Isopropanol, 80 percent. Mix 80 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 362 nanometers on a spectrophotometer. If absorbance exceeds 0.1, reject alcohol for use.

Peroxides may be removed from isopropanol by redistilling or by passage through a column of activated alumina; 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, 5 Percent. Dilute 30 percent hydrogen peroxide 1:9 (v/v) with deionized, distilled water (80 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.

3.2 Sample Recovery.

3.2.1 Water. Deionized, distilled, as in 3.1.1.

3.2.2 Isopropanol, 80 Percent. Mix 80 ml of isopropanol with 20 ml of deionized, distilled water.

3.3 Analysis

3.3.1 Water. Deionized, distilled, as in 3.1.1.

3.3.2 Isopropanol, 100 percent.

3.3.3 Thorin. Indicator 1-(o-arsenophenylazo)-2-naphthol-3,6-disulfonic acid, disodium salt, or equivalent. Dissolve 0.20 g in 100 ml of deionized, distilled water.

3.3.4 Barium Perchlorate Solution, 0.0100 N. Dissolve 1.93 g of barium perchlorate trihydrate [$\text{Ba}(\text{ClO}_4)_3 \cdot 3\text{H}_2\text{O}$] in 200 ml distilled water and dilute to 1 liter with isopropanol. Alternatively, 1.22 g of [$\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$] may be used instead of the perchlorate. Standardize as in Section 5.5.

3.3.5 Sulfuric Acid Standard, 0.0100 N. Purchase or standardize to ± 0.0002 N against 0.0100 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 80 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 gauge at the inlet to the bubbler 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 end 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. The procedure used in Method 5 is not suitable for diaphragm pumps.

4.1.3 Sample collection. Record the initial 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 (± 10 percent) during the entire sampling run. Take readings (dry gas meter, temperatures 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 temperature of the gases leaving the last impinger at 20°C (68°F) or less. At the conclusion of each run, turn off the pump, remove probe from the stack, and record the final readings. 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 extra midge impinger with 15 ml of 3 percent H_2O_2 . The tester may opt to simply use ambient air, without purification.

4.2 Sample Recovery. Disconnect the impingers after pumping. 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 fluid 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 methods, subject to the approval of the Administrator, to correct the final results.

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 thorin indicator, and titrate to a pink endpoint using 0.0100 N barium perchlorate. Repeat and average the titration volumes. Run a blank with each series of samples. Replicate titrations must agree within 1 percent or 0.2 ml, whichever is larger.

(NOTE.—Protect the 0.0100 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 or 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 end.

Next, calibrate the metering system (at the sampling flow rate defined by the method) as follows: connect an appropriately sized wet test meter (e.g., 1 liter per revolution) 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, V (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 V value deviates by more than 3 percent from the average, the metering system is unacceptable for use. Otherwise, use the average as 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 volumes 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, and for the calculations, use the calibration factor (initial or recalibration) that yields the lower gas volume for each test run.

5.2 Thermometers. Calibrate against mercury-in-glass thermometers.

5.3 Rotameter. The rotameter need not be calibrated but should be cleaned and maintained according to the manufacturer's instruction.

5.4 Barometer. Calibrate against a mercury barometer.

5.5 Barium Perchlorate Solution. Standardize the barium perchlorate solution against 25 ml of standard sulfuric acid to which 100 ml of 100 percent isopropanol has been added.

6. Calculations

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, milliequivalents/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_a = Volume of sample aliquot titrated, ml.

V_m = Dry gas volume as measured by the dry gas meter, dcm (dcf).

$V_{m(std)}$ = Dry gas volume measured by the dry gas meter, corrected to standard conditions, dscm (dscf).

V_{sola} = 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).

$V_{t,b}$ = 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 Dry sample gas volume, corrected to standard conditions.

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

Equation 6-1

where:

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

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

6.3 Sulfur dioxide concentration.

$$C_{SO_2} = K_2 \frac{(V_t - V_{t,b}) N \left(\frac{V_{sola}}{V_a} \right)}{V_{m(std)}}$$

Equation 6-2

where:

$K_2 = 32.03 \text{ mg/meq.}$ for metric units.

$= 7.061 \times 10^{-4} \text{ lb/meq.}$ for English units.

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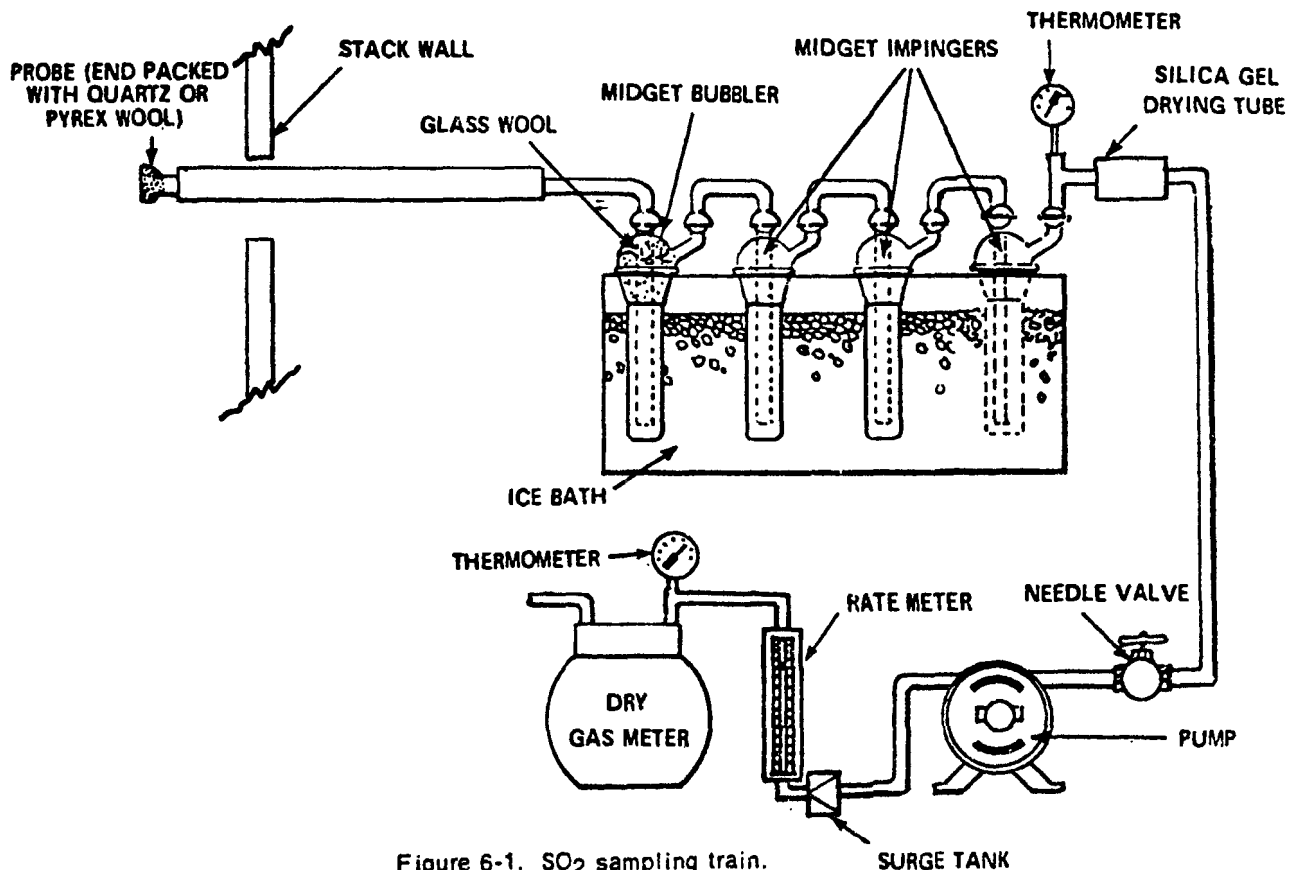


Figure 6-1. SO_2 sampling train.

In Method 6 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 "siliac" 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 4.1.2, 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."

11.0 REFERENCES

1. 40 Code of Federal Regulations 60. July 1, 1978.
2. Hamil, F. Laboratory and Field Evaluations of EPA Methods 2, 6, and 7. Report No. EPA-650/4-74-026. Southwest Research Institute, San Antonio, Tex. 1974.
3. Hamil, F., and David E. Camann. Collaborative Study of Method for the Determination of Sulfur Dioxide Emissions from Stationary Sources. Report No. EPA-650/4-74-024. National Environmental Research Center, Environmental Protection Agency, Research Triangle Park, N.C. December 1973.
4. Hamil, F., David E. Camann, and Richard E. Thomas. The Collaborative Study of EPA Methods 5, 6, and 7 in Fossil Fuel-Fired Steam Generators. Final Report No. EPA-650/4-74-013. Southwest Research Institute, San Antonio, Tex. September 1974.
5. Quality Assurance Handbook for Air Pollution Measurement Systems, Vol. I, Principles. EPA-600/9-76-005. Environmental Protection Agency, Research Triangle Park, N.C. March 1976.
6. Guidelines for Development of a Quality Assurance Program: Volume V - Determination of Sulfur Dioxide Emissions from Stationary Sources. EPA-650/4-74-005. Research Triangle Institute, Research Triangle Park, N.C. November 1975.
7. McCoy, Richard A., David E. Camann, and Herbert C. McKee. Collaborative Study. Reference Method for Determination of Sulfur Dioxide in the Atmosphere (Pararosaniline Method). EPA-650/4-74-027. December 1973.
8. Smith, Franklin, and Carl Nelson, Jr. Guidelines for Development of a Quality Assurance Program. EPA-R4-73-028d. August 1973.
9. Fuerst, Robert G. Improved Temperature Stability of Sulfur Dioxide Samples Collected by the Federal Reference Method. EPA-600/4-78-018, April 1978.

10. Knoll, Joseph E., and Midgett, M. Rodney. The Application of EPA Method 6 to High Sulfur Dioxide Concentrations. EPA-600/4-76-038. July 1976.
11. Osborne, Michael C., and Midgett, M. Rodney. Survey of Continuous Source Emission Monitors: Survey No. 1 NO_x and SO₂. EPA-600/4-77-022. April 1977.
12. Buchanan, J. N., and Wagoner, D. E. Guidelines for Development of a Quality Assurance Program: Volume VII - Determination of Sulfuric Acid Mist and Sulfur Dioxide Emissions from Stationary Sources. EPA-650/4-74-005g. March 1976.
13. Fuerst, R. G., R. L. Denny, and M. R. Midgett. A Summary of Interlaboratory Source Performance Surveys for EPA Reference Methods 6 and 7 - 1977. Available from U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory (MD-77), Research Triangle Park, N.C. 27711.
14. Fuerst, R. G., and M. R. Midgett. A Summary of Interlaboratory Source Performance Surveys for EPA Reference Methods 6 and 7 - 1978. Report in preparation by U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory (MD-77), Research Triangle Park, N.C. 27711.

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 ₂
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

Section No. 3.5.12
Revision No. 0
Date May 1, 1979
Page 2 of 13

6.1A and 6.1B

Sulfur Dioxide Calculation Forms
(English and metric units)

8.1

Method 6 Checklist To Be Used by
Auditors

PROCUREMENT LOG

Item description	Qty.	Purchase order number	Vendor	Date		Cost	Dispo- sition	Comments
				Ord.	Rec.			

WET TEST METER CALIBRATION LOG

Wet test meter serial number _____

Date _____

Range of wet test meter flow rate _____

Volume of test flask $V_s =$ _____

Satisfactory leak check? _____

Ambient temperature of equilibrate liquid in wet test meter and reservoir _____

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

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

Calculations:

^b $V_m = V_f - V_i$.

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

_____ Signature of calibration person

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 _____ $^{\circ}\text{F}$

Wet test meter pressure drop (D_m), ^a in. H_2O	Rota-meter setting (R_s), ft^3/min	Wet test meter gas volume (V_w), ^b ft^3	Dry test meter gas volume (V_d), ^b ft^3		Wet test meter gas temp (t_w), $^{\circ}\text{F}$	Dry test meter					(Y_{r_i}) , ^f
			Initial	Final		Inlet gas temp (t_{d_i}), $^{\circ}\text{F}$	Outlet gas temp (t_{d_o}), $^{\circ}\text{F}$	Average gas temp (t_d), ^c $^{\circ}\text{F}$	Time of run (Θ), ^d min	Average ratio (Y_i), ^e	

^a D_m expressed as negative number.

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

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

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

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

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

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

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

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

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

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), ^a mm H ₂ O	Rota- meter setting (R_s), ℓ/min	Wet test meter gas volume (V_w), ^b ℓ	Dry test meter gas volume (V_d), ^b ℓ		Wet test meter gas temp (t_w), °C	Dry test meter					
						Inlet gas temp (t_{d_i}), °C	Outlet gas temp (t_{d_o}), °C	Average gas temp (t_d), ^c °C	Time of run (θ), ^d min	Average ratio (Y_i), ^e	
			Initial	Final							

^a D_m expressed as negative number.

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

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

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

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

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

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

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

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

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

SAMPLING DATA FORM FOR SO₂

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 ³)	Sample flow rate setting, l/min (ft ³ /min)	Sample volume metered (ΔV_m), l (ft ³)	Percent deviation, ^a %	Dry gas meter temp, °C (°F)	Impinger temp, °C (°F)
Total		Total		ΔV_m avg	Avg dev	Avg	Max temp

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

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 _____

SULFUR DIOXIDE ANALYTICAL DATA

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

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

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

^b $\frac{\text{1st titration}}{\text{2nd titration}} = 0.99 \text{ to } 1.01$ or $|\text{1st titration} - \text{2nd titration}| \leq 0.2 \text{ ml}$.

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, ^a ml			
		1st	2nd	3rd	Avg

^a Two titrant volumes must agree within 0.2 ml.

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

_____ ml \times _____ N = _____

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

Does value agree? ___yes ___no

_____ Signature of analyst

_____ Signature of reviewer

Quality Assurance Handbook M6-5.3

SULFUR DIOXIDE CALCULATION FORM
(English units)

Sample Volume^a

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

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

Equation 6-1

SO₂ 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

^a 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 $V_{m(\text{std})} = \text{---} \text{ ft}^3$.

SULFUR DIOXIDE CALCULATION FORM
(metric units)

Sample Volume ^a

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

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

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

Equation 6-1

SO₂ Concentration

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

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

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

Equation 6-2

^a 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 $V_{m(\text{std})} = \text{---} \cdot \text{---} \text{---} \text{ m}^3$.

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

Section 3.6

METHOD 7--DETERMINATION OF NITROGEN OXIDE
EMISSIONS FROM STATIONARY SOURCES

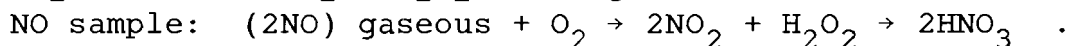
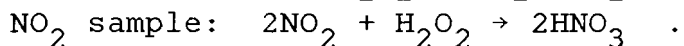
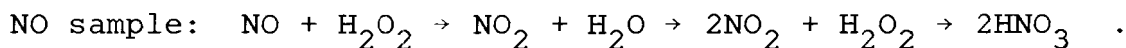
OUTLINE

Section	<u>Documentation</u>	<u>Number of Pages</u>
SUMMARY	3.6	2
METHOD HIGHLIGHTS	3.6	8
METHOD DESCRIPTION		
1. PROCUREMENT OF APPARATUS AND SUPPLIES	3.6.1	13
2. CALIBRATION OF APPARATUS	3.6.2	7
3. PRESAMPLING OPERATIONS	3.6.3	9
4. ON-SITE MEASUREMENTS	3.6.4	11
5. POSTSAMPLING OPERATIONS	3.6.5	14
6. CALCULATIONS	3.6.6	6
7. MAINTENANCE	3.6.7	2
8. AUDITING PROCEDURE	3.6.8	8
9. RECOMMENDED STANDARDS FOR ESTABLISHING TRACEABILITY	3.6.9	1
10. REFERENCE METHOD	3.6.10	3
11. REFERENCES	3.6.11	2
12. DATA FORMS	3.6.12	16

SUMMARY

A gas sample is extracted from the sampling point in the stack. The sample is collected in an evacuated 2-l round bottom borosilicate flask containing 25 ml of dilute sulfuric acid-hydrogen peroxide absorbing solution. The nitrogen oxides, except nitrous oxide, are measured colorimetrically using the phenoldisulfonic acid (PDS) method for analysis.

If the gas being sampled contains insufficient oxygen for the conversion of NO to NO₂, then oxygen should be introduced into the flask to permit this conversion. Oxygen may be introduced into the flask by one of three methods: (1) Before evacuating the sampling flask, flush with pure cylinder oxygen, and then evacuate flask to 75 mm (3.0 in.) Hg absolute pressure or less; or (2) inject oxygen into the flask after sampling; or (3) terminate sampling with a minimum of 50 mm (2.0 in.) Hg vacuum remaining in the flask, record this final pressure, and then open the flask to the atmosphere until the flask pressure is almost equal to atmospheric pressure. The chemical reactions that occur during sampling absorption are:



Method 7 is applicable to the measurement of nitrogen oxides emitted from stationary sources. The range of the method has been determined to be 2 to 400 mg NO_x, expressed as NO₂ per dry standard cubic meter without having to dilute the sample.

The precision of the method (as measured by repeatability and reproducibility of the measurements) in the collaborative

studies varies from 6.6% to 15% (repeatability) and from 9.5% to 19% (reproducibility). See Appendixes A and K, Volume I of this Handbook¹ for definition and discussion of these measures of data quality.

The method description given herein draws heavily on the corresponding guideline document,² the collaborative test reports,^{3,4,5} and the Reference Method from the 40 CFR 60, July 1, 1978. Section 3.6.10 contains a complete copy of the Reference Method. Blank data forms are provided in Section 3.6.12 for the convenience of the Handbook user.

METHOD HIGHLIGHTS

Section 3.6 provides the procedures for collecting and analyzing a grab sample of oxides of nitrogen (NO_x). The results are expressed as concentrations of nitrogen dioxide (NO_2). The applicable regulation should be consulted to determine any additional requirements (i.e., velocity traverse or O_2 grab sample). Method 7 requires less experience and manpower to collect the sample than most of the other reference methods. However, based on the wide variations in the collaborative results of analyses on aqueous ammonia nitrate audit samples, it is imperative that the analyst be familiar with the analytical techniques described in the Reference Method in Section 3.6.10. A larger number of samples (normally 12) is also required to be taken because the method collects a grab sample not an integrated sample over an extended time.

The four blank data forms at the end of this section may be removed from the Handbook and used in the pretest, test, and posttest operations. Each form has a subtitle (e.g., Method 7, Figure 3.1) for helping the user find a similar filled-in form in the method description (Section 3.6.3). On the blank and filled-in forms, the items/parameters that can cause the most significant errors are starred.

1. Procurement of Equipment

Section 3.6.1 (Procurement of Apparatus and Supplies) gives the specifications, criteria, and design features of the equipment and material required to perform Method 7 tests with the evacuated flask sampling train. This section is designed to guide the tester in the procurement and initial check of equipment and supplies. The activity matrix (Table 1.1) at the end of Section 3.6.1 can be used as a quick reference and is a summary of the corresponding written description.

2. Pretest Preparations

Section 3.6.2 (Calibration of Apparatus) provides a step-by-step description of the calibration procedures along with the

required accuracy for each component. The optimum wavelength should be determined every 6 mo, and the calibration factor should be determined each time the spectrophotometer is used to analyze NO_x samples. The volume of each collection flask must be determined with stopcock in place. This volume measurement is required only on the initial calibration, provided the stopcock is not changed. The calibration section may be removed along with the corresponding sections from the other methods and made into a separate quality assurance reference manual for use by calibration personnel.

Section 3.6.3 (Presampling Operations) provides the tester with a guide for equipment and supplies preparation for the field test. The calibration data should be summarized on a pretest checklist (Figure 3.1, Section 3.6.3) or similar form. A pretest preparation form (Figure 3.2, Section 3.6.3) can be used as an equipment checkout and packing list. The flasks may be charged with the absorbing reagent in the base laboratory. The method of packing and the use of the described packing containers should help protect the equipment, but neither is required by the Reference Method.

3. On-Site Measurements

Section 3.6.4 (On-Site Measurements) contains step-by-step procedures for the sample collection and for the sample recovery. The on-site checklist (Figure 4.3, Section 3.6.4) provides the tester with a quick method of checking the requirements. When high negative stack pressures are present, extra care should be taken to purge the leak-tested sample system and to be sure the flask is ≤ 75 mm (3 in.) Hg absolute pressure prior to testing. Also the 16-h sample residence time in the flask must be observed.

4. Posttest Operations

Section 3.6.5 (Postsampling Operations) gives the posttest equipment procedures and a step-by-step analytical procedure for determination of NO_x, expressed as NO₂. Posttest calibration is not required on any of the sampling equipment. The posttest

operation forms (Figure 5.3, Section 3.6.5) provide some key parameters to be checked by the tester and laboratory personnel. The step-by-step analytical procedure description 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. Strict adherence to the Reference Method analytical procedures must be observed; for example in the evaporation of the sample, the substitution of a hot plate for the steam bath is not acceptable.

Section 3.6.6 (Calculations) provides the tester with the required equations, nomenclature, and significant digits. It is suggested that a calculator be used if available to reduce the chance of calculation error.

Section 3.6.7 (Maintenance) provides the tester with a guide for a maintenance program. This program is not required, but should reduce equipment malfunctions.

5. Auditing Procedure

Section 3.6.8 (Auditing Procedure) provides a description of necessary activities for conducting performance and system audits. The performance audit of the analytical phase can be conducted using an aqueous ammonium nitrate solution. Performance audits for the analytical phase and the data processing are described in Section 3.6.8. A checklist for a systems audit is also included in this section.

Section 3.6.9 (Recommended Standards for Establishing Traceability) provides the primary standards to which the data should be traceable. The analysis of NO_x is traceable to primary standard grade ammonium nitrate.

6. Reference Material

Section 3.6.10 (Reference Method) is a copy of the Reference Method, on which the quality assurance method description was based.

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Section 3.6.11 (References) is a listing of the references that were used in this method description.

PRETEST SAMPLING CHECKS
(Method 7, Figure 3.1)

Date _____ Calibrated by _____

Flask Volume

Flask volumes measured with valves? ____yes ____no

Volume measured within ± 10 ml of actual volume? ____yes ____no

Temperature Gauge

Was a pretest temperature correction used? ____yes ____no

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

Vacuum Gauge

Was gauge calibrated against a U-tube mercury manometer
(If it was a mechanical gauge)? ____yes ____no ____not
applicable?

Barometer

Was the pretest field barometer reading within ± 2.5 mm (0.1 in.)
Hg of the mercury-in-glass barometer? ____yes ____no

* Most significant items/parameters to be checked.

PRETEST PREPARATIONS
(Method 7, Figure 3.2)

Apparatus check	Acceptable		Quantity required	Ready		Loaded and packed	
	Yes	No		Yes	No	Yes	No
<u>Probe</u> Glass liner clean Heated properly Leak checked							
<u>Collection Flask</u> Clean Leak checked Temperature gauge							
<u>Evacuation System</u> Leak-free pumps Manifold and tubing U-tube manometer Barometer							
<u>Reagents</u> Distilled water Absorbing solu- tion* Sodium hydrox- ide, 1N pH paper							
<u>Sample Recovery</u> Dropper or burette Sample bottles Pipette, 25 ml							

* Most significant items/parameters to be checked.

ON-SITE MEASUREMENTS
(Method 7, Figure 4.3)

Sampling

Volume of 25 ml of absorbing solution placed in flask? _____

Flask valve stopper in purge position? _____

Sampling train properly assembled? _____

Leak free?* _____ Stopcock grease used? _____

Type? _____

Flask evacuated to 75 mm (3 in.) Hg pressure? _____

Leakage from manometer observation?* _____

(e.g., maximum change in manometer of ≤ 10 mm (0.4 in.)

Hg/min) _____

Initial pressure of flask recorded?* _____

Initial temperature of flask recorded? _____

Probe purged before sampling? _____

Sample collected properly?* _____

Flask shaken for 5 min after collection and disassembly
from train?* _____

Oxygen introduced to flask? _____ Method used? _____

Samples properly labeled and sealed and stored for shipment?

Sample Recovery

Samples allowed to remain in flasks for minimum of 16 h?* _____

Final flask temperature and pressure recorded?* _____

Sample transferred to leak-free polyethylene bottle? _____

Flask rinsed twice with 5-ml portions of distilled water
and rinse added to bottle containing sample? _____

pH adjusted to between 9 and 12?* _____

* Most significant items/parameters to be checked.

POSTTEST OPERATIONS
(Method 7, Figure 5.3)

Reagents

Phenoldisulfonic acid stored in dark stoppered bottle? _____

Sulfuric acid, concentrated, 95% minimum assay reagent
grade? _____

Ammonium hydroxide, concentrated reagent grade? _____

Sample Preparation

Has liquid level noticeably changed?* _____

Original volume _____ Corrected volume _____

Analysis

Spectrophotometer calibrated?* _____

Setting for maximum absorbance of standard _____ nm

Control sample prepared?* _____

Any solids in sample removed through Whatman No. 41 filter
paper? _____

Absorbance measured at optimum wavelength used for the stand-
ards, using the blank solution as a zero reference? _____

All analytical data recorded on checklist and laboratory form?

* Most significant items/parameters to be checked.

1.0 PROCUREMENT OF APPARATUS AND SUPPLIES

The activity matrix for apparatus is given in Table 1.1 at the end of this section. The required apparatus for a Method 7 sampling train is shown in Figure 1.1. Additional specifications, criteria, and/or design features as applicable are given here to aid in the selection of equipment to ensure the collection of good quality data. All new items of equipment are to be inspected visually for identification and damage before acceptance. Also, if applicable, new equipment is to be calibrated according to Section 3.6.2, as part of the acceptance check.

During the procurement of equipment and supplies, it is suggested that a procurement log be used to record the descriptive title of the equipment, identification number (if applicable), and the results of acceptance checks. An example of a procurement log is shown in Figure 1.2. A blank copy of this form is given in Section 3.6.12 for the Handbook user. Calibration data generated in the acceptance check are to be recorded in the calibration log book. Alternative grab sampling systems or equipment capable of measuring sample volume to within $\pm 2\%$ and collecting a sufficient sample volume to allow analytical repeatability to within $\pm 5\%$ is acceptable, subject to approval. The following equipment is specified in the Reference Method.

1.1 Sampling

1.1.1 Sampling Probe - The sampling probe should be made of glass (borosilicate) encased in a stainless steel sheath and equipped with a heating system capable of preventing water condensation and with a filter (either in-stack or heated out of stack) to remove particulate matter. A plug of glass wool in the sample probe is satisfactory for the in-stack filter. Stainless

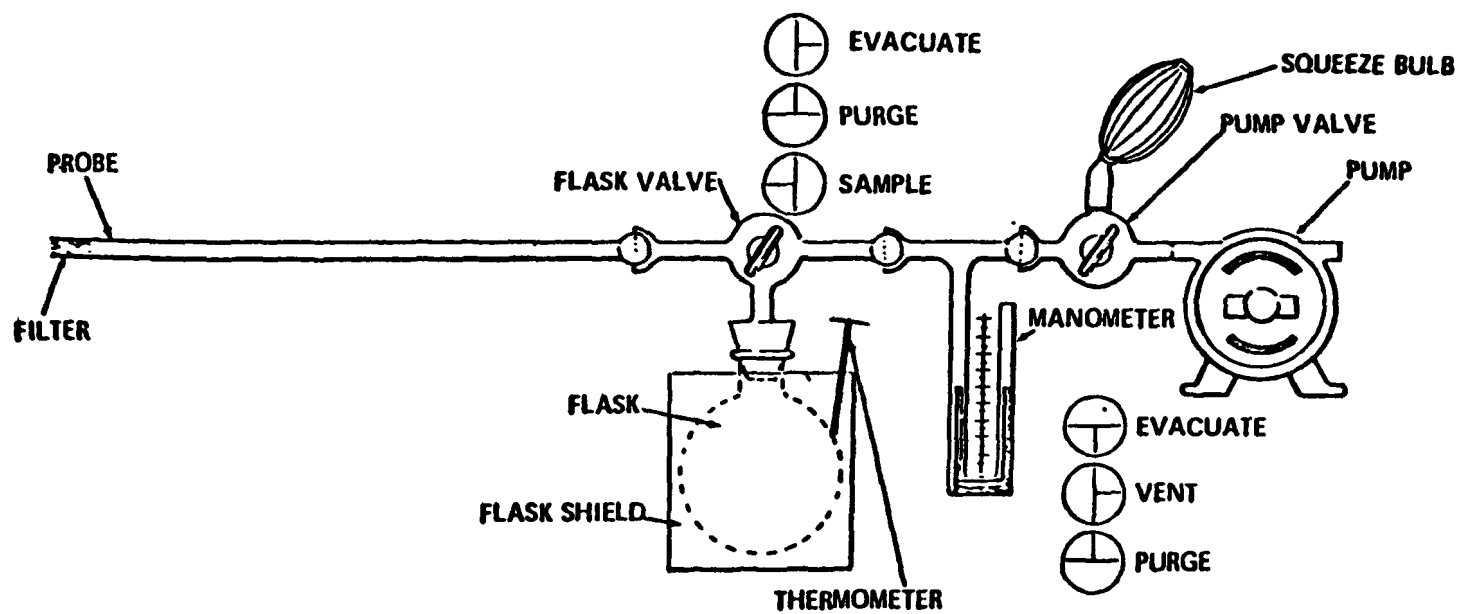


Figure 1.1. Evacuated flask sampling train.

Item description	Qty.	Purchase order number	Vendor	Date		Cost	Disposition	Comments
				Ord.	Rec.			
Spectrophotometer	1	1035	Bausch + Lomb	2/11/77	2/14/77	\$2500	ok	

Figure 1.2. Example of a procurement log.

steel or Teflon^R tubing may also be used for the probe liner. Heating is not required if the probe remains dry during the purging period, but it is recommended that the probe have provision for heating. The in-stack end of the probe should have an expanded diameter for about the first 4 cm to be used for the glass-wool filter. A probe of approximately 1.2 m (4 ft) total length is usually sufficient for sampling. However, the probe tip can be no closer 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 (Vycor) should be used along with quartz wool for filter material. The main criterion in selecting a probe material is that it be nonreactive with the gas constituents and therefore not introduce a bias into the analysis.

A new probe should be checked visually for specifications (i.e., the length and composition ordered). It should be checked for cracks, breaks, and leaks on a sampling train. 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 for a flow rate of about 1.0 l/min.
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 the above conditions. If it cannot, the probe should be replaced. Any probe not satisfying the acceptance check should be repaired if possible, or returned to the supplier.

1.1.2 Collection Flask - A 2-l borosilicate round bottom flask, with a short neck and 24/40 standard taper opening is required.

^RTrade name.

The collection flask should be protected from implosion or breakage by using (1) tape, (2) a commercial unit encased in foam, or (3) a fabricated closed-cell foam enclosure. Once the flask has been connected to the flask valve, both should be marked as a set and neither should be used at random with other flasks as this will cause volume fluctuations with the sample.

1.1.3 Flask Valve - A T-bore stopcock is connected to a 24/40 standard taper joint. Bores should be numbered but not switched to prevent leakage problems. The T-bore should be marked to avoid turning the stopcock in the wrong direction when sampling. The flask valve should be marked to identify its matched flask.

1.1.4 Temperature Gauge - A temperature gauge should consist of a dial-type thermometer, or equivalent, capable of measuring 1°C (2°F) intervals from -5° to 50°C (25° to 125°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°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 replaced.

1.1.5 Vacuum Line - The vacuum line should be of a nonreactive, thick wall type and should be leak checked at 75 mm (3 in.) Hg of absolute pressure while connected to the sampling train. The tubing should be flexible and approximately 1 to 1.6 m (3 to 5 ft) in total length. If the tubing is found to leak, it should be rejected.

1.1.6 Vacuum Gauge - A U-tube manometer should be about 1 m (36 in.) in length with 1-mm (0.1 in.) divisions, or the equivalent, capable of measuring pressure to within ± 2.5 mm (0.1 in.) Hg. If a U-tube manometer is used, no calibration is required. Upon receipt, the user should verify by reading the instructions that the manometer was designed to use mercury. If the manometer is acceptable, it must then be leak checked. When a mechanical vacuum gauge is used, it must be calibrated upon receipt by the

procedures described in Section 3.6.2. If it fails to calibrate, it should be replaced.

The vacuum gauge should be leak checked as follows: (1) connect vacuum line to the manometer at the end that connects to the sampling train, as shown in Figure 1.1 (2) pull a vacuum of 75 mm (3 in.) Hg or less, (3) shut off the valve between the manometer and the pump, (4) shut off the pump, (5) observe the vacuum registered on the manometer for any deviation over a 1-min period. If there is no deviation, the vacuum gauge is acceptable; if there is a deviation, the gauge is unacceptable and should be corrected or replaced.

1.1.7 Vacuum Pump - The vacuum pump should be capable of producing a vacuum of 75 mm (3 in.) Hg or less. The pump must be leak free when running and when pulling a vacuum (inlet plugged) of 75 mm (3 in.) Hg. Two types of vacuum pumps are commonly used--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 75 mm (3 in.) Hg of vacuum. The vacuum reading should remain stable for 30 seconds.

1.1.8 Squeeze Bulb - A one-way, hard rubber bulb with about a 50-ml capacity is needed to purge the sampling system.

1.1.9 Volumetric Pipette - A 25-ml volumetric glass pipette (Class A) is needed for addition of reagent to the collection flask.

1.1.10 Stopcock Grease - An inert, high-vacuum, high-temperature chlorofluorocarbon grease should be used. Halocarbon 25 - 55 has been found to be effective.

1.1.11 Barometer - Mercury, aneroid, or other barometers capable of measuring atmospheric pressure to within 2.5 mm (0.1 in.) Hg are required. 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) should be requested and an adjustment for elevation differences between the weather station and the sampling point should be 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. Upon receipt, check the barometer against a mercury-in-glass barometer. Replace it if it cannot be calibrated to read correctly.

1.2 Sample Recovery

1.2.1 Graduated Cylinder - A 50-ml glass or polyethylene graduated cylinder with 1-ml divisions is required.

1.2.2 Storage Bottles - A minimum of 12 leak-free polyethylene bottles for recovery of samples are needed. The bottles should be packed in a cushioned, locked container (box or footlocker) for shipment. The leak-free seal can be initially checked by putting water in each, sealing, and then shaking the container upside down.

1.2.3 Wash Bottle - Glass or polyethylene wash bottles are needed for rinsing (transferral) of the sample solution to storage bottles.

1.2.4 Stirring Rod - A stirring rod (glass or polyethylene) is required to check the pH of the absorbing reagent.

1.2.5 pH Indicating Paper - pH paper with the range of 7 - 14 is required to test the alkalinity of the samples.

1.3 Analysis

1.3.1 Pipettes - Several volumetric pipettes are required (two 1 ml, two 2 ml, one 3 ml, one 4 ml, two 10 ml, and one 25 ml); one transfer pipette (10 ml with 0.1-ml divisions) is required.

1.3.2 Volumetric Flasks - One 100-ml volumetric flask, is needed for each sample and each standard. Two 1000-ml volumetric flasks are required for the blank and the standard nitrate. Additional volumetric flasks (50 ml) are required for aliquots for analysis and for dilution of samples that fall outside the calibration range (absorbance >400- μ g standard).

1.3.3 Evaporating Dishes - Several 175- to 250-ml capacity porcelain dishes with lip for pouring are needed, one for each sample and one for each standard. The Coors No. 45006 (shallow, 195 ml) has been found to be satisfactory. Alternatively, polymethyl-pentene beakers (Nalge No. 1203, 150 ml) or glass beakers (150 ml) may be used. When glass beakers are used, etching of the beakers may cause solid matter to be present in the analytical step; the solids should be removed by filtration. For this reason, glass beakers should be used only if necessary.

1.3.4 Steam Bath - A steam bath is required to evaporate the absorbing solution. Low-temperature ovens or thermostatically controlled hot plates kept below 70°C (160°F) are acceptable alternatives.

1.3.5 Polyethylene Policeman - One stirring rod (polyethylene policeman) is required for each sample and standard. A glass stirring rod is not recommended.

1.3.6 Graduated Cylinder - A 100-ml graduated glass cylinder (Class A) with 1-ml divisions is required for additions of distilled water.

1.3.7 Spectrophotometer - A spectrophotometer capable of measuring the absorption at 410 nm (or the maximum peak), a set of neutral density filters, and a filter for wavelength calibration are required.

1.3.8 pH Paper - The paper should cover the pH range of 7 - 14 with intervals of 1-pH unit.

1.3.9 Analytical Balance - One analytical balance that weighs to 0.1 mg and a set of Class-S calibration weights to check the accuracy of the balance (± 0.3 mg) upon receipt are needed. The balance should be serviced by or returned to the manufacturer if agreement cannot be met.

1.3.10 Dropping Pipette or Dropper - A dropping pipette, or a dropper, or its equivalent for addition of ammonium hydroxide to the evaporation dish is needed.

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, use the best available grade.

1.4.1 Sampling - To prepare the absorbing solution, cautiously add 2.8 ml of concentrated H_2SO_4 to 1 l of deionized distilled water and mix well. Add 6 ml of 3% hydrogen peroxide, freshly prepared from 30% hydrogen peroxide (ACS reagent grade) solution. The absorbing solution must be used within 1 week of its preparation and if possible within 24 h. Store in a dark-colored bottle. Do not expose to extreme heat or direct sunlight. Note: The 30% hydrogen should be stored in the refrigerator.

1.4.2 Sample Recovery - Two reagents are required for sample recovery.

Sodium hydroxide (1N) - Dissolve 40 g of NaOH ACS reagent grade in deionized distilled water and dilute to 1 l.

Water - Use deionized distilled to conform to ASTM specification D1193-74, Type 3. At the option of the analyst, the KMnO_4 test for oxidizable organic matter may be omitted whenever high concentrations of organic matter are not expected to be present.

1.4.3 Analysis - For the analysis, the following reagents are required.

Fuming sulfuric acid - Use 15% to 18% by weight of free sulfur trioxide, ACS reagent grade. Note: Handle with caution.

Phenol - Use white solid, ACS reagent grade.

Sulfuric acid - Use concentrated, 95% minimum assay, ACS reagent grade. Note: Handle with caution.

Potassium nitrate - Dry at 105° to 110°C (220° to 230°F) for a minimum of 2 h just prior to preparation of standard solution, ACS reagent grade.

Standard KNO_3 solution - Dissolve exactly 2.198 g of dried potassium nitrate (KNO_3) in deionized distilled water and dilute

to 1 l with deionized distilled water. One ml of the working standard solution is equivalent to 100 µg of nitrogen dioxide (NO₂).

Water - Deionized distilled as in Subsection 1.4.2.

Phenoldisulfonic acid solution - Dissolve 25 g of pure white phenol in 150 ml of concentrated sulfuric acid on a steam bath. Cool; add 75 ml of fuming sulfuric acid; and heat at 100°C (212°F) for 2 h. Store in a dark, stoppered bottle. Alternatively, this solution may be purchased prepared, if it meets the American Public Health Association specification for nitrate-nitrogen in water.

Ammonium hydroxide - Use concentrated, ACS reagent grade.

Table 1.1. ACTIVITY MATRIX FOR PROCUREMENT OF APPARATUS AND SUPPLIES

Apparatus/ reagents	Acceptance limits	Frequency and method of measurement	Action if requirements are not met
Probe	Borosilicate glass tubing, stainless steel or Teflon capable of removing particulate and preventing moisture condensation	Upon receipt, visually check for cracks or flaws and heating capability	Return to supplier and note in procurement log
Collection flask	Two-liter borosilicate glass round bottom, short neck w/24/40 standard taper opening	Upon receipt visually check and leak check	As above
Flask valve	Borosilicate glass T-bore stopcock w/24/40 standard taper male joint (joint connection to be made by glass-blower)	Visually check upon receipt	As above
Temperature gauge	Dial-type, capable of measuring from -5° to +50°C within 1°C	Visually check upon receipt, and compare against Hg-in-glass thermometer	As above
Vacuum line tubing	Capable of withstanding 75 mm absolute pressure	Upon receipt visually check and leak check	As above
Vacuum gauge	U-tube manometer, open end, 1 m with 1-mm divisions	Visually check upon receipt	As above
Vacuum pump	Pump capable of pulling vacuum of 75 mm Hg or less	Upon receipt check with suitable pressure gauge	As above
Squeeze bulb	Rubber, one-way	Visually check upon receipt	As above
Volumetric pipettes	1-, 2-, 3-, 4-, 10-, 25-ml glass (Class A)	As above	As above

(continued)

Table 1.1 (continued)

Apparatus/ reagents	Acceptance limits	Frequency and method of measurement	Action if requirements are not met
Stopcock grease	High vacuum, high temperature chlorofluoro-carbon grease	As above	As above
Barometer (or consult local weather station)	Capable of reading atmospheric pressure to ± 2.5 mm Hg	Visually check; calibrate against mercury-in-glass barometer	As above
Storage bottle	Polyethylene, 100-ml, or greater capacity, screw cap	Visually check upon receipt	Return to supplier and note in procurement log
Wash bottle	Polyethylene or glass	Visually check label upon receipt	As above
Glass stirring rod	As above	As above	As above
pH paper	Sensitive in pH range 7-14	As above	Return to supplier
Volumetric flasks	50-, 100-, 1000-ml glass (Class A)	As above	As above
Evaporating dishes	Porcelain evaporating dishes or polymethylpentene beakers	As above	Discard when the bottoms become etched
Steam bath	Evaporate the sample solution at a low controlled temperature	As above	Return to supplier
Polyethylene policeman	Polyethylene stirring rod	As above	As above
Graduated cylinders	50, 100 ml (Class A) with 1-ml divisions	As above	As above

(continued)

Table 1.1 (continued)

Apparatus/ reagents	Acceptance limits	Frequency and method of measurement	Action if requirements are not met
Spectrophotometer	Capable of measuring absorbance at 410 nm (such as Bausch & Lomb Spectronic 70)	Upon receipt, either check wavelength with filters or ensure optimum wavelength is between 400 and 415 nm	Adjust, recalibrate as per manufacturer's instructions, and note in procurement log
Dropping pipette or dropper	Able to add reagents dropwise	Visually check upon receipt	Return to supplier
Sulfuric acid	Concentrated, ACS reagent grade	Visually check upon receipt; check specifications	As above
Hydrogen peroxide	30% aqueous solution, ACS reagent grade	As above	As above
Sodium hydroxide	ACS reagent grade pellets	Visually check upon receipt; check specifications	Return to supplier
Sulfuric acid	Fuming, 15-18% free sulfur trioxide	As above	As above
Phenol	White solid, ACS reagent grade	As above	As above
Potassium nitrate	ACS reagent grade	As above	As above

2.0 CALIBRATION OF APPARATUS

Calibration of the apparatus is one of the most important functions in maintaining data quality. The detailed calibration procedures included in this section are designed for the equipment specified by Method 7 and described in the previous section. Table 2.1 at the end of this section summarizes the quality assurance functions for calibration. All calibrations should be recorded on standardized record forms and retained in a calibration log book.

2.1 Collection Flask

Assemble the clean flasks and valves and fill with water (room temperature) to the stopcock. Measure the volume to ± 10 ml by transferring the water to a 500-ml glass (Class A) graduated cylinder. Do duplicate volume determinations, and use the mean value. Number and record the volume mean value on the flask or foam encasement and in the laboratory log book. This volume measurement is required only on the initial calibration if the flask valves are not switched.

2.2 Spectrophotometer

2.2.1 Determination of Optimum Wavelength - Calibrate the wavelength scale of the spectrophotometer every 6 mo. The calibration may be accomplished by using an energy source with an intense line emission such as a mercury lamp, or by using a series of glass filters spanning the measuring range of the spectrophotometer. Calibration materials are available commercially and from the National Bureau of Standards. Specific details on the uses of such materials should be supplied by the vendor.

In general, when using glass filters, each filter is inserted into the light path and the wavelength dial is rotated until the instrument response is greatest. Then the reading on the dial is noted and can be compared with the true value. When using an alternate light source, the instrument lamp is replaced

by the alternate lamp. The wavelength dial is rotated, and the dial reading is noted at each peak for comparison with the true value. The wavelength scale of the spectrophotometer must read correctly within ± 5 nm of the true wavelength at all calibration points; otherwise, the spectrophotometer should be repaired and recalibrated. Once the wavelength scale of the spectrophotometer is properly calibrated, use 410 nm as the optimum wavelength for the measurement of the absorbance of the standards and samples.

Alternatively, a scanning procedure may be employed to determine the optimum wavelength. If the instrument is a double-beam spectrophotometer, scan the spectrum between 400 and 415 nm using a 200 μg NO_2 standard solution in the sample cell and a blank solution in the reference cell. If a peak does not occur, the spectrophotometer is probably malfunctioning and should be repaired. If a peak is obtained within the 400- to 415-nm range, the wavelength at which this peak occurs should be the optimum wavelength for the measurement of absorbance of both the standards and the samples. For a single-beam spectrophotometer, follow the scanning procedure described, but scan the blank and the standard solutions separately. The optimum wavelength should be the one at which the maximum difference in absorbance between the standard and the blank occurs. The data obtained for this alternative optimum wavelength determination should be recorded on the data form as shown in Figure 2.1.

2.2.2 Determination of Calibration Factor - K_C - The calibration factor (K_C) must be determined in the verification of the analytical technique and solution preparation prior to sample analysis with the control sample. After the analytical technique and solutions have been verified as to their accuracy and precision, a new calibration factor should be determined simultaneously with the field sample analysis. Since a detailed discussion of this procedure is included in the sample analysis Section 3.6.5, it is omitted here.

2.3 Barometer

The field barometer should be adjusted initially and before each test series to agree within 2.5 mm (0.1 in.) Hg of the

Spectrophotometer number PEI-2

Date 2/10/77

Calibrated by B. Plummer

Reviewed by T. Seaver

Spectrophotometer setting, nm	Absorbance of standard OD ^a	Absorbance of blank OD ^b	Actual absorbance of OD ^c
399	.955	.185	.770
400	.934	.157	.777
401	.920	.136	.784
402	.905	.116	.789
403	.895	.097	.798
404	.891	.086	.805
405	.888	.080	.808
406	.884	.074	.810
407	.879	.066	.813
408	.877	.056	.821
409	.873	.057	.816
410	.844	.043	.801
411	.830	.036	.794
412	.823	.031	.892
413	.811	.028	.783
414	.806	.015	.791
415	.785	.009	.776
416	.777	.000	.777

^a Absorbance of the 200 μg NO_2 standard in a single beam spectrophotometer.

^b Absorbance of the blank in a single-beam spectrophotometer.

^c For a single-beam spectrophotometer--absorbance of the standard minus absorbance of the blank. For a double beam spectrophotometer--absorbance of the 200 μg NO_2 standard with the blank in the reference cell.

Spectrophotometer setting for maximum actual absorbance of standard 408 nm.

If the maximum actual absorbance occurs at a spectrophotometer setting of ≤ 399 or ≥ 416 nm, the spectrophotometer must be repaired or recalibrated.

Figure 2.1. Optimun wavelength determination data form.

mercury-in-glass barometer or with the pressure value reported from a nearby National Weather Service Station and corrected for elevation. The correction for elevation difference between the station and sampling point should be applied at a rate of -2.5 mm Hg/30 m (-0.1 in Hg/100 ft) elevation increase, or vice versa for elevation decrease.

2.4 Thermometer

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

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

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

3. The dial-type or equivalent thermometer is acceptable if values agree within 1°C (2°F) at both room and ice bath temperatures. If the difference is greater than $\pm 1^\circ\text{C}$ (2°F), the thermometer should be either adjusted and recalibrated until the above criteria are met, or replaced.

4. Prior to each field trip the temperatures should then be compared at room temperature with the thermometer in the equipment. If the value is not within $\pm 2^\circ\text{C}$ (4°F) of the mercury-in-glass thermometer value, the meter thermometer should be replaced or recalibrated.

2.5 Vacuum Gauge

When a mercury U-tube manometer is used, no calibration is required. The U-tube manometer should be checked initially to ensure that it is leak free.

When a mechanical gauge is used, it must be calibrated against a mercury U-tube manometer before the field test unless otherwise specified by the administrator. The mechanical gauge should be calibrated in the following manner:

1. Connect the mechanical gauge and the U-tube manometer in parallel with the vacuum pump. This can be accomplished with a T-connection. One line should be placed on the vacuum side of the pump, and the other two lines should be placed on the vacuum side of the gauge and manometer.

2. Turn the pump on, and pull a vacuum of about 25 to 50 mm (1 to 2 in.) Hg. Shut off main pump valve and then shut off pump.

3. Observe the U-tube manometer to be sure that the system is leak free. Any variation >10 mm (0.4 in.) Hg over a 1-min period is not acceptable. The manometer and gauge readings must agree within ± 2.5 mm (0.1 in.) Hg, or the gauge should be repaired or replaced.

4. Turn the pump on, and pull the maximum vacuum for which the pump is capable (must be within 75 mm (3 in.) Hg of absolute pressure). Shut off the main valve, and then the pump.

5. Be sure that the system is leak free and again compare readings.

6. The gauge must agree within 2.5 mm (0.1 in.) Hg at both vacuums, or the gauge is not acceptable.

2.6 Analytical Balance

The analytical balance should always be zeroed and calibrated against a standard Class-S weight(s) just before the potassium nitrate (KNO_3) is weighed for the formulation of the working standard. This calibration should be done in the following manner:

1. Zero the balance.

2. Place a 5-g and then a 10-g standard weight on the balance.

3. Be sure the balance readings of the standardized weights agree within ± 2 mg of the standard weights.

4. Enter the data on the calibration form, Figure 2.2.

5. The weight of the weighing boat and the potassium nitrate should be <10 g; if not, heavier standard weights should be used to calibrate the balance.

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Classification of standard weights

B 21

Figure 2.2. Analytical balance calibration form.

Table 2.1. ACTIVITY MATRIX FOR CALIBRATION OF EQUIPMENT

Apparatus	Acceptance limits	Frequency and method of measurement	Action if requirements are not met
Collection flask	Measure volume within ± 10 ml	On receipt, measure with graduated cylinder	Recalibrate
Spectrophotometer	1. *Calibrate wavelength scale 2. *Determine optimum wavelength within 399 to 416 nm	1. Upon receipt and every 6 mo, use glass filters or light source 2. Upon receipt and every 6 mo scan between 400 and 415 nm with 200 mg NO ₂ standard solution	1. Return to manufacturer for repair 2. As above
Barometer	Reading agrees within ± 2.5 mm (0.1 in.) Hg of mercury-in-glass barometer	Upon receipt and before each field test	Repair or return
Thermometer	Reading agrees within $\pm 1^{\circ}\text{C}$ (2°F) of mercury-in-glass thermometer	As above	As above
Vacuum gauge (mechanical only)	Reading agrees within ± 2.5 mm (0.1 in.) Hg of mercury U-tube manometer	As above	As above
Analytical balance	Weight within ± 2 mg of standard weights (Class S)	Use standard weight before preparation of working solution	Repair or return to manufacturer

* The tester may opt to perform either step 1 or 2, both are not required.

3.0 PRESAMPLING OPERATIONS

The quality assurance functions for presampling operations are summarized in Table 3.1 at the end of this section. See Section 3.0.1, Planning the Test Program, of this Handbook for details on preliminary site visits.

3.1 Apparatus Check and Calibration

Previously used equipment should be visually checked for damage and/or excessive wear before each field test. Items should be repaired or replaced (as applicable) if judged to be unsuitable for use. A pretest checklist (Figure 3.1) summarizes equipment calibration. The pretest operations form (Figure 3.2) can be used as an equipment check and packing list. The completed form should be dated, signed by the field crew supervisor, and filed in the operational log book. The replacement of worn or damaged items of equipment should be initiated. Procedures for performing the checks are given herein; a check is placed in the proper row and column as the check/operation is completed. Each team will have to construct its own checklist according to the type of sampling train and equipment it uses.

3.1.1 Probe (Filter) - Clean the probe internally by brushing first using tap water, then with distilled deionized water, next with acetone, and finally allow it to dry in the air. In extreme cases, the glass liner can be cleaned with stronger reagents. Note: Do not use nitric acid to clean the probe unless a thorough cleaning is performed to remove all the nitrates. In either case, the object is to leave the glass liner chemically inert to oxides of nitrogen. If the probe is equipped with a heating system, check to see whether it is operating properly. The probe should be sealed on the filter side and checked for leaks at an absolute pressure of <380 mm (15 in.) Hg. The probe must be leak free under these conditions. This leak check may be performed following the leak check of the sample flask and using the same

Date 2/15/77 Calibrated by B. Plummer

Flask Volume

Flask volumes measured with valves? ☒ yes ☐ no

Volume measured within ± 10 ml? ☐ yes ☐ no

Temperature Gauge

Was a pretest temperature correction used? ☐ yes ☒ no

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

Vacuum Gauge

Was gauge calibrated against a U-tube mercury manometer
(If it was a mechanical gauge)? ☐ yes ☐ no ☒ not
applicable?

Barometer

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

* Most significant items/parameters to be checked.

Figure 3.1. Pretest sampling checks.

Apparatus check	Acceptable		Quantity required	Ready		Loaded and packed	
	Yes	No		Yes	No	Yes	No
<u>Probe</u>			3	✓		✓	
Glass liner clean	✓						
Heated properly	✓						
Leak checked	✓						
<u>Collection Flask</u>			14	✓		✓	
Clean	✓						
Leak checked	✓						
Temperature gauge	✓						
<u>Evacuation System</u>				✓		✓	
Leak-free pumps	✓		2				
Manifold and tubing	✓		3	✓		✓	
U-tube manometer	✓		2	✓		✓	
Barometer	✓		1	✓		✓	
<u>Reagents</u>							
Distilled water	✓		1 liter	✓		✓	
Absorbing solu- tion*	✓		1 liter	✓		✓	
Sodium hydrox- ide, 1 N	✓		1 liter	✓		✓	
pH paper	✓		1 pkg.	✓		✓	
<u>Sample Recovery</u>				✓		✓	
Dropper or burette	✓		2				
Sample bottles	✓		14	✓		✓	
Pipette, 25 ml	✓		2	✓		✓	

* Most significant items/parameters to be checked.

Figure 3.2. Pretest preparations.

setup as described below in Subsection 3.1.2. The glass liner should be sealed inside the metal sheath to prevent ambient air from entering the duct.

3.1.2 Collection Flask, Flask Valve, and Evacuation System - The collection flask and valve in contact with sample gas should be cleaned with a strong detergent and hot water, and rinsed with tap water and deionized distilled water. Periodically, the glassware can be cleaned with a grease remover such as decahydro-naphthalene ($C_{10}H_{18}$), followed with acetone, and then with the cleaning agents named above. An alternate procedure is to use dichromate cleaning solution. Do not use solutions containing nitrogen. Vapor degreaser can be used to remove the stale vacuum grease.

Stopcocks and joints should be lubricated with a chemically inert lubricant. An inert hydrogen-free chlorofluorocarbon lubricant can be used.

The evacuation system (Figure 1.1) is assembled, and a minimum vacuum of 75 mm (3 in.) Hg absolute pressure is produced in each flask with the flask valve in the "evacuation" position. The vacuum should be held for at least 1 min with the pump valve in the "vent" position without appreciable fluctuation (≤ 10 mm (0.4 in.) Hg); if this is not possible, check for leaks.

If the leak check of the probe is to be performed using the same setup, the probe tip should be plugged with a rubber stopper. Immediately after the sample flask has been determined to be leak free, turn the flask valve to the "purge" position. The vacuum will initially drop. After the vacuum stabilizes there should not be any appreciable fluctuation--that is ≤ 10 mm (0.4 in.) Hg over a 1-min period. If stabilization is not obtained, check for leaks and correct.

3.2 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, use the best available grade.

Chloride is an interference in the phenoldisulfonic acid method because even rather low concentrations of chloride result in nitrate losses. It is important that the chloride content be reduced to a minimum, preferably below 10 mg/l.

3.2.1 Sampling - The absorbing reagent is prepared by adding 2.8 ml of concentrated sulfuric acid (H_2SO_4) to 1 l of deionized distilled water. Mix well, and add 6 ml of 3% hydrogen peroxide (H_2O_2). Prepare a fresh absorbing solution weekly, store in a dark-colored pyrex container, and do not expose to extreme heat or direct sunlight. If the reagent must be shipped to the field site, it is advisable that the absorbing reagent be prepared fresh on site.

3.2.2 Sample Recovery - A sodium hydroxide solution (NaOH) is prepared by dissolving 40 g NaOH in distilled water and diluting to 1 l. This solution can be transferred to a polyethylene 1000-ml (32-oz) jar for shipment. Deionized distilled water and pH paper are required to test for basicity and for transferral of samples.

3.2.3 Analysis - The following reagents are needed for analysis and standardization:

Fuming sulfuric acid - 15% to 18% (by weight) free sulfur trioxide (SO_3).

Phenol - White solid ACS reagent grade.

Sulfuric acid - Concentrated reagent, 95% minimum assay, ACS reagent grade.

Standard solution - Dissolve 2.198 g of dried potassium nitrate (KNO_3) ACS reagent grade in distilled water, and dilute to 1 l in a volumetric flask. For the working standard solution, pipette 10 ml of the resulting solution into a 100-ml volumetric flask and dilute to the mark. Note: One ml of the working standard solution is equivalent to 100 μg of nitrogen dioxide.

Water - Deionized distilled.

Phenoldisulfonic acid solution - Dissolve 25 g of pure white phenol (no discoloration) in 150 ml of concentrated sulfuric acid on a steam bath. Cool. Add 75 ml of fuming sulfuric acid, and heat at 100°C (212°F) on a steam bath for 2 h. Store in a dark stoppered bottle. This acid may also be purchased if it meets the American Public Health Association specification for nitrate-nitrogen in water.

3.3 Packing 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 - Pack the probe in a case protected by polyethylene foam or other suitable packing material. An ideal container is a wooden case (or the equivalent) lined with foam material in which separate compartments are cut to hold the individual devices. This case can also contain a Pitot tube for velocity determinations. The case should have handles that can withstand hoisting and should be rigid enough to prevent bending or twisting of the devices during shipping and handling.

3.3.2 Collection Flask and Valve - The collection flasks and valves should be packed securely in a suitable shipping container. An ideal container is a case or footlocker of approximately the following dimensions: 30 in. × 15 in. × 15 in. This container, when lined with foam, will accommodate eight collection flasks with the appropriate mated flask valves.

3.3.3 Evacuation System, Temperature Gauges, Vacuum Lines, and Reagents - A sturdy case lined with foam material can contain the evacuation manifold, squeeze bulb, manometer, and reagents for sample recovery. Special care should be taken with mercury U-tube manometers to avoid any spillages.

3.3.4 Evacuation Pump - The vacuum pump should be packed in a shipping container unless its housing is sufficient for travel. Additional pump oil and oiler jar should be packed with the pump if oil is required for its operation.

3.3.5 Glass Storage Containers - All glass storage containers must be packed with cushion material at the top and bottom of the case, and with some form of dividers to separate the components.

Table 3.1. ACTIVITY MATRIX FOR PRESAMPLING PREPARATION

Characteristic	Acceptance limits	Frequency and method of measurement	Action if requirements are not met
<u>Apparatus Check</u>			
Probe	1. Clean; glass liner inert to oxides of nitrogen 2. Heating properly if equipped with heating system 3. Leak free	1. Before each test 2. As above 3. Pressure <380 mm (15 in.) Hg	Must be replaced
Collection flask	Clean; volume within ± 10 ml	Before each test, clean with strong detergent and hot water and rinse with tap and deionized distilled water; periodically clean with grease remover	Repeat cleansing of flask and/or measure volume
Evacuation system	Vacuum of 75 mm (3 in.) Hg absolute pressure in each flask; leakage rate <10 mm (0.4 in.) Hg/min	Before each test, check for leaks using Hg-filled U-tube manometer	Correct leaks
<u>Absorbing Reagents</u>			
Sulfuric acid, concentrated	2.8 ml/l	Prepare fresh absorbing solution weekly; use graduated pipette	Make up new solution
Hydrogen peroxide, 3%	6 ml/l	As above	As above

(continued)

Table 3.1. (continued)

Characteristic	Acceptance limits	Frequency and method of measurement	Action if requirements are not met
<u>Sample Recovery Reagents</u>			
Sodium hydroxide	40 g ACS reagent grade NaOH in a 1-l volumetric flask (Class A)	On makeup of solution, use triple-beam balance and Class A volumetric flask	As above
Water	Deionized distilled to ASTM specifications D11 93-82, Type 3		Prepare fresh for each analysis period
<u>Analytical Reagent</u>			
Potassium nitrate	2.198 \pm 0.001 g KNO ₃ ACS reagent grade into a 1-l volumetric flask (Class A)	On makeup of solution, use analytical balance	Purchase new solution
Phenoldisulfonic acid solution	25 g white phenol ACS reagent grade in 150-ml concentrated cylinder (Class A) 75 ml fuming sulfuric acid	On makeup of solution, use triple-beam balance and graduated cylinder On makeup of solution, graduated cylinder (Class A)	Make up new solution. As above

4.0 ON-SITE MEASUREMENTS

The on-site measurement activities include transporting the equipment to the test site, unpacking and assembling the equipment, confirming duct measurements and traverse points (if volumetric flow rate is to be determined), velocity traverse, molecular weight determination of the stack gas, moisture content, sampling for oxides of nitrogen, and data recording. Table 4.1 at the end of this section summarizes the quality assurance activities relative to on-site measurements.

4.1 Transport of Equipment to the Sampling Site

The most efficient means of transporting or moving the equipment from ground level to the sampling site (as decided during the preliminary site visit) should be used to place the equipment on site. Care should always be exercised against damage to the test equipment or injury to test personnel during the moving phase. A "laboratory" type area should be designated for preparation of absorbing reagent and charging of the flasks. An acceptable alternative is to charge the flasks in the home laboratory. Utilization of plant personnel or equipment (winches and forklifts) in movement of the sampling gear is highly recommended.

4.2 Preliminary Measurements and Setup

The Reference Method outlines the determination of the concentration of oxides of nitrogen in the gas stream. The volumetric flow rate must be determined utilizing Method 2, Section 3.1, and Method 4, Section 3.3 of this Handbook so that mass emission rate may be determined.

4.3 Sampling

The on-site sampling includes preparation and/or addition of the absorbing reagent to collection flasks (if not performed at home laboratory), setup of the evacuation system, connection

of the electric service, preparation of the probe (leak check and addition of particulate filter), insertion of probe into the stack, purging of the probe, sealing of the port, evacuation of flasks, sampling and recording of the data, and a final leak check. In addition, EPA Reference Methods 1, 2, 3, and/or 4 may have to be performed simultaneously with Method 7. This will be specified by the applicable regulation, and the applicable reference method should be followed.

4.3.1 Preparation and/or Addition of Absorbing Reagent

to Collection Flasks - If preparation of absorbing reagent is necessary on site, follow directions given in Section 3.6.3. Pipette exactly 25 ml of absorbing reagent into the sample flask. Place a properly lubricated flask valve into the collection flask with the valve turned in the "purge" position. Lubrication of joints is intended to prevent leaks and should not seal the bore of the stopcock or contaminate the sample.

4.3.2 Assembling Sampling Train - Assemble the sampling train as shown in Figure 1.1 and perform the following:

1. Visually check probe for liner separation (cracks, etc.).
2. Place a loosely packed filter of glass or quartz wool in the inlet end of the probe to trap any particulates.
3. Insert the probe into the stack to the sampling point, and seal the opening around the probe.

4.3.3 Evacuation, Purge, and Sampling - A sample is taken as follows:

1. Turn the pump and flask valves to the "evacuate" positions and evacuate to a minimum of 75 mm (3 in.) Hg absolute pressure or until the apparent boiling point is reached (bubbling of absorbing solution).
2. Turn the pump valve to the "vent" position, turn off the pump and check the manometer for fluctuations. The manometer should stay stable (maximum deviation ≤ 10 mm (0.4 in.) Hg) for at least 1 minute. If the mercury level changes, check for leaks

and eliminate the problem. Pressure in the flask should be ≤ 75 mm (3 in.) Hg absolute when sampling is commenced.

3. Record the volume of the flask and valve (V_F), the flask temperature (t_i), and the barometric pressure (P_{bar}) on a data form (see Figure 4.1A or 4.1B) or in a field laboratory notebook.

4. Turn the flask valve counterclockwise to the "purge" position.

5. Turn the pump valve to the "purge" position.

6. Purge the probe and the vacuum line using the one-way squeeze bulb.

7. If condensation occurs in the probe or the flask valve, heat the probe until (upon purging) the condensation disappears.

8. Turn the pump valve to the "vent" position.

9. Turn the flask valve clockwise to its "evacuate" position, and record the difference in the mercury levels in the manometer. The absolute internal pressure in the flask (P_i) is equal to the barometric pressure less the manometer reading (Leg A and Leg B).

10. Immediately turn the flask valve to the sample position, and permit the gas to enter the flask until pressures in the flask and sample line (i.e., duct, stack) are equal. This will usually require about 15 s; a longer period indicates a "plug" in the probe, which must be corrected before sampling is continued.

11. After collecting the sample, turn the flask valve to its "purge" position.

12. Disconnect the flask and valve from the sampling train and shake the flask for at least 5 min.

4.3.4 Chemical Reactions of Sample Collection - If the gas being sampled contains insufficient oxygen for the conversion of NO to NO₂ (e.g., an applicable subpart of the standard may require taking a sample of a calibration gas mixture of NO in N₂), then oxygen should be introduced into the flask to permit this

Plant Acme Power Plant City Acme, Ohio
 Sample location ESP Outlet Boiler #1 Date 2/31/77
 Operator _____ Barometric pressure (P_{bar}) 29.84 in. Hg

Sample number	Sample point location	Sample time 24-hr	Probe temperature, °F	Flask and valve number	Volume of flask and valve (V_F), ml	Initial pressure in. Hg			Initial temperature	
						Leg A _i	Leg B _i	P_i^a	°F (t_i)	°R (T_i) ^b
AP-1	B-11	0733	210	PE-13	2013	13.6	13.7	2.54	73	533
AP-2	B-10	0745	210	PE-10	2010	13.7	13.8	2.34	73	533
AP-3	C-10	0801	210	PE-8	2008	13.7	13.7	2.44	74	534

$$^a P_i = P_{\text{bar}} - (A_i + B_i).$$

$$^b T_i = t_i + 460^\circ\text{F}.$$

Figure 4.1A. Nitrogen oxide field data form (English units).

Plant Acme Power PlantCity Acme, OhioSample location ESP Outlet Boiler # 1Date 2/29/77Operator P. RoseBarometric pressure (P_{bar}) 706.2 mm Hg

Sample number	Sample point location	Sample time 24-hr	Probe temperature, °C	Flask and valve number	Volume of flask and valve (V_F), ml	Initial pressure mm Hg			Initial temperature	
						Leg A _i	Leg B _i	P_i^a	°C (t_i)	°K (T_i) ^b
AP-1	B-11	0733	100	PE-13	2013	372	371	17.2	22.2	295.2
AP-2	B-10	0745	100	PE-10	2010	373	370.5	16.7	21.2	294.2
AP-3	C-10	0801	100	PE-8	2008	372.5	370	17.7	23.5	296.5

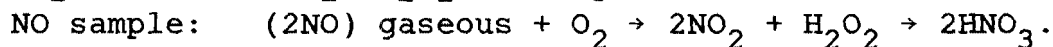
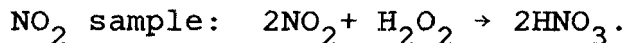
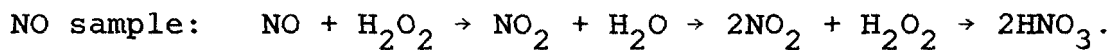
$$^a P_i = P_{\text{bar}} - (A_i + B_i).$$

$$^b T_i = t_i + 273^\circ\text{C}.$$

Figure 4.1B. Nitrogen oxide field data form (metric units).

conversion. Oxygen may be introduced into the flask by one of three methods: (1) Before evacuating the sampling flask, flush with pure cylinder oxygen, and then evacuate flask to 75 mm (3.0 in.) Hg absolute pressure or less; or (2) inject oxygen into the flask after sampling; or (3) terminate sampling with a minimum of 50 mm (2.0 in.) Hg vacuum remaining in the flask, record this final pressure, and then vent the flask to the atmosphere until the flask pressure is almost equal to atmospheric pressure.

Chemical reactions which occur during sampling adsorption are:



4.4 Sample Recovery

The Reference Method requires a minimum sample absorption period of 16 h in the flask. If the laboratory is close by, the sample may be left in the flasks for return to the laboratory. Otherwise, the appropriate data may be taken in the field, solutions made alkaline and transferred to leak-free polyethylene bottles after the required absorption period.

4.4.1 Flask Pressure, Temperature, and Barometric Pressure - After the absorption period is completed (≥ 16 h), record the barometric pressure and the room temperature (final temperature (t_f) on the integrity data forms (Figures 4.2A or 4.2B.)

1. Shake the flask and contents for 2 min.
2. Connect the flask to a mercury-filled U-tube manometer.
3. Open the valve from the flask to the manometer and record the flask temperature (t_f), the barometric pressure, and the difference between the mercury levels in the manometer (Leg A and Leg B). The absolute internal pressure in the flask (P_f) is the barometric pressure less the manometer reading.

4. Transfer the contents of the flask to a leak-free polyethylene bottle.

Plant Acme Power Plant Date 2/3/77
 Sample recovery personnel J. Morgan Barometric pressure, (P_{bar}) 29.84 in. Hg
 Person with direct responsibility for recovered samples P. Rose

Sample number	Final pressure, in. Hg			Final temperature,		Sample recovery time, 24-h	pH adjusted 9 to 12	Liquid level marked	Samples stored in locked container
	Leg A _f	Leg B _f	P _f ^a	°F (t _f)	°R (T _f) ^b				
AP-1	1.6	0.6	27.64	73	533	1322	✓	✓	✓
AP-2	1.2	0.8	27.84	72	532	1340	✓	✓	✓
AP-3	2.0	1.0	25.84	73	533	1415	✓	✓	✓

$$P_f = P_{\text{bar}} - (A_f + B_f). \quad T_f = t_f + 460^\circ\text{F}.$$

Lab person with direct responsibility for recovered samples G. Foster

Date recovered samples received 3/2/77 Analyst J. Morgan

All samples identifiable? yes All liquids at marked level? yes

Remarks _____

Signature of lab sample trustee George Foster

Figure 4.2A. NO_x sample recovery and integrity data form (English units).

Plant Acme Power Plant Date 2/31/77
 Sample recovery personnel J. Morgan Barometric pressure, (P_{bar}) 758 mm Hg
 Person with direct responsibility for recovered samples P. Rose

Sample number	Final pressure, mm Hg			Final temperature,		Sample recovery time, 24-h	pH adjusted 9 to 12	Liquid level marked	Samples stored in locked container
	Leg A _f	Leg B _f	P _f	°C (t _f)	K (T _f)				
AP-1	40.6	15.2	702	22.7	295.7	1322	✓	✓	✓
AP-2	30.5	20.3	707	22.2	295.2	1330	✓	✓	✓
AP-3	50.8	25.4	682	22.7	295.7	1341	✓	✓	✓

$$P_f = P_{\text{bar}} - (A_f + B_f). \quad T_f = t_f + 273^\circ\text{C}.$$

Lab person with direct responsibility for recovered samples G. Foster

Date recovered samples received 3/2/77 Analyst J. Morgan

All samples identifiable? yes All liquids at marked level? yes

Remarks _____

Signature of lab sample trustee George Foster

Figure 4.2B. NO_x sample recovery and integrity data form (metric units).

5. Rinse the flask three times with 5-ml portions of deionized distilled water, and add the rinse water to the bottle.

6. Adjust the pH to between 9 and 12 by adding sodium hydroxide (1N) dropwise (about 25 to 35 drops). Check the pH by dipping a stirring rod into the solution and then touching the rod to the pH test paper. Remove as little material as possible during this step. The pH adjustment is mandatory. The NaOH changes the sample, which is in the form of HNO_3 , to NaNO_3 . If the pH is not adjusted, the HNO_3 will be liberated during the evaporation phase of analysis.

4.5 Sample Logistics (Data) and Packing of Equipment

The above procedures are followed until the required number of runs are completed. Log all data on the form shown in Figure 4.2 A or 4.2.B

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 and duplicate by the best means available. One set of data should be mailed to the base laboratory, or given to another team member or to the Agency; the original data should be hand carried.

3. Examine all sample containers and sampling equipment for damage, and pack them properly for shipment to the base laboratory. All shipping containers should be properly labeled to prevent loss of samples or equipment.

4. The sampling procedures can be reviewed after testing or during the testing using an on site measurement checklist (Figure 4.3).

Sampling

Volume of 25 ml of absorbing solution placed in flask? ✓
Flask valve stopper in purge position? ✓
Sampling train properly assembled? ✓
Leak free?* ✓ Stopcock grease used? ✓
Type? C-7340
Flask evacuated to 75 mm (3 in.) Hg pressure? ✓
Leakage from manometer observation?* 0.1/min
(e.g., maximum change in manometer of ≤ 10 mm (0.4 in.)
Hg/min) _____
Initial pressure of flask recorded?* ✓
Initial temperature of flask recorded? ✓
Probe purged before sampling? ✓
Sample collected properly?* ✓
Flask shaken for 5 min after collection and disassembly
from train?* ✓
Oxygen introduced to flask? N/A Method used? _____
Samples properly labeled and sealed and stored for shipment?
Flasks labeled

Sample Recovery

Samples allowed to remain in flasks for minimum of 16 h?*
✓
Final flask temperature and pressure recorded?* ✓
Sample transferred to leak-free polyethylene bottle? ✓
Flask rinsed twice with 5-ml portions of distilled water
and rinse added to bottle containing sample? ✓
pH adjusted to between 9 and 12?* ✓

* Most significant items/parameters to be checked.

Figure 4.3. On-site measurements.

Table 4.1. ACTIVITY MATRIX FOR ON-SITE MEASUREMENTS

Characteristic	Acceptance limits	Frequency and method of measurement	Action if requirements are not met
Apparatus assembly	Assemble using Fig. 1.1; no leakage	Before sample collection, visually and physically inspect all connections	Check for leaks; repair system; repair test
Operational check	Maximum vacuum of 75 mm (3 in.) Hg absolute pressure	Before sample collection, use Hg-filled U-tube manometer	Check system for leaks; check vacuum pump
	Leakage rate ≤ 10 mm (0.4 in.) Hg/min	As above	Check all joints and valves for source of leakage
Sample recovery	Shake flask for 5 min	During each sample collection, use manometer, centigrade thermometer, and pH paper	Reject sample, re-run test
	Let flask set for a minimum of 16 h		
	Shake flask for 2 min		
	Determine flask pressure and temperature		
	Adjust pH of sample to 9-12 with NaOH		
	Mark sample level on container		
Sample logistics	Record data on data form (Fig. 4.2)	Visually check each sample	Complete the labeling
	Properly label all containers, etc		
Sample logistics	Record all data on field data forms (Fig. 4.1 and Fig. 4.2)	As above	Complete the data records

5.0 POSTSAMPLING OPERATIONS

Table 5.1 at the end of this section summarizes the quality assurance activities for sample analysis. If the laboratory receives the samples in the sample flask, laboratory personnel will have to complete the sample recovery procedures previously explained in Section 3.6.4.

5.1 Procedures For Operating a Spectrophotometer

The correct manipulations of blanks and sample cells are critical. Careless technique is unacceptable. The following points are recommended and should be adhered to.

1. Designate the cuvettes as either a blank or a sample cell. Do not interchange the cells during an analysis because they are not always matched.
2. Do not touch the bottom of the cuvette with your fingers.
3. Rinse the cuvette at least twice with the solution you are about to measure.
4. Remove lint, liquid, and so forth with a lens tissue or its equivalent.

5.2 Base Laboratory (Analysis)

5.2.1 Check of Field Sample Integrity - If the field samples have been shipped in sample containers, be sure that all samples are identifiable and that the liquid level of each is at its mark. If a sample is not identifiable or if a loss of liquid is detected, note it on the data form, as shown in Figures 4.2A and 4.2B. When a noticeable amount of leakage has occurred, use an alternative method, subject to the approval of the administrator, to correct the final value; approval should have been requested prior to testing. An alternative method is as follows:

1. Mark the new level of the sample.

2. Transfer the sample to a 50-ml volumetric flask, along with two 5-ml deionized distilled water rinsings of the container.

3. Add water to the sample storage container to the initial sample mark, and measure the initial sample volume (V_{soln_i}) in ml.

4. Add water to the sample storage container to the mark of the transferred sample, and measure the final volume (V_{soln_f}) in ml.

5. If (V_{soln_f}) $< V_{\text{soln}_i}$, correct the sample volume (V_{soln}) by using Equation 5-1.

$$V_{\text{soln}'} = V_{\text{soln}} \left[\frac{V_{\text{soln}_i}}{V_{\text{soln}_f}} \right]. \quad \text{Equation 5-1}$$

where

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

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

V_{soln_i} = initial sample volume placed in storage container, ml, and

V_{soln_f} = final sample volume removed from storage container, ml.

6. Both the corrected and uncorrected values should be submitted in the test report to the Agency.

5.2.2 Control Samples and Working Standards Preparation - The accuracy and precision of the analytical technique can be determined with control samples. For analysts that are unfamiliar with these procedures it is recommended that acceptable accuracy and precision be demonstrated with the working solution prior to the analysis of the field samples. This procedure may help the testing company to detect analytical errors prior to

sample analysis and thus prevent having to invalidate the field samples and to require a complete retest of the source.

The control samples and the standard KNO_3 solution should be prepared using the following procedure.

1. Dry the potassium nitrate (KNO_3) ACS reagent grade at 105° to 110°C for a minimum of 2 h prior to the preparation of the control sample and the standard solution.

2. Place a 2 g Class-S weight on the balance. The balance must agree within ± 2 mg of the Class-S standard weight.

3. Cool and store KNO_3 in desiccator. Weigh and then dissolve 2.198 ± 0.002 g of dried KNO_3 in about 800 ml of deionized distilled water in a 1-l volumetric flask (Class A).

4. Dilute to the mark with deionized distilled water, and label and date the solution.

5. Dilute 10.0 ml of the standard solution to the mark in a 100-ml volumetric flask with deionized distilled water, and label as "control sample" for analysis.

6. Weigh and then dissolve 2.198 ± 0.002 g of dried KNO_3 in about 800 ml of deionized distilled water in a 1-l volumetric flask (Class A).

7. Dilute to the mark with distilled deionized water, and label and date as the standard KNO_3 solution.

8. Dilute 10.0 ml of the standard KNO_3 solution to the mark in a 100-ml volumetric flask with deionized distilled water, and label as "working standard KNO_3 solution" for analysis.

9. Pipette 0.0, 2.0, 4.0, 6.0, and 8.0 ml of the working standard KNO_3 solution into five 50-ml volumetric flasks.

10. Pipette 2.0, 4.0, and 6.0 ml of the control sample into another set of 50-ml volumetric flasks.

11. Add 25 ml of absorbing solution, 10 ml of deionized distilled water, and then sodium hydroxide (1N) dropwise to each of the eight flasks until the pH is between 9 and 12 (about 25 to 35 drops each). Check for alkalinity by touching a glass rod first to the solution and then to pH paper. Note: The pH check is mandatory.

12. Dilute to the mark with deionized distilled water, and mix thoroughly.

5.2.3 Analysis of Control Samples, Standard Solutions, and Field Samples - The analysis of the samples has a time-dependent color change. To provide an estimate of the accuracy and precision of the analysis, the control sample is analyzed at the same time as the field sample. The standard solutions, field samples, and control samples should be analyzed in the following manner.

1. Pipette a 25-ml aliquot of each solution into a separate porcelain evaporating dish.

2. Evaporate the solutions (standards, field samples, and control samples) to dryness on a steam bath and then cool. Note: Do not evaporate on a hot plate or in an oven unless it is thermostatically controlled below 70°C (160°F). Remove samples from steam bath just before complete dryness is reached (the bottom of the dish should be covered with a smooth film), so that the last droplet evaporates as the dishes cool.

3. Add 2.0 ml of phenoldisulfonic acid reagent to each dried residue and either mix thoroughly with a polyethylene policeman or let the solution stand for 5 min.

4. Add 1.0 ml of deionized distilled water and four drops of concentrated sulfuric acid, and then heat the solution on a steam bath for 3 min with occasional stirring.

5. Cool. Add 20 ml of deionized distilled water, and mix well by stirring.

6. Add concentrated ammonium hydroxide dropwise (a 50-ml burette is suggested) with constant stirring until the pH is 10, as determined either by pH paper or by the first yellow color that does not fade.

7. Transfer directly to a 100-ml volumetric flask if the sample does not contain solids. Rinse the evaporating dish with at least three 5-ml portions of deionized distilled water, and then add the washings to the contents of the flask.

8. Remove any solids from the sample by filtering the sample through a Whatman No. 41 filter paper into a 100-ml volumetric flask; rinse each evaporating dish with three 5-ml portions of deionized distilled water; filter these three rinses. Wash the filter with at least three 15-ml portions of deionized distilled water, and then add the filter washings to the contents of the volumetric flask.

9. Dilute to the 100-ml mark with deionized distilled water and mix the contents of the flask thoroughly.

10. Measure the absorbance of the standard solutions at the optimum wavelength, using the blank solution as a zero reference. Note: The flasks should not sit in warm or light areas for very long before analysis because precipitates may form.

11. Record the standard solutions and control sample data on Figure 5.1 or similar form.

12. Read the absorbance of the field samples from Run 1 and then one of the control samples; Run 2 and another control sample; and Run 3 and the last control sample.

13. If the absorbance reading of any field sample is greater than the absorbance reading of the standard sample A_4 (the absorbance of the 400 $\mu\text{g NO}_2$ standard), then dilute the sample and the blank with equal volumes of deionized distilled water using pipettes to get ratios of 25/5, 25/10, and so forth.

14. Record all field sample analysis data as shown in Figure 5.2, and calculate the mass (m) of NO_x for each sample as μg of NO_2 .

15. Perform the calculations and the accuracy checks of the three control samples as shown in Figure 5.1. It is recommended that the agreement for each control sample be within $\pm 15\%$. The standard solution and control sample analytical form should be included in the emission test report as a documentation of the analytical accuracy. This accuracy limit of $\pm 15\%$ for intra-laboratory control samples is recommended based on the control limit of $\pm 20\%$ for interlaboratory audit results discussed in Section 3.6.8.

Plant ACME POWER PLANT Date 3-3-77
Analyst J. Morgan Optimum wavelength 408 nm
Blank used as reference? Yes

Sample number	Sample, μg	Working solution	Control sample	Measured, absorbance, OD	Calculated absorbance, ^a OD	Absorbance comparison error, ^b %
A1	100	x		0.192	-	-
A2	200	x		0.380	-	-
A3	300	x		0.560	-	-
A4	400	x		0.770	-	-
S1	100		x	0.190	0.191	- 0.5
S2	200		x	0.381	0.381	0.0
S3	300		x	0.570	0.571	- 0.2
						Avg ^c 0.2

^a $\text{OD} = (\mu\text{g})/K_c$; i.e., S1 calculated absorbance = $100/K_c$.

$$K_c = 100 \left[\frac{A_1 + 2A_2 + 3A_3 + 4A_4}{A_1^2 + A_2^2 + A_3^2 + A_4^2} \right] = \underline{525}.$$

^b Absorbance comparison errors:

$$\% = 100 \times \left[\frac{(\text{measured absorbance, OD}) - (\text{calculated absorbance, OD})}{\text{calculated absorbance, OD}} \right].$$

^c Average of absolute values.

Figure 5.1. Standard solution and control sample analytical data form.

Plant ACME POWER PLANT Run number(s) AP-1 THROUGH AP-12
Date samples received 3/2/77 Date analyzed 3/3/77
Aliquot factor 2 Samples analyzed by J. MORGAN
Blank absorbance USED AS REFERENCE Date reviewed by T. SEAYER
Calibration factor (K_c) 528 Date of review 3/5/77

Sample number	Sample absorbance, A	Dilution factor, F	Total mass of NO ₂ in sample, m
AP-1	0.743	1.0	784
AP-2	0.631	1.0	666
AP-3	0.450	2.0	950

$m = 2 K_c AF$, Note: If other than a 25 ml aliquot is used for analysis, the factor 2 must be replaced by a corresponding factor.

Figure 5.2 NO_x laboratory data form.

16. When the above criteria cannot be met, it is recommended that the analytical techniques be checked and then the field sample and control sample analysis be repeated using a 20.0-ml aliquot of the remaining field samples.

17. The main parameters of the analytical procedures may be checked during or after the analysis, using a posttest operations form (Figure 5.3).

Reagents

Phenoldisulfonic acid stored in dark stoppered bottle? ✓
Sulfuric acid, concentrated, 95% minimum assay reagent grade? ✓
Ammonium hydroxide, concentrated reagent grade? ✓

Sample Preparation

Has liquid level noticeably changed?* No
Original volume _____ Corrected volume _____

Analysis

Spectrophotometer calibrated?* ✓
Setting for maximum absorbance of standard 408 nm
Control sample prepared?* ✓
Any solids in sample removed through Whatman No. 41 filter paper? N/A
Absorbance measured at optimum wavelength used for the standards, using the blank solution as a zero reference? ✓
All analytical data recorded on checklist and laboratory form? ✓

* Most significant items/parameters to be checked.

Figure 5.3. Posttest operations.

Table 5.1. ACTIVITY MATRIX FOR SAMPLE ANALYSIS

Characteristic	Acceptance limits	Frequency and method of measurement	Action if requirements are not met
Control sample analysis (recommended)	Agree within 15% of the working standards for each sample	Compare control sample analysis to working standards analysis	Redo field and control samples and/or seek assistance with analytical technique
Field sample analysis	No sample volume lost, or final results corrected	Compare liquid level to mark before analysis	Void sample
	Working standard analyzed simultaneously with field sample	Use same solutions and techniques used for control samples	As above
	No absorbance readings outside working standard solution concentration	Dilute sample and blank with equal amounts of deionized distilled water	Dilute and reanalyze
Data recording	All pertinent data recorded on Figs. 5.1 and 5.2	Visually check	Supply missing data

6.0 CALCULATIONS

Calculation errors due to procedural or mathematical mistakes can be a large component 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 checked, and 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 at least one extra decimal figure beyond that of the acquired data and should be rounded after final calculation to two significant digits for each run or sample. All rounding of numbers should be performed in accordance with the ASTM 380-76 procedures. All calculations are then recorded on a form such as the one in Figure 6.1A or 6.1B, following the nomenclature list.

6.1 Nomenclature

The following nomenclature is used in the calculations.

A = Absorbance of sample.

C = Concentration of NO_x as NO_2 , dry basis, corrected to standard conditions, mg/dscm (lb/dscf).

F = Dilution factor (i.e., 25/5, 25/10, etc.) required only if sample dilution was needed to reduce the absorbance to the range of calibration.

K_C = Spectrophotometer calibration factor.

m = Mass of NO_x as NO_2 in gas sample, μg .

P_f = Final absolute pressure of flask, mm (in.) Hg.
 P_i = Initial absolute pressure of flask, mm (in.) Hg.
 P_{std} = Standard absolute pressure, 760 mm (29.92 in.) Hg
 T_f = Final absolute temperature of flask, K ($^{\circ}$ R).
 T_i = Initial absolute temperature of flask, K ($^{\circ}$ R).
 T_{std} = Standard absolute temperature, 293K (528 $^{\circ}$ R).
 V_{sc} = Sample volume at standard conditions, dry basis,
ml.
 V_f = Volume of flask and valve, ml.
 V_a = Volume of absorbing solution, 25 ml.

6.2 Calculations

The following are the equations used with example calculation forms Figures 6.1A and 6.1B to calculate the concentration of nitrogen oxides.

6.2.1 Sample Volume - Calculate the sample volume on a dry basis at standard conditions (760 mm (29.92 in.) Hg and 293K (528 $^{\circ}$ R)) by using the following equation.

$$V_{sc} = \frac{T_{std}(V_f - V_a)}{P_{std}} \left(\frac{P_f}{T_f} - \frac{P_i}{T_i} \right)$$

$$= K_1 (V_f - 25 \text{ ml}) \left(\frac{P_f}{T_f} - \frac{P_i}{T_i} \right) \quad \text{Equation 6-1}$$

where

$$K_1 = 0.3858 \frac{K}{\text{mm Hg}} \quad \text{for metric units, or}$$

$$K_1 = 17.64 \frac{^{\circ}R}{\text{in. Hg}} \quad \text{for English units.}$$

6.2.2 Total μg of NO_2 Per Sample - Calculate the total μg of NO_2 per sample by using Equation 6-2.

$$m = 2 K_c AF \quad . \quad \text{Equation 6-2}$$

where

2 = 50/25, the aliquot factor (if other than a 25-ml aliquot was used for analysis, the corresponding factor must be substituted).

6.2.3 Sample Concentration - Calculate the sample concentration on a dry basis at standard conditions using Equation 6-3.

$$C = K_2 \left[\frac{m}{V_{sc}} \right] \quad \text{Equation 6-3}$$

where

$$K_2 = 10^3 \frac{\text{mg}/\text{m}^3}{\mu\text{g}/\text{ml}} \quad \text{for metric units, or}$$

$$K_2 = 6.243 \times 10^{-5} \frac{\text{lb}/\text{scf}}{\mu\text{g}/\text{ml}} \quad \text{for English units.}$$

Sample Volume

$$V_f = \underline{2013} \text{ ml}, P_f = \underline{27.64} \text{ in. Hg}, T_f = \underline{533} \text{ }^\circ\text{R}$$

$$P_i = \underline{0.59} \text{ in. Hg}, T_i = \underline{532} \text{ }^\circ\text{R}$$

$$V_{sc} = 17.64 (V_f - 25) \left[\frac{P_f}{T_f} - \frac{P_i}{T_i} \right] = \underline{1780} \text{ ml} \quad \text{Equation 6-1}$$

Total $\mu\text{g NO}_2$ Per Sample

$$K_C = \underline{528.}, A = \underline{0.743} \text{ OD}, F = \underline{1.00} \quad \text{Equation 6.2}$$

$$m = 2K_C AF = \underline{785.} \text{ } \mu\text{g of NO}_2$$

Sample Concentration

$$C = 6.243 \times 10^{-5} \left[\frac{m}{V_{sc}} \right] = \underline{2.75} \times 10^{-5} \text{ lb/dscf}$$

Figure 6.1A. Nitrogen oxide calculation form
(English units).

Sample Volume

$$V_f = \underline{2013} \text{ ml}, P_f = \underline{702.0} \text{ mm Hg}, T_f = \underline{295.2} \text{ K}$$

$$P_i = \underline{12.0} \text{ mm Hg}, T_i = \underline{295.5} \text{ K}$$

$$V_{sc} = 0.3858 (V_f - 25) \left[\frac{P_f}{T_f} - \frac{P_i}{T_i} \right] = \underline{1775} \text{ ml} \quad \text{Equation 6-1}$$

Total $\mu\text{g NO}_2$ Per Sample

$$K_c = \underline{528}, A = \underline{0.743} \text{ OD}, F = \underline{1.00}$$

$$m = 2K_c AF = \underline{784} \text{ } \mu\text{g of NO}_2. \quad \text{Equation 6-2}$$

Sample Concentration

$$C = 10^3 \left[\frac{m}{V_{sc}} \right] = \underline{0.442} \times 10^3 \text{ mg/dscf.} \quad \text{Equation 6-3}$$

Figure 6.1B. Nitrogen oxide calculation form
(metric units).

Table 6.1 ACTIVITY MATRIX FOR CALCULATIONS

Characteristic	Acceptance limits	Frequency and method of measurement	Action if requirements are not met
Sample volume calculation	All data available; calculations correct within round-off error	For each sample, examine the data form	Complete the data or void the sample
Sample mass calculation	As above	As above	As above
Sample concentration	As above	As above	As above
Calculation check	Original and check calculations agree within round-off error	For each sample, perform independent calculation using data on Figs. 4.1, 4.2, and 4.3	Check and correct all data
Document and report results	All data available; calculations correct within round-off error	For each sample, examine the data form	Complete the data or void the sample

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 routine maintenance program which should be performed quarterly or upon improper functioning of the apparatus. It is suggested that the vacuum pump be disassembled and cleaned yearly. A summary of the components with maintenance procedures is presented in Table 7.1 at the end of this section. The following procedures are not required, but are recommended to increase the reliability of the equipment.

7.1 Pumps

Several types of pumps are used in the present commercial sampling trains. 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. The oil should be translucent. During the yearly disassembly or if the fiber vane pump starts to run erratically, the head should be removed and the fiber vanes changed. The diaphragm pump will show a leak when the diaphragm needs changing. If the diaphragm pump runs erratically, it is usually due to a bad diaphragm (causing leakage) or to malfunctions in the valves. The valves should be cleaned annually by complete disassembly of the pump.

7.2 Shipping Containers

Since the majority of the sampling train is glassware, the shipping containers are very important for protection and safety. All shipping containers should be inspected quarterly for their condition, and repaired or modified to assure the safety of the equipment.

Table 7.1 ACTIVITY MATRIX FOR MAINTENANCE

Apparatus	Acceptance limits	Frequency and method of measurement	Action if requirements are not met
Routine maintenance	Proper functioning	Perform routine maintenance quarterly; disassemble and clean yearly	Replace parts as needed
Fiber vane pump	Oil translucent pump leakless and capable of pulling a vacuum of less than 75 mm (3 in.) Hg absolute pressure	Check of oiler jar periodically; remove head and change fiber vanes	Replace as needed
Diaphragm pump	Leak free, valves functioning properly, and capable of pulling a vacuum of <75 mm (3 in.) Hg absolute pressure	Clean valves during disassembly; replace diaphragm as needed	Replace when leaking or malfunctioning
Shipping container	Protect equipment from damage	Inspect quarterly; repair as needed	Replace

8.0 AUDITING PROCEDURE

An audit is an independent assessment of data quality. Independence is achieved if the individual(s) performing the audit and their standards and equipment are different from the regular field crew and their standards and equipment. Routine quality assurance checks by a field team are necessary in generation of good quality data, but they are not part of the auditing procedure. Table 8.1 at the end of this section summarizes the quality assurance functions for auditing.

Based on the results of collaborative tests^{3,4,5} of Method 7, two specific performance audits are recommended:

1. Audit of the analytical phase of Method 7.
2. Audit of data processing.

It is suggested that a systems audit be conducted as specified by the quality assurance coordinator, in addition to these performance audits. The two performance audits and the systems audit are described in detail in Subsections 8.1 and 8.2, respectively.

8.1 Performance Audits

Performance audits are made to 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. 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 actual analysis of the field samples which is required.

8.1.1 Pretest Audit of Analytical Phase Using Aqueous

Potassium Nitrate (Optional) - The pretest audit described in this subsection can be used to determine the proficiency of the analyst and the standardization of solutions in the Method 7

analysis and should be performed at the discretion of the agency auditor. The analytical phase of Method 7 can be audited with the use of aqueous potassium nitrate samples provided to the testing laboratory before the enforcement source test. Aqueous potassium nitrate samples may be prepared by the procedure described in Section 3.6.5 on control samples preparation.

The pretest audit provides the opportunity for the testing laboratory to check the accuracy of its analytical procedure. This audit is especially recommended for a laboratory with little or no experience with the Method 7 analysis procedure as described in this Handbook.

The testing laboratory should provide the agency/organization requesting the performance test with a notification of the intent to test 30 days prior to the enforcement source test. The testing laboratory should also request that the agency/organization provide the following performance audit samples: two samples at a low concentration (250 to 500 mg NO₂/dscm of gas sampled) and two samples at a high concentration (600 to 1000 mg NO₂/dscm of gas sampled). At least 10 days prior to the enforcement source test, the agency/organization should provide the four audit samples. The concentrations of the two low and two high samples should not be identical.

The testing laboratory will analyze one sample at the low concentration and one at the high concentration, and submit their results to the agency/organization prior to the enforcement source test. Note: The analyst performing this optional audit must be the same analyst audited during the field sample analysis described in Subsection 8.1.2.

The agency/organization determines the percent accuracy, %A, between the measured NO₂ concentration and the audit or known values of concentration. This %A is a measure of the bias of the analytical phase of Method 7. Calculate %A using Equation 8-1.

$$\%A = \frac{C_{NO_2} (M) - C_{NO_2} (A)}{C_{NO_2} (A)} \times 100 \quad \text{Equation 8-1}$$

where

$C_{NO_2} (M)$ = concentration measured by the lab analyst
mg/ml, and

$C_{NO_2} (A)$ = audit or known concentration of the audit
sample, mg/ml.

The recommended control limit for the pretest audit is the 80th percentile value for %A based on the results of three audits (11/77, 5/78, and 10/78) performed by the Environmental Monitoring and Support Laboratory, USEPA, Research Triangle Park, North Carolina.^{12,13} The 80th percentile values and the known audit concentrations are given below for each concentration range, 250 to 500 mg NO_x/dscm and 600 to 1000 mg NO_x/dscm. By definition, 80% of the laboratory participants in the audit obtained values of %A less than the 80th percentile values tabulated below. The 80th percentile is recommended for NO_x instead of the 90th percentile as used for SO₂ in Method 6, Section 3.5.8, even though it is recognized that about one out of five laboratories audited would be expected to exceed the 80th percentile limits for the pretest audits.

250 to 500 mg NO_x/dscm

<u>Audit date</u>	<u>Known audit concentration mg NO_x/dscm</u>	<u>80th percentile for %A, %</u>
11/77	421	16.2
5/78	516	13.6
5/78	328	14.9
10/78	246	15.6
10/78	458	17.2

600 to 1000 mg NO_x/dscm

<u>Audit date</u>	<u>Known audit concentration mg NO_x/dscm</u>	<u>80th percentile for %A, %</u>
11/77	804	16.4
5/78	703	19.7
5/78	938	21.3
10/78	731	17.5
10/78	880	18.7

Based on the results in the previous tables, a control limit of 20% is suggested for both concentrations levels.

If the results of the pretest audit exceed 20% the agency/organization should provide the correct results to the testing laboratory. After taking any necessary corrective action, the testing laboratory should then proceed to analyze the two remaining samples and report the results immediately to the agency/organization before the enforcement source test analysis.

8.1.2 Audit of Analytical Phase Using Aqueous Potassium

Nitrate (Required) - The agency should provide 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 %A of the audit samples is determined using Equation 8-1. The results of the calculated %A should be included in the enforcement source test report as an assessment of accuracy of the analytical phase of Method 7 during the actual enforcement source test.

8.1.3 Audit of Data Processing - Calculation errors are prevalent in Method 7.^{3,4,5} 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 occur in the field) and by requesting that the data calculation be

completed and the results 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 in the following:

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 charts 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 the absorbing solution and adding it to the collection flasks.
3. Collecting the sample.

4. Sample absorption, recovery, and preparation for shipment.

Figure 8.1 is a suggested checklist for the auditor.

Presampling Preparation

- | Yes | No | |
|----------|------------|------------------------------------------------------------------------------|
| <u>✓</u> | <u> </u> | 1. Information concerning combustion effluents that may act as interferences |
| <u>✓</u> | <u> </u> | 2. Plant operation parameters variation |
| <u>✓</u> | <u> </u> | 3. Calibration of the flask and valve volume---three determinations |
| <u>✓</u> | <u> </u> | 4. Absorbing reagent preparation |

On-site Measurements

- | | | |
|----------|------------|------------------------------------------------------------------------|
| <u>✓</u> | <u> </u> | 5. Leak testing of the sampling train |
| <u>✓</u> | <u> </u> | 6. Preparation and pipetting of absorbing solution into sampling flask |

Postsampling (Analysis and Calculation)

- | | | |
|----------|------------|-------------------------------------------------|
| <u>*</u> | <u> </u> | 7. Control sample analysis |
| <u>✓</u> | <u> </u> | 8. Sample aliquotting technique |
| <u>✓</u> | <u> </u> | 9. Evaporation and chemical treatment of sample |
| <u>✓</u> | <u> </u> | 10. Spectrophotometric technique |
| | | a. Preparation of standard nitrate samples |
| | | b. Measurement of absorbance, including blanks |
| | | c. Calibration factor |
| | | d. Wavelength and absorbance, including blanks |
| <u>✓</u> | <u> </u> | 11. Calculation procedure and checks |
| | | a. Use of computer program |
| | | b. Independent check of calculations |

Comments

** Unable to obtain agreement on first analysis but second analysis was acceptable.*

Figure 8.1. Method 7 checklist to be used by auditors.

Table 8.1. ACTIVITY MATRIX FOR AUDITING PROCEDURE

Audit	Acceptance limits	Frequency and method of measurement	Action if requirements are not met
Spectrophotometer analysis using reference samples of dilute KNO_3 solutions	$0.80 < \frac{C_{\text{NO}_2}(\text{M})}{C_{\text{NO}_2}(\text{A})} < 1.20$ $C_{\text{NO}_2}(\text{M}) = \text{measured}$ $C_{\text{NO}_2}(\text{A}) = \text{true conc.}$	<u>Frequency:</u> Once during every enforcement source test* <u>Method:</u> Measure reference samples and compare to their true values	Review operating technique and/or calibration check
Data processing errors	Original and check calculations agree within round-off error	<u>Frequency:</u> Once during every enforcement source test* <u>Method:</u> Independent calculations starting with recorded data on Figures 4.1 and 5.1	Check and correct all data for the audit period represented by the sampled data
Systems audit--observance of technique	Operational technique as described in this section of the Handbook	<u>Frequency:</u> Once during every enforcement source test* until experience gained, then every fourth test <u>Method:</u> Observation of techniques assisted by audit checklist, Fig. 8.1	Explain to team their deviations from recommended techniques and note on Fig. 8.1

* As defined here, a source test for enforcement comprises a series of runs at one source. Source tests for purposes other than enforcement (e.g., a research project) may be audited at a lower frequency.

9.0 RECOMMENDED STANDARDS FOR ESTABLISHING TRACEABILITY

To achieve data of desired quality, two essential considerations are necessary: (1) the measurement process must be in a state of statistical control at the time of the measurement and (2) the systematic errors, when combined with the random variation (errors or measurement), must result in an acceptable uncertainty. As evidence in support of good quality data, it is necessary to perform quality control checks and independent audits of the measurement process; to document these data; 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 standard reference samples (primary, secondary, and/or working standards) and the establishment of a condition of process control. The working calibration standards should be traceable to standards of higher accuracy, such as that below.

Class-S weights (made to NBS specifications) are recommended for the analytical balance calibration. See Section 3.6.2 for details on balance calibration checks.

10.0 REFERENCE METHOD *

METHOD 7—DETERMINATION OF NITROGEN OXIDE EMISSIONS FROM STATIONARY SOURCES

1. Principle and Applicability

1.1 Principle. A grab sample is collected in an evacuated flask containing a dilute sulfuric acid-hydrogen peroxide absorbing solution, and the nitrogen oxides, except nitrous oxide, are measured colorimetrically using the phenoldisulfonic acid (PDS) procedure.

1.2 Applicability. This method is applicable to the measurement of nitrogen oxides emitted from stationary sources. The range of the method has been determined to be 2 to 400 milligrams NO_x (as NO_2) per dry standard cubic meter, without having to dilute the sample.

2. Apparatus

2.1 Sampling (see Figure 7-1). Other grab sampling systems or equipment, capable of measuring sample volume to within ± 2.0 percent and collecting a sufficient sample volume to allow analytical reproducibility to within ± 3 percent, will be considered acceptable alternatives, subject to approval of the Administrator, U.S. Environmental Protection Agency. The following equipment is used in sampling:

2.1.1 Probe. Borosilicate glass tubing, sufficiently heated to prevent water condensation and equipped with an in-stack or out-stack filter to remove particulate matter (a plug of glass wool is satisfactory for this purpose). Stainless steel or Teflon³ tubing may also be used for the probe. Heating is not necessary if the probe remains dry during the purging period.

³ Mention of trade names or specific products does not constitute endorsement by the Environmental Protection Agency.

2.1.2 Collection Flask. Two-liter borosilicate, round bottom flask, with short neck and 24/40 standard taper opening, protected against implosion or breakage.

2.1.3 Flask Valve. T-bore stopcock connected to a 24/40 standard taper joint.

2.1.4 Temperature Gauge. Dial-type thermometer, or other temperature gauge, capable of measuring 1°C (2°F) intervals from -5 to 50°C (23 to 123°F).

2.1.5 Vacuum Line. Tubing capable of withstanding a vacuum of 75 mm Hg (3 in. Hg) absolute pressure, with "T" connection and T-bore stopcock.

2.1.6 Vacuum Gauge. U-tube manometer, 1 meter (36 in.), with 1-mm (0.1 in.) divisions, or other gauge capable of measuring pressure to within ± 2.5 mm Hg (0.10 in. Hg).

2.1.7 Pump. Capable of evacuating the collection flask to a pressure equal to or less than 75 mm Hg (3 in. Hg) absolute.

2.1.8 Squeeze Bulb. One-way.

2.1.9 Volumetric Pipette. 25 ml.

2.1.10 Stopcock and Ground Joint Grease. A high-vacuum, high-temperature chlorofluorocarbon grease is required. Halocarbon 25-58 has been found to be effective.

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.

2.2 Sample Recovery. The following equipment is required for sample recovery:

2.2.1 Graduated Cylinder. 50 ml with 1-ml divisions.

2.2.2 Storage Containers. Leak-free polyethylene bottles.

2.2.3 Wash Bottle. Polyethylene or glass.

2.2.4 Glass Stirring Rod.

2.2.5 Test Paper for Indicating pH. To cover the pH range of 7 to 14.

2.3 Analysis. For the analysis, the following equipment is needed:

2.3.1 Volumetric Pipettes. Two 1 ml, two 2 ml, one 3 ml, one 4 ml, two 10 ml, and one 25 ml for each sample and standard.

2.3.2 Porcelain Evaporating Dishes. 175- to 250-ml capacity with lip for pouring, one for each sample and each standard. The Coors No. 45008 (shallow-form, 195 ml) has been found to be satisfactory. Alternatively, polymethyl pentene beakers (Nalgae No. 1203, 150 ml), or glass beakers (150 ml) may be used. When glass beakers are used, etching of the beakers may cause solid matter to be present in the analytical step, the solids should be removed by filtration (see Section 4.3).

2.3.3 Steam Bath. Low-temperature ovens or thermostatically controlled hot plates kept below 70°C (160°F) are acceptable alternatives.

2.3.4 Dropping Pipette or Dropper. Three required.

2.3.5 Polyethylene Policeman. One for each sample and each standard.

2.3.6 Graduated Cylinder. 100 ml with 1-ml divisions.

2.3.7 Volumetric Flasks. 50 ml (one for each sample), 100 ml (one for each sample and each standard, and one for the working standard KNO_3 solution), and 1000 ml (one).

2.3.8 Spectrophotometer. To measure absorbance at 410 nm.

2.3.9 Graduated Pipette. 10 ml with 0.1-ml divisions.

2.3.10 Test Paper for Indicating pH. To cover the pH range of 7 to 14.

2.3.11 Analytical Balance. To measure to within 0.1 mg.

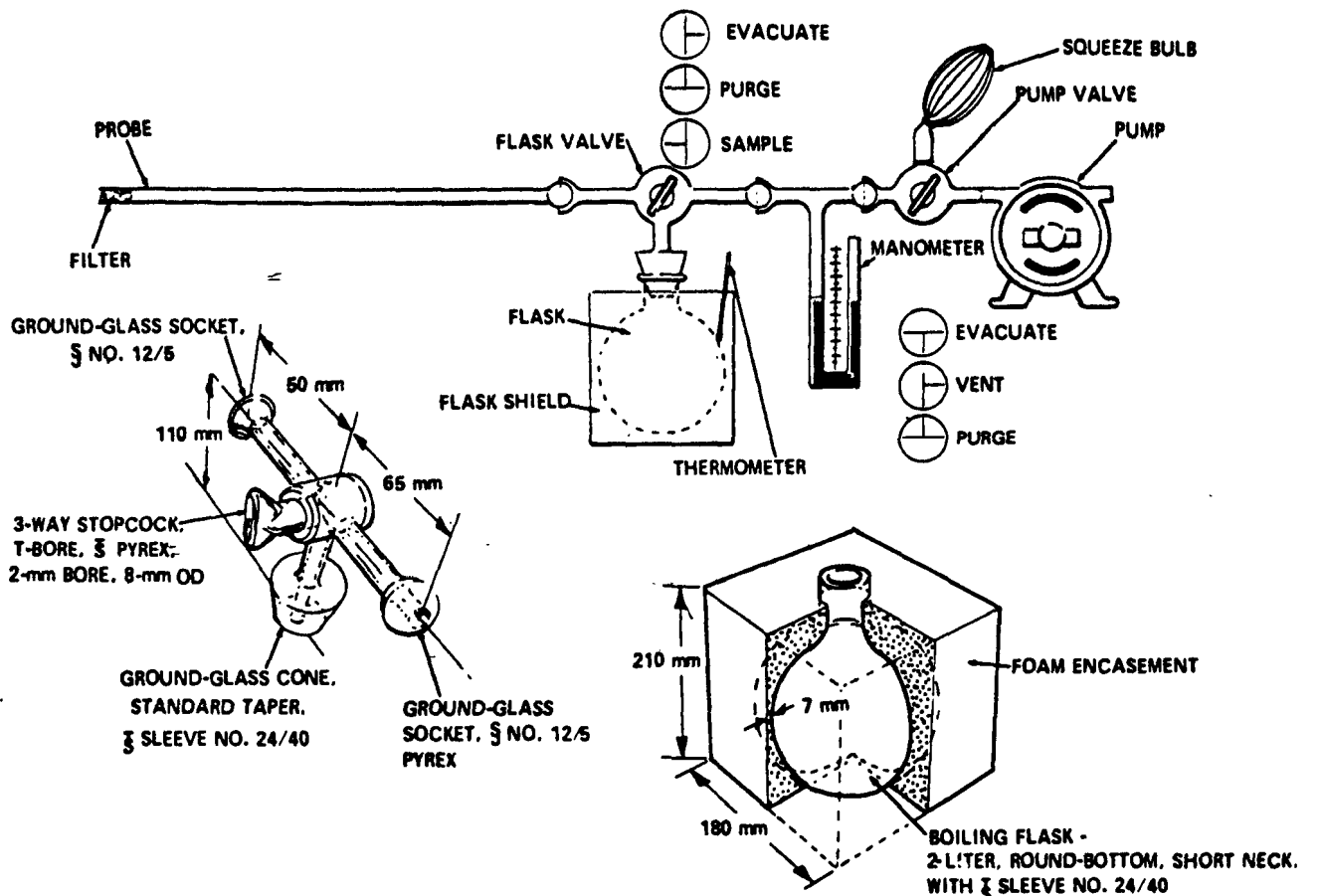


Figure 7-1. Sampling train, flask valve, and flask.

3. 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, where such specifications are available; otherwise, use the best available grade.

3.1 Sampling. To prepare the absorbing solution, cautiously add 2.5 ml concentrated H_2SO_4 to 1 liter of deionized, distilled water. Mix well and add 6 ml of 3 percent hydrogen peroxide, freshly prepared from 30 percent hydrogen peroxide solution. The absorbing solution should be used within 1 week of its preparation. Do not expose to extreme heat or direct sunlight.

3.2 Sample Recovery. Two reagents are required for sample recovery:

3.2.1 Sodium Hydroxide (1N). Dissolve 40 g NaOH in deionized, distilled water and dilute to 1 liter.

3.2.2 Water. Deionized, distilled to conform to ASTM specification D1193-74, Type 3. At the option of the analyst, the $KMnO_4$ test for oxidizable organic matter may be omitted when high concentrations of organic matter are not expected to be present.

3.3 Analysis. For the analysis, the following reagents are required:

3.3.1 Fuming Sulfuric Acid. 15 to 18 percent by weight free sulfur trioxide. HANDLE WITH CAUTION.

3.3.2 Phenol. White solid.

3.3.3 Sulfuric Acid. Concentrated, 95 percent minimum assay. HANDLE WITH CAUTION.

3.3.4 Potassium Nitrate. Dried 105 to 110° C (220 to 230° F) for a minimum of 2 hours just prior to preparation of standard solution.

3.3.5 Standard KNO_3 Solution. Dissolve exactly 2.168 g of dried potassium nitrate (KNO_3) in deionized, distilled water and dilute to 1 liter with deionized, distilled water in a 1,000-ml volumetric flask.

3.3.6 Working Standard KNO_3 Solution. Dilute 10 ml of the standard solution to 100 ml with deionized, distilled water. One milliliter of the working standard solution is equivalent to 100 μg nitrogen dioxide (NO_2).

3.3.7 Water. Deionized, distilled as in Section 3.2.2.

3.3.8 Phenoldisulfonic Acid Solution. Dissolve 25 g of pure white phenol in 150 ml concentrated sulfuric acid on a steam bath. Cool, add 75 ml fuming sulfuric acid, and heat at 100° C (212° F) for 2 hours. Store in a dark, stoppered bottle.

4. Procedure

4.1 Sampling

4.1.1 Pipette 25 ml of absorbing solution into a sample flask, retaining a sufficient quantity for use in preparing the calibration standards. Insert the flask valve stopper into the flask with the valve in the "purge" position. Assemble the sampling train as shown in Figure 7-1 and place the probe at the sampling point. Make sure that all fittings are tight and leak-free, and that all ground glass joints have been properly greased with a high-vacuum, high-temperature chlorofluorocarbon-based stopcock grease. Turn the flask valve and the pump valve to their "evacuate" positions. Evacuate the flask to 75 mm Hg (3 in. Hg) absolute pressure, or less. Evacuation to a pressure approaching the vapor pressure of water at the existing temperature is desirable. Turn the pump valve to its "vent" position and turn off the pump. Check for leakage by observing the manometer for any pressure fluctuation. (Any variation greater than 10 mm Hg (0.4 in. Hg) over a period of 1 minute is not acceptable, and the flask is not to be used until the leakage problem is corrected. Pressure in the flask is not to exceed 75 mm Hg (3 in. Hg) absolute at the time sampling is commenced.) Record the volume of the flask and valve (V_f), the flask temperature (T_f), and the barometric pressure. Turn the flask valve counterclockwise to its "purge" position and do the same with the pump valve. Purge the probe and the vacuum tube using the squeeze bulb. If condensation occurs in the probe and the flask valve area, heat the probe and purge until the condensation disappears. Next, turn the pump valve to its "vent" position. Turn the flask valve clockwise to its "evacuate" position and record the difference in the mercury levels in the manometer. The absolute internal pressure in the flask (P_i) is equal to the barometric pressure less the manometer reading. Immediately turn the flask valve to the "sample" position and permit the gas to enter the flask until pressure in the flask and sample line (i.e., duct, stack) are equal. This will usually require about 15 seconds; a longer period indicates a "plug" in the probe, which must be corrected before sampling is continued. After collecting the sample, turn the flask valve to its "purge" position and disconnect the flask from the sampling train. Shake the flask for at least 5 minutes.

4.1.2 If the gas being sampled contains insufficient oxygen for the conversion of NO to NO_2 (e.g., an applicable subpart of the standard may require taking a sample of a calibration gas mixture of NO in N_2), then oxygen shall be introduced into the flask to permit this conversion. Oxygen may be introduced into the flask by one of three methods: (1) Before evacuating the sampling flask, flush with pure cylinder oxygen, then evacuate flask to 75 mm Hg (3 in. Hg) absolute pressure or less; or (2) Inject oxygen into the flask after sampling; or (3) terminate sampling with a minimum of 50 mm Hg (2 in. Hg) vacuum remaining in the flask, record this final pressure, and then vent the flask to the atmosphere until the flask pressure is almost equal to atmospheric pressure.

4.2 Sample Recovery. Let the flask set for a minimum of 16 hours and then shake the contents for 2 minutes. Connect the flask to a mercury-filled U-tube manometer. Open the valve from the flask to the manometer and

record the flask temperature (T_f), the barometric pressure, and the difference between the mercury levels in the manometer. The absolute internal pressure in the flask (P_i) is the barometric pressure less the manometer reading. Transfer the contents of the flask to a leak-free polyethylene bottle. Rinse the flask twice with 5-ml portions of deionized, distilled water and add the rinse water to the bottle. Adjust the pH to between 9 and 12 by adding sodium hydroxide (1 N), dropwise (about 25 to 35 drops). Check the pH by dipping a stirring rod into the solution and then touching the rod to the pH test paper. Remove as little material as possible during this step. Mark the height of the liquid level so that the container can be checked for leakage after transport. Label the container to clearly identify its contents. Seal the container for shipping.

4.3 Analysis. Note the level of the liquid in container and confirm whether or not any sample was lost during shipment; note this on the analytical data sheet. If a noticeable amount of leakage has occurred, either void the sample or use methods, subject to the approval of the Administrator, to correct the final results. Immediately prior to analysis, transfer the contents of the shipping container to a 50-ml volumetric flask, and rinse the container twice with 5-ml portions of deionized, distilled water. Add the rinse water to the flask and dilute to the mark with deionized, distilled water; mix thoroughly. Pipette a 25-ml aliquot into the porcelain evaporating dish. Return any unused portion of the sample to the polyethylene storage bottle. Evaporate the 25-ml aliquot to dryness on a steam bath and allow to cool. Add 2 ml phenoldisulfonic acid solution to the dried residue and triturate thoroughly with a polyethylene policeman. Make sure the solution contacts all the residue. Add 1 ml deionized, distilled water and four drops of concentrated sulfuric acid. Heat the solution on a steam bath for 5 minutes with occasional stirring. Allow the solution to cool, add 20 ml deionized, distilled water, mix well by stirring, and add concentrated ammonium hydroxide, dropwise, with constant stirring, until the pH is 10 (as determined by pH paper). If the sample contains solids, these must be removed by filtration (centrifugation is an acceptable alternative, subject to the approval of the Administrator), as follows: filter through Whatman No. 41 filter paper into a 100-ml volumetric flask; rinse the evaporating dish with three 5-ml portions of deionized, distilled water; filter these three rinses. Wash the filter with at least three 15-ml portions of deionized, distilled water. Add the filter washings to the contents of the volumetric flask and dilute to the mark with deionized, distilled water. If solids are absent, the solution can be transferred directly to the 100-ml volumetric flask and diluted to the mark with deionized, distilled water. Mix the contents of the flask thoroughly, and measure the absorbance at the optimum wavelength used for the standards (Section 5.2.1), using the blank solution as a zero reference. Dilute the sample and the blank with equal volumes of deionized, distilled water if the absorbance exceeds 4.4, the absorbance of the 400 μg NO_2 standard (see Section 5.2.2).

5. Calibration

5.1 Flask Volume. The volume of the collection flask, flask valve combination must be known prior to sampling. Assemble the flask and flask valve and fill with water, to the stopcock. Measure the volume of water to ± 0.1 ml. Record this volume in the flask.

5.2 Spectrophotometer Calibration

5.2.1 Optimum Wavelength Determination. For both fixed and variable wavelength spectrophotometers, calibrate against standard certified wavelength of 410 nm, every 6 months. Alternatively, for variable wavelength spectrophotometers, scan the spectrum between 400 and 415 nm using a 200 μg NO_2 standard solution (see Section 5.2.2). If a peak does not occur, the spectrophotometer is probably malfunctioning, and should be repaired. When a peak is obtained within the 400 to 415 nm range, the wavelength at which this peak occurs shall be the optimum wavelength for the measurement of absorbance for both the standards and samples.

5.2.2 Determination of Spectrophotometer Calibration Factor K_c . Add 0.0, 1.0, 2.0, 3.0, and 4.0 ml of the KNO_3 working standard solution (1 ml=100 μg NO_2) to a series of five porcelain evaporating dishes. To each, add 25 ml of absorbing solution, 10 ml deionized, distilled water, and sodium hydroxide (1N), dropwise, until the pH is between 9 and 12 (about 25 to 35 drops each). Beginning with the evaporation step, follow the analysis procedure of Section 4.3, until the solution has been transferred to the 100 ml volumetric flask and diluted to the mark. Measure the absorbance of each solution, at the optimum wavelength, as determined in Section 5.2.1. This calibration procedure must be repeated on each day that samples are analyzed. Calculate the spectrophotometer calibration factor as follows

$$K_c = 100 \frac{A_1 + 2A_2 + 3A_3 + 4A_4}{A_1^2 + A_2^2 + A_3^2 + A_4^2}$$

Equation 7-1

where:

K_c = Calibration factor

A_1 = Absorbance of the 100- μg NO_2 standard

A_2 = Absorbance of the 200- μg NO_2 standard

A_3 = Absorbance of the 300- μg NO_2 standard

A_4 = Absorbance of the 400- μg NO_2 standard

5.3 Barometer. Calibrate against a mercury barometer.

5.4 Temperature Gauge. Calibrate dual thermometer against mercury-in-glass thermometers.

5.5 Vacuum Gauge. Calibrate mechanical gauges, if used, against a mercury manometer such as that specified in 2.1.6.

5.6 Analytical Balance. Calibrate against standard weights.

6. Calculations

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

6.1 Nomenclature

A = Absorbance of sample.

C = Concentration of NO_2 , as NO_2 , dry basis, corrected to standard conditions, mg/dscm (lb/dscf).

F = Dilution factor (i.e., 25/5, 25/10, etc., required only if sample dilution was needed to reduce the absorbance into the range of calibration).

K_c = Spectrophotometer calibration factor.

m = Mass of NO_2 , as NO_2 , in gas sample, μg .

P_f = Final absolute pressure of flask, mm Hg (in. Hg).

P_i = Initial absolute pressure of flask, mm Hg (in. Hg).

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

T_f = Final absolute temperature of flask, °K (°R).

T_i = Initial absolute temperature of flask, °K (°R).

T_{std} = Standard absolute temperature, 293° K (528° R).

V_{std} = Sample volume at standard conditions (dry basis), ml.

V_f = Volume of flask and valve, ml.

V_a = Volume of absorbing solution, 25 ml.

2=50/25, the aliquot factor. (If other than a 25-ml aliquot was used for analysis, the corresponding factor must be substituted).

6.2 Sample volume, dry basis, corrected to standard conditions.

$$V_{std} = \frac{T_{std}}{P_{std}} (V_f - V_a) \left[\frac{P_f}{T_f} - \frac{P_i}{T_i} \right] = K_1 (V_f - 25 \text{ ml}) \left[\frac{P_f}{T_f} - \frac{P_i}{T_i} \right]$$

Equation 7-2

where:

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

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

6.3 Total μg NO_2 per sample.

$$m = 2 K_c A F$$

Equation 7-3

NOTE.—If other than a 25-ml aliquot is used for analysis, the factor 2 must be replaced by a corresponding factor.

6.4 Sample concentration, dry basis, corrected to standard conditions.

$$C = K_2 \frac{m}{V_{std}}$$

Equation 7-4

where:

$$K_2 = 10^3 \frac{\text{mg}/\text{m}^3}{\mu\text{g}/\text{ml}} \text{ for metric units}$$

$$= 6.243 \times 10^{-5} \frac{\text{lb}/\text{scf}}{\mu\text{g}/\text{ml}} \text{ for English units}$$

7. Bibliography

1. Standard Methods of Chemical Analysis, 6th ed. New York, D. Van Nostrand Co., Inc. 1962. Vol. 1, p. 329-330.
2. Standard Method of Test for Oxides of Nitrogen in Gaseous Combustion Products (Phenoldisulfonic Acid Procedure). In: 1968 Book of ASTM Standards, Part 26. Philadelphia, Pa. 1968. ASTM Designation D-1605-60. p. 725-729.
3. Jacob, M. B. The Chemical Analysis of Air Pollutants. New York, Interscience Publishers, Inc. 1960. Vol. 10, p. 351-356.
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5. Hamill, H. F. and D. E. Cammann. Collaborative Study of Method for the Determination of Nitrogen Oxide Emissions from Stationary Sources (Fossil Fuel-Fired Steam Generators). Southwest Research Institute report for Environmental Protection Agency. Research Triangle Park, N.C. October 5, 1973.
6. Hamill, H. F. and R. E. Thomas. Collaborative Study of Method for the Determination of Nitrogen Oxide Emissions from Stationary Sources (Nitric Acid Plants). Southwest Research Institute report for Environmental Protection Agency. Research Triangle Park, N.C. May 8, 1974.

In Method 7 of Appendix A, Sections

2.3.2, 2.3.7, 4.2, 4.3, 5.2.1, 5.2.2, 6 and 7 are amended as follows:

1. In Section 2.3.2, a semicolon replaces the comma between the words "step" and "the."

2. In Section 2.3.7, the phrase "(one for each sample)" in the first line is corrected to read "(one for each sample and each standard)."

3. In Section 4.2, the letter "n" in the seventh line is corrected to read "in."

4. In Section 4.3, the word "polyethylene" in the seventeenth line is corrected to read "polyethylene."

5. In Section 5.2.1, delete the entire section and insert the following:

Optimum Wavelength Determination. Calibrate the wavelength scale of the spectrophotometer every 6 months. The calibration may be accomplished by using an energy source with an intense line emission such as a mercury lamp, or by using a series of glass filters spanning the measuring range of the spectrophotometer. Calibration materials are available commercially and from the National Bureau of Standards. Specific details on the use of such materials should be supplied by the vendor; general information about calibration techniques can be obtained from general reference books on analytical chemistry. The wavelength scale of the spectrophotometer must read correctly within ± 5 nm at all calibration points; otherwise, the spectrophotometer shall be repaired and recalibrated. Once the wavelength scale of the spectrophotometer is in proper calibration, use 410 nm as the optimum wavelength for the measurement of the absorbance of the standards and samples.

Alternatively, a scanning procedure may be employed to determine the proper measuring wavelength. If the instrument is a double-beam spectrophotometer, scan the spectrum between 400 and 415 nm using a 200 μ g NO_3 standard solution in the sample cell and a blank solution in the reference cell. If a peak does not occur, the spectrophotometer is probably malfunctioning and should be repaired. When a peak is obtained within the 400 to 415 nm range, the wavelength at which this peak occurs shall be the optimum wavelength for the measurement of absorbance of both the standards and the samples. For a single-beam spectrophotometer, follow the scanning procedure described above, except that the blank and standard solutions shall be scanned separately. The optimum wavelength shall be the wavelength at which the maximum difference in absorbance between the standard and the blank occurs.

6. In Section 5.2.2, delete the first seven lines and insert the following:

Determination of Spectrophotometer Calibration Factor K_s . Add 0.0 ml, 2 ml, 4 ml, 6 ml, and 8 ml of the KNO_3 working standard solution (1 ml = 100 μ g NO_3) to a series of five 50-ml volumetric flasks. To each flask, add 25 ml of absorbing solution, 10 ml deionized, distilled water, and sodium hydroxide (1 N) dropwise until the pH is be-

tween 9 and 12 (about 25 to 35 drops each). Dilute to the mark with deionized, distilled water. Mix thoroughly and pipette a 25-ml aliquot of each solution into a separate porcelain evaporating dish.

7. In Section 6.1, the word "Hass" in the tenth line is corrected to read "Mass."

8. In Section 7, the word "Vna" in (1) is corrected to read "Van." The word "drtermination" in (6) is corrected to read "Determination."

11.0 REFERENCES

1. Quality Assurance Handbook for Air Pollution Measurement Systems, Volume I - Principles. U.S. Environmental Protection Agency, Office of Research and Development, Environmental Monitoring and Support Laboratory, Research Triangle Park, N.C. EPA-600/9-76-005, March 1976.
2. Buchanan, J. W. and D. E. Wagoner. Guidelines for Development of a Quality Assurance Program, Determination of Nitrogen Oxide Emissions from Stationary Sources. EPA.
3. Hamil, Henry F. et. al. The Collaborative Study of EPA Methods 5, 6, and 7 in Fossil Fuel Fired Steam Generators. Final Report, EPA-650/4-74-013, May 1974.
4. Hamil, H. F., and R. E. Thomas. Collaborative Study of Method for the Determination of Nitrogen Oxide Emissions from Stationary Sources (Nitric Acid Plants), EPA-650/4074-028, May 1974.
5. Hamil, Henry F. Laboratory and Field Evaluations of EPA Methods 2, 6, and 7. Final Report, EPA Contract No. 68-02-0626. Southwest Research Institute, San Antonio, Tex., October 1973.
6. Standard Methods of Chemical Analysis, 6th Edition. D. Van Nostrand Co., Inc., N.Y., 1962. Vol. 1, pp. 329-330.
7. Standard Method of Test for Oxides of Nitrogen in Gaseous Combustion Products (Phenoldisulfonic Acid Procedure) In: 1968 Book of ASTM Standards, Part 26. Philadelphia, Pa. 1968. ASTM Designation D-1608-60, pp. 725-729.
8. Jacob, M. B. The Chemical Analysis of Air Pollutants. Interscience Publishers, Inc., N.Y., 1960. Vol. 10, pp. 351-356.
9. Beatty, R. L., L. B. Berger, and H. H. Schrenk. Determination of Oxides of Nitrogen by the Phenoldisulfonic Acid Method. Bureau of Mines, U.S. Department of Interior, R.I. 3687. February 1943.

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12. Fuerst, R. G., R. L. Denny, and M. R. Midgett. A Summary of Interlaboratory Source Performance Surveys for EPA Reference Methods 6 and 7-1977. Available from U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory (MD-77), Research Triangle Park, N.C. 27711.
13. Fuerst, R. G. and M. R. Midgett. A Summary of Interlaboratory Source Performance Surveys for EPA Reference Methods 6 and 7-1978. Report in preparation by U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory (MD-77), Research Triangle Park, North Carolina 27711.

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 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 M7-1.2, indicates that the form is Figure 1.2 in Section 3.6.1 of the Method 7 Handbook. Future revisions of these forms, if any, can be documented by 1.2A, 1.2B, etc. Twelve of the blank forms listed below are included in this section. Four 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
2.1	Optimum Wavelength Determination Data Form
2.2	Analytical Balance Calibration Form
3.1 (MH)	Pretest Checklist
3.2 (MH)	Pretest Preparations
4.1A and 4.1B	Nitrogen Oxide Field Data Form (English and metric units)
4.2A and 4.2B	NO _x Sample Recovery and Integrity Data Form (English and metric units)
4.3 (MH)	On-site Measurements
5.1	Standard Solution and Control Sample Analytical Data Form
5.2	NO _x Laboratory Data Form
5.3 (MH)	Posttest Operations
6.1A and 6.1B	Nitrogen Oxide Calculation Form (English and metric units)
8.1	Method 7 Checklist to be Used by Auditors

PROCUREMENT LOG

Item description	Qty.	Purchase order number	Vendor	Date		Cost	Dispo- sition	Comments
				Ord.	Rec.			

OPTIMUM WAVELENGTH DETERMINATION DATA FORM

Spectrophotometer number _____ Date _____

Calibrated by _____ Reviewed by _____

Spectrophotometer setting, nm	Absorbance of standard OD ^a	Absorbance of blank OD ^b	Actual absorbance of OD ^c
399			
400			
401			
402			
403			
404			
405			
406			
407			
408			
409			
410			
411			
412			
413			
414			
415			
416			

^a Absorbance of the 200 µg NO₂ standard in a single beam spectrophotometer.

^b Absorbance of the blank in a single-beam spectrophotometer.

^c For a single-beam spectrophotometer-- absorbance of the standard minus absorbance of the blank. For a double beam spectrophotometer-- absorbance of the 200 µg NO₂ standard with the blank in the reference cell.

Spectrophotometer setting for maximum actual absorbance of standard _____ nm.

If the maximum actual absorbance occurs at a spectrophotometer setting of <399 or >416 nm, the spectrophotometer must be repaired or recalibrated.

ANALYTICAL BALANCE CALIBRATION FORM

Balance name _____ Number _____

Classification of standard weights

Date	0.5000 g	1.0000 g	10.000 g	50.0000 g	100.0000 g	Analyst

NITROGEN OXIDE FIELD DATA FORM
(English units)

Plant _____ City _____
 Sample location _____ Date _____
 Operator _____ Barometric pressure (P_{bar}) _____ in. Hg

Sample number	Sample point location	Sample time 24-hr	Probe temperature, °F	Flask and valve number	Volume of flask and valve (V_F), ml	Initial pressure in. Hg			Initial temperature	
						Leg A_i	Leg B_i	P_i^a	°F (t_i)	°R (T_i) ^b

^a $P_i = P_{\text{bar}} - (A_i + B_i)$.

^b $T_i = t_i + 460^\circ\text{F}$.

NITROGEN OXIDE FIELD DATA FORM
(metric units)

Plant _____ City _____
 Sample location _____ Date _____
 Operator _____ Barometric pressure (P_{bar}) _____ mm Hg

Sample number	Sample point location	Sample time 24-hr	Probe temperature, °C	Flask and valve number	Volume of flask and valve (V_F), ml	Initial pressure mm Hg			Initial temperature	
						Leg A_i	Leg B_i	P_i^a	°C (t_i)	°K (T_i) ^b

^a $P_i = P_{\text{bar}} - (A_i + B_i)$.

^b $T_i = t_i + 273^\circ\text{C}$.

NO _x SAMPLE RECOVERY AND INTEGRITY DATA FORM
(English units)

Plant _____ Date _____

Sample recovery personnel _____ Barometric pressure, (P_{bar}) _____ in. Hg

Person with direct responsibility for recovered samples _____

Sample number	Final pressure, in. Hg			Final temperature,		Sample recovery time, 24-h	pH adjusted 9 to 12	Liquid level marked	Samples stored in locked container
	Leg A _f	Leg B _f	P _f ^a	°F (t _f)	°R (T _f) ^b				

$$P_f = P_{\text{bar}} - (A_f + B_f) . \quad T_f = t_f + 460^{\circ}\text{F} .$$

Lab person with direct responsibility for recovered samples _____

Date recovered samples received _____ Analyst _____

All samples identifiable? _____ All liquids at marked level? _____

Remarks _____

Signature of lab sample trustee _____

NO_x SAMPLE RECOVERY AND INTEGRITY DATA FORM
(metric units)

Plant _____ Date _____

Sample recovery personnel _____ Barometric pressure, (P_{bar}) _____ mm Hg

Person with direct responsibility for recovered samples _____

Sample number	Final pressure, mm Hg			Final temperature,		Sample recovery time, 24-hr	pH adjusted 9 to 12	Liquid level marked	Samples stored in locked container
	Leg A _f	Leg B _f	P _f	°C (t _f)	K (T _f)				

$$P_f = P_{bar} - (A_f + B_f). \quad T_f = t_f + 273^{\circ}\text{C}.$$

Lab person with direct responsibility for recovered samples _____

Date recovered samples received _____ Analyst _____

All samples identifiable? _____ All liquids at marked level? _____

Remarks _____

Signature of lab sample trustee _____

STANDARD SOLUTION AND CONTROL SAMPLE
ANALYTICAL DATA FORM

Plant _____ Date _____

Analyst _____ Optimum wavelength _____ nm

Blank used as reference? _____

Sample number	Sample, μg	Working solution	Control sample	Measured, absorbance, OD	Calculated absorbance, ^a OD	Absorbance comparison error, ^b %
A1	100	x			-	-
A2	200	x			-	-
A3	300	x			-	-
A4	400	x			-	-
S1	100		x			
S2	200		x			
S3	300		x			
						Avg ^c

$$K_c = 100 \left[\frac{A_1 + 2A_2 + 3A_3 + 4A_4}{A_1^2 + A_2^2 + A_3^2 + A_4^2} \right] = \text{_____}.$$

^a Calculated absorbance: $\text{OD} = (\mu\text{g})/K_c$ i.e., S1 calculated absorbance = $100/K_c$.

^b Absorbance comparison errors:

$$\% = 100 \times \frac{(\text{measured absorbance, OD}) - (\text{calculated absorbance, OD})}{\text{calculated absorbance, OD}}$$

^c Average of absolute values.

NO_x LABORATORY DATA FORM

Plant _____ Run number(s) _____

Date samples received _____ Date analyzed _____

Aliquot factor _____ Samples analyzed by _____

Blank absorbance _____ Date reviewed by _____

Calibration factor (K_C) _____ Date of review _____

Sample number	Sample absorbance, A	Dilution factor, F	Total mass of NO _x as NO ₂ in sample, m

$m = 2 K_C AF$, Note: If other than a 25 ml aliquot is used for analysis, the factor 2 must be replaced by a corresponding factor.

NITROGEN OXIDE CALCULATION FORM
(English units)

Sample Volume

$$V_f = _ _ _ _ \text{ ml}, P_f = _ _ _ _ \text{ in. Hg}, T_f = _ _ _ _ ^\circ\text{R}$$

$$P_i = _ _ _ _ \text{ in. Hg}, T_i = _ _ _ _ ^\circ\text{R}$$

$$V_{sc} = 17.64 (V_f - 25) \left[\frac{P_f}{T_f} - \frac{P_i}{T_i} \right] = _ _ _ _ \text{ ml} \quad \text{Equation 6.1}$$

Total $\mu\text{g NO}_2$ Per Sample

$$K_c = _ _ _ _ _, A = _ _ _ _ \text{ OD}, F = _ _ _ _ \quad \text{Equation 6.2}$$

$$m = 2K_c AF = _ _ _ _ _ \mu\text{g of NO}_2$$

Sample Concentration

$$C = 6.243 \times 10^{-5} \left[\frac{m}{V_{sc}} \right] = _ _ _ _ \times 10^{-5} \text{ lb/dscf}$$

NITROGEN OXIDE CALCULATION FORM
(metric units)

Sample Volume

$$V_f = \text{---} \cdot \text{ml}, P_f = \text{---} \cdot \text{mm Hg}, T_f = \text{---} \cdot \text{K}$$

$$P_i = \text{---} \cdot \text{mm Hg}, T_i = \text{---} \cdot \text{K}$$

$$V_{sc} = 0.3858 (V_f - 25) \left[\frac{P_f}{T_f} - \frac{P_i}{T_i} \right] = \text{---} \cdot \text{ml} \quad \text{Equation 6-1}$$

Total $\mu\text{g NO}_2$ Per Sample

$$K_c = \text{---} \cdot, A = \text{---} \cdot \text{OD}, F = \text{---} \cdot$$

$$m = 2K_c AF = \text{---} \cdot \mu\text{g of NO}_2. \quad \text{Equation 6-2}$$

Sample Concentration

$$C = 10^3 \left[\frac{m}{V_{sc}} \right] = \text{---} \cdot \times 10^3 \text{ mg/dscf.} \quad \text{Equation 6-3}$$

METHOD 7 CHECKLIST TO BE USED BY AUDITORS

Presampling Preparation

Yes No

- | | | |
|-----|-----|------------------------------------------------------------------------------|
| ___ | ___ | 1. Information concerning combustion effluents that may act as interferences |
| ___ | ___ | 2. Plant operation parameters variation |
| ___ | ___ | 3. Calibration of the flask and valve volume---three determinations |
| ___ | ___ | 4. Absorbing reagent preparation |

On-site Measurements

- | | | |
|-----|-----|------------------------------------------------------------------------|
| ___ | ___ | 5. Leak testing of the sampling train |
| ___ | ___ | 6. Preparation and pipetting of absorbing solution into sampling flask |

Postsampling (Analysis and Calculation)

- | | | |
|-----|-----|-------------------------------------------------|
| ___ | ___ | 7. Control sample analysis |
| ___ | ___ | 8. Sample aliquotting technique |
| ___ | ___ | 9. Evaporation and chemical treatment of sample |
| ___ | ___ | 10. Spectrophotometric technique |
| | | a. Preparation of standard nitrate samples |
| | | b. Measurement of absorbance, including blanks |
| | | c. Calibration factor |
| | | d. Wavelength and absorbance, including blanks |
| ___ | ___ | 11. Calculation procedure and checks |
| | | a. Use of computer program |
| | | b. Independent check of calculations |

Comments

Section 3.7

METHOD 8--DETERMINATION OF SULFURIC ACID MIST
AND SULFUR DIOXIDE EMISSIONS FROM STATIONARY SOURCES

OUTLINE

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METHOD DESCRIPTION		
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3. PRESAMPLING OPERATIONS	3.7.3	7
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5. POSTSAMPLING OPERATIONS	3.7.5	17
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8. AUDITING PROCEDURE	3.7.8	7
9. RECOMMENDED STANDARDS FOR ESTABLISHING TRACEABILITY	3.7.9	1
10. REFERENCE METHOD	3.7.10	4
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SUMMARY

A gas sample is extracted isokinetically from the stack. The sulfuric acid mist (including sulfur trioxide, or SO_3) and the SO_2 are separated, and both fractions are measured separately by the barium-thorin titration method. The barium ions react preferentially with sulfate ions in solution to form a highly insoluble barium sulfate precipitate. When the barium has reacted with all sulfate ions, the excess barium reacts with the thorin indicator to form a metal salt of the indicator and to give a color change.

This method is applicable for the determination of sulfuric acid mist (including SO_3) emissions from stationary sources. Collaborative tests have shown that the minimum detectable limits of the method are $0.05 \text{ mg SO}_3/\text{m}^3$ ($0.03 \times 10^{-7} \text{ lb/ft}^3$) and $1.2 \text{ mg SO}_2/\text{m}^3$ ($0.74 \times 10^{-7} \text{ lb/ft}^3$). No upper limits have been established. Based on theoretical calculations for 200 ml of 3% hydrogen peroxide solution, the upper concentration limit in a 1.0 m^3 (35.3 ft^3) gas sample is about $12,500 \text{ mg SO}_2/\text{m}^3$ ($7.7 \times 10^{-4} \text{ lb/ft}^3$). The upper limit can be extended by increasing the quantity of peroxide solution in the impingers.

Possible interferences with this method are fluorides, free ammonia, and dimethyl aniline. If any of these interferences are present (as determined by knowledge of the process), alternative methods subject to the approval of the administrator, U.S. Environmental Protection Agency, are required. For example, if free ammonia is present, white particulates can be seen in the probe and in the isopropanol impinger.

Filterable particulate matter may be determined along with SO_3 and SO_2 (subject to the approval of the administrator); however, the procedure used for particulate matter must

be consistent with the specifications and procedures given in Method 5.

The Method 8 description which follows is based on the Reference Method that was promulgated on August 18, 1977. A complete copy of the Reference Method is in Section 3.7.10. Data forms are provided in Subsection 12 for the convenience of the Handbook user.

Reference 1 was used extensively in preparing the method description. References 2 and 3 are the collaborative test studies of this method and other related methods; data from these test studies were used in establishing quality control limits. References 4 and 5 were used extensively in those sections which include the description, calibration, and maintenance of the sampling train. All references are listed in Section 3.7.11.

A collaborative test program was conducted at a sulfuric acid (H_2SO_4) plant to determine the accuracy of Method 8. Six laboratories simultaneously sampled the same stack, using two Method 8 sampling trains per laboratory.⁶ The collaborative test determined that the repeatability (within-laboratory precision) of the method was $7.19 \text{ mg H}_2\text{SO}_4/\text{m}^3$ and $22.30 \text{ mg SO}_2/\text{m}^3$ and that reproducibility (between-laboratory precision) of the method was $8.03 \text{ mg H}_2\text{SO}_4/\text{m}^3$ and $31.10 \text{ mg SO}_2/\text{m}^3$.⁶

METHOD HIGHLIGHTS

Specifications described in Section 3.7 are for sampling and analysis of sulfuric acid mist (including sulfur trioxide) and sulfur dioxide emissions from stationary sources. The sampling system consists of the EPA Method 5 sampling train modified by placing the filter (unheated) between the first and second impingers. Filterable particulate matter may be determined along with SO_3 and SO_2 (subject to the approval of the administrator); however, the procedure used for particulate matter must be consistent with the specifications and procedures given in Method 5.

The results of collaborative tests have shown that the overall precision of the test method is good if sound quality assurance procedures are applied.⁶ On the basis of these results these procedures are recommended:

1. On-site checks of the orifice and dry gas meter calibration coefficients of all control consoles with a dry gas meter that has been calibrated with a spirometer.
2. Certification that all reagent isopropyl alcohol is peroxide-free prior to the test.
3. Leak checks are performed at the beginning and at the end of each sampling run before and after every port change. Care should be taken to be sure that the sulfur dioxide absorbing reagent, hydrogen peroxide, does not contact the filter when the leak check is conducted; if peroxide does contact the filter, the filter should be replaced before sampling is continued.

The five blank data forms at the end of the highlights may be removed from the Handbook and used in the pretest, test, and posttest operations. Each form has a subtitle (e.g., Method 8, Figure 3.1) for helping the user find a similar filled-in form in the method description (e.g., in Section 3.7.3). On the blank and filled-in forms, the items/parameters that can cause the most significant errors are starred.

1. Procurement of Equipment

Section 3.7.1 (Procurement of Apparatus and Supplies) gives the specifications, criteria, and design features for equipment and materials required for performing Method 8 tests. The sampling apparatus has the same design criteria as Method 5, with the exception of the filter-impinger arrangement. This section is designed as a guide in the procurement and initial check of equipment and supplies. The activity matrix (Table 1.1) at the end of Section 3.7.1 can be used as a quick reference; it follows the same order as the written descriptions in the main text.

2. Pretest Preparations

Section 3.7.2 (Calibration of Apparatus) provides a step-by-step description of the required calibration procedures. The calibration of the Method 8 equipment is similar to that of Method 5, with the exception that the Method 8 sampling rate is not to exceed 28.3 l/min (1 scfm), and the stack thermometer need not be calibrated at the higher temperatures if the equipment is used to measure acid plant emissions only. The calibration section can be removed and compiled, along with calibration sections from all other methods, into a separate quality assurance reference manual for use by calibration personnel. A pretest checklist (Figure 2.5 of Section 3.7.2) or similar form should be used to summarize the calibration data.

Section 3.7.3 (Presampling Operations) provides the tester with a guide for supplies and equipment preparation for field tests. Sample impingers may be charged in the base laboratory if testing is to be performed within 24 h of charging. The pretest preparation form (Figure 3.1 of Section 3.7.3) can be used as an equipment checkout and packing list. The method for packing and the descriptions of the packing containers should help protect the equipment, but are not required.

3. On-Site Measurements

Section 3.7.4 (On-Site Measurements) contains a step-by-step procedure for performing sampling and sample recovery. Testing is performed isokinetically and similarly to Method 5, with the exception that the sample rate is not to exceed 1 ft³/min. The most common error results when hydrogen peroxide solution is allowed to backup, wet the filter, and enter the isopropanol impinger. Also precautions must be taken to ensure that the isopropanol does not have hydrogen peroxide impurities and that the same pipette or graduated cylinder is not used to charge both isopropanol and hydrogen peroxide. The on-site measurement checklist (Figure 4.4 of Section 3.7.4) is provided to assist the tester with a quick method of checking requirements.

4. Posttest Operations

Section 3.7.5 (Postsampling Operations) gives the post-test equipment check procedures and a step-by-step analytical procedure. Figure 5.1 (Section 3.7.5) or a similar form should be used to summarize the posttest calibration checks and should be included in the emission test report. The posttest operation form (Figure 5.4 of Section 3.7.5) will provide the tester and laboratory personnel with key parameters to be checked. The step-by-step analytical procedure description can be removed and made into a separate quality assurance analytical reference manual for 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 a quality control check on the accuracy and precision of the analytical techniques.

Section 3.7.6 (Calculations) provides the tester with the required equations, the nomenclature, and the suggested number of significant digits. It is suggested that a programmed calculator be used if available to reduce the chance of calculation error.

Section 3.7.7 (Maintenance) provides the tester with a guide for a routine maintenance program. This program is not required, but should reduce equipment malfunctions.

5. Auditing Procedure

Section 3.7.8 (Auditing Procedure) provides a description of necessary activities for conducting performance and system audits. The performance audit of the analytical phase can be conducted using an aqueous ammonium sulfate solution. Performance audits for the analytical phase and the data processing are described in Section 3.7.8. A checklist for a systems audit is also included in this section.

Section 3.7.9 (Recommended Standards for Establishing Traceability) recommends the primary standards to which the working standards should be traceable.

6. References

Sections 3.7.10 and 3.7.11 contain the Reference Method and the suggested references.

PRETEST SAMPLING CHECKS
(Method 8, Figure 2.5)

Date _____ Calibrated by _____

Meter box number _____ $\Delta H@$ _____

Dry Gas Meter*

Pretest calibration factor = _____ (within $\pm 2\%$ of the 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°F) of reference values for calibration and within $\pm 2^\circ\text{C}$ (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 $\pm 3^\circ\text{C}$ (5.4°F) of reference values for calibration and 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.

PRETEST PREPARATIONS
(Method 8, Figure 3.1)

Apparatus check	Acceptable		Quantity required	Ready		Loaded and packed
	Yes	No		Yes	No	
<u>Probe</u>						
Type glass liner						
Borosilicate ____						
Quartz ____						
Heated						
Leak checked						
<u>Nozzle</u>						
Glass ____						
Stainless steel ____						
Other ____						
<u>Pitot Tube</u>						
Types ____						
Other ____						
Properly attached ____						
Modifications ____						
C _p ____						
<u>Differential Pressure Gauge</u>						
Inclined manometer ____						
Other ____						
<u>Filter Holder</u>						
Borosilicate glass						
Glass frit						
Gasket						
Silicone ____						
Teflon ____						
Viton ____						

(continued)

Apparatus check	Acceptable		Quantity required	Ready		Loaded and packed
	Yes	No		Yes	No	
<u>Condenser</u> Impingers Greenburg-Smith Modified Green- burg-Smith						
<u>Impinger Temper- ature Sensor</u> Thermometer _____ Other _____ Calibrated _____						
<u>Other</u> Barometer Mercury _____ Aneroid _____ Other _____ Calibrated* _____						
<u>Stack Temperature Sensor</u> Type _____ Calibrated* _____						
<u>Reagents</u> Distilled water Hydrogen perox- ide (30%) Isopropanol (80%) (checked for peroxides) Silica gel						
<u>Meter System</u> Pump leak free* Orifice meter* Dry gas meter*						

* Most significant items/parameters to be checked.

ON-SITE MEASUREMENTS
(Method 8, Figure 4.4)

Sampling

Impingers properly assembled? _____
Contents:* 1st _____
 2nd _____
 3rd _____
 4th _____
Cooling system _____
Filter between 1st and 2nd impinger? _____
Proper connections? _____
Silicone grease added to all ground-glass joints? _____
Pretest leak check? _____ (optional) Leakage? _____
Pitot tube lines checked for plugging or leaks?* _____
Meter box leveled? _____ Periodically? _____
Manometers zeroed?* _____
Heat uniform along length of probe?* _____
 $\Delta H@$ from most recent calibration _____
Nomograph set up properly? _____
Care taken to avoid scraping sample port or stack wall? _____

Seal around in-stack probe effective? _____
Probe moved at proper time? _____
Nozzle and Pitot tube parallel to stack wall at all times? _____

Data forms complete and data properly recorded? _____
Nomograph setting changed when stack temperature changes
significantly? _____
Velocity pressures and orifice pressure readings recorded
accurately? _____
Posttest leak check performed?* _____ (mandatory)
Leakage rate* _____

Sampling Recovery

System purged at least 15 min at test sampling rate?* _____
Filter placed in 1st impinger contents? _____
Ice removed before purging? _____
Contents of impingers placed in polyethylene bottles? _____
Glassware rinsed with distilled water? _____
Fluid level marked?* _____
Sample containers sealed and identified?* _____
Blanks obtained?* _____

* Most significant items/parameters to be checked.

POSTTEST SAMPLING CHECKS
(Method 8, 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 average)
Lower calibration factor, $Y =$ _____ for pretest or posttest
calculations

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°C (10.8°F) of reference values)
Recalibration required? _____ yes _____ no
Recalibration temperature correction, if used ____ (within +3°C
(5.4°F) of reference values)
If yes, no correction is needed whenever meter thermometer
temperature is higher
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 ±5.0 mm (0.2 in.)
Hg of mercury-in-glass barometer)
Was recalibration required? _____ yes _____ no
If yes, no correction is needed whenever the field barometer
has the lower reading
If the mercury-in-glass reading is lower, subtract the dif-
ference from the field data readings for the calculations

*Most significant items/parameters to be checked.

POSTTEST OPERATIONS
(Method 8, Figure 5.4)

Reagents

Normality of sulfuric acid standard* _____
Date of purchase _____ 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 _____
Sulfuric acid samples diluted to 250 ml?* _____
Sulfur dioxide samples diluted to 1000 ml?* _____

Analysis

Aliquot analyzed* _____
Do replicate titrant volumes agree within 1% or 0.2 ml? ____
Number of control samples analyzed _____
Are replicate control samples within 0.2 ml? _____
Is accuracy of control sample analysis $\pm 10\%$?* _____
All data recorded? _____ Reviewed _____

* Most significant items/parameters to be checked.

1.0 PROCUREMENT OF APPARATUS AND SUPPLIES

A schematic of the sampling train used in Method 8 is shown in Figure 1.1. It is similar to the Method 5 train, but the filter position is different and the filter holder does not have to be heated. Commercial models of this train are available. For those who desire to build their own, complete construction details are described in APTD-0581.⁴ Changes from the APTD-0581 document and allowable modifications to Figure 1.1 are discussed in the following subsections.

The operating and maintenance procedures for the sampling train are described in APTD-0576.⁵ Since correct usage is important in obtaining valid results, all users should read the APTD-0576 document and adopt the operating and maintenance procedures therein, unless otherwise specified. Further details and guidelines on operation and maintenance in Method 5 should be read and followed whenever they are applicable. Maintenance of equipment is also covered in Section 3.7.7.

Specifications, criteria, and/or design features as applicable, are given in this section to aid in the selection of equipment to ensure the collection of data 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 (Figure 1.2) be used to record the descriptive title of the equipment; the identification number, if applicable; and the results of acceptance checks. Also, if calibration is required as part of the acceptance check, the data are to be recorded in the calibration log book. Table 1.1 at the end of this section contains a summary of the quality assurance activities for procurement and acceptance of apparatus and supplies.

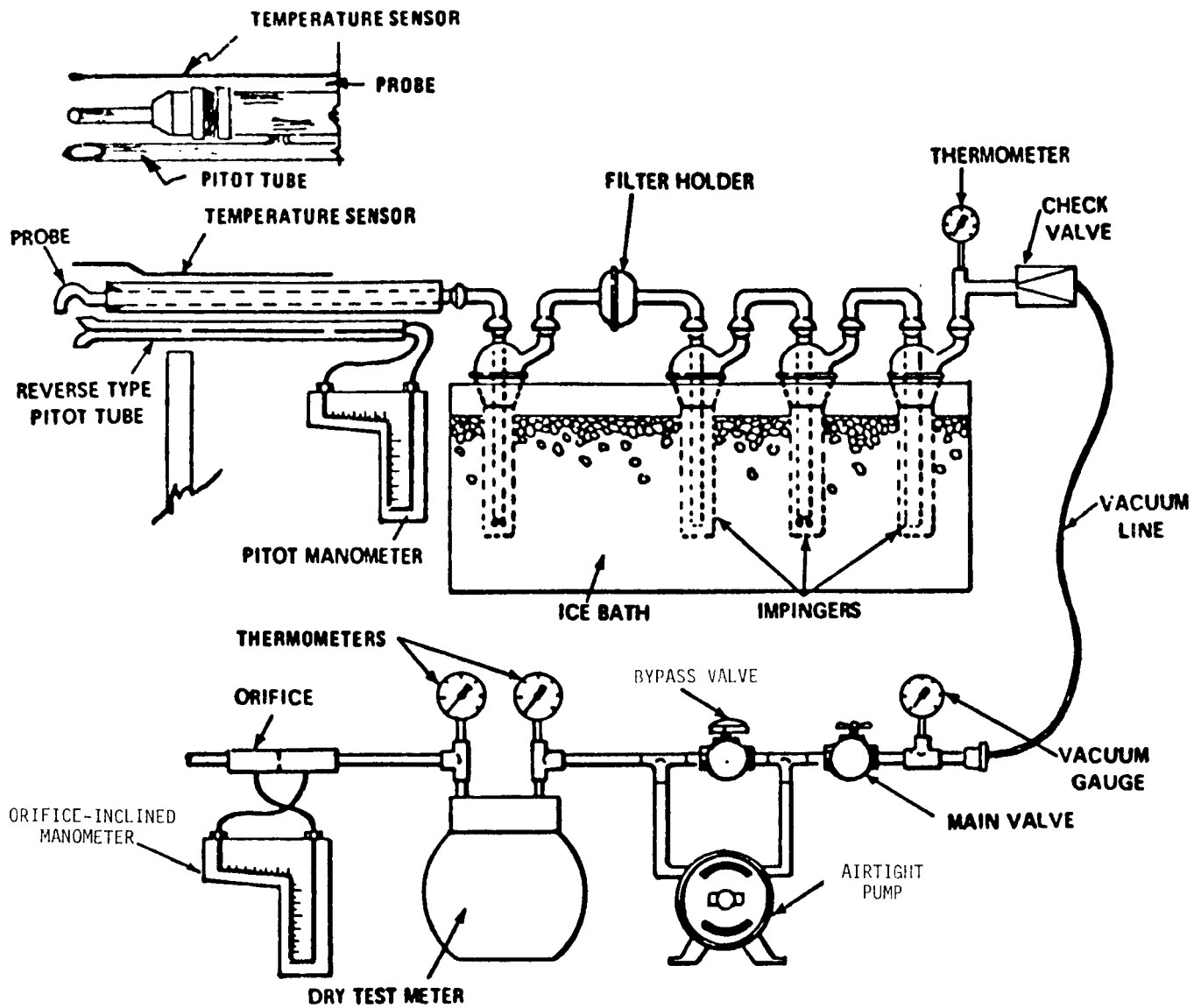


Figure 1.1. Schematic of Method 8 sampling train.

Item description	Qty.	Purchase order number	Vendor	Date		Cost	Disposition	Comments
				Ord.	Rec.			
(1) Meter Box w/ Fiber Vane Pump, Magnahelic Gauges	1	77A25	ARC Technology	12/23/76	1/20/77	\$5,000	Calibrated Ready for Use	Calibrated 2/4/77 by GLS

Figure 1.2. Example of a procurement log.

Determination of filterable particulate matter simultaneously with sulfuric acid mist (and with SO_3 and SO_2) will not be discussed in this subsection.

1.1 Sampling

1.1.1 Probe Liner - Borosilicate or quartz glass tubing equipped with a heating system capable of preventing visible condensation during sampling should be protected with an outer sheath of stainless steel. Borosilicate or quartz probe liners can be used for stack temperatures up to about 480°C (900°F). Quartz liners should be used for high-temperature probes for stacks with temperatures between 480° and 900°C (900° and 1650°F). Both types of liners may be used at temperatures higher than specified for short periods of time, subject to the approval of the administrator. Metal probe liners may not be used because of the requirement that the liner material must not react with the gas constituents.

Upon receiving a new probe, it should be visually checked for the length and composition ordered and for breaks or cracks and then leak checked on a sampling train as shown in Figure 1.1. Also the probe heating system should be checked as follows:

1. Connect the probe with a nozzle attached to the inlet of the pump.
2. Electrically connect and turn on the probe heater for 2 or 3 min. It should become warm to the touch.
3. Start the pump and adjust the needle valve until a flow rate of about $0.02 \text{ m}^3/\text{min}$ ($0.75 \text{ ft}^3/\text{min}$) is achieved.
4. Check the probe. It should remain warm to the touch. The heater should be capable of maintaining the exit air at a minimum of 100°C (212°F) under these conditions. If it cannot, the probe should be repaired, returned to the supplier, or rejected.

1.1.2 Probe Nozzle - Same as Method 5, Section 3.4.2.

1.1.3 Pitot Tube - Same as Method 5, Section 3.4.2.

1.1.4 Differential Pressure Gauge - Same as Method 5, Section 3.4.2.

1.1.5 Filter Holder - A borosilicate glass filter holder with a glass frit filter support and a silicone rubber gasket is required by the Reference Method. Other gasket materials (e.g., Teflon or Viton) may be used, subject to the approval of the administrator. The holder design must provide a positive seal against leakage from the outside or around the filter. A filter holder should be durable, easy to load, and leak free in normal applications. The filter holder is placed between the first and second impingers, and the filter is located toward the direction of flow. Do not heat the filter holder.

1.1.6 Impingers - Four impingers are required, as shown in Figure 1.1. The first and third impinger must be of the Greenburg-Smith design with standard tips. The second and fourth should be of the Greenburg-Smith design, but modified by replacing the insert with an approximately 13-mm (0.5-in.) inside diameter (ID) glass tube having an unobstructed tip located 13 mm (0.5 in.) from the bottom of the flask. Connections between impingers should be of glass. (Plastic or rubber tubing is not permitted because of absorption and desorption of gaseous species.) Silicone grease may be used, if necessary, to prevent leakage.

Upon receipt of a new Greenburg-Smith impinger, fill the inner impinger tube with water. If the water does not drain through orifice within 6 to 8 s, the impinger tip should be replaced or enlarged to prevent an excessive pressure drop in the sampling system. Each impinger is checked visually for damages such as breaks or cracks and for manufacturing flaws such as poorly shaped connections.

Collection absorbers and flow rates other than the specified ones may be used subject to the approval of the administrator. The collection efficiency must, however, be shown to be at least 99% for each test run to obtain approval and must be documented in the emission test 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, extra absorbers must be added for the sulfuric acid mist and the SO_2 , and then each must be analyzed separately. These extra absorbers must not contain more than 1% of the total H_2SO_4 or SO_2 .

1.1.7 Metering System - Same as Method 5, Section 3.4.1.

1.1.8 Barometer - Same as Method 5, Section 3.4.1.

1.1.9 Gas Density Determination Equipment - Same as Method 5, Section 3.4.1.

1.1.10 Temperature Gauge - Same as Method 5, Section 3.4.1.

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 - Two 1000-ml polyethylene bottles are required for each sample run, plus one 100-ml polyethylene bottle to retain a blank for each absorbing solution used in testing. Visually check wash bottles and/or storage bottles for damage. Also check each storage bottle seal to prevent sample leakage during transport.

1.2.3 Graduated Cylinders - One 250-ml and one 1000-ml glass graduated cylinder (Class A) or volumetric flasks are needed to measure the impinger contents.

1.2.4 Trip Balance - A trip balance with a 500-g capacity and an accuracy of ± 0.5 g is needed to weigh the silica gel, only if a moisture content analysis is to be done. A moisture determination has to be performed unless the gas stream can be considered dry. Check the trip balance by using a range of

standard weights, and adjust or return to supplier if necessary.

1.3 Analysis Glassware

1.3.1 Pipettes - Several volumetric pipettes (Class A), including 5-, 10-, 20-, 25-, and 100-ml sizes, should be available for the analysis.

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

1.3.3 Burette - A 50-ml 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 graduated cylinder (Class A) is needed in the preparation of the thorin indicator and the sample. Check all glassware for cracks, breaks, and discernible manufacturing flaws.

1.3.7 Trip Balance - Same as Subsection 1.2.4.

1.4 Reagents

Unless otherwise indicated, all reagents should conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society (ACS), when such specifications are available; otherwise use best available grade.

1.4.1 Sampling - The following are required for sampling:

Filters - Same as Method 5, Section 3.4.1.

Silica Gel - Same as Method 5, Section 3.4.1.

Water - Deionized distilled water to conform to ASTM specification D1193-74, Type 3. At the option of the analyst, the potassium permanganate (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 800 ml of reagent grade or certified ACS isopropanol with 200 ml of deionized distilled water. Check each lot of isopropanol for peroxide (H_2O_2) 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 at 352 nm on a spectrophotometer; if the absorbance exceeds 0.1, reject the isopropanol.

Peroxides may be removed from isopropanol by redistilling or by passing the mixture 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.

Potassium iodide solution, 10% - Dissolve 10.0 g of reagent grade or certified ACS KI 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.

Hydrogen peroxide, 3% - Dilute 30% reagent grade or certified ACS H_2O_2 1:9 (v/v) with deionized distilled water. Prepare fresh daily.

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

Water - Deionized distilled water, as in Subsection 1.4.1 above.

Isopropanol 100% - See Subsection 1.4.1.

1.4.3 Analysis - The following are required for sample analysis.

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

Isopropanol 100% - Use reagent grade or certified ACS isopropanol, and check for peroxide impurities, as in Subsection 1.4.1 above.

Thorin indicator - 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 deionized distilled water, and dilute to 1 l with isopropanol. Alternatively, 1.22 g of ($\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$) may be used. Standardize as in Section 3.7.5.

Sulfuric acid standard, 0.0100N - Either purchase the manufacturer's certified 0.0100N H_2SO_4 , or standardize the H_2SO_4 to 0.0100N $\pm 0.0002\text{N}$ against 0.0100N reagent grade or certified ACS sodium hydroxide (NaOH) that has previously been standardized against primary standard grade potassium acid phthalate.

1.5 Analytical Equipment

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

Table 1.1. ACTIVITY MATRIX FOR PROCUREMENT OF APPARATUS & SUPPLIES

Apparatus	Acceptance limits	Frequency and method of measurement	Action if requirements are not met
<u>Sampling</u>			
Sampling probe with heating system	Capable of 100°C (212°F) exit air at flow rate of 20 l/min	Visually check; run heating system check-out	Repair, re-return to supplier, or reject
Probe nozzle	Stainless steel (316); sharp, tapered leading edge (angle $\leq 30^\circ$); difference between measured ID's ≤ 0.1 mm (0.004 in.); no nicks, dents, or corrosion; uniquely identified (Meth. 5, Sec. 3.4.2)	Visually check before each test; use a micrometer to measure ID before field use after each repair	Reshape and sharpen, re-return to the supplier, or reject
Pitot tube	Type-S (Meth. 2, Sec. 3.1.2); attached to probe with impact (high pressure) opening plane even with or above nozzle entry plane	Calibrate according to Meth. 2, Sec. 3.1.2	Repair or re-return to supplier
Differential pressure gauge (manometer)	Criteria in Meth. 2, Sec. 3.1.2; agree within 5% of gauge-oil manometer used to calibrate	Check against gauge-oil manometer at a minimum of three points: [0.64(0.025), 12.7(0.5), 25.4(1.0)] mm (in.) H ₂ O	As above
Vacuum gauge	0-760 mm Hg range; ± 25 mm (1 in.) Hg accuracy at 380 mm (15 in.) Hg	Check against a mercury U-tube manometer upon receipt	Adjust or re-return to supplier
Vacuum pump	Capable of maintaining a flow rate of 0.03-0.05 m ³ /min (1-1.7 ft ³ /min) for pump inlet vacuum of 380 mm (15 in.) Hg with pump outlet at 760 mm (29.92 in.) Hg; leak free at 380 mm (15 in.) Hg	Check upon receipt for leaks and capacity	Repair or re-return to supplier

(continued)

Table 1.1 (continued)

Apparatus	Acceptance limits	Frequency and method of measurement	Action if requirements are not met
Orifice meter	ΔH_Q of 46.74 \pm 6.35 mm (1.84 \pm 0.25 in.) (recommended)	Visually check upon receipt for damage; calibrate against wet test meter	Repair, if possible; otherwise, return to supplier
Impingers	Standard stock glass; pressure drop across impingers not excessive (Sec. 3.7.1)	Visually check upon receipt; check pressure drop (Sec. 3.7.1)	Return to supplier
Filter holder	Leak free	Visually check before use	As above
Filters	Glass fiber without organic binder designed to remove 99.95% (\leq 0.05% penetration) of 0.3- μ dioctyl phthalate smoke particles	Manufacturer's guarantee that filters meet ASTM standard method D2986-71; observe under light for defects	Return to supplier and replace
Dry gas meter	Capable of measuring total volume with accuracy of \pm 2% at flow rate of 0.02 m ³ /min (0.75 ft ³ /min)	Check for damage upon receipt; calibrate against wet test meter (Sec. 3.7.2)	Reject if damaged, behaves erratically, or cannot be properly adjusted
Wet test meter	Capable of measuring total volume with accuracy of \pm 1%	Upon assembly, leak check all connections and check calibration by a liquid displacement method	As above
Thermometers	Within \pm 1°C (2°F) of value in range of 0°C to 25°C (32°F to 67°F) for impinger thermometer; \pm 3°C (6°F) of true value in range of 0°C to 90°C (32°F to 194°F) for dry gas meter thermometers	Check each thermometer upon receipt for damage--i.e., dents or bent stem; calibrate (Sec. 3.7.2)	Reject if unable to calibrate

(continued)

Table 1.1 (continued)

Apparatus	Acceptance limits	Frequency and method of measurement	Action if requirements are not met
Barometer	Capable of measuring atmospheric pressure to within 2.5 mm (0.1 in.) Hg	Check against a mercury-in-glass barometer or equivalent; calibrate (Sec. 3.7.2)	Determine correction factor, or reject if difference in the readings exceeds +2.5 mm (0.1 in.) Hg
<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, 1000 ml and 100 ml	Visually check for damage upon receipt; be sure caps make proper seals	As above
Graduated cylinders	Glass (Class A), 250 ml and 1000 ml	Visually check upon receipt	As above
Trip balance	500-g capacity, ± 0.5 g; needed to weigh silica gel only if moisture measurement desired	Check with standard weights up to 500 g	Adjust or return to supplier
<u>Analysis Glassware</u>			
Pipettes, volumetric flasks, burette, and graduated cylinder	Glass (Class A)	Upon receipt, check for stock number, cracks, breaks, and manufacturer's flaws	As above
<u>Reagents</u>			
Distilled water	ASTM-D1193-74, Type 3	Check each lot or specify type when ordering	As above

(continued)

Table 1.1 (continued)

Apparatus	Acceptance limits	Frequency and method of measurement	Action if requirements are not met
Isopropanol	100% isopropanol, reagent grade or certified ACS with no peroxide impurities; absorbance ≤ 0.1 at 352 nm on spectrophotometer	Upon receipt, check each lot for peroxide impurities with a spectrophotometer	Redistill, pass through alumina column, or replace
Hydrogen peroxide	30% H_2O_2 , reagent grade or certified ACS	Upon receipt, check label for grade or certification	Replace or return to
Potassium iodide	KI 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	Upon receipt, check label for grade or certification	As above
Barium perchlorate trihydrate solution	$Ba(ClO_4)_2 \cdot 3H_2O$, reagent grade or certified ACS	As above	As above
Sulfuric acid solution	H_2SO_4 , 0.0100N $\pm 0.0002N$	Certified by manufacturer, or standardize against 0.0100N NaOH previously standardized against potassium acid phthalate (primary standard grade)	As above

2.0 CALIBRATION OF APPARATUS

Calibration of the apparatus is one of the most important functions in maintaining data quality. The detailed calibration procedures included in this section are designed for the equipment specified by Method 8 and described in the previous section. A laboratory log book of all calibrations must be maintained. Table 2.1 at the end of this section summarizes the quality assurance functions for calibration.

2.1 Metering System

2.1.1 Wet Test Meter - Wet test meters are calibrated by the manufacturer to an accuracy of $\pm 0.5\%$. The calibration of the wet test meter must be checked initially upon receipt and yearly thereafter. A wet test meter with a capacity of $3.4 \text{ m}^3/\text{h}$ ($120 \text{ ft}^3/\text{h}$) will be necessary to calibrate the dry gas meter. For large wet test meters ($>3\ell/\text{rev}$), there is no convenient method to check the calibration. For this reason, several methods are suggested, and other methods may be approved by the administrator. The initial calibration may be checked by any of the following methods:

1. Certification from the manufacturer that the wet test meter is within $\pm 1\%$ of true value at the wet test meter discharge, so that only a leak check of the system is then required. Determine from manufacturer if the air entering the wet test meter should be saturated.

2. Calibration by any primary air or liquid displacement method that displaces at least one complete revolution of the wet test meter.

3. Comparison against a smaller wet test meter that has previously been calibrated against a primary air or liquid displacement method, as described in Section 3.5.2.

4. Comparison against a dry gas meter that has previously been calibrated against a primary air or liquid displacement method.

The calibration of the test meter should be checked annually. The calibration check can be made by the same method as that of the original calibration, with the exception that the comparison method need not be recalibrated if the calibration check is within $\pm 1\%$ of the true value. When this agreement is not obtained, then the comparison method or wet test meter must be recalibrated against a primary air or liquid displacement method.

2.1.2 Sample Meter System - The sample meter system--consisting of the pump, vacuum gauge, valves, orifice meter, and dry gas meter--is initially calibrated by stringent laboratory methods before it is used in the field. After the initial acceptance, the calibration is rechecked after each field test series. This recheck is designed to provide the tester with a method that can be used more often and with less effort to ensure that the calibration has not changed. When the quick check indicates that the calibration factor has changed, the tester must again use the complete laboratory procedure to obtain the new calibration factor. After recalibration, the metered sample volume must be multiplied by either the initial or the recalibrated calibration factor--that is, the one that yields the lower gas volume for each test run.

Before initial calibration of the metering system, a leak check should be conducted. The meter system should be leak free. Both positive (pressure) and negative (vacuum) leak checks should be performed. Following is a pressure leak-check procedure that will check the metering system from the quick disconnect inlet to the orifice outlet and will check the orifice-inclined manometer:

1. Disconnect the orifice meter line from the downstream orifice pressure tap (the one closest to the exhaust of the orifice), and plug this tap.

2. Vent the negative side of the inclined manometer to the atmosphere. If the inclined manometer is equipped with a three-way valve, this step can be performed by merely turning the three-way valve that is on the negative side of the orifice-inclined manometer to the vent position.

3. Place a one-hole rubber stopper with a tube through its one hole in the exit of the orifice, and connect a piece of rubber or plastic tubing to the tube, as shown in Figure 2.1.

4. Open the positive side of the orifice-inclined manometer to the "reading" position. If the inclined manometer is equipped with a three-way valve, this will be the line position.

5. Plug the inlet to the vacuum pump. If a quick disconnect with a leak-free check valve is used on the control module, the inlet will not have to be plugged.

6. Open the main valve and the bypass valve.

7. Blow into the tubing connected to the end of the orifice until a pressure of 127 to 178 mm (5 to 7 in.) H_2O has built up in the system.

8. Plug or crimp the tubing to maintain this pressure.

9. Observe the pressure reading for a 1-min period. No noticeable movement in the manometer fluid level should occur. If the meter box has a leak, a bubbling-type leak-check solution may aid in locating the leak(s).

After the metering system is determined to be leak free by the positive leak-check procedure, the vacuum system to and including the pump should be checked by plugging the air inlet to the meter box. If a quick disconnect with a leak-free stopper system is presently on the meter box, then the inlet will not have to be plugged. Turn the pump on, pull a vacuum within

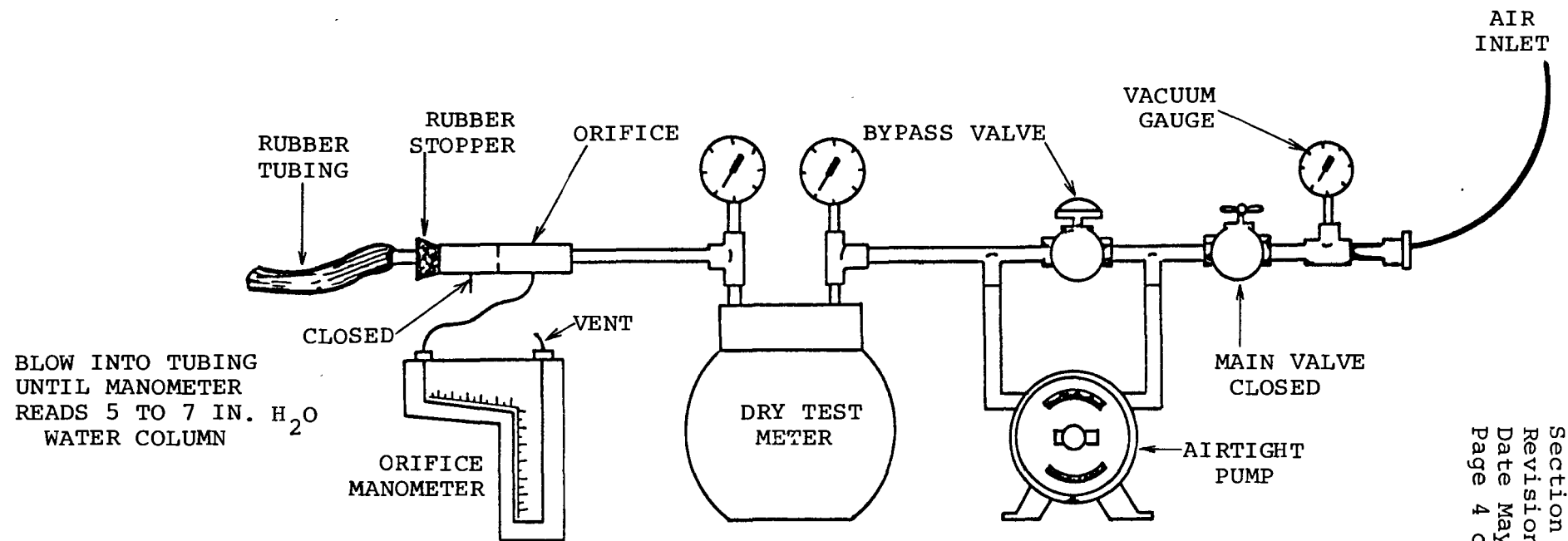


Figure 2.1. Positive leak check of metering system.

7.5 cm (3 in.) Hg of absolute zero, and observe the dry gas meter. If the leakage exceeds $1.5 \times 10^{-4} \text{ m}^3/\text{min}$ ($0.005 \text{ ft}^3/\text{min}$), the leak(s) must be found and minimized until the above specifications are satisfied.

Leak checking the meter system before initial calibration is not mandatory, but is recommended.

Note: For metering systems having diaphragm pumps, the normal leak-check procedure described above will not detect leakages within the pump. For these cases, the following leak-check procedure is suggested: make a 10-min calibration run at $0.00057 \text{ m}^3/\text{min}$ ($0.02 \text{ ft}^3/\text{min}$); at the end of the run, take the difference of the measured wet test meter and dry gas meter volumes; divide the difference by 10, to get the leak rate. The leak rate should not exceed $0.00057 \text{ m}^3/\text{min}$ ($0.02 \text{ ft}^3/\text{min}$).

Initial calibration - The dry gas meter and orifice meter can be calibrated simultaneously and should be calibrated when first purchased and any time the posttest check yields a Y outside the range of the calibration factor $Y \pm 0.05Y$. A calibrated wet test meter (properly sized, with $\pm 1\%$ accuracy) should be used to calibrate the dry gas meter and the orifice meter.

The dry gas meter and the orifice meter should be calibrated in the following manner:

1. Before its initial use in the field, leak check the metering system, as described in Subsection 2.1.2. Leaks, if present, must be eliminated before proceeding.

2. Assemble the apparatus, as shown in Figure 2.2, with the wet test meter replacing the probe and impingers--that is, with the outlet of the wet test meter connected to a needle valve that is connected to the inlet side of the meter box and with the inlet side of the wet test meter connected to an impinger with water or to a saturator.

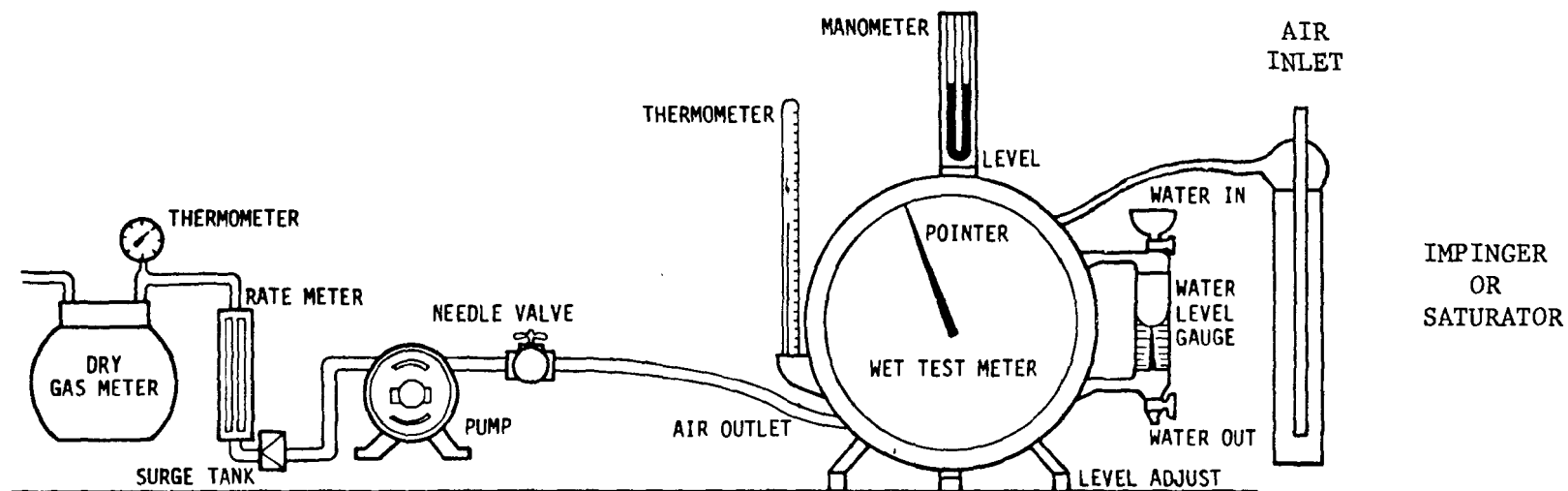


Figure 2.2. Sample meter system calibration setup.

3. Run the pump for 15 min with the orifice meter differential (ΔH) set at 12.7 mm (0.5 in.) H_2O to allow the pump to warm up and to permit the interior surface of the wet test meter to be wetted.

4. Adjust the needle valve so that the vacuum gauge on the meter box will read between 50 and 100 mm (2 to 4 in.) Hg during calibration.

5. Collect the information required in the forms provided (Figure 2.3A or 2.3B). Sample volumes, as shown, should be used.

6. Calculate Y_i for each of the six runs, using the equation in Figure 2.3A or B under the Y_i column, and record the results on the form in the space provided.

7. Calculate the average Y for the six runs using the following equation:

$$Y = \frac{Y_1 + Y_2 + Y_3 + Y_4 + Y_5 + Y_6}{6} .$$

Record the average on Figure 2.3A or B in the space provided.

8. The dry gas meter should be cleaned, adjusted, and recalibrated, or rejected if one or more values of Y fall outside the interval $Y \pm 0.02Y$. Otherwise, the average Y (calibration factor) is acceptable and will be used for future checks and subsequent test runs.

9. Calculate $\Delta H@_i$ for each of the six runs using the equation in Figure 2.3A or B under the $\Delta H@_i$ column, and record on the form in the space provided.

10. Calculate the average $\Delta H@$ for the six runs using the following equation:

$$\Delta H@ = \frac{\Delta H@_1 + \Delta H@_2 + \Delta H@_3 + \Delta H@_4 + \Delta H@_5 + \Delta H@_6}{6} .$$

Date 8/10/78

Meter box number FM-2

Barometric pressure, $P_b = 29.64$ in. Hg.

Calibrated by WGD

Orifice manometer setting (ΔH), in. H ₂ O	Gas Volume		Temperature ^a				Time (Θ), min	Y _i	$\Delta H@_i$
	Wet test meter (V _w), ft ³	Dry gas meter (V _d), ft ³	Wet test meter (t _w), °F	Dry gas meter					
				Inlet (t _{d_i}), °F	Outlet (t _{d_o}), °F	Average ^a (t _d), °F			
0.5	5	130.000 135.140	71.5 71.5	91 98	82 85	89	12.4%	1.00%	1.79
1.0	5								
1.5	10								
2.0	10								
3.0	10								
4.0	10								
Average									

ΔH	$\frac{\Delta H}{13.6}$	$Y_i = \frac{V_w P_b (t_d + 460)}{V_d (P_b + \frac{\Delta H}{13.6}) (t_w + 460)}$	$\Delta H@_i = \frac{0.0317 \Delta H}{P_b (t_d + 460)} \left[\frac{(t_w + 460) \Theta}{V_w} \right]^2$
0.5	0.0368	$\frac{5 (29.64) (549)}{5.14 (29.67) (531.5)}$	$\frac{(0.0317) (0.5)}{(29.64) (549)} \left[\frac{(531.5) (12.78)}{5} \right]^2$
1.0	0.0737		
1.5	0.110		
2.0	0.147		
3.0	0.221		
4.0	0.294		

^a If there is only one thermometer on the dry gas meter, record the temperature under t_d .

Figure 2.3A. Dry gas meter calibration data (English units).
(front side)

Nomenclature:

V_w = Gas volume passing through the wet test meter, ft^3 .

V_d = Gas volume passing through the dry test meter, ft^3 .

t_w = Temperature of the gas in the wet test meter, $^{\circ}\text{F}$.

t_{d_i} = Temperature of the inlet gas of the dry test meter, $^{\circ}\text{F}$.

t_{d_o} = Temperature of the outlet gas of the dry test meter, $^{\circ}\text{F}$.

t_d = Average temperature of the gas in the dry test meter, obtained by the average t_{d_i} and t_{d_o} , $^{\circ}\text{F}$.

ΔH = Pressure differential across orifice, in. H_2O .

Y_i = Ratio of accuracy of wet test meter to dry test meter for each run. Tolerance $Y_i = Y \pm 0.02 Y$.

Y = Average ratio of accuracy of wet test meter to dry test meter for all six runs.
Tolerance $Y = Y \pm 0.01 Y$.

$\Delta H@_i$ = Orifice pressure differential at each flow rate that gives $0.75 \text{ ft}^3/\text{min}$ of air at standard conditions for each calibration run, in. H_2O . Tolerance = $\Delta H@ \pm 0.15$ (recommended).

$\Delta H@$ = Average orifice pressure differential that gives $0.75 \text{ ft}^3/\text{min}$ of air at standard conditions for all six runs, in. H_2O . Tolerance = 1.84 ± 0.25 (recommended).

Θ = Time for each calibration run, min.

P_b = Barometric pressure, in. Hg.

Figure 2.3A. Dry gas meter calibration data (English units).
(back side)

Date 8/10/78

Meter box number FM-2

Barometric pressure, $P_b = 736$ mm Hg.

Calibrated by WDS

Orifice manometer setting (ΔH), mm H ₂ O	Wet test meter (v_w), m ³	Gas volume	Temperature ^a				Time (θ), min	Y_i	$\Delta H@_i$
		Dry gas meter (V_d), m ³	Wet test meter (t_w), °C	Dry gas meter					
				Inlet (t_{d_i}), °C	Outlet (t_{d_o}), °C	Average (t_d), °C			
10	0.15	25.0320 24.8800	18 18	20 19	18 17	18	10.4% 10	.986	23
25	0.15								
40	0.30								
50	0.30								
75	0.30								
100	0.30								
Average									

ΔH	$\frac{\Delta H}{13.6}$	$Y_i = \frac{V_w P_b (t_d + 273)}{V_d (P_b + \frac{\Delta H}{13.6}) (t_w + 273)}$	$\Delta H@_i = \frac{0.00117 \Delta H}{P_b (t_d + 273)} \left[\frac{(t_w + 273) \theta}{V_w} \right]^2$
10	0.7	$\frac{(0.15)(736)(291)}{(0.152)(737)(291)}$	$\frac{(0.00117)(10)}{(736)(29)} \left[\frac{(291)(10.82)}{0.152} \right]^2$
25	1.8		
40	2.94		
50	3.68		
75	5.51		
100	7.35		

^a If there is only one thermometer on the dry gas meter, record it under t_d .

Figure 2.3B. Dry gas meter calibration data (metric units).
(front side)

Nomenclature:

V_w = Gas volume passing through the wet test meter, m^3 .

V_d = Gas volume passing through the dry test meter, m^3 .

t_w = Temperature of the gas in the wet test meter, $^{\circ}C$.

t_{d_i} = Temperature of the inlet gas of the dry test meter, $^{\circ}C$.

t_{d_o} = Temperature of the outlet gas of the dry test meter, $^{\circ}C$.

t_d = Average temperature of the gas in the dry test meter, obtained by the average of t_{d_i} and t_{d_o} , $^{\circ}C$.

ΔH = Pressure differential across orifice, mm H_2O .

Y_i = Ratio of accuracy of wet test meter to dry test meter for each run. Tolerance $Y_i = Y \pm 0.02 Y$.

Y = Average ratio of accuracy of wet test meter to dry test meter for all six runs.
Tolerance $Y = Y \pm 0.01 Y$.

$\Delta H@_i$ = Orifice pressure differential at each flow rate that gives $0.021 m^3$ of air at standard conditions for each calibration run, mm H_2O . Tolerance $\Delta H@_i = \Delta H@ \pm 3.8 \text{ mm } H_2O$ (recommended).

$\Delta H@$ = Average orifice pressure differential that gives $0.021 m^3$ of air at standard conditions for all six runs, mm H_2O . Tolerance $\Delta H@ = 46.74 \pm 6.3 \text{ mm } H_2O$ (recommended).

Θ = Time of each calibration run, min.

P_b = Barometric pressure, mm Hg.

Figure 2.3B. Dry gas meter calibration data (metric units).
(back side)

Record the average on Figure 2.3A or B in the space provided.

11. Adjust the orifice meter or reject it if $\Delta H@_1$ varies by more than ± 3.9 mm (0.15 in.) H_2O over the range of 10 to 100 mm (0.4 to 4.0 in.) H_2O . Otherwise, the average $\Delta H@$ is acceptable and will be used for subsequent test runs.

Posttest calibration check - After each field test series, conduct a calibration check of the metering system, as in Subsection 2.1.2, except for the following variations:

1. Three calibration runs at a single intermediate orifice meter setting may be used with the vacuum set at the maximum value reached during the test series. The single intermediate orifice meter setting should be based on the previous field test. A valve must be inserted between the wet test meter and the inlet of the metering system to adjust the vacuum.

2. 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 during the test series.

3. Use Figure 2.4A or 2.4B, and record the required information.

If the calibration factor Y deviates 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 Y deviates by $>5\%$, recalibrate the metering system (as in Subsection 2.1.2), and use whichever meter coefficient (initial or recalibrated) yields the lower gas volume for each test run.

Alternate procedures--for example, using the orifice meter coefficients--may be used, subject to the approval of the administrator.

2.2 Thermometers

The thermometers used to measure the temperature of gas leaving the impinger train should be initially compared with a

Date 9/13/78 Test numbers AB1-3
 Meter box number FM-7 Plant Acme Power Plant
 Barometric pressure, $P_b = 28.72$ in. Hg Dry gas meter number FM-7 Pretest Y 0.986

Orifice manometer setting, (ΔH), in H_2O	Gas volume wet test meter (V_w), ft^3	Gas volume dry gas meter (V_d), ft^3	Temperature				Time (Θ), min	Vacuum setting, in. Hg	Y_i	$Y_i =$
			Wet test meter (t_w), $^{\circ}F$	Dry gas meter						$\frac{V_w P_b (t_d + 460)}{V_d P_b + \frac{\Delta H}{13.6} (t_w + 460)}$
				Inlet (t_{d_i}), $^{\circ}F$	Outlet (t_{d_o}), $^{\circ}F$	Average ^a (t_d), $^{\circ}F$				
1.41	10	886.544 876.321	72	83	75	79	13.35	3	0.987	$\frac{10(28.72)(79 + 460)}{10(223)(28.72 + \frac{1.41}{13.6})(72 + 460)}$
	10									
	10									
										Y=

^a If there is only one thermometer on the dry gas meter, record the temperature under t_d .

where

V_w = Gas volume passing through the wet test meter, ft^3 .

V_d = Gas volume passing through the dry test meter, ft^3 .

t_w = Temperature of the gas in the wet test meter, $^{\circ}F$.

t_{d_i} = Temperature of the inlet gas of the dry test meter, $^{\circ}F$.

t_{d_o} = Temperature of the outlet gas of the dry test meter, $^{\circ}F$.

t_d = Average temperature of the gas in the dry test meter, obtained by the average of t_{d_i} and t_{d_o} , $^{\circ}F$.

ΔH = Pressure differential across orifice, in H_2O .

Y_i = Ratio of accuracy of wet test meter to dry test meter for each run.

Y = Average ratio of accuracy of wet test meter to dry test meter for all three runs.
 Tolerance = Pretest Y $\pm 0.05Y$

P_b = Barometric pressure, in. Hg.

Θ = Time of calibration run, min.

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 Revision No. 0
 Date May 1, 1979
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Figure 2.4A. Posttest meter calibration data form (English units).

Test numbers AB1-3

Date 9/13/78 Meter box number FM-7 Plant Acme Power Plant

Barometric pressure, $P_b = 730$ mm Hg Dry gas meter number FM-7 Pretest Y 0.993

Orifice manometer setting, (ΔH), mm H ₂ O	Gas volume wet test meter (V_w), m ³	Gas volume dry gas meter (V_d), m ³	Temperature			Time (Θ), min	Vacuum setting, mm Hg	Y_i	$Y_i =$ $\frac{V_w P_b (t_d + 273)}{V_d P_b + \frac{\Delta H}{13.6} (t_w + 273)}$	
			Wet test meter (t_w), °C	Dry gas meter						
				Inlet (t_{d_i}), °C	Outlet (t_{d_o}), °C					Average (t_d), ^a °C
<u>36</u>	<u>0.30</u>	<u>26.1742</u> <u>19.8730</u>	<u>21</u>	<u>23.5</u>	<u>21.5</u>	<u>22.5</u>	<u>13.50</u>	<u>75</u>	<u>0.990</u>	<u>$\frac{0.30(730)(21.5 + 273)}{0.3012(730 + \frac{75}{13.6})(21 + 23)}$</u>
									Y=	

^a If there is only one thermometer on the dry gas meter, record the temperature under t_d .

where

V_w = Gas volume passing through the wet test meter, m³.

V_d = Gas volume passing through the dry test meter, m³.

t_w = Temperature of the gas in the wet test meter, °C.

t_{d_i} = Temperature of the inlet gas of the dry test meter, °C.

t_{d_o} = Temperature of the outlet gas of the dry test meter, °C.

t_d = Average temperature of the gas in the dry test meter, obtained by the average of t_{d_i} and t_{d_o} , °C.

ΔH = Pressure differential across orifice, mm H₂O.

Y_i = Ratio of accuracy of wet test meter to dry test meter for each run.

Y = Average ratio of accuracy of wet test meter to dry test meter for all three runs.

Tolerance = Pretest Y $\pm 0.05Y$

P_b = Barometric pressure, mm Hg.

Θ = Time of calibration run, min.

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

mercury-in-glass thermometer that meets ASTM E-1 No. 63C or 63F specifications as follows:

1. Place both the mercury-in-glass and the dial type or equivalent thermometer in an ice bath. Compare readings after the bath stabilizes.
2. Allow both thermometers to come to room temperature. Compare readings after both stabilize.
3. Accept the dial type or equivalent thermometer if values agree within $\pm 1^{\circ}\text{C}$ (2°F) at both points. If the difference is greater than $\pm 1^{\circ}\text{C}$ (2°F), the thermometer should be either adjusted and recalibrated until the above criteria are met, or rejected.
4. Prior to each field trip, compare the temperature reading of the mercury-in-glass thermometer at room temperature with that of the meter thermometer in the equipment. If the readings are not within $\pm 2^{\circ}\text{C}$ (4°F) the meter thermometer should be replaced or recalibrated.

The thermometers used to measure the metered sample gas temperature should also 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 equivalent thermometer and the mercury-in-glass thermometer in a hot water bath, 40° to 50°C (105° to 122°F). Compare readings after the bath stabilizes.
2. Allow both thermometers to come to room temperature. Compare readings after thermometers stabilize.
3. Accept the dial type or equivalent thermometer if: (1) values agree within $\pm 3^{\circ}\text{C}$ (5.4°F) at both points or (2) 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 pretest sampling checks form (Figure 2.5).

Date 9/15/78 Calibrated by WGD
Meter box number FM-1 $\Delta H@$ 1.41

Dry Gas Meter*

Pretest calibration factor = 0.986 (within $\pm 2\%$ of the average factor for each calibration run).

Impinger Thermometer

Was a pretest temperature correction used? yes ☒ no.
If yes, temperature correction (within $+1^{\circ}\text{C}$ (2°F) of reference values for calibration and within $\pm 2^{\circ}\text{C}$ (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 $+3^{\circ}\text{C}$ (3.4°F) of reference values for calibration and within $\pm 6^{\circ}\text{C}$ (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 the mercury-in-glass barometer).

*
Most significant items/parameters to be checked.

Figure 2.5. Pretest sampling checks.

4. Prior to each field trip, compare the temperature reading of the mercury-in-glass thermometer at room temperature with that of the meter system thermometer. The values or corrected values should be within $\pm 6^{\circ}\text{C}$ (10.8°F) of one another, or the meter thermometer should be replaced or recalibrated. Record any temperature correction factors on Figure 2.5 or on a similar form.

2.3 Barometer

The field barometer should be adjusted initially and before each test series to agree within ± 2.5 mm (0.1 in.) Hg of the mercury-in-glass barometer or the station pressure value reported from a nearby National Weather Service station, corrected for elevation. The tester should be aware that the reported pressure is normally corrected to sea level; the tester should request the uncorrected reading. The correction for elevation difference between the weather station and the sampling point should be applied at a rate of -2.5 mm Hg/30 m (-0.1 in./100 ft). Record results on Figure 2.5 or on a similar form.

2.4 Probe Nozzle

The nozzle should be stainless steel (316) or glass with sharp, tapered leading edges. The angle of taper should be $\leq 30^{\circ}$, and the taper should be on the outside to preserve a constant ID. Also the probe nozzles should be calibrated before their initial use in the field. Using a micrometer, measure the ID of the nozzle to the nearest 0.025 mm (0.001 in.). Make three separate measurements using different diameters each time, and then average the measurements. The difference between the high and low numbers should not exceed 0.1 mm (0.004 in.).

When nozzles become nicked, dented, or corroded, they should be reshaped, sharpened, and recalibrated before use. Each nozzle should be permanently and uniquely identified. Figure 2.6 is an example sample nozzle calibration data form.

Date 9/15/78

Calibrated by WGD

Nozzle identification number	D_1 , mm, (in.)	D_2 , mm, (in.)	D_3 , mm, (in.)	ΔD , mm, (in.)	D_{avg}
37	0.251	0.253	0.252	0.002	0.252

where:

D_1, D_2, D_3 = Nozzle diameter measured on a different diameter, mm (in.).
Tolerance = measure within 0.025 mm (0.001 in.).

ΔD = maximum difference in any two measurements, mm (in.).
Tolerance = 0.1 mm (0.004 in.).

D_{avg} = average of D_1 , D_2 , D_3 .

Figure 2.6. Nozzle calibration form.

2.5 Pitot Tube

The type-S Pitot tube assembly should be calibrated according to the procedure outlined in Method 2, Section 3.1.2.

2.6 Trip Balance

The trip balance should be calibrated initially by using Class-S standard weights and should be within ± 0.5 g of the standard weight. Adjust or return the balance to the manufacturer if limits are not met.

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 $3.4 \text{ m}^3/\text{h}$ ($120 \text{ ft}^3/\text{h}$) and an accuracy within $\pm 1.0\%$	Calibrate initially and then yearly by the liquid displacement technique	Adjust until specifications are met, or return to manufacturer
Dry gas meter	$Y_1 = Y \pm 0.02 Y$ at a flow rate of $0.02\text{--}0.03 \text{ m}^3/\text{min}$ ($0.66\text{--}1$)	Calibrate vs. wet test meter initially, and when the posttest check is not within $Y \pm 0.05 Y$	Repair or replace and then recalibrate
Thermometers	Impinger thermometer $\pm 1^\circ\text{C}$ (2°F); dry gas meter thermometer within $\pm 3^\circ\text{C}$ (5.4°F) over range	Calibrate each initially as a separate component against a mercury-in-glass thermometer and then before each field trip compare each as part of the train with the mercury-in-glass thermometer	Adjust; determine a constant correction factor; or reject
Barometer	$\pm 2.5 \text{ mm}$ (0.1 in.) Hg of mercury-in-glass barometer	Calibrate initially using mercury-in-glass barometer, and check before and after each field test	Adjust to agree with certified barometer
Probe nozzle	Average of three ID measurements of nozzle; difference between high and low not to exceed 0.1 mm (0.004 in.). $\alpha \leq 30^\circ$	Use a micrometer to measure to the nearest 0.025 mm (0.001 in.)	Recalibrate, reshape, and sharpen when nozzles are nicked, dented, or corroded
Trip balance	Standard weights measured within $\pm 0.5 \text{ g}$ of stated value	Balance calibration verified when first purchased, any time moved or subjected to rough handling, and during routine operations when cannot weigh within $\pm 0.5 \text{ g}$	Manufacturer should recalibrate or adjust
Type-S Pitot tube	Initially calibrated according to Sec. 2 of Method 2, and tube tips undamaged	Visually check before each field test	Repair or replace

3.0 PRESAMPLING OPERATIONS

The quality assurance functions for presampling preparations 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 form, and packing list.

3.1.1 Sampling Train - The schematic of the Method 8 sampling 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 3.7.10.

3.1.2 Probe and Nozzle - The probe and nozzle should be cleaned internally by brushing first with tap water, then with deionized distilled water followed by acetone, and finally allowed to dry in the air. In extreme cases, the glass probe liner can be cleaned with stronger reagents. The objective is to leave the glass liner free from contaminants. The probe heating system should be checked to see that it is operating properly. The probe must be leak free at a vacuum of 380 mm (15 in.) Hg when sealed at the inlet or tip.

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

3.1.4 Pump - The vacuum pump and oiler should be serviced as recommended by the manufacturer, every 3 mo, or after the 10th test (whichever comes first), or upon erratic behavior (nonuniform or insufficient pumping action).

Apparatus check	Acceptable		Quantity required	Ready		Loaded and packed
	Yes	No		Yes	No	
<u>Probe</u>			4-6' ebb	✓		✓
Type glass liner						
Borosilicate ____	✓					
Quartz ____						
Heated	✓					
Leak checked	✓					
<u>Nozzle</u>			3 sets	✓		✓
Glass ____						
Stainless steel ____	✓					
Other ____						
<u>Pitot Tube</u>			4-6' ebb.	✓		✓
Type ____	✓		"5"			
Other ____						
Properly attached	✓					
Modifications ____						
C _p ____	.84					
<u>Differential Pressure Gauge</u>						
Inclined manometer	✓		1			
Other ____			0-0.25	✓		✓
<u>Filter Holder</u>			5	✓		✓
Borosilicate glass	✓					
Glass frit	✓					
Gasket						
Silicone ____	✓					
Teflon ____						
Viton ____						

(continued)

Figure 3.1. Example of a pretest preparation checklist.

Apparatus check	Acceptable		Quantity required	Ready		Loaded and packed
	Yes	No		Yes	No	
<u>Condenser</u>						
Impingers						
Greenburg-Smith	✓		6	✓		✓
Modified Greenburg-Smith	✓		14	✓		✓
<u>Impinger Temperature Sensor</u>						
Thermometer _____	✓		4	✓		✓
Other _____						
Calibrated _____	✓			✓		✓
<u>Other</u>						
Barometer						
Mercury _____						
Aneroid _____	✓		1	✓		✓
Other _____						
Calibrated* _____						
<u>Stack Temperature Sensor</u>						
Type _____	✓		2	✓		✓
Calibrated* _____	✓					
<u>Reagents</u>						
Distilled water	✓		3 gal	✓		✓
Hydrogen peroxide (30%)	✓		2 pt	✓		✓
Isopropanol (80%) (checked for peroxides)	✓		1 gal	✓		✓
Silica gel	✓		5#	✓		✓
<u>Meter System</u>						
Pump leak free*	✓		2	✓		✓
Orifice meter*	✓			✓		✓
Dry gas meter*	✓			✓		✓

* Most significant items/parameters to be checked.

Figure 3.1 (continued)

3.1.5 Dry Gas Meter - A dry gas meter calibration check should be made in accordance with the procedure in Section 3.7.2.

3.1.6 Silica Gel - Either dry the used silica gel at 120° - 150°C (248° - 302°F) or weigh out fresh silica gel in several 200- to 300-g portions in airtight containers to the nearest 0.5 g. Record the total weight (silica gel plus container) on each container. The silica gel does not have to be weighed if the moisture content is not to be determined.

3.1.7 Filters - Check filters visually against light for irregularities, flaws, or pinhole leaks. The filters do not have to be weighed, labeled, or numbered.

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 the weather station reading after making an elevation correction, prior to each field trip.

3.2 Reagents and Equipment

3.2.1 Sampling - The first impinger solution (80% isopropanol) is prepared by mixing 800 ml of reagent grade or certified ACS isopropanol (100%) with 200 ml of deionized distilled water. The second and third impinger absorbing reagent (H_2O_2 , 3%) is prepared by diluting 100 ml of 30% H_2O_2 to 1 l (1000 ml) with deionized distilled water. The 3% H_2O_2 should be prepared fresh daily, using certified ACS reagent grade components. Solutions containing isopropanol must be kept in sealed containers to prevent evaporation and must be prepared fresh for each test series.

3.2.2 Sample Recovery - Deionized distilled water and 80% isopropanol are required on site for quantitative transfer of impinger solutions to storage containers. The water and isopropanol are used to clean the sampling train in the process of sample recovery.

3.3 Packing Equipment for Shipment

The condition of equipment may depend upon the careful packing of equipment with regard to (1) accessibility in the field, (2) care of movement on site, and (3) optimum functioning of measurement devices in the field. Equipment should be packed under the assumption that it will receive severe treatment during shipping and field operations. One major consideration in shipping cases is the construction materials.

3.3.1 Probe - Pack the probe in a case protected by polyethylene foam or other suitable packing material. The inlet and outlet should be sealed and protected from breakage. An ideal container is a wooden case, or equivalent, lined with foam material in which separate compartments are cut to hold individual devices. The case, equipped with handles or eye-hooks that can withstand hoisting, should be rigid enough to prevent bending or twisting of the devices during shipping and handling.

3.3.2 Impingers, Connectors, and Assorted Glassware - All impingers and glassware should be packed in rigid containers and protected by polyethylene foam or other suitable packing material. Individual compartments for glassware help to organize and protect each individual item.

3.3.3 Volumetric Glassware - A sturdy case lined with polyethylene foam material protects drying tubes and assorted volumetric glassware.

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

3.3.5 Wash Bottles and Storage Containers - Storage containers and miscellaneous glassware should be packed in rigid foam-lined containers.

Table 3.1. ACTIVITY MATRIX FOR PRESAMPLING OPERATIONS

Apparatus	Acceptance limits	Frequency and method of measurement	Action if requirements are not met
Probe	<p>1. Probe liner should be free of contaminants and constructed of borosilicate glass, or quartz, or the equivalent (no metal liners)</p> <p>2. Probe must be leak free at 380 mm (15 in.) Hg</p> <p>3. Probe must prevent condensation of moisture</p>	<p>1. Clean probe internally by brushing with tap deionized distilled water, then acetone; allow to dry in air before test</p> <p>2. Visually check before test</p> <p>3. Check out heating system initially and when moisture cannot be prevented during testing (Sec. 3.7.1)</p>	<p>1. Retrace cleaning procedure and assembly</p> <p>2. Replace</p> <p>3. Repair or replace</p>
Impingers, filter holders, and glass connectors	Clean, free of breaks, cracks, leaks, etc.	Clean with detergent and tap water, then deionized distilled water	Repair or discard
Pump	Maintain a smooth sampling rate of about 0.3-0.5 m ³ /min (1-1.7 ft ³ /min) at up to 380 mm (15 in.) Hg vacuum at pump inlet	Service every 3 mo or upon erratic behavior; check oiler jars every 10 tests	Repair or return to manufacturer
Dry gas meter	+2% of calibration factor and clean	Calibrate according to Sec. 3.7.2, and check for excess oil	As above
<u>Reagents and Equipment</u>			
Sampling	All reagents must be certified ACS or reagent grade	Prepare fresh daily and store in sealed containers	Prepare new reagent

(continued)

Table 3.1 (continued)

Apparatus	Acceptance limits	Frequency and method of measurement	Action if requirements are not met
Sample recovery	Deionized distilled water on-site and leak-free sample storage bottles as specified in Sec. 3.7.1	Water and reagent grade isopropanol are used to clean impinger after testing and prior to taking sample.	Prepare new reagent
<u>Package Equipment for Shipment</u>			
Probe	Pack in rigid container and protect with polyethylene foam	Pack prior to each shipment	Repack
Impingers, connectors, and assorted glassware	Pack in rigid containers and protect with polyethylene foam	Pack prior to each shipment	Repack
Pump	Sturdy case lined with polyethylene foam material or as part of meter box	As above	As above
Meter box	Meter box case and/or additional material to protect train components; pack spare meter box	As above	As above
Wash bottles and storage containers	Pack in rigid foam-lined containers	As above	As above

4.0 ON-SITE MEASUREMENTS

The on-site measurement activities include transporting the equipment to the test site, unpacking and assembling the equipment, making duct measurements, velocity traverse, determination of molecular weight and stack gas moisture content (in certain cases the moisture content can be assumed to be zero), sampling for sulfuric acid mist and sulfur dioxide, and recording data. Table 4.1 at the end of this section summarizes the quality assurance activities for on-site measurements. A copy of all field data forms mentioned are contained in Section 3.7.12.

4.1 Transport of Equipment to the Sampling Site

The most efficient means of transporting the equipment from ground level to the sampling site should be decided during the preliminary site visit (or prior correspondence). Care should be exercised to prevent damage to the test equipment or injury to test personnel during the moving phase. A laboratory type area should be designated for preparation of absorbing reagents, placing the filter in the filter holder, charging of the impingers, sample recovery, and documentation. This area should be fairly clean and should not have excessive drafts.

4.2 Sampling

The on-site sampling includes the following steps:

1. Preliminary measurements and setup,
2. Preparation and/or addition of the absorbing reagents to the impingers,
3. Placement of the filter in the filter holder,
4. Setup of the sampling train,
5. Preparation of the probe,
6. Leak check of entire train,

7. Insertion of the probe into the stack,
8. Sealing the port,
9. Checking the temperature of the probe,
10. Sampling at designated points, and
11. Recording of the data.

A final leak check of the train must always be performed upon completion of sampling.

4.2.1 Preliminary Measurements and Setup - The sampling site location should be selected in accordance with Method 2. If this is not possible due to duct configuration or other reasons, the sampling site location should be approved by the administrator. A 115-V, 30-amp electrical supply is necessary to operate the standard sampling train. Measure the stack and either determine the minimum number of traverse points by Method 1 or check the traverse points determined from the preliminary site visit, Section 3.0 of this Handbook. Record all data on the traverse point location form, as shown in Section 3.0. These measurements will be used to locate the Pitot tube and the sampling probe during preliminary measurements and actual sampling.

4.2.2 Stack Parameters - Check the sampling site for cyclonic or nonparallel flow as described in Method 1 (Section 3.0). The sampling site must be acceptable before a valid sample can be made. Determine the stack pressure, temperature, and the range of velocity heads using Method 2; it is recommended that a leak check of the velocity pressure system (Method 2) be performed. Be sure that the proper differential pressure gauge is chosen for the range of velocity heads encountered (see Method 2). Determine the moisture content using the approximation Method 4 or its alternatives for the purpose of setting the isokinetic sampling rate. If the particular source has been tested before or a good estimate of the moisture is available, this should be sufficient. The Reference Method uses the condensate collected during sampling to determine the moisture content used in final calculations.

Note: For contact-process sulfuric acid plants, the moisture can be assumed to be zero if a scrubber is not in use.

Determine the dry molecular weight of the stack gas, as required in Method 2. If an integrated gas sample is required, follow Method 3 procedures and take the sample simultaneously with, and for the same total length of time as, the sulfuric acid mist and SO₂ sample run. Sampling and analytical data forms for molecular weight determinations are presented in Method 3.

Using the stack parameters obtained by these preliminary measurements, the nomograph can be set up as outlined in APTD-0576. An example of a nomograph data form is presented in Method 5.

Method 8 sampling is performed isokinetically like Method 5, but the sampling rate is not to exceed 0.03 m³/min (1.0 ft³/min) during the test. To accomplish this, select a nozzle size based on the range of velocity heads, so that it is not necessary to change the nozzle size in order to maintain isokinetic sampling rates. Select also a nozzle that will not allow the maximum sampling rate to exceed 0.03 m³/min (1.0 ft³/min) during the run. Check the maximum ΔH, using the following equation:

$$\text{Maximum } \Delta H \leq \frac{1.09 P_m M \Delta H@}{T_m} \quad \text{Equation 4-1}$$

where

Maximum ΔH = pressure differential across the orifice, in. H₂O, that will produce a flow of 1.0 ft³/min;

P_m = pressure of the dry gas meter, in. Hg;

M = molecular weight of stack gas;

ΔH@ = pressure differential across the orifice that will produce a flow of 0.75 scfm, in. H₂O; and

T_m = temperature of the meter, °R.

This maximum ΔH will limit the sampling flow rate to $<0.03 \text{ m}^3/\text{min}$ ($1.0 \text{ ft}^3/\text{min}$).

During the run, do not change the nozzle size. Install the selected nozzle using a Viton-A O-ring when stack temperatures are $<260^\circ\text{C}$ (500°F) and using an asbestos string gasket when temperatures are higher (see APTD-0576 for details). Other connecting systems such as Teflon ferrules may be used. Mark the probe with heat resistant tape or by some other technique to denote the proper distance into the stack or duct for each sampling point.

Select a suitable probe liner and probe length so that all traverse points can be sampled. For large stacks, consider sampling from opposite sides of the stack to reduce the length of the probe.

Select a total sampling time greater than or equal to the minimum total sampling time specified in the test procedures for the specific industry so that (1) the sampling time per point is ≥ 2 min (or some greater time interval specified by the administrator) and (2) the sample volume taken (corrected to standard conditions) will exceed the required minimum total gas sample volume (normally 1.15 dscm (40.6 dscf)). The latter can be based on an approximate average sampling rate.

It is recommended that the number of minutes sampled at each point be an integer or an integer plus one-half min, in order to avoid timekeeping errors.

In some circumstances (e.g., batch cycles), it may be necessary to sample for shorter times at the traverse points and to obtain smaller gas sample volumes. In these cases, the administrator's approval must first be obtained.

4.2.3 Preparation and/or Addition of Absorbing Reagents and Filter to Collection System - Absorbing reagents can be prepared on site if necessary, according to the

directions given in Section 3.7.3. A pipette or graduated cylinder should be used to place 100 ml of 80% isopropanol into the first impinger. Be sure that the pipette or graduated cylinder was not used previously to add the H_2O_2 solution. It is suggested that the graduated cylinders or pipettes be marked to reduce the chance of interchanging. Place 100 ml of 3% H_2O_2 into the second impinger and 100 ml of 3% H_2O_2 into the third impinger. Also, place approximately 200 g of silica gel into the fourth impinger.

Note: If moisture content is to be determined by impinger analysis, either weigh each of the first three impingers (plus absorbing solution) to the nearest 0.5 g and record these weights, or determine to the nearest 1 ml volumetrically. The weight of the silica gel (or silica gel plus container) must also be determined to the nearest 0.5 g, and recorded.

Using tweezers or clean disposable surgical gloves, place a filter in the filter holder. Be sure that the filter is properly centered and that the gasket is properly placed in order to prevent the sample gas stream from circumventing the filter. Check the filter for tears after assembly is completed.

4.2.4 Assembling Sampling Train - During preparation and assembly of the sampling train, keep all sample train surfaces that are to be exposed to the sample covered until just prior to assembly or until sampling is about to begin.

Assemble the sampling train as shown in Figure 1.1, using (if necessary) a very light coat of silicone grease on all ground-glass joints. Apply grease only to the outer portion of the glass joint to avoid the possibility of contaminating the sample. Place crushed ice and water around the impingers.

4.2.5 Leak Checks - Leak checks are necessary to assure that the sample has not been biased low by dilution air. The Reference Method specifies that leak checks be performed at certain times. These are discussed below in this subsection.

Pretest leak check - A pretest leak check is recommended, but not required. If the tester opts to conduct the pretest leak check, the following procedure should be used:

1. After the sampling train has been assembled, turn on the probe heating system, set it at the desired operating temperature, and allow time for the temperature to stabilize.

2. If a Viton A O-ring or other leak-free connection is used in assembling the probe nozzle to the probe liner, leak check the train at the sampling site by plugging the nozzle and pulling a 380 mm (15 in.) Hg vacuum. Note: A lower vacuum may be used, if it is not exceeded during the test.

If an asbestos string is used for the probe gasket, do not connect the probe to the train during the leak check. Instead, leak check the train by first plugging the inlet to the first impinger and pulling a 380 mm (15 in.) Hg vacuum (see note immediately above). Then connect the probe to the train and leak check at about 25 mm (1 in.) Hg vacuum; alternatively, the probe may be leak checked with the rest of the sampling train in one step at a vacuum of 380 mm (15 in.) Hg. Leakage rates in excess of 4% of the average sampling rate or at $0.00057 \text{ m}^3/\text{min}$ ($0.02 \text{ ft}^3/\text{min}$), whichever is less, are not acceptable.

The following leak-check instructions for the sampling train described in APTD-0576 and APTD-0581 may be helpful:

1. Start the pump with the bypass valve fully open and the coarse adjust valve completely closed.

2. Partially open the coarse adjust valve and slowly close the bypass valve until the desired vacuum is reached. Do not reverse the direction of the bypass valve; this will cause hydrogen peroxide to back up into the filter holder. If the desired vacuum is exceeded, either leak check at this higher vacuum or end the leak check as shown below and start over.

When the leak check is completed, first slowly remove the plug from the inlet to the probe or the first impinger and then immediately turn off the vacuum pump. This prevents the absorbing solution in the impingers from being forced backward into the filter holder and prevents the silica gel from being entrained backward into the third impinger. Visually check to be sure that H_2O_2 did not contact the filter and that the filter has no breaks, and so forth.

Leak checks during the sample run - If during the sampling run a component (e.g., a filter assembly) change becomes necessary, a leak check should be conducted immediately before the change is made. The leak check should be done according to the procedure outlined above, except that it should be done at a vacuum equal to or greater than the maximum value recorded up to that point in the test. If the leakage rate is found to be no greater than $0.00057 \text{ m}^3/\text{min}$ ($0.02 \text{ ft}^3/\text{min}$) or 4% of the average sampling rate (whichever is less), the results are acceptable, and no correction will need to be applied to the total volume of dry gas metered; if, however, a higher leakage rate is obtained, the tester either should record the leakage rate and plan to correct the sample volume (as shown in Section 3.7.6 of this method) or should void the sampling run.

Note: Be sure to record the dry gas meter reading before and after each leak check performed during and after each test run so that the sample volume can be corrected.

Immediately after component changes, leak checks are again optional; if such leak checks are done, the procedure outlined above should be used.

Posttest leak check - A leak check is mandatory at the conclusion of each sampling run. The leak check should be done in accordance with the procedures previously outlined, except that it should be conducted at a vacuum equal to or

greater than the maximum value reached during the sampling run. If the leakage rate is found to be no greater than $0.00057 \text{ m}^3/\text{min}$ ($0.02 \text{ ft}^3/\text{min}$) or 4% of the average sampling rate (whichever is less), the results are acceptable, and no correction will need to be applied to the total volume of dry gas metered. If, however, a higher leakage rate is obtained, the tester should record the leakage rate and should correct the sample volume as shown in Section 3.7.6 of this method.

Note: Be sure to record the dry gas meter reading before performing the leak check in order to determine the sample volume.

4.2.6 Sampling Train Operation - Just prior to sampling, clean the portholes to minimize the chance of sampling any deposited material. Particulate matter can interfere with the wet chemical analysis for sulfuric acid mist. Verify that the probe heating system is at the desired temperature and that both the Pitot tube and the nozzle are located properly. Follow the procedure outlined below for sampling:

1. Record the initial dry gas meter readings, barometer readings, and other data as indicated in Figure 4.1.
2. Position the tip of the probe at the first sampling point so that the nozzle tip is pointing directly into the gas stream; then turn on the pump.
3. Immediately adjust the sample flow to isokinetic conditions.
4. Take other readings required by Figure 4.1 at least once at each sampling point during each time increment.
5. Record the dry gas meter readings at the end of each sampling time increment.
6. Repeat steps 3 through 5 for each sampling point.
7. At the conclusion of each traverse, turn off the pump, remove the probe from the stack, and record the final readings.

Plant Sulfuric Acid Plant
 Location Unit 1 outlet
 Operator BD
 Date 9/18/78
 Run number SAD-1
 Sample box number RG-12
 Meter box number FM-16
 Meter $\Delta H\theta$ 1.41
 Meter calibration Y 1.016
 Pitot tube CP 0.84

Probe length 6 ft.
 Probe liner material glass
 Probe heater setting 250
 Ambient temperature 70
 Barometric pressure 29.96
 Assumed moisture 0
 Static pressure -0.06
 C factor 0.88
 Reference ΔP 0.90
 Maximum ΔH 2.38

Sheet 1 of 1
 Nozzle identification number 37
 Nozzle diameter 0.252
 Final leak rate 0.013
 Vacuum during leak check 3 in. Hg
 Remarks: _____

Traverse point number	Sampling time (t), min	Clock time 24 h	Vacuum, mm Hg (in. Hg)	Stack temperature (T), °C (°F)	Velocity head (ΔP), mm H ₂ O (in. H ₂ O)	Pressure differential across orifice meter, mm H ₂ O (in. H ₂ O)	Gas sample volume, m ³ (ft ³)	Gas sample temperature at dry gas meter		Temperature of gas leaving condenser or last impinger, °C (°F)
								Inlet, °C (°F)	Outlet, °C (°F)	
Start	0	1152	—	—	—	—	111.431	—	—	—
1	5		2.0	120	0.95	1.9	115.18	70	70	66
2	10		2.5	121	1.05	2.0	118.99	73	71	64
3	15		2.5	123	1.05	2.0	122.79	76	72	62
4	20		2.5	120	1.05	2.0	126.60	79	74	62
5	25		3.0	122	.95	1.9	130.35	83	76	60
6	30	1222	2.5	122	.93	1.8	134.11	87	78	61
7	35	1233	2.5	119	.86	1.7	137.86	84	82	61
8	40		2.5	123	.88	1.75	141.61	87	83	63
9	45		3.0	122	.95	1.9	146.31	93	85	64
10	50		3.0	123	1.05	2.0	149.01	97	87	64
11	55		3.0	123	1.00	1.95	152.76	99	88	64
12	60	1258	3.0	122	.95	1.9	156.51	100	89	65
Total or Avg	60		3.0	121.7		1.89	145.080		82.6	

Figure 4.1. Method 8 field test data form.

8. Conduct a leak check, as described in Subsection 4.2.4, at the conclusion of the last traverse. This leak check is mandatory. Record all leakage rates. Note: If the velocity determination is required for the emissions calculation, a leak check of the Pitot-tube-manometer system is mandatory. The procedures are detailed in Section 4 of Method 2.

9. Disconnect the probe and then cap the nozzle and the end of the probe with polyethylene caps or the equivalent. See Subsection 4.3 on how to recover the probe contents.

10. Drain the ice bath, and purge the remaining part of the train by drawing clean ambient air through the system for 15 min at the average sampling rate. Provide clean ambient air by passing the air through a charcoal filter, or use ambient air without purification. See Subsection 4.3 for details on how to protect the probe from contamination during purging, and so forth. Note: Ambient air that is in compliance with normal state or Federal ambient air standards for SO₂ will have less than a 0.5% effect on the final results when not cleaned by passing it through a charcoal filter.

During the sampling run, maintain an isokinetic sampling rate within +10% unless otherwise specified by the administrator. Adjust the sampling flow rates when a 20% variation in the velocity head reading occurs. Make periodic checks of the manometer level and zero during each traverse. Vibrations and temperature fluctuations can cause the manometer zero to drift.

Periodically during the test, observe the connecting line between the probe and the first impinger for signs of condensation. If signs do occur, adjust the probe heater setting upward to the minimum temperature required to prevent condensation.

4.3 Sample Recovery

The Reference Method requires the sample to be recovered from the probe, the impingers, all connecting glassware, and the filter. Sample recovery should be performed in a labora-

tory type area to prevent contamination of the test sample. Upon completion of sampling, the probe should have been disconnected and capped off with polyethylene caps or the equivalent. Also, the impinger section should be capped off with polyethylene caps or the equivalent upon completion of purging with clean ambient air. Then the impinger box and the sampling probe can be transported safely to the clean-up area without contaminating or losing the sample.

4.3.1 Sulfuric Acid Mist Sample Recovery - The sulfuric acid mist (including SO_3) sample is collected in the probe, the first impinger, all connecting glassware before the filter, the front half of the filter holder, and the filter. To recover the sample:

1. Transfer the contents of the first impinger into a 250-ml graduated cylinder. (If a moisture content analysis is to be done, each impinger and its contents should be weighed to the nearest 0.5 g and recorded before transferring its contents.)

2. Rinse the probe, the first impinger, all connecting glassware before the filter, and the front half of the filter holder with 80% reagent grade or certified ACS isopropanol.

3. Add the rinse solution to the graduated cylinder and dilute to 250 ml with 80% reagent grade or certified ACS isopropanol.

4. Remove the filter with a pair of tweezers, and add to the solution; mix; and transfer to the 1000-ml storage containers. Protect the solution from evaporation.

5. Mark the level of liquid on the container, and identify the sample container. An example of a sample label is shown in Figure 4.2.

6. Place about 100 ml of the 80% isopropanol in a polyethylene bottle, and label the bottle for use as a blank during sample analysis.

4.3.2 Sulfur Dioxide Sample Recovery - The SO_2 is captured in the second and third impingers and in all connecting glassware. To recover the SO_2 sample:

Plant	<u>Sulfuric Acid Plant</u>	City	<u>Acidville, USA</u>	Remarks
Site	<u>Unit 2 Outlet</u>	Sample type	<u>H₂SO₄</u>	
Date	<u>9/18/78</u>	Run number	<u>SAP-1A</u>	
Front rinse	<input checked="" type="checkbox"/>	Front filter	<input type="checkbox"/>	
Back rinse	<input type="checkbox"/>	Back filter	<input type="checkbox"/>	
Solution	<u>80% IPA</u>	Level marked	<input checked="" type="checkbox"/>	
Volume:	Initial	<u>100 mL</u>	Final	<u>98/250</u>
Cleanup by	<u>WGD</u>			

Figure 4.2. Example of a sample label.

1. Transfer the solutions from the second and third impingers to a 1000-ml graduated cylinder. (If a moisture content analysis is to be done, each impinger and its contents should be weighed to the nearest 0.5 g and recorded before transferring its contents.)

2. Rinse all connecting glassware (including back half of the filter holder) between the filter and the silica gel impinger with deionized distilled water; add this rinse water to the graduated cylinder; and dilute to a volume of 1000 ml with deionized distilled water.

3. Transfer the solution to a storage container; mark the level of liquid on the container; and seal and identify the sample container.

4. Place 100 ml of the absorbing reagent (3% H_2O_2) in a polyethylene bottle, and label the bottle for use as a blank during sample analysis.

4.4 Sample Logistics (Data) and Packing of Equipment

The above procedures are followed until the required number of runs are completed. Log all data on the form shown in Figure 4.3. If the probe and the glassware (impingers, filter holder, and connectors) are to be used in the next test, rinse all of the glassware and the probe with deionized distilled water. Rinse the probe, the first impinger, all connecting glassware before the filter, and the front half of the filter holder with 80% isopropanol.

The following are recommended at the completion of the test series:

1. Check all sample containers for proper labeling (time and date of test, location of test, number of test, and any pertinent documentation). Be sure that a blank has been taken.

2. All data recorded during the field test should be recorded and duplicated by the best means available. One set of data can then be either mailed to the base laboratory or given to another team member or to the Agency; the original data should be hand-carried.

Plant Sulfuric Acid Plant Sample location Unit 1 Acidville

Field Data Checks

Sample recovery personnel W. Mason

Person with direct responsibility for recovered samples B. DeWees

Sample number	Sample identification number		Date of recovery	Liquid level marked	Stored in locked container
	H ₂ SO ₄	SO ₂			
1	SAP-1A	SAP-1B	9/18/78	Yes	Yes
2					
3					
Blanks	SAP-A Blank	SAP-B Blank	9/18/78	Yes	Yes

Remarks

Signature of field sample trustee W. DeWees

Laboratory Data Checks

Lab person with direct responsibility for recovered samples G. Caldwell

Date recovered samples received 9/21/78

Analyst R. Kuntz

Sample number	Sample identification number		Date of analysis	Liquid at marked level	Sample identified
	H ₂ SO ₄	SO ₂			
1	SAP-1A	SAP-1B	9/22/78	Yes	Yes
2					
3					
Blanks	SAP-A Blank	SAP-B Blank	9/22/78	Yes	Yes

Remarks

Signature of lab sample trustee Ronda Kuntz

Figure 4.3. Sample recovery and integrity data.

3. All sample containers and sampling equipment should be examined for damage, and then properly packed for shipment to the base laboratory. All shipping containers should be properly labeled to prevent loss of samples or equipment.

4. A quick check of the sampling and sample recovery procedures can be made using the data form, Figure 4.4.

Sampling

Impingers properly assembled? Yes
Contents: * 1st 80% IPA - 100 ml
2nd 3% H₂O₂ - 100 ml
3rd 3% H₂O₂ - 100 ml
4th 200g of Silicagel
Cooling system ICE AND WATER
Filter between 1st and 2nd impinger? Yes
Proper connections? Yes
Silicone grease added to all ground-glass joints? Yes
Pretest leak check? Yes (optional) Leakage? 0.01 ft³/min
Pitot tube lines checked for plugging and leaks? Yes
Meter box leveled? Yes Periodically? Yes - checked
Manometers zeroed? * Yes
Heat uniform along length of probe? * Yes
ΔH@ from most recent calibration 1.83
Nomograph set up properly? Yes
Care taken to avoid scraping sample port or stack wall?
Yes
Seal around in-stack probe effective? Yes
Probe moved at proper time? Yes
Nozzle and Pitot tube parallel to stack wall at all times?
Yes
Data forms complete and data properly recorded? Yes
Nomograph setting changed when stack temperature changes
significantly? Yes
Velocity pressures and orifice pressure readings recorded
accurately? Yes
Posttest leak check performed? * Yes (mandatory)
Leakage rate * 0.01 ft³/min

Sampling Recovery

System purged at least 15 min at test sampling rate? * Yes
Filter placed in 1st impinger contents? Yes
Ice removed before purging? Yes
Contents of impingers placed in polyethylene bottles? Yes
Glassware rinsed with distilled water? Yes
Fluid level marked? * Yes
Sample containers sealed and identified? * Yes
Blanks obtained? * Yes

* Most significant items/parameters to be checked.

Figure 4.4. On-site measurements checklist.

Table 4.1. ACTIVITY MATRIX FOR ON-SITE MEASUREMENT CHECKS

Apparatus	Acceptance limits	Frequency and method of measurement	Action if requirements are not met
<u>Sampling</u>			
Preparation and/or addition of absorbing reagents to collection system	100 ml of 80% isopropanol to first impinger and 100 ml of 3% H_2O_2 to each of the second and third impingers	Prepare H_2O_2 and 80% isopropanol fresh daily; use pipette or graduated cylinder to add solutions	Reassemble collection system
Filter	Properly centered; no breaks, damage, or contamination during loading	Use tweezers or surgical gloves to load	Discard filter and reload
Assembling sampling train	1. Assemble to specifications in Fig. 1.1 2. Leakage rate $<4\%$ or $0.00057 \text{ m}^3/\text{min}$ ($0.02 \text{ ft}^3/\text{min}$)	1. Before each sampling 2. A leak check before sampling is recommended; plug the nozzle or inlet to the first impinger and pull a vacuum of 380 mm (15 in.) Hg	1. Reassemble 2. Correct leak
Sampling (isokinetically)	1. Sampling must be performed within $\pm 10\%$ of isokinetic 2. Check applicable standard for minimum sampling time and volume; minimum sampling time/point should be 2 min 3. Sampling rate ₃ should not exceed $0.03 \text{ m}^3/\text{min}$ ($1.0 \text{ ft}^3/\text{min}$)	1. Calculate for each sample run 2. Make a quick calculation before and an exact calculation after testing 3. Select proper nozzle size. Sec. 3.7.4, Eq. 4-1	1. Repeat sample or obtain acceptance from a representative of the Administrator 2. As above 3. As above

(continued)

Table 4.1 (continued)

Apparatus	Acceptance limits	Frequency and method of measurement	Action if requirements are not met
	<p>4. Minimum number of points sampled, as specified by Meth. 1</p> <p>5. Leakage rate, not to exceed $0.00057 \text{ m}^3/\text{min}$ ($0.02 \text{ ft}^3/\text{min}$) or 4% of average sampling rate; apply correction to sample volume if rate is exceeded</p> <p>6. Purge remaining SO_2 from isopropanol</p>	<p>4. Check before the first test run by measuring duct and sampling site location</p> <p>5. Leak check after each test run or before equipment replacement during a run at maximum vacuum occurring during the run (mandatory)</p> <p>6. Drain ice, and purge with clean air for 15 min</p>	<p>4. As above</p> <p>5. Correct sample volume or repeat sample</p> <p>6. Repeat sample</p>
Sample recovery	Noncontaminated sample	Transfer sample to labeled polyethylene container after each test run. Mark level of solution in the container	Repeat sample
Sample logistics (data) and packing of equipment	<p>1. All data recorded correctly</p> <p>2. All equipment examined for damage and labeled for shipment</p> <p>3. All sample containers properly labeled and packaged</p>	<p>1. Upon the completion of each sample and before packing for shipment</p> <p>2. As above</p> <p>3. Visually check up on completion of each sample</p>	<p>1. Complete data</p> <p>2. Repeat sampling if damage occurred during testing</p> <p>3. Correct when possible</p>

5.0 POSTSAMPLING OPERATIONS

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

5.1 Apparatus Checks

Posttest checks have to be conducted on most of the sampling apparatus. These checks include three calibration runs at a single orifice meter setting; cleaning; and/or routine maintenance. The cleaning and maintenance will be discussed in Section 3.7.7, and is discussed in APTD-0576.⁵ Figure 5.1 should be used to record data from the posttest checks.

5.1.1 Metering System - The metering system has two components that must be checked--the dry gas meter and the dry gas meter thermometer(s).

The dry gas meter thermometer(s) should be checked by comparison with the ASTM mercury-in-glass thermometer at room temperature. If the readings agree within 6°C (10.8°F), they are acceptable; if not, the thermometer must be recalibrated according to Section 3.7.2 after the posttest check of the dry gas meter. For calculations, the dry gas meter thermometer readings (field or recalibration) that would give the higher temperature is used; that is, if the field reading is higher, no correction of the data is necessary; if the recalibration value is higher, the difference in the two readings should be added to the average dry gas meter temperature reading.

The posttest check of the dry gas meter is described in Section 3.7.2. If the posttest dry gas meter calibration factor (Y) is within 5% of the initial calibration factor, the initial calibration is used for calculations; if it deviates by >5%, recalibrate the metering system (as shown in Section 3.7.2) and use for the calculations the calibration factor (initial or recal-

Meter box number Fm-1

Dry Gas Meter

Pretest calibration factor $Y = 0.986$
Posttest check $Y_1 = 0.987$ $Y_2 =$ (±5% of pretest calibration factor)*
Recalibration required? yes ☒ no
If yes, recalibration factor $Y =$ (within ±2% of the average factor for each calibration run)
Lower calibration factor, $Y = 0.986$ for pretest or posttest calculations

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°C (10.8°F) of the reference values)
Recalibration required? yes no
Recalibration temperature correction, if used - (within ±3°C (5.4°F) of the reference values)
If yes, no correction is needed whenever meter thermometer temperature is higher
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 (±5.0 mm (0.2 in.) Hg of mercury-in-glass barometer)
Was recalibration required? yes ☒ no
If yes, no correction is needed whenever the field barometer has the lower reading
If the mercury-in-glass reading is lower, subtract the difference from the field data readings for the calculations

*Most significant items/parameters to be checked.

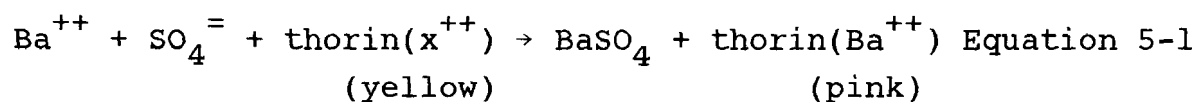
Figure 5.1. Posttest sampling checks.

brated) that yields the lesser gas volume. For each test run, the lesser calibration factor will give the lower gas volume.

5.1.2 Barometer - The field barometers are acceptable if they agree within ± 5 mm (0.2 in.) Hg when compared with the mercury-in-glass barometer. When they do not agree, the lesser calibration value should be used for the calculations. If the field barometer reads lower, no correction is necessary. If the mercury-in-glass barometer reads lower, subtract the difference from the field data readings for the calculations.

5.2 Analysis (Base Laboratory)

Calibrations and standardizations are of primary importance to a precise and accurate analysis. The analytical method is based on the insolubility of barium sulfate (BaSO_4) and the formation of a colored complex between barium ions and the thorin indicator (1-(o-arsonophenylazo)-2-naphthol-3,6-disulfonic acid disodium salt). Aliquots from the impinger solutions are analyzed by titration with barium perchlorate to the pink endpoint. The chemical reaction for this standardization is shown in Equation 5-1. The barium ions (Ba^{++}) react preferentially with sulfate ions ($\text{SO}_4^{=}$) in solution to form a highly insoluble barium sulfate (BaSO_4) precipitate. After the Ba^{++} has reacted with all $\text{SO}_4^{=}$, excess Ba^{++} reacts with the thorin indicator (x^{++}) to form a metal salt of the indicator and to give a color change:



Upon completion of each step of the standardization or of each sample analysis, the data should be entered on the proper data form. At the conclusion of the sample analysis, the data form should be reviewed and signed by the laboratory person with direct responsibility for the sample.

5.2.1 Reagents (Standardization and Analysis) - The following reagents are required for the analysis of the sulfuric acid mist (including SO_3) and the SO_2 samples.

Water - Deionized distilled water to conform to ASTM specification D1193-74, Type 3. At the option of the analyst, the KMnO_4 test for oxidizable organic matter may be omitted when high concentrations of organic matter are not expected to be present. Note: It is imperative that the distilled water meet the ASTM specifications since $\text{SO}_4^{=}$ and other polyvalent ions present in distilled water are not determined in the normal standardization of the acid by NaOH titration (which measures the hydrogen ion (H^+) concentration rather than the $\text{SO}_4^{=}$ concentration). This added $\text{SO}_4^{=}$ concentration would result in an erroneous standardization of the $\text{Ba}(\text{ClO}_4)_2$ titration, which directly measures $\text{SO}_4^{=}$ concentration and not H^+ concentration. A check on the acceptability of the distilled water is detailed in Section 3.7.1.

Isopropanol, 100% - Certified ACS reagent grade isopropanol. Check for peroxide impurities as described in Section 3.7.1.

Thorin indicator - 1-o-arsonophenylazo-2-naphthol-3, 6-disulfonic acid disodium salt, or equivalent. Dissolve 0.20 g ± 0.002 g in 100 ml of deionized distilled water. Measure the distilled water in a 100-ml Class-A graduated cylinder.

Barium perchlorate solution 0.0100N - Dissolve 1.95 g of barium perchlorate trihydrate ($\text{Ba}(\text{ClO}_4)_2 \cdot 3\text{H}_2\text{O}$) in 200 ml of deionized distilled water and dilute to 1 l with isopropanol. Alternatively, 1.22 g of barium chloride dihydrate ($\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$) may be used instead of the trihydrate. Standardize as in the subsection below with H_2SO_4 . Note: Protect the 0.0100N barium perchlorate solution from evaporation at all times by keeping the bottle capped between uses.

Sulfuric acid standard, 0.0100N - Either purchase a standard guaranteed by the manufacturer or standardize to

$\pm 0.0002N$ H_2SO_4 against $0.0100N$ $NaOH$ that has been standardized against potassium acid phthalate (primary standard grade), as described in the subsection below.

The $0.01N$ H_2SO_4 may be prepared in the following manner:

- a. Prepare $0.5N$ H_2SO_4 by adding approximately 1500 ml of deionized distilled water into a 2 l volumetric flask.
- b. Cautiously add 28 ml of concentrated H_2SO_4 and mix. Cool, if necessary.
- c. Dilute to 2 l with deionized distilled water.
- d. Prepare $0.01N$ H_2SO_4 by adding approximately 800 ml of deionized distilled water to a 1 l volumetric flask.
- e. Add 20.0 ml of the $0.5N$ H_2SO_4 .
- f. Dilute to 1 l with distilled water and mix thoroughly. Note: It is recommended that $0.1N$ sulfuric acid be purchased. Pipette 10.0 ml of $H_2SO_4(0.1N)$ 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 the 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 (KHP) for 1 to 2 h at $110^\circ C$ ($230^\circ F$), and cool in desiccator.
3. Weigh, to the nearest 0.1 mg, three 40-mg portions of the phthalate. Dissolve each portion in 100 ml of freshly boiled deionized distilled water in a 250-ml Erlenmeyer flask.
4. Add two drops of phenolphthalein indicator, and titrate the phthalate solutions with the $NaOH$ solution. All titrations should be done against a white background to

facilitate the detection of the endpoint--the first faint pink color that persists for at least 30 s.

5. Compare the endpoint colors of the other two titrations against the first one. The normality is the average of the three individual values calculated using Equation 5-1.

$$N_{\text{NaOH}} = \frac{\text{mg KHP}}{\text{ml titrant} \times 204.23} \quad \text{Equation 5-1}$$

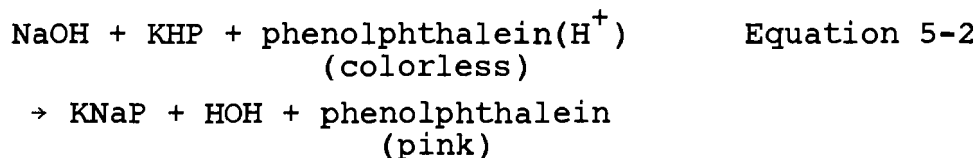
where

N_{NaOH} = calculated normality of NaOH, N,

mg KHP = the weight of KHP, mg, and

ml titrant = the volume of NaOH titrant, ml.

The chemical reaction for this standardization is shown in Equation 5-2. The NaOH is added to the KHP and the colorless phenolphthalein solution until an excess of sodium ions (Na^+) causes the phenolphthalein to change to a pink color.



5.2.3 Standardization of Sulfuric Acid - To standardize H_2SO_4 , proceed as follows:

1. Pipette 25 ml of H_2SO_4 into three 250-ml Erlenmeyer flasks.
2. Add 25 ml of deionized distilled water.
3. Add two drops of phenolphthalein indicator, and titrate with the standardized NaOH solution to a persistent pink endpoint, using a white background.
4. Titrate a blank of 25 ml of deionized distilled

water, using the same technique as step 3 above. The normality will be the average of the three independent values calculated using Equation 5-3.

$$N_{H_2SO_4} = \frac{(\text{ml NaOH}_{H_2SO_4} - \text{ml NaOH}_{\text{blank}}) \times N_{NaOH}}{25} \quad \text{Equation 5-3}$$

where

$N_{H_2SO_4}$ = calculated normality of H_2SO_4 , N,

$\text{ml NaOH}_{H_2SO_4}$ = volume of NaOH titrant used for H_2SO_4 , ml,

$\text{ml NaOH}_{\text{blank}}$ = volume of NaOH titrant used for blank, ml, and

N_{NaOH} = normality of NaOH, N.

5.2.4 Standardization of Barium Perchlorate (0.0100N) - To standardize $Ba(ClO_4)_2$, proceed as follows:

1. Pipette 25 ml of standard 0.0100N H_2SO_4 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 $Ba(ClO_4)_2$. All thorin titrations should be done against a white background to facilitate the detection of the pink endpoint.

3. Run a blank that contains 25 ml of deionized distilled water and 100 ml of isopropanol. The blank must not exceed 0.5 ml of titrant to obtain the endpoint; otherwise the distilled water has excess $SO_4^{=}$. If this 0.5-ml volume is exceeded, all reagents made with the distilled water will have to be remade using acceptable distilled water.

4. Use the endpoint of the first titration as a visual comparator for the succeeding titrations.

5. Record data on the form in Figure 5.2. The normality of the $Ba(ClO_4)_2$ will be the average of the three independent values calculated using Equation 5-4.

Plant Sulfuric Acid Plant Date 9/22/78

Sample location Unit 1 Acidville Analyst R. Kuntz

Volume and normality of
barium perchlorate

1. 25.0 ml $\text{Ba}(\text{ClO}_4)_2$
2. 25.0 ml $\text{Ba}(\text{ClO}_4)_2$ N = 0.010
Blank 25.0 ml $\text{Ba}(\text{ClO}_4)_2$

Sulfur Trioxide Analysis

V_{soln} - Total volume of solution in which the
sulfuric acid sample is contained, ml

V_a - Volume of sample aliquot, ml

V_t - Volume of barium perchlorate 1st titration
titrant used for sample, ml 2nd titration
Average

V_{tb}^* - Volume of barium perchlorate 1st titration
titrant used for blank, ml 2nd titration
Average

Run 1	Run 2	Run 3
250		
100		
19.0		
19.1		
19.05		
0.0		
0.0		
0.0		

$\frac{\text{1st titration}}{\text{2nd titration}} = 0.99 \text{ to } 1.01$ or $|\text{1st titration} - \text{2nd titration}| \leq 0.2 \text{ ml}$

Sulfur Dioxide Analysis

V_{soln} - Total volume of solution in which the
sulfur dioxide sample is contained, ml

V_a - Volume of sample aliquot, ml

V_t - Volume of barium perchlorate 1st titration
titrant used for sample, ml 2nd titration
Average

V_{tb}^* - Volume of barium perchlorate 1st titration
titrant used for blank, ml 2nd titration
Average

Run 1	Run 2	Run 3
1000		
10		
11.3		
11.3		
11.3		
0.0		
0.0		
0.0		

$\frac{\text{1st titration}}{\text{2nd titration}} = 0.99 \text{ to } 1.01$ or $|\text{1st titration} - \text{2nd titration}| \leq 0.2 \text{ ml}$

Signature of analyst Ronda Kuntz

Signature of reviewer or supervisor Craig Caldwell

* Volume of blank and sample titrated should be the same; otherwise a volume correction must be made.

Figure 5.2. Method 8 analytical data form.

$$N_{\text{Ba}(\text{ClO}_4)_2} = \frac{N_{\text{H}_2\text{SO}_4} \times 25}{\text{ml Ba}(\text{ClO}_4)_2} \quad \text{Equation 5-4}$$

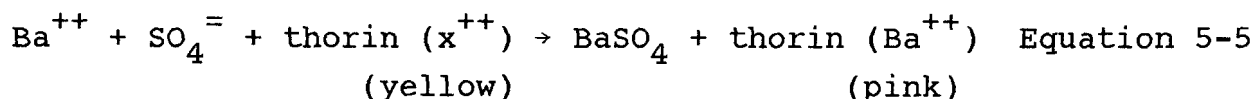
where

$N_{\text{Ba}(\text{ClO}_4)_2}$ = calculated normality of $\text{Ba}(\text{ClO}_4)_2$, N,

$N_{\text{H}_2\text{SO}_4}$ = normality of standard H_2SO_4 , N, and

ml $\text{Ba}(\text{ClO}_4)_2$ = volume of $\text{Ba}(\text{ClO}_4)_2$ required to titrate H_2SO_4 , ml.

The chemical reaction for this standardization is shown in Equation 5-5. The Ba^{++} reacts preferentially with $\text{SO}_4^{=}$ in solution to form a highly insoluble BaSO_4 precipitate. When the Ba^{++} has reacted with all of the $\text{SO}_4^{=}$, the excess Ba^{++} reacts with the thorin indicator (x^{++}) to form a metal salt of the indicator and to give a color change.



The standardized $\text{Ba}(\text{ClO}_4)_2$ 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 of low, medium, and high concentrations in the following manner:

1. Pipette 3.0-, 10.0-, and 20-ml aliquots of 0.01N H_2SO_4 into three 250-ml Erlenmeyer flasks.
2. Dilute each 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 flask.
4. Titrate with $\text{Ba}(\text{ClO}_4)_2$ 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 analysis technique is determined by control samples; the

precision, by duplicate analyses of both the control and the field samples. Acceptable accuracy and precision should be demonstrated on the analysis of the control samples prior to the analysis for the field samples.

Each 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 $(\text{NH}_4)_2\text{SO}_4$.

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 0.01N $(\text{NH}_4)_2\text{SO}_4$.

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

6. Pipette 25 ml of the control sample into each of four 250-ml Erlenmeyer flasks, and prepare a 25-ml blank of distilled water in 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 and two to four drops of thorin indicator to each flask.

8. Initially titrate the blank to a faint pink endpoint using the standardized $\text{Ba}(\text{ClO}_4)_2$. The blank must contain <0.5 ml of titrant; otherwise, the distilled water is unacceptable for use in this method.

9. Titrate two of the control samples with the standardized $\text{Ba}(\text{ClO}_4)_2$ to a faint pink endpoint, using the blank endpoint that persists for at least 30 s. All titrations should be done using 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 the agreement is not within 0.2 ml, titrate the third control sample. If the third titrant volume agrees within 0.2 ml of either of the first two samples, use the two titrant volumes

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 gram? YES

Dissolved in 2 l of distilled water? YES

Titration of blank 0.0 ml $\text{Ba}(\text{ClO}_4)_2$
(must be less than the 0.5 ml titrant)

Control Sample Number	Time of Analysis 24 h	Titrant volume, ml			
		1st	2nd	3rd	Ave.
1	0930	25.0	25.0		25.0

(Two consecutive volumes must agree within 0.2 ml)

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

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

(must agree within $\pm 5\%$, i.e., 0.233 to 0.268)

Does value agree? yes no

Ronda Kuntz Signature of analyst

Craig Caldwell Signature of reviewer

Figure 5.3. Control sample analytical data form.

that are consistent for the remaining calculations. When this criterion cannot be met with the first set of two control samples, the analyst should 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.

12. After consistent titrant volumes are obtained, the calculation of the analytical accuracy should be completed, as shown in Figure 5.3. If the measured value is within $\pm 5\%$ of the stated value, the technique is considered acceptable, and the field samples may be analyzed. When the $\pm 5\%$ 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 5% accuracy limit is based on the control limit from EPA audits discussed in Section 3.5.8.

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, determine whether any sample was lost during shipment, and note this on 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 prescribed below. Approval should have been requested prior to testing in case of subsequent leakage. The alternative method is as follows:

Reagents

Normality of sulfuric acid standard* 0.0100
Date of purchase 6/7/78 Date standardized N/A
Normality of barium perchlorate titrant* 0.010
Date standardized 9/22/78
Normality of control sample* 0.010
Date prepared 9/22/78
Volume of burette* 200 Graduations 0.1

Sample Preparation

Has liquid level noticeably changed? No
Original volume N/A Corrected volume N/A
Sulfuric acid samples diluted to 250 ml?* ✓
Sulfur dioxide samples diluted to 1000 ml?* ✓

Analysis

Volume of aliquots analyzed* 10 ml / SO₂ 100 ml / H₂SO₄
Do replicate titrant volumes agree within 1% or 0.2 ml? yes
Number of control samples analyzed 1
Are replicate control samples within 0.2 ml? yes
Is accuracy of control sample analysis $\pm 4\%$? yes
All data recorded? yes Reviewed by WGD

* Most significant items/parameters to be checked.

Figure 5.4. Posttest operations.

1. Mark the new volume level of the sample.
2. Transfer the sample to a 100-ml volumetric flask.
3. Put water in the sample storage container to the initial sample mark, and measure the initial sample volume (V_{soln_i}).
4. Put water in the sample storage container to the mark of the transferred sample, and measure the final volume (V_{soln_f}).
5. Use Equation 5-6 to correct the sample volume (V_{soln}) if the final volume (V_{soln_f}) is >50% of the initial volume.

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

where

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

V_{soln} = total volume of solution in which the sample is contained, ml,

V_{soln_i} = initial sample volume placed in sample storage container, ml, and

V_{soln_f} = final sample volume removed from sample storage container, ml.

6. Report both the corrected and the uncorrected values to the Agency, and proceed with the applicable analysis listed below.

Sulfuric acid mist (including SO_3) analysis - Proceed with the analysis as follows:

1. Shake the container holding the isopropanol solution and the filter. If the filter breaks up, allow the fragments to settle for a few minutes before removing a sample.
2. Pipette a 100-ml aliquot of this solution into a 250-ml Erlenmeyer flask.

3. Add two to four drops of thorin indicator, and titrate to a pink endpoint using 0.0100N $\text{Ba}(\text{ClO}_4)_2$.

4. Repeat the titration with a second aliquot from the same sample. Replicate titrant volumes should be within 1% or 0.2 ml, whichever is greater. If the titrant volumes do not meet this criterion, repeat analyses on new aliquots until two consecutive titrations agree within 1% or 0.2 ml, whichever is greater.

5. Record all data on Figure 5.2. The consistent titrant volumes should be averaged and used as V_t in subsequent calculations. All analytical data must then be reviewed by an individual familiar with procedures. The review of the data will also be noted on Figure 5.2. Note: Protect the 0.0100N $\text{Ba}(\text{ClO}_4)_2$ solution from evaporation at all times.

Sulfur dioxide analysis - Proceed with the SO_2 analysis as follows:

1. Thoroughly mix the solution in the container holding the contents of the second and third impingers.

2. Pipette a 10-ml aliquot of the sample into a 250-ml Erlenmeyer flask.

3. Add 40 ml of isopropanol and two to four drops of thorin indicator.

4. Titrate to a pink endpoint using 0.0100N $\text{Ba}(\text{ClO}_4)_2$. Note: Protect the 0.0100N $\text{Ba}(\text{ClO}_4)_2$ solution from evaporation at all times. Repeat titration with a second aliquot from the same sample. Replicate titrant volumes should be within 1% or 0.2 ml, whichever is greater. If the titrant volumes do not meet this criterion, repeat analyses on new aliquots until two consecutive titrations are within 1% or 0.2 ml, whichever is greater.

5. Record all data on the Method 8, Figure 5.2. The consistent titrant volumes should be averaged and used as V_t in subsequent calculations. All analytical data must then be reviewed by an individual familiar with procedures. The review of the data should also be noted on Figure 5.2.

Blanks - Prepare blanks by adding two to four drops of thorin indicator to 100 ml of 80% isopropanol. Titrate the blanks in the same manner as the samples. Record on Figure 5.2 in the space provided.

To aid the analyst or reviewer in a method of checking the analytical steps or procedures, the posttest operations form Figure 5.4 is given.

Table 5.1. ACTIVITY MATRIX FOR POSTSAMPLING OPERATIONS

Apparatus	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 three runs at one intermediate orifice setting and at highest vacuum of test (Sec. 3.7.2)	Recalibrate and use calibration factor that gives lower sample volume
Meter thermometer	Within $\pm 6^\circ\text{C}$ (10.8°F) at ambient temperature	Compare with mercury-in-glass thermometer after each test	Recalibrate and use higher temperature for calculations
Barometer	Within ± 5.0 mm (0.2 in.) Hg at ambient pressure	Compare with mercury-in-glass barometer after each test	Recalibrate and use lower barometric values for calculations
<u>Analysis</u>			
Reagents	Prepare according to Sec. 3.7.5	Prepare and/or standardize within 24 h of analysis	Prepare new solutions and/or restandardize
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 restandardize
Sample analysis	Titriments differ by $\leq 1\%$ or 0.2 ml, whichever is greater	Titrate until two or more aliquots agree within 1% or 0.2 ml, whichever is greater; review all analytical data	Void sample if any two consecutive titrations do not meet criterion

6.0 CALCULATIONS

Calculation errors due to procedural or mathematical mistakes can be a large component 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. Use a computer program that prints the input data back out so that it can be checked. If a standardized computer program is used, the original data entry should 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 retaining at least one decimal figure beyond that of the acquired data and should be rounded after final calculation to two significant digits for each run or sample. All rounding of numbers should be in accordance with the ASTM 380-76 procedures. Record all calculations on Figures 6.1A or B and on Figures 6.2A or B, or on similar forms, following the nomenclature list.

6.1 Nomenclature

The nomenclature is used in the calculations that follow this alphabetical list.

A_n = Cross-sectional area of nozzle, m^2 (ft^2).

B_{ws} = Water vapor in the gas stream, proportion by volume.

$C_{H_2SO_4}$ = Sulfuric acid (including SO_3) concentration, g/dscm (lb/dscf).

C_{SO_2} = Sulfur dioxide concentration, g/dscm (lb/dscf).

I = Percent of isokinetic sampling, %.

N = Normality of $Ba(ClO_4)_2$ titrant, g-eq/l.

P_{bar} = Barometric pressure at the sampling site, mm (in.) Hg.

P_s = Absolute stack gas pressure, mm (in.) Hg.

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

T_m = Average absolute dry gas meter temperature, K ($^{\circ}R$).

T_s = Average absolute stack gas temperature, K ($^{\circ}R$).

T_{std} = Standard absolute temperature, 293K (528 $^{\circ}R$).

V_a = Volume of sample aliquot titrated, 100 ml for H_2SO_4 and 10 ml for SO_2 .

V_{lc} = Total volume of liquid collected in impingers and silica gel, ml.

V_m = Volume of gas sample measured by dry gas meter, dcm (dcf).

$V_{m(std)}$ = Volume of gas sample measured by the dry gas meter and corrected to standard conditions, dscm (dscf).

V_s = Average stack gas velocity calculated by Method 2, using data from Method 8, m/s (ft/s).

V_{soln} = Total volume of solution in which the H_2SO_4 or SO_2 sample is contained, 250 ml or 1000²ml, respectively.

V_t = Volume of $Ba(ClO_4)_2$ titrant used for the sample, ml.

V_{tb} = Volume of barium perchlorate titrant used for the blank, ml.

Y = Dry gas meter calibration factor.

ΔH = Average pressure drop across orifice meter, mm
(in.) H_2O .

θ = Total sampling time, min.

13.6 = Specific gravity of mercury.

60 = s/min.

100 = Conversion to percent.

6.2 Calculations

The following are the formulas used to calculate the concentrations of sulfuric acid mist (including SO_3 and SO_2) along with the calculation forms (Figures 6.1A, 6.1B, 6.2A, and 6.2B) used to record the data.

6.2.1 Dry Sample Gas Volume, Corrected to Standard Conditions -

Correct the sample volume measured by the dry gas meter to standard conditions $20^\circ C$ and 760 mm ($68^\circ F$ and 29.92 in. Hg) by using Equation 6-1. The average dry gas meter temperature and average orifice pressure drop are obtained by averaging the field data (see Figure 4.1).

$$V_{m(std)} = V_m Y \left(\frac{T_{std}}{T_m} \right) \left[\frac{P_{bar} + \frac{\Delta H}{13.6}}{P_{std}} \right] \quad \text{Equation 6-1}$$

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

where

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

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

Note: If the leakage rate observed during any mandatory leak check exceeds the specified acceptable rate, the tester should either correct the value of V_m in Equation 6-1 (as described in Reference Method 5) or invalidate the test run.

Sample Volume

$$V_m = 45.080 \text{ ft}^3, T_m = 542.6^\circ\text{R}, P_{\text{bar}} = 29.96 \text{ in. Hg}$$

$$Y = 1.016, \Delta H = 1.89 \text{ in. H}_2\text{O}$$

Equation 6-1

$$V_{m_{\text{std}}} = 17.64 V_m Y \left[\frac{P_{\text{bar}} + (\Delta H/13.6)}{T_m} \right] = 44.82 \text{ ft}^3$$

Sulfuric Acid Mist (Including SO₃) Concentrations

$$N = .0100 \text{ g-eg/l}, V_t = 19.05 \text{ ml}, V_{tb} = 0.02 \text{ ml}$$

$$V_{\text{soln}} = 250.0 \text{ ml}, V_a = 100.0 \text{ ml}, V_{m_{\text{std}}} = 44.82 \text{ ft}^3$$

Equation 6-2

$$C_{\text{H}_2\text{SO}_4} = 1.081 \times 10^{-4} \frac{N(V_t - V_{tb}) \left(\frac{V_{\text{soln}}}{V_a} \right)}{V_{m_{\text{std}}}} = .0115 \times 10^{-4} \text{ lb/dscf}$$

Figure 6.1A. Sulfuric acid mist (including SO₃) calculation form (English units).

Sample Volume

$$V_m = 1.276 \text{ m}^3, T_m = 301.1 \text{ K}, P_{\text{bar}} = 761.0 \text{ mm Hg}$$

$$Y = 1.016, \Delta H = 42.0 \text{ mm. H}_2\text{O}$$

Equation 6-1

$$V_{m_{\text{std}}} = 0.3858 V_m Y \left[\frac{P_{\text{bar}} + (\Delta H/13.6)}{T_m} \right] = 1.270 \text{ m}^3$$

Sulfuric Acid Mist (Including SO₃) Concentrations

$$N = .0100 \text{ g-eg/l}, V_t = 19.05 \text{ ml}, V_{tb} = 0.02 \text{ ml}$$

$$V_{\text{soln}} = 250. \text{ ml}, V_a = 100.0 \text{ ml}, V_{m_{\text{std}}} = 1.270 \text{ m}^3$$

Equation 6-2

$$C_{\text{H}_2\text{SO}_4} = 0.04904 \left[\frac{N(V_t - V_{tb}) \left(\frac{V_{\text{soln}}}{V_a} \right)}{V_{m_{\text{std}}}} \right] = .01837 \text{ g/dscm}$$

Figure 6.1B. Sulfuric acid mist (including SO₃)
calculation form (metric units).³

Sample Volume

$$V_m = \underline{45.080} \text{ ft}^3, T_m = \underline{542.6} ^\circ\text{R}, P_{\text{bar}} = \underline{29.96} \text{ in. Hg}$$

$$Y = \underline{1.016}, \Delta H = \underline{1.89} \text{ in. H}_2\text{O}$$

Equation 6-1

$$V_{m_{\text{std}}} = 17.64 V_m Y \left[\frac{P_{\text{bar}} + (\Delta H/13.6)}{T_m} \right] = \underline{44.82} \text{ ft}^3$$

Sulfuric Acid Mist (Including SO₃) Concentrations

$$N = \underline{.0100} \text{ g-eg/l}, V_t = \underline{11.34} \text{ ml}, V_{tb} = \underline{0.02} \text{ ml}$$

$$V_{\text{soln}} = \underline{1000.0} \text{ ml}, V_a = \underline{10.0} \text{ ml},$$

Equation 6-2

$$C_{\text{SO}_2} = 7.061 \times 10^{-5} \frac{N(V_t - V_{tb}) \left(\frac{V_{\text{soln}}}{V_a} \right)}{V_{m_{\text{std}}}} = \underline{0.177} \times 10^{-4} \text{ lb/dscf}$$

Figure 6.2A. Sulfur dioxide calculation form (English units).

Sample Volume

$$V_m = 1.276 \text{ m}^3, T_m = 301.1 \text{ K}, P_{\text{bar}} = 761.0 \text{ mm Hg}$$

$$Y = 1.016, \Delta H = 48.0 \text{ mm H}_2\text{O}$$

Equation 6-1

$$V_{m_{\text{std}}} = 0.3858 V_m Y \left[\frac{P_{\text{bar}} + (\Delta H/13.6)}{T_m} \right] = 1.270 \text{ m}^3$$

SO₂ Concentration

$$N = .0100 \text{ g-eg/l}, V_t = 11.34 \text{ ml}, V_{tb} = 0.02 \text{ ml}$$

$$V_{\text{soln}} = 1000. \text{ ml}, V_a = 10.0 \text{ ml},$$

Equation 6-2

$$C_{\text{SO}_2} = 3.203 \times 10^{-2} \left[\frac{N(V_t - V_{tb}) \left(\frac{V_{\text{soln}}}{V_a} \right)}{V_{m_{\text{std}}}} \right] = 0.286 \text{ g/dscm}$$

Figure 6.2B. Sulfur dioxide calculation form (metric units).

6.2.2 Volume of Water Vapor and Moisture Content - Calculate the volume of water vapor and moisture content of the stack gas as described in Sections 6.4 and 6.5 of Method 5, respectively.

6.2.3 Sulfuric Acid Mist (Including SO₃) Concentration -

$$C_{H_2SO_4} = K_2 \left[\frac{N (V_t - V_{tb}) \left[\frac{V_{soln}}{V_a} \right]}{V_{m(std)}} \right] \quad \text{Equation 6-2}$$

where

$$K_2 = 0.04904 \text{ g/meq for metric units, or} \\ = 1.081 \times 10^{-4} \text{ lb/meq for English units.}$$

6.2.4 Sulfur Dioxide Concentration -

$$C_{SO_2} = K_3 \left[\frac{N (V_t - V_{tb}) \left[\frac{V_{soln}}{V_a} \right]}{V_{m(std)}} \right] \quad \text{Equation 6-3}$$

where

$$K_3 = 0.03203 \text{ g/meq for metric units, or} \\ = 7.061 \times 10^{-5} \text{ lb/meq for English units.}$$

6.2.5 Isokinetic Variation (I) in Raw Data -

$$I = \frac{T_s \left\{ K_4 V_{lc} + \left[\frac{YV_m}{T_m} \right] \left[P_{bar} + \frac{\Delta H}{13.6} \right] \right\} \times 100}{60 \theta V_s P_s A_n} \quad \text{Equation 6-4}$$

where

$$K_4 = 0.003464 \text{ mm Hg-m}^3/\text{ml-K for metric units, or} \\ = 0.002676 \text{ in. Hg-ft}^3/\text{ml-}^\circ\text{R for English units.}$$

6.2.6 Isokinetic Variation (I) in Intermediate Values -

$$I = \frac{\left[T_s V_{m(std)} P_{std} \right] 100}{T_{std} 60 \theta V_s P_s A_n [1 - B_{ws}]} \quad \text{Equation 6-5}$$

$$= K_5 \frac{T_s V_{m(std)}}{\theta V_s P_s A_n [1 - B_{ws}]}$$

where

$$K_5 = 4.320 \text{ for metric units, or}$$

$$= 0.09450 \text{ for English units.}$$

6.3 Acceptable Results

If $90\% \leq I \leq 110\%$, the results are acceptable. If the results are low in comparison with the standards and if the I is beyond the acceptable range, the administrator may opt to accept the results. Otherwise, the results may be rejected and the test repeated. It is suggested that, for Method 8 tests, the data not be rejected only because of noncompliance with isokinetic requirements.

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 given	Visually check	Complete missing data values
Calculations	Difference between check and original calculations not to exceed round-off error; retain at least one decimal figure beyond that of acquired data	Repeat all calculations, starting with raw data for hand calculations; check all raw data input to computer calculations; hand calculate one sample/test	Indicate errors on analysis data form, Fig. 6.3
Isokinetic variations	$90\% \leq I \leq 110\%$	For each traverse point, calculate I	Repeat test and adjust flow rates to maintain I within 10% variation

7.0 MAINTENANCE

The normal use of emission testing equipment subjects it to corrosive gases, extremes in temperature, vibrations, and shocks. Keeping the equipment in good operating order over an extended period of time requires a knowledge of the equipment and a program of routine maintenance which is performed quarterly or after 28.4 m³ (1000 ft³) 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 this subsection.

The following procedures are not required, but are recommended to increase the reliability of the equipment.

7.1 Pumps

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 at the time of filling and at each periodic check, and it is recommended that the oil be changed if it is not translucent. Use the oil specified by the manufacturer; if none is specified, use SAE 10, nondetergent oil. Whenever the fiber vane pump starts to run erratically or during the yearly disassembly, the head should be removed, and the fiber vanes should be changed. Erratic operation of the diaphragm pump is normally due either to a bad diaphragm, which will cause leakage, or to malfunction of the valves, which should be cleaned annually by complete disassembly of the train.

7.2 Dry Gas Meters

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 should be cleaned and checked when the rotation of the dials is erratic, when the meter will not calibrate properly over the required flow rate range, and during yearly maintenance.

7.3 Sample Train

All remaining sample train components should be checked visually every 3 mo and disassembled completely and cleaned or replaced yearly. Many of the items such as quick disconnects should be replaced when 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 the meter box) rather than to replace individual components.

7.4 Inclined Manometer

The fluid in the inclined thermometer should be changed whenever there is discoloration or visible matter in the fluid and during the yearly disassembly. No other routine maintenance is required since the inclined manometers will be leak checked during both the leak check of the Pitot tube and the leak check of the entire control console.

Table 7.1. ACTIVITY MATRIX FOR EQUIPMENT MAINTENANCE CHECKS

Apparatus	Acceptance limits	Frequency and method of measurement	Action if requirements are not met
Routine main-tenance	No erratic behavior	Routine maintenance quarterly. Disassemble and clean yearly	Replace parts as needed
Fiber vane pump	In-line oiler free of leaks	Periodic check of 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 top plate. Check valves and diaphragm when meter dial runs erratically or when meter will not calibrate	Replace parts as needed, or replace meter
Inclined manometer	No discoloration or visible matter in the fluid	Check periodically during yearly disassembly	Replace parts as needed
Sample train	No damage	Visually check every 3 mo and completely disassemble and clean or replace yearly	If failure noted, use another entire control console, sample box, or umbilical cord
Nozzle	No dents, corrosion, or other damage	Visually check before and after each test run	Use another nozzle or clean out, sharpen, and recalibrate

8.0 AUDITING PROCEDURE

An audit is an independent assessment of data quality. Independence is achieved if the individual(s) performing the audit and their standards and equipment are different from the regular field crew and their standards and equipment. Routine quality assurance checks by a field team are necessary in generation of good quality data, but they are not part of the auditing procedure. Table 8.1 at the end of this section summarizes the quality assurance functions for auditing.

Based on the results of a collaborative test² of Method 8, two specific performance audits are recommended:

1. Audit of the analytical phase of Method 8, and
2. Audit of data processing.

It is suggested that a systems audit be conducted as specified by the quality assurance coordinator, in addition to these performance audits. The two performance audits and the systems audit are described in detail in Subsections 8.1 and 8.2, respectively.

8.1 Performance Audits

Performance audits are made to 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. 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 actual analysis of the field samples which is required.

8.1.1 Pretest Audit of Analytical Phase Using Aqueous

Ammonium Sulfate (Optional) - The pretest audit described in this subsection can be used to determine the

proficiency of the analyst and the standardization of solutions in the Method 8 analysis and should be performed at the discretion of the agency auditor. The analytical phase of Method 8 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 3.7.5 on control sample preparation.

The pretest audit provides the opportunity for the testing laboratory to check the accuracy of its analytical procedure. This audit is especially recommended for a laboratory with little or no experience with the Method 8 analysis procedure described in this Handbook.

The testing laboratory should provide the agency/organization requesting the performance test with a notification of the intent to test 30 days prior to the enforcement source test. The testing laboratory should request that the agency/organization provide the following performance pretest audit samples: two samples at a low concentration (500 to 1000 mg SO₂/dscm of gas sampled or approximately 10 to 20 mg of ammonium sulfate/sample) and two samples at a high concentration (1500 to 2500 mg SO₂/dscm of gas sampled or about 30 to 50 mg of ammonium sulfate/sample). At least 10 days prior to the time of the enforcement source test, the agency/organization should provide the four audit samples. The concentration of the two low and the two high audit samples should not be identical.

The testing laboratory will analyze one sample at the low concentration and one at the high concentration, and submit their results to the agency/organization prior to the enforcement source test. (Note: The analyst performing this optional audit must be the same analyst audited during the field sample analysis described in Subsection 8.1.2 below).

The agency/organization determines the percent accuracy, %A, between the measured SO₂ concentration and the audit or known values of concentration. The %A is a measure of the

bias of the analytical phase of Method 8. Calculate %A using Equation 8-1.

$$\%A = \frac{C_{SO_2}(M) - C_{SO_2}(A)}{C_{SO_2}(A)} \times 100 \quad \text{Equation 8-1}$$

where

$C_{SO_2}(M)$ = concentration measured by the lab analyst
mg/ml, and

$C_{SO_2}(A)$ = audit or known concentration of the audit
sample, mg/ml.

The recommended control limit for the pretest audit is the 90th percentile value for %A based on the results of three audits (11/77, 5/78, and 10/78) performed by the Environmental Monitoring and Support Laboratory, USEPA, Research Triangle Park, North Carolina.^{6,7} By definition, 90% of the laboratory participants in the audit obtained values of %A less than the values tabulated below. The control limit is expected to be exceeded by 10% of the laboratories to be audited, based on these three audits. The 90th percentile values and the known audit concentrations are given below for each concentration range, 500 to 1000 mg SO₂/dscm and 1500 to 2500 mg SO₂/dscm.

500 to 1000 mg SO₂/dscm

<u>Audit date</u>	<u>Known audit concentration, mg SO₂/dscm</u>	<u>90th percentile for %A, %</u>
5/78	686	4.1
10/78	572	6.4

1500 to 2500 mg SO₂/dscm

<u>Audit date</u>	<u>Known audit concentration, mg SO₂/dscm</u>	<u>90th percentile for %A, %</u>
11/77	1411	6.6
11/77	2593	4.0
5/78	2479	4.5
5/78	1907	4.5
10/78	2555	4.9
10/78	1754	5.2

Based on the results of these audits, the recommended 90th percentile control limit for pretest audits is 7% for both concentration ranges.

If the results of the pretest audit exceed 7% the agency/organization should provide the correct results to the testing laboratory. After taking any necessary corrective action, the testing laboratory should then analyze the two remaining samples and report the results immediately to the agency/organization before the enforcement source test analysis.

8.1.2 Audit of Analytical Phase Using Aqueous Ammonium

Sulfate (Required) - The agency should provide 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 percent accuracy of the audit samples is determined using Equation 8-1. The results of the calculated %A should be included in the enforcement source test report as an assessment of accuracy of the analytical phase of Method 8 during the actual enforcement source test.

8.1.3 Audit of Data Processing - Calculation errors are prevalent in Method 8. Data-processing errors can be determined by auditing the data recorded on the field and laboratory forms. The original and audit (check) calculation should agree within roundoff; 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 occur 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--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 in the following:

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. Checking for isokinetic sampling.
4. Purging the sampling train.

Figure 8.1 is a suggested checklist for the auditor.

Presampling Preparation

Yes No Comment

- | | | | |
|-------------|-------------|-------------|---------------------------------------------------------------------------------------------------|
| <u> </u> | <u> </u> | <u>OK</u> | 1. Knowledge of process conditions |
| <u>✓</u> | <u> </u> | <u> </u> | 2. Calibration of pertinent equipment, in particular, the dry gas meter, prior to each field test |

On-site Measurements

- | | | | |
|-------------|-------------|-------------|----------------------------------------------------------------------------------------------------------|
| <u>✓</u> | <u> </u> | <u> </u> | 3. Leak-testing of sampling train after sample run |
| <u>✓</u> | <u> </u> | <u> </u> | 4. Preparation and addition of absorbing solutions to impingers |
| <u> </u> | <u> </u> | <u>OK</u> | 5. Isokinetic sampling |
| <u>✓</u> | <u> </u> | <u> </u> | 6. Purging of the sampling train and rinsing of the impingers and connecting tubes to recover the sample |
| <u>✓</u> | <u> </u> | <u> </u> | 7. Recording of pertinent process condition during sample collection |
| <u> </u> | <u> </u> | <u>*</u> | 8. Maintaining the probe at a given temperature |

Postsampling

- | | | | |
|-------------|-------------|-------------|----------------------------------------------------------------|
| <u>**</u> | <u> </u> | <u> </u> | 9. Control sample analysis - accuracy and precision |
| <u> </u> | <u> </u> | <u>OK</u> | 10. Sample aliquotting techniques |
| <u> </u> | <u> </u> | <u>OK</u> | 11. Titration technique, particularly endpoint precision |
| <u>✓</u> | <u> </u> | <u> </u> | 12. Use of detection blanks in correcting field sample results |
| <u> </u> | <u> </u> | <u>OK</u> | 13. Calculation procedure/check |
| <u> </u> | <u> </u> | <u>OK</u> | 14. Calibration checks |
| <u> </u> | <u> </u> | <u>OK</u> | 15. Standard barium perchlorate solution |

General Comments

** probe shorted out during run 3 but sampling was allowed to be continued*

*** first set of audit samples were acceptable*

Figure 8.1 Method 8 checklist to be used by auditors.

Table 8.1. ACTIVITY MATRIX FOR AUDITING PROCEDURE

Audit	Acceptance limits	Frequency and method of measurement	Action if requirements are not met
Analytical phase of Method 8 using aqueous ammonium sulfate	The measured value of the pretest audit sample should be less than the 90th percentile value, 7%	Once during every enforcement source test, measure reference samples and compare with their true values	Review operating technique
Data-processing errors	The original and check calculations should agree within round-off error	Once during every enforcement source test, perform independent calculations, starting with recorded data	Check and correct all data for the source test
Systems audit--observance of technique	Operation technique described in this section of the Handbook	Once during every enforcement test until experience gained; then every fourth test. Observation of technique, assisted by audit checklist, Fig. 8.1	Explain to team its deviations from recommended techniques, and note on Fig. 8.1

9.0 RECOMMENDED STANDARDS FOR ESTABLISHING TRACEABILITY

To achieve data of desired quality, two considerations are necessary: (1) the measurement process must be in a state of statistical control at the time of the measurement, and (2) the systematic errors, when combined with the random variation (errors of measurement), must result in a small uncertainty.

To ensure good quality data, it is necessary to perform quality control checks and independent audits of the measurement process; to document these checks and audits by recording the results on quality control charts, 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 to be primary. Two primary standards recommended for establishing traceability are:

1. Dry gas meter should be calibrated against a wet test meter that has been verified by an independent liquid displacement meter, as described in Section 2.1.1.

2. Barium perchlorate should be standardized against sulfuric acid that has already been standardized with primary grade potassium acid phthalate. Then standardized barium perchlorate should be validated with an aqueous ammonium sulfate to make the titrant solution traceable to two primary standard grade reagents.

10.0 REFERENCE METHOD*

METHOD 8—DETERMINATION OF SULFURIC ACID MIST AND SULFUR DIOXIDE EMISSIONS FROM STATIONARY SOURCES

1. Principle and Applicability

1.1 Principle A gas sample is extracted isokinetically from the stack. The sulfuric acid mist (including sulfur trioxide) and the sulfur dioxide are separated, and both fractions are measured separately by the barium-thorium titration method.

1.2 Applicability. This method is applicable for the determination of sulfuric acid mist (including sulfur trioxide, and in the absence of other particulate matter) and sulfur dioxide emissions from stationary sources. Collaborative tests have shown that the minimum detectable limits of the method are 0.05 milligrams/cubic meter (0.03 $\times 10^{-3}$ pounds/cubic foot) for sulfur trioxide and 1.2 mg/m³ (0.74 $\times 10^{-3}$ lb/ft³) for sulfur dioxide. No upper limits have been established. Based on theoretical calculations for 200 milliliters of 3 percent hydrogen peroxide solution, the upper concentration limit for sulfur dioxide in a 1.0 m³ (35.3 ft³) gas sample is about 12,500 mg/m³ (7.7 $\times 10^{-4}$ lb/ft³). The upper limit can be extended by increasing the quantity of peroxide solution in the impingers.

Possible interfering agents of this method are fluorides, free ammonia, and dimethyl aniline. If any of these interfering agents are present (this can be determined by knowledge of the process), alternative methods, subject to the approval of the Administrator, are required.

Filterable particulate matter may be determined along with SO₃ and SO₂ (subject to the approval of the Administrator), however, the procedure used for particulate matter must be consistent with the specifications and procedures given in Method 5.

2. Apparatus

2.1 Sampling A schematic of the sampling train used in this method is shown in Figure 8-1; it is similar to the Method 5 train except that the filter position is different and the filter holder does not have to be heated. Commercial models of this train are available. For those who desire to build their own, however, complete construction details are described in APTD-4581. Changes from the APTD-4581 document and allowable modifications to Figure 8-1 are discussed in the following subsections.

The operating and maintenance procedures for the sampling train are described in APTD-0576. Since correct usage is important in obtaining valid results, all users should read the APTD-0576 document and adopt the operating and maintenance procedures outlined in it, unless otherwise specified herein. Further details and guidelines on operation and maintenance are given in Method 5 and should be read and followed whenever they are applicable.

2.1.1 Probe Nozzle. Same as Method 5, Section 2.1.1.

2.1.2 Probe Liner. Borosilicate or quartz glass, with a heating system to prevent visible condensation during sampling. Do not use metal probe liners.

2.1.3 Pitot Tube. Same as Method 5, Section 2.1.3.

2.1.4 Differential Pressure Gauge. Same as Method 5, Section 2.1.4.

2.1.5 Filter Holder. Borosilicate glass, with a glass frit filter support and a silicone rubber gasket. Other gasket materials, e.g., Teflon or Viton, may be used subject to the approval of the Administrator. The holder design shall provide a positive seal against leakage from the outside or around the filter. The filter holder shall be placed between the first and second impingers. Note: Do not heat the filter holder.

2.1.6 Impingers—Four, as shown in Figure 8-1. The first and third shall be of the Greenburg-Smith design with standard tips. The second and fourth shall be of the Greenburg-Smith design, modified by replacing the insert with an approximately 13 millimeter (0.5 in.) ID glass tube, having an unobstructed tip located 13 mm (0.5 in.) from the bottom of the flask. Similar collection systems, which have been approved by the Administrator, may be used.

2.1.7 Metering System. Same as Method 5, Section 2.1.8.

2.1.8 Barometer. Same as Method 5, Section 2.1.9.

2.1.9 Gas Density Determination Equipment. Same as Method 5, Section 2.1.10.

2.1.10 Temperature Gauge. Thermometer, or equivalent, to measure the temperature of the gas leaving the impinger train to within 1° C (2° F).

2.2 Sample Recovery.

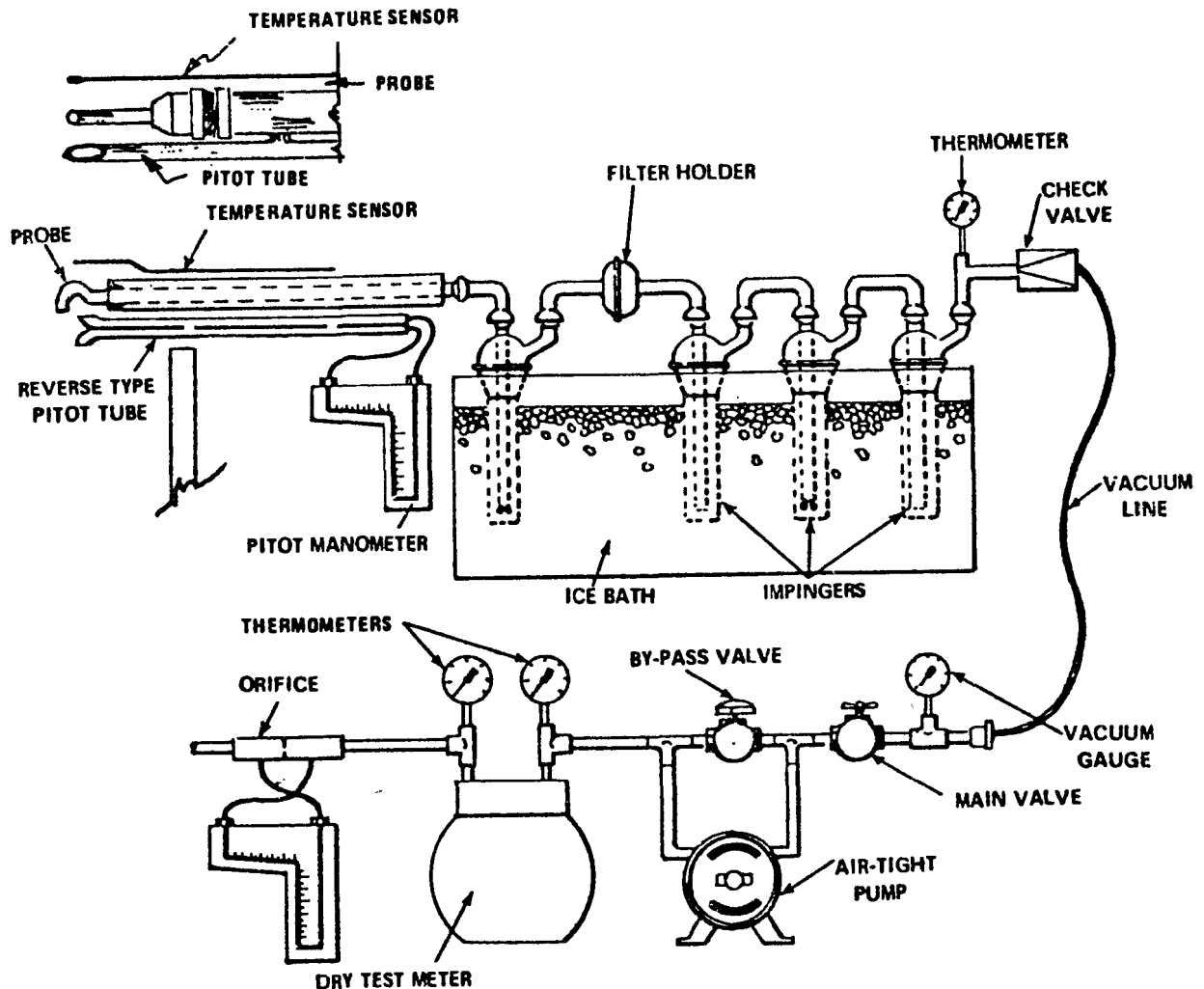


Figure 8-1. Sulfuric acid mist sampling train.

- Figure 8-2. Field data.**

NOTE.—If moisture content is to be determined by impinger analysis, weigh each of the first three impingers (plus absorbing solution) to the nearest 0.5 g and record these weights. The weight of the silica gel (or silica gel plus container) must also be determined to the nearest 0.5 g and recorded.

4.1.4 Pretest Leak-Check Procedure. Follow the basic procedure outlined in Method 5, Section 4.1.4.1, noting that the probe heater shall be adjusted to the minimum temperature required to prevent condensation, and also that verbiage such as, "... plugging the inlet to the filter holder ..." shall be replaced by, "... plugging the inlet to the first impinger ...". The pretest leak-check is optional.

4.1.5 Train Operation. Follow the basic procedures outlined in Method 5, Section 4.1.5, in conjunction with the following special instructions. Data shall be recorded on a sheet similar to the one in Figure 8-2. The sampling rate shall not exceed 0.030 m³/min (1.0 cfm) during the run. Periodically during the test, observe the connecting line between the probe and first impinger for signs of condensation. If it does occur, adjust the probe heater setting upward to the minimum temperature required to prevent condensation. If component changes become necessary during a run, a leak-check shall be done immediately before each change, according to the procedure outlined in Section 4.1.4.2 of Method 5 (with appropriate modifications; as mentioned in Section 4.1.4 of this method); record all leak rates. If the leakage rate(s) exceed the specified rate, the tester shall either void the run or shall plan to correct the sample volume as outlined in Section 6.3 of Method 5. Immediately after component changes, leak-checks are optional. If these leak-checks are done, the procedure outlined in Section 4.1.4.1 of Method 5 (with appropriate modifications) shall be used.

After turning off the pump and recording the final readings at the conclusion of each run, remove the probe from the stack. Conduct a post-test (mandatory) leak-check as in Section 4.1.4.3 of Method 5 (with appropriate modification) and record the leak rate. If the post-test leakage rate exceeds the specified acceptable rate, the tester shall either correct the sample volume, as outlined in Section 6.3 of Method 5, or shall void the run.

Drain the ice bath and, with the probe disconnected, purge the remaining part of the train, by drawing clean ambient air through the system for 15 minutes at the average flow rate used for sampling.

NOTE.—Clean ambient air can be provided by passing air through a charcoal filter. As the option of the tester, ambient air (without cleaning) may be used.

4.1.6 Calculation of Percent Isokinetic. Follow the procedure outlined in Method 5, Section 4.1.6.

4.2 Sample Recovery.

4.2.1 Container No. 1. If a moisture content analysis is to be done, weigh the first impinger plus contents to the nearest 0.5 g and record this weight.

Transfer the contents of the first impinger to a 250-ml graduated cylinder. Rinse the probe, first impinger, all connecting glassware before the filter, and the front half of the filter holder with 80 percent isopropanol. Add the rinse solution to the cylinder. Dilute to 250 ml with 80 percent isopropanol. Add the filter to the solution, mix, and transfer to the storage container. Protect the solution against evaporation. Mark the level of liquid on the container and identify the sample container.

4.2.2 Container No. 2. If a moisture content analysis is to be done, weigh the second and third impingers (plus contents) to the nearest 0.5 g and record these weights. Also, weigh the spent silica gel (or silica gel plus impinger) to the nearest 0.5 g.

Transfer the solutions from the second and third impingers to a 1000-ml graduated cylinder. Rinse all connecting glassware (including back half of filter holder) between the filter and silica gel impinger with deionized, distilled water, and add this rinse water to the cylinder. Dilute to a volume of 1000 ml with deionized, distilled water. Transfer the solution to a storage container. Mark the level of liquid on the container. Seal and identify the sample container.

4.3 Analysis.

Note the level of liquid in containers 1 and 2, and confirm whether or not any sample was lost during shipment; note this on the analytical data sheet. If a noticeable amount of leakage has occurred, either void the sample or use methods, subject to the approval of the Administrator, to correct the final results.

4.3.1 Container No. 1. Shake the container holding the isopropanol solution and the filter. If the filter breaks up, allow the fragments to settle for a few minutes before removing a sample. Pipette a 100-ml aliquot of this solution into a 250-ml Erlenmeyer flask, add 2 to 4 drops of thion indicator, and titrate to a pink endpoint using 0.0100 N barium perchlorate. Repeat the titration with a second aliquot of sample and average the titration values. Replicate titrations must agree within 1 percent or 0.2 ml, whichever is greater.

4.3.2 Container No. 2. Thoroughly mix the solution in the container holding the contents of the second and third impingers. Pipette a 10-ml aliquot of sample into a 250-ml Erlenmeyer flask. Add ml of isopropanol, 2 to 4 drops of thion indicator, and titrate to a pink endpoint

using 0.0100 N barium perchlorate. Repeat the titration with a second aliquot of sample and average the titration values. Replicate titrations must agree within 1 percent or 0.2 ml, whichever is greater.

4.3.3 Blanks. Prepare blanks by adding 2 to 4 drops of thion indicator to 100 ml of 80 percent isopropanol. Titrate the blanks in the same manner as the samples.

5. Calibration

5.1 Calibrate equipment using the procedures specified in the following sections of Method 5: Section 5.3 (metering system); Section 5.5 (temperature gauges); Section 5.7 (barometer). Note that the recommended leak-check of the metering system, described in Section 5.6 of Method 5, also applies to this method.

5.2 Standardize the barium perchlorate solution with 25 ml of standard sulfuric acid, to which 100 ml of 100 percent isopropanol has been added.

6. Calculations

NOTE.—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.

A_s = Cross-sectional area of nozzle, m² (ft²).

B_m = Water vapor in the gas stream, proportion by volume.

CH_3SO_3 = Sulfuric acid (including SO_3) concentration, g/dscm (lb/dscf).

CSO_2 = Sulfur dioxide concentration, g/dscm (lb/dscf).

I = Percent of isokinetic sampling.

N = Normality of barium perchlorate titrant, g equivalents/liter.

P_{bar} = Barometric pressure at the sampling site, mm Hg (in. Hg).

P_s = Absolute stack gas pressure, mm Hg (in. Hg).

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

T_m = Average absolute dry gas meter temperature (see Figure 8-2), °K (°R).

T_s = Average absolute stack gas temperature (see Figure 8-2), °K (°R).

T_{std} = Standard absolute temperature, 293° K (32° R).

V_s = Volume of sample aliquot titrated, 100 ml for H_2SO_4 and 10 ml for SO_3 .

V_{li} = Total volume of liquid collected in impingers and silica gel, ml.

V_m = Volume of gas sample as measured by dry gas meter, dcm (dcf).

$V_m(std)$ = Volume of gas sample measured by the dry gas meter corrected to standard conditions, dcm (dscf).

v_s = Average stack gas velocity, calculated by Method 2, Equation 2-9, using data obtained from Method 8, m/sec (ft/sec).

V_{soln} = Total volume of solution in which the sulfuric acid or sulfur dioxide sample is contained, 250 ml or 1,000 ml, respectively.

V_{tr} = Volume of barium perchlorate titrant used for the sample, ml.

V_{tr} = Volume of barium perchlorate titrant used for the blank, ml.

Y = Dry gas meter calibration factor.

ΔH = Average pressure drop across orifice meter, mm (in.) H₂O.

θ = Total sampling time, min.

13.6 = Specific gravity of mercury.

60 = sec/min.

100 = Conversion to percent.

6.2 Average dry gas meter temperature and average orifice pressure drop. See data sheet (Figure 8-2).

6.3 Dry Gas Volume. Correct the sample volume measured by the dry gas meter to standard conditions (20° C and 760 mm Hg or 68° F and 29.92 in. Hg) by using Equation 8-1.

$$V_m(std) = V_m Y \left(\frac{T_{std}}{T_m} \right) \frac{P_{bar} + \left(\frac{\Delta H}{13.6} \right)}{P_{std}} \\ = K_1 V_m Y \frac{P_{bar} + (\Delta H/13.6)}{T_m} \quad \text{Equation 8-1}$$

where:
 K_1 = 0.3858 °K/mm Hg for metric units.

= 17.64 °R/in. Hg for English units.

NOTE.—If the leak rate observed during any mandatory leak-checks exceeds the specified acceptable rate, the tester shall either correct the value of V_m in Equation 8-1 (as described in Section 6.3 of Method 5), or shall invalidate the test run.

6.4 Volume of Water Vapor and Moisture Content. Calculate the volume of water vapor using Equation 8-2 of Method 5; the weight of water collected in the impingers and silica gel can be directly converted to milliliters (the specific gravity of water is 1 g/ml). Cal-

culate the moisture content of the stack gas, using Equation 5-3 of Method 5. The "Note" in Section 6.5 of Method 5 also applies to this method. Note that if the effluent gas stream can be considered dry, the volume of water vapor and moisture content need not be calculated.

6.5 Sulfuric acid mist (including SO_3) concentration.

$$CH_3SO_3 = K_2 \frac{N(V_i - V_{li}) \left(\frac{V_{soln}}{V_s} \right)}{V_m(std)} \quad \text{Equation 8-2}$$

where:
 K_2 = 0.04904 g/milliequivalent for metric units.

= 1.081 × 10⁻⁴ lb/meq for English units.

6.6 Sulfur dioxide concentration.

$$CSO_2 = K_3 \frac{N(V_i - V_{li}) \left(\frac{V_{soln}}{V_s} \right)}{V_m(std)} \quad \text{Equation 8-3}$$

where:
 K_3 = 0.03203 g/meq for metric units.

= 7.061 × 10⁻⁴ lb/meq for English units.

6.7 Isokinetic Variation.

6.7.1 Calculation from raw data.

$$I = \frac{100 T_s [K_4 V_{li} + (V_m/T_m) P_{bar} + \Delta H/13.6]}{60 \theta v_s P_s A_s} \quad \text{Equation 8-4}$$

where:
 K_4 = 0.003444 mm Hg·m³/ml·°K for metric units.

= 0.002876 in. Hg·ft³/ml·°R for English units.

6.7.2 Calculation from intermediate values.

$$I = \frac{T_s V_m(std) P_{std} 100}{T_{std} v_s \theta A_s P_s 60 (1 - B_m)} \\ = K_5 \frac{T_s V_m(std)}{P_s v_s \theta (1 - B_m)} \quad \text{Equation 8-5}$$

where:
 K_5 = 4.330 for metric units.

= 0.09450 for English units.

6.8 Acceptable Results. If 90 percent ≤ I ≤ 110 percent, the results are acceptable. If the results are low in comparison to the standards and I is beyond the acceptable range, the Administrator may opt to accept the results. Use Citation 4 in the Bibliography of Method 5 to make judgments. Otherwise, reject the results and repeat the test.

7. Bibliography

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Amendment to Reference Method 8; Correction*

In Method 8 of Appendix A, Sections 1.2, 2.3.2, 4.1.4, 4.2.1, 4.3.2, 6.1, and 6.7.1 are amended as follows:

1. In Section 1.2, the phrase "U.S. EPA," is inserted in the fifth line of the second paragraph between the words "Administrator," and "are." Also, delete the third paragraph and insert the following:

Filterable particulate matter may be determined along with SO₂ and SO₃ (subject to the approval of the Administrator) by inserting a heated glass fiber filter between the probe and isopropanol impinger (see Section 2.1 of Method 6). If this option is chosen, particulate analysis is gravimetric only; H₂SO₄ acid mist is not determined separately.

2. In Section 2.3.2, the word "Burette" is corrected to read "Burette."

3. In Section 4.1.4, the stars " * * *" are corrected to read as periods " . . . ".

4. In Section 4.2.1, the word "het" on the eighth line of the second paragraph is corrected to read "the."

5. In Section 4.3.2, the number "40" is inserted in the fourth line between the words "Add" and "ml."

6. In Section 6.1, Nomenclature, the following are corrected to read as shown with subscripts "C_{H2SO4}, C_{SO2}, P_{bar}, P_{std}, T_{std}, V_{m(std)}, and V_{soin}."

7. In Section 6.7.1, Equation 8-4 is corrected to read as follows:

$$I = \frac{100 T_s [K_s V_{1c} + (V_m V / T_m) (P_{bar} + \Delta H / 13.6)]}{60 \theta V_s P_s A_n}$$

(Secs. 111, 114, 301(a), Clean Air Act as amended (42 U.S.C. 7411, 7414, 7601).)

[FR Doc. 78-7686 Filed 3-22-78; 8:45 am]

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 M8-1.2 indicates that the form is Figure 1.2 in Section 3.7.1 of the Method 8 Handbook. Future revisions of these forms, if any, can be documented by 1.2A, 1.2B, etc. Sixteen 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
2.3A and 2.3B	Meter Box Calibration Data and Calculation Form (English and metric units)
2.4A and 2.4B	Posttest Meter Calibration Data Form (English and metric units)
2.5 (MH)	Pretest Sampling Checks
2.6	Nozzle Calibration Form
3.1 (MH)	Pretest Preparations
4.1	Method 8 Field Data Form
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	Method 8 Analytical Data Form
5.3	Control Sample Analytical Data Form
5.4 (MH)	Posttest Operations

<u>Form</u>	<u>Title</u>
6.1A and 6.1B	Sulfuric Acid Mist Calculation Form (English and metric units)
6.2A and 6.2B	Sulfur Dioxide Calculation Form (English and metric units)
8.1	Method 8 Checklist to be Used by Auditors

PROCUREMENT LOG

Item description	Qty.	Purchase order number	Vendor	Date		Cost	Dispo- sition	Comments
				Ord.	Rec.			

METER BOX CALIBRATION DATA AND CALCULATION FORM
(English units)

Date _____

Meter box number _____

Barometric pressure, P_b = _____ in. Hg.

Calibrated by _____

Orifice manometer setting (ΔH), in. H ₂ O	Wet test meter (v_w), ft ³	Gas volume	Temperature ^a			Time (Θ), min	Y_i	$\Delta H@_i$
		Dry gas meter (V_d), ft ³	Wet test meter (t_w), °F	Dry gas meter				
				Inlet (t_{d_i}), °F	Outlet (t_{d_o}), °F	Average (t_d), °F		
0.5	5							
1.0	5							
1.5	10							
2.0	10							
3.0	10							
4.0	10							
Average								

ΔH	$\frac{\Delta H}{13.6}$	$Y_i = \frac{V_w P_b (t_d + 460)}{V_d (P_b + \frac{\Delta H}{13.6}) (t_w + 460)}$	$\Delta H @_i = \frac{0.0317 \Delta H}{P_b (t_d + 460)} \left[\frac{(t_w + 460) \theta}{V_w} \right]^2$
0.5	0.0368		
1.0	0.0737		
1.5	0.110		
2.0	0.147		
3.0	0.221		
4.0	0.294		

^a If there is only one thermometer on the dry gas meter, record the temperature under t_d .

METER BOX CALIBRATION DATA AND CALCULATION FORM

Nomenclature:

V_w = Gas volume passing through the wet test meter, ft^3 .

V_d = Gas volume passing through the dry test meter, ft^3 .

t_w = Temperature of the gas in the wet test meter, $^{\circ}\text{F}$.

t_{d_i} = Temperature of the inlet gas of the dry test meter, $^{\circ}\text{F}$.

t_{d_o} = Temperature of the outlet gas of the dry test meter, $^{\circ}\text{F}$.

t_d = Average temperature of the gas in the dry test meter, obtained by the average t_{d_i} and t_{d_o} , $^{\circ}\text{F}$.

ΔH = Pressure differential across orifice, in. H_2O .

Y_i = Ratio of accuracy of wet test meter to dry test meter for each run. Tolerance $Y_i = Y \pm 0.02 Y$.

Y = Average ratio of accuracy of wet test meter to dry test meter for all six runs.
Tolerance $Y = Y \pm 0.01 Y$.

$\Delta H@_i$ = Orifice pressure differential at each flow rate that gives $0.75 \text{ ft}^3/\text{min}$ of air at standard conditions for each calibration run, in. H_2O . Tolerance = $\Delta H@ \pm 0.15$ (recommended).

$\Delta H@$ = Average orifice pressure differential that gives $0.75 \text{ ft}^3/\text{min}$ of air at standard conditions for all six runs, in. H_2O . Tolerance = 1.84 ± 0.25 (recommended).

Θ = Time for each calibration run, min.

P_b = Barometric pressure, in. Hg.

METER BOX CALIBRATION DATA AND CALCULATION FORM
(metric units)

Date _____

Meter box number _____

Barometric pressure, P_b = _____ mm Hg.

Calibrated by _____

Orifice manometer setting (ΔH), mm H ₂ O	wet test meter (v_w), m ³	Gas volume	Temperature ^a			Time (Θ), min	Y_i	$\Delta H@_i$	
		dry gas meter (V_d), m ³	Wet test meter (t_w), °C	Dry gas meter					
				Inlet (t_{d_i}), °C	Outlet (t_{d_o}), °C				Average ^a (t_d), °C
10	0.15								
25	0.15								
40	0.30								
50	0.30								
75	0.30								
100	0.30								
Average									

ΔH	$\frac{\Delta H}{13.6}$	$Y_1 = \frac{V_w P_b (t_d + 273)}{V_d (P_b + \frac{\Delta H}{13.6}) (t_w + 273)}$	$\Delta H@_1 = \frac{0.00117 \Delta H}{P_b (t_d + 273)} \left[\frac{(t_w + 273) \Theta}{V_w} \right]^2$
10	0.7		
25	1.8		
40	2.94		
50	3.68		
75	5.51		
100	7.35		

^a If there is only one thermometer on the dry gas meter, record it under t_d .

METER BOX CALIBRATION DATA AND CALCULATION FORM

Nomenclature:

V_w = Gas volume passing through the wet test meter, m^3 .

V_d = Gas volume passing through the dry test meter, m^3 .

t_w = Temperature of the gas in the wet test meter, $^{\circ}C$.

t_{d_i} = Temperature of the inlet gas of the dry test meter, $^{\circ}C$.

t_{d_o} = Temperature of the outlet gas of the dry test meter, $^{\circ}C$.

t_d = Average temperature of the gas in the dry test meter, obtained by the average of t_{d_i} and t_{d_o} , $^{\circ}C$.

Θ = Time of calibration run, min.

ΔH = Pressure differential across orifice, mm H_2O .

Y_i = Ratio of accuracy of wet test meter to dry test meter for each run. Tolerance $Y_i = Y \pm 0.02 Y$.

Y = Average ratio of accuracy of wet test meter to dry test meter for all six runs.
Tolerance $Y = Y \pm 0.01 Y$.

$\Delta H\Theta_i$ = Orifice pressure differential that gives $0.021 m^3$ of air at standard conditions for each calibration run, mm H_2O . Tolerance $\Delta H\Theta_i = \Delta H\Theta \pm 3.8 mm H_2O$ (recommended).

$\Delta H\Theta$ = Average orifice pressure differential that gives $0.021 m^3$ of air at standard conditions for all six runs, mm H_2O . Tolerance $\Delta H\Theta = 46.74 \pm 6.3 mm H_2O$ (recommended).

P_b = Barometric pressure, mm Hg.

POSTTEST METER CALIBRATION DATA FORM (English units)

Test numbers _____

Date _____

Meter box number _____

Plant _____

Barometric pressure, P_b = _____ in. Hg

Dry gas meter number _____

Pretest Y _____

Orifice manometer setting, (ΔH), in H_2O	Gas volume wet test meter (V_w), ft^3	Gas volume dry gas meter (V_d), ft^3	Temperature			Time (Θ), min	Vacuum setting, in. Hg	Y_i	$Y_i =$
			Wet test meter (t_w), $^{\circ}F$	Dry gas meter					$\frac{V_w P_b (t_d + 460)}{V_d P_b + \frac{\Delta H}{13.6} (t_w + 460)}$
				Inlet (t_{d_i}), $^{\circ}F$	Outlet (t_{d_o}), $^{\circ}F$				
	10								
	10								
	10								
									$Y =$

^a If there is only one thermometer on the dry gas meter, record the temperature under t_d .

where

V_w = Gas volume passing through the wet test meter, ft^3 .

V_d = Gas volume passing through the dry test meter, ft^3 .

t_w = Temperature of the gas in the wet test meter, $^{\circ}F$.

t_{d_i} = Temperature of the inlet gas of the dry test meter, $^{\circ}F$.

t_{d_o} = Temperature of the outlet gas of the dry test meter, $^{\circ}F$.

t_d = Average temperature of the gas in the dry test meter, obtained by the average of t_{d_i} and t_{d_o} , $^{\circ}F$.

ΔH = Pressure differential across orifice, in H_2O .

Y_i = Ratio of accuracy of wet test meter to dry test meter for each run.

Y = Average ratio of accuracy of wet test meter to dry test meter for all three runs.

Tolerance = Pretest Y $\pm 0.05Y$

P_b = Barometric pressure, in. Hg.

R = Time of calibration run, min.

POSTTEST METER CALIBRATION DATA FORM (metric units)

Test numbers _____

Date _____

Meter box number _____

Plant _____

Barometric pressure, $P_b =$ _____ mm Hg

Dry gas meter number _____

Pretest Y _____

Orifice manometer setting, (ΔH), mm H ₂ O	Gas volume wet test meter (V _w), m ³	Gas volume dry gas meter (V _d), m ³	Temperature			Time (Θ), min	Vacuum setting, mm Hg	Y _i	Y _i =
			Wet test meter (t _w), °C	Dry gas meter					
				Inlet (t _{d_i}), °C	Outlet (t _{d_o}), °C				Average (t _d) _a , °C
									$\frac{V_w P_b (t_d + 273)}{V_d P_b + \frac{\Delta H}{13.6} (t_w + 273)}$
									Y=

^a If there is only one thermometer on the dry gas meter, record the temperature under t_d .

where

V_w = Gas volume passing through the wet test meter, m^3 .

$$V_d = \text{Gas volume passing through the dry test meter, m}^3.$$

t_w = Temperature of the gas in the wet test meter, °C.

t_{d_1} = Temperature of the inlet gas of the dry test meter, °C.

t_{d_o} = Temperature of the outlet gas of the dry test meter, °C.

t_d = Average temperature of the gas in the dry test meter, obtained by the average of t_{d_1} and t_{d_0} , °C.

$$\Delta H = \text{Pressure differential across orifice, mm H}_2\text{O.}$$

Y_i = Ratio of accuracy of wet test meter to dry test meter for each run.

Y = Average ratio of accuracy of wet test meter to dry test meter for all three runs.

$$\text{Tolerance} = \text{Pretest } Y + 0.05Y$$

P_h = Barometric pressure, mm Hg.

Θ = Time of calibration run, min.

NOZZLE CALIBRATION

Date _____

Calibrated by _____

Nozzle identification number	$D_{1'} \text{ (in.)}$	$D_{2'} \text{ (in.)}$	$D_{3'} \text{ (in.)}$	$\Delta D, \text{ (in.)}$	D_{avg}

where:

D_{1,2,3}' = nozzle diameter measured on a different diameter, mm (in.).
Tolerance = measure within 0.25 mm (0.001 in.).

ΔD = maximum difference in any two measurements, mm (in.).
Tolerance = 0.1 mm (0.004 in.).

$$D_{\text{avg}} = \text{average of } D_1, D_2, D_3.$$

METHOD 8 FIELD TEST DATA FORM

Plant _____

Location

Operator

Date _____

Run number

Sample box number

Meter box number

Meter ΔH°

Meter calibration Y _____

Pitot tube CP

Probe length _____

Probe liner material

Probe heater setting

Ambient temperature

Barometric pressure

Assumed moisture

Static pressure

C factor

Reference ΔP _____Maximum ΔH

Sheet _____ of _____

Nozzle identification number _____

Nozzle diameter _____

Final leak rate _____

Vacuum during leak check _____

Remarks:

[illegible]

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
	H ₂ SO ₄	SO ₂			
1					
2					
3					
Blanks					

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
	H ₂ SO ₄	SO ₂			
1					
2					
3					
Blanks					

Remarks _____

Signature of lab sample trustee _____

METHOD 8 ANALYTICAL DATA FORM

Plant _____ Date _____

Sample location _____ Analyst _____

Volume and normality of
barium perchlorate

1. _____ ml $\text{Ba}(\text{ClO}_4)_2$
2. _____ ml $\text{Ba}(\text{ClO}_4)_2$ N = _____
Blank _____ ml $\text{Ba}(\text{ClO}_4)_2$

Sulfur Trioxide Analysis

V_{soln} - Total volume of solution in which the
sulfuric acid sample is contained, ml

V_a - Volume of sample aliquot, ml

V_t - Volume of barium perchlorate titrant used for sample, ml

1st titration
2nd titration
Average

V_{tb}^* - Volume of barium perchlorate titrant used for blank, ml

1st titration
2nd titration
Average

Run 1	Run 2	Run 3

$\frac{\text{1st titration}}{\text{2nd titration}} = 0.99 \text{ to } 1.01$ or $|\text{1st titration} - \text{2nd titration}| \leq 0.2 \text{ ml}$

Sulfur Dioxide Analysis

V_{soln} - Total volume of solution in which the
sulfur dioxide sample is contained, ml

V_a - Volume of sample aliquot, ml

V_t - Volume of barium perchlorate titrant used for sample, ml

1st titration
2nd titration
Average

V_{tb}^* - Volume of barium perchlorate titrant used for blank, ml

1st titration
2nd titration
Average

Run 1	Run 2	Run 3

$\frac{\text{1st titration}}{\text{2nd titration}} = 0.99 \text{ to } 1.01$ or $|\text{1st titration} - \text{2nd titration}| \leq 0.2 \text{ ml}$

Signature of analyst _____

Signature of reviewer or supervisor _____

* Volume of blank and sample titrated should be the same; otherwise a volume correction must be made.

CONTROL SAMPLE ANALYTICAL DATA FORM

Plant _____ Date analyzed _____

Analyst _____ $N_{\text{Ba}(\text{ClO}_4)_2}$ _____

Weight of ammonium sulfate is 1.3214 gram? _____

Dissolved in 2 l of distilled water? _____

Titration of blank _____ ml $\text{Ba}(\text{ClO}_4)_2$
(must be less than the 0.5 ml titrant)

Control Sample Number	Time of Analysis 24 h	Titrant volume, ml			
		1st	2nd	3rd	Ave.

(Two consecutive volumes must agree within 0.2 ml)

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

_____ ml \times _____ N = _____

(must agree within $\pm 5\%$, i.e., 0.233 to 0.268)

Does value agree? ☐ yes ☐ no

_____ Signature of analyst

_____ Signature of reviewer

Sulfuric Acid Mist (Including SO₃) Calculation Form
(English units)

Sample Volume

$V_m = \text{---} \text{ft}^3$, $T_m = \text{---} \text{ } ^\circ\text{R}$, $P_{\text{bar}} = \text{---} \text{ in. Hg}$
 $Y = \text{---}$, $\Delta H = \text{---} \text{ in. H}_2\text{O}$

Equation 6-1

$$V_{m_{\text{std}}} = 17.64 V_m Y \left[\frac{P_{\text{bar}} + (\Delta H/13.6)}{T_m} \right] = \text{---} \text{ft}^3$$

Sulfuric Acid Mist (Including SO₃) Concentrations

$N = \text{---} \text{ g-eg/l}$, $V_t = \text{---} \text{ ml}$, $V_{tb} = \text{---} \text{ ml}$
 $V_{\text{soln}} = \text{---} \text{ ml}$, $V_a = \text{---} \text{ ml}$, $V_{m_{\text{std}}} = \text{---} \text{ft}^3$

Equation 6-2

$$C_{\text{H}_2\text{SO}_4} = 1.081 \times 10^{-4} \left\{ \frac{N(V_t - V_{tb}) \left(\frac{V_{\text{soln}}}{V_a} \right)}{V_{m_{\text{std}}}} \right\} = \text{---} \times 10^{-4} \text{ lb/dscf}$$

Sulfuric Acid Mist (Including SO₃) Calculation Form
(metric units)

Sample Volume

$$V_m = \text{---} \text{ m}^3, T_m = \text{---} \text{ K}, P_{\text{bar}} = \text{---} \text{ mm Hg}$$

$$Y = \text{---}, \Delta H = \text{---} \text{ mm. H}_2\text{O}$$

Equation 6-1

$$V_{m_{\text{std}}} = 17.64 V_m Y \left[\frac{P_{\text{bar}} + (\Delta H/13.6)}{T_m} \right] = \text{---} \text{ m}^3$$

Sulfuric Acid Mist (Including SO₃) Concentrations

$$N = \text{---} \text{ g-eg/l}, V_t = \text{---} \text{ ml}, V_{\text{tb}} = \text{---} \text{ ml}$$

$$V_{\text{soln}} = \text{---} \text{ ml}, V_a = \text{---} \text{ ml}, V_{m_{\text{std}}} = \text{---} \text{ m}^3$$

Equation 6-2

$$C_{\text{H}_2\text{SO}_4} = 0.04904 \left[\frac{N(V_t - V_{\text{tb}}) \left(\frac{V_{\text{soln}}}{V_a} \right)}{V_{m_{\text{std}}}} \right] = \text{---} \text{ g/dscm}$$

Sulfur Dioxide Calculation Form
(English units)

Sample Volume

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

$$Y = \text{---}, \Delta H = \text{---} \text{ in. H}_2\text{O}$$

Equation 6-1

$$V_{m\text{std}} = 17.64 V_m Y \left[\frac{P_{\text{bar}} + (\Delta H/13.6)}{T_m} \right] = \text{---} \text{ ft}^3$$

Sulfuric Acid Mist (Including SO₃) Concentrations

$$N = \text{---} \text{ g-eg/l}, V_t = \text{---} \text{ ml}, V_{tb} = \text{---} \text{ ml}$$

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

Equation 6-2

$$C_{\text{SO}_2} = 7.061 \times 10^{-5} \left[\frac{N(V_t - V_{tb}) \left(\frac{V_{\text{soln}}}{V_a} \right)}{V_{m\text{std}}} \right] = \text{---} \times 10^{-4} \text{ lb/dscf}$$

Sulfur Dioxide Calculation Form
(metric units)

Sample Volume

$$V_m = \text{---} \text{ m}^3, T_m = \text{---} \text{ K}, P_{\text{bar}} = \text{---} \text{ mm Hg}$$

$$Y = \text{---}, \Delta H = \text{---} \text{ mm H}_2\text{O}$$

Equation 6-1

$$V_{m_{\text{std}}} = 0.3858 V_m Y \left[\frac{P_{\text{bar}} + (\Delta H/13.6)}{T_m} \right] = \text{---} \text{ m}^3$$

SO₂ Concentration

$$N = \text{---} \text{ g-eg/l}, V_t = \text{---} \text{ ml}, V_{tb} = \text{---} \text{ ml}$$

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

Equation 6-2

$$C_{\text{SO}_2} = 3.203 \times 10^{-2} \left[\frac{N(V_t - V_{tb}) \left(\frac{V_{\text{soln}}}{V_a} \right)}{V_{m_{\text{std}}}} \right] = \text{---} \text{ g/dscm}$$

Quality Assurance Handbood M8-6.2B.

METHOD 8 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 condition during sample collection
_____	_____	_____	8.	Maintaining the probe at a given temperature
Postsampling				
_____	_____	_____	9.	Control sample analysis - accuracy and precision
_____	_____	_____	10.	Sample aliquotting 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.	Standard barium perchlorate solution

General Comments

TECHNICAL REPORT DATA (Please read instructions on the reverse before completing)		
1. REPORT NO EPA-600/4-77-027b	2.	3. RECIPIENT'S ACCESSION NO.
4. TITLE AND SUBTITLE QUALITY ASSURANCE HANDBOOK FOR AIR POLLUTION MEASUREMENT SYSTEMS, VOLUME III - STATIONARY SOURCE SPECIFIC METHODS	5. REPORT DATE May 1979	
	6. PERFORMING ORGANIZATION CODE	
7. AUTHOR(S) Darryl J. von Lehmden, U.S. EPA, RTP, NC William G. DeWees, PEDCo-Environmental, Inc., Cin., OH Carl Nelson, PEDCo-Environmental, Inc., Cincinnati, OH	8. PERFORMING ORGANIZATION REPORT NO.	
9. PERFORMING ORGANIZATION NAME AND ADDRESS U.S. Environmental Protection Agency, Environmental Monitoring & Support Laboratory, RTP, NC 27711, and PEDCo-Environmental, Inc., Cincinnati, Ohio 45246	10. PROGRAM ELEMENT NO. 1AD 800	
	11. CONTRACT/GRANT NO 68-02-2725	
12. SPONSORING AGENCY NAME AND ADDRESS Environmental Monitoring & Support Laboratory, QAB Office of Research and Development U.S. Environmental Protection Agency Research Triangle Park, NC 27711	13. TYPE OF REPORT AND PERIOD COVERED	
	14. SPONSORING AGENCY CODE	
15. SUPPLEMENTARY NOTES The Handbook will be reproduced in the current format (3-ring binder) and maintained up-to-date by a document control system operated by EMSL/RTP. Distribution will be to personnel in EPA, and its contractors, state and selected		
16. ABSTRACT air pollution control agencies in foreign countries. This Handbook includes quality assurance guidelines on stationary source emission measurements. Regardless of the scope and magnitude of the stationary source emission measurement program, there are a number of common considerations pertinent to the production of quality data. These common parameters are discussed in Section 3.0 of Volume III and include quality assurance guidelines in the areas of: (1) planning the test program; (2) general factors in stationary source testing; (3) chain-of-custody procedure; and (4) traceability protocol for gases used for continuous source emission monitors. The remainder of Volume III contains pollutant-specific quality assurance guidelines. Initially Volume III includes guidelines for the following pollutant-specific measurement systems: Section 3.5 Method 6 - determination of sulfur dioxide emissions from stationary sources, Section 3.6 Method 7 - determination of nitrogen oxide emissions from stationary sources, and Section 3.7 Method 8 - determination of sulfuric acid mist and sulfur dioxide from stationary sources. Source testers and managers responsible for stationary source emission measurements will find Volume III useful in planning quality assurance.		
17. KEY WORDS AND DOCUMENT ANALYSIS		
a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Quality assurance, source testing, performance and system audits, chain-of-custody, traceability protocol, sulfur dioxide emission method, nitrogen oxide emission method, sulfuric acid mist emission method		
18. DISTRIBUTION STATEMENT RELEASE TO PUBLIC	19. SECURITY CLASS (This Report) Unclassified	21. NO. OF PAGES 404
	20. SECURITY CLASS (This page) Unclassified	22. PRICE