



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

**Sections 3.0.1, 3.0.2
3.0.3, 3.0.4,
3.5, 3.6, and
3.7**

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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 measurement studies. 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 programs 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. Performance 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 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. Equivalent Method for the Determination of Sulfur Dioxide in the Atmosphere (Fluorescence).

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.
5. Specific procedures to assess accuracy of Reference Methods used for SPNSS.
6. Specific procedures to assess accuracy of Reference Methods used for NESHAP.
7. Interpretation and application of CEM precision and accuracy data.

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 9 - Visual Determination of the Opacity of Emissions from Stationary Sources.

Method 10 - Determination of Carbon Monoxide Emissions from Stationary Sources.

Methods 13A and B - 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.

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Research and Development



Section 3.0

General Aspects of Quality Assurance for Stationary Source Emission Testing Programs

Outline

Section	Documentation	Number of Pages
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2. General Factors Involved In Stationary Source Testing	3.0.2	2
3. Chain-of-Custody Procedure for Source Sampling	3.0.3	7
4. Traceability Protocol for Establishing True Concentra- tions of Gases Used for Cali- brations and Audits of Con- tinuous Source Emission Mon- itors (Protocol No. 1)	3.0.4	3

Summary

Section 3.0 provides guidelines for quality assurance in performance of emission testing of stationary sources by federally prescribed procedures. The guidelines may be applied to all categories of sources commonly monitored.

The purpose of emission testing (also called "source sampling" or "stack sampling") is to extract from the stack or duct a sample that is representative of emissions from that source during a time period in which the process is under a desired operating condition. The sampling methods prescribed by Federal agencies are for specific substances and types of sources, and are designed to provide representative and reliable data. Since the Federal New Source Performance Standards are promulgated from data obtained by these methods, adherence to these standard procedures for sampling and analysis is essential.

Although personnel engaged in emission testing learn to perform these

tests routinely, some of the procedures may not be readily understood by laymen who are involved in hearings or litigations concerning an emission source. When an enforcement agency must rely on results of emissions testing, the test results may be subjected to the requirements of legal rules of evidence. Emissions monitoring personnel, therefore, should not only follow standard testing procedures but should also document each step of the test by maintaining complete and accurate records.

The following guidelines for assurance of high quality emissions test data are presented in four major phases: planning the test program, performing the test, chain-of-custody procedure, and establishing the traceability of calibration gases. Specific method descriptions are given in subsequent sections of this Handbook.

General Quality Assurance Guidelines

1.0 Planning the Test Program

Although a detailed and specific plan will be developed for each test program, the factors discussed here apply to all cases and provide a basis for formulation of a test plan.

The reason for conducting the emission test must first be carefully determined. Data may be required to check for compliance with a specific regulation, to measure process stream losses, or to obtain engineering data for designing control equipment. The guidelines presented in this Handbook are designed to provide more accurate data regardless of the test purpose. The test methods discussed here are those used to determine compliance with U.S. EPA emission regulations. These methods can also be used in other applications, but caution must be exercised against overloading the equipment due to higher pollutant concentrations or introducing interferences.

For compliance testing, the first planning step is to determine the applicable emission control regulation. Since most control regulations designate specific process conditions to be monitored and recorded as part of a valid emission test, a thorough understanding of the regulation is a prerequisite to formulating the sampling plan. Monitoring personnel may become familiar with specific industry operations and the required test data through inspection manuals published by EPA.

1.1 Preliminary Plant Survey

The next step in developing the test program is a preliminary survey of the process and the test site. Except in the most routine cases, an on-site inspection or presurvey should be performed to determine process information, emission parameters, and locations of sampling points. The presurvey may be made by telephone, particularly when the monitoring personnel have had experience with the specific industry/process.

Considerable information concerning the process to be monitored may be gained in advance of the on-site survey by consulting a registration form or permit application pertaining to the plant operations. These forms provide valuable data on process throughput, emission factors, material balances, types and sizes of fans and motors, and similar items. From these data, one can

often estimate gas flow rates and compositions of effluents. For testing of new sources, the plant's construction permit may provide a guide to locations of test ports and scaffolding.

A further step in preparing for the on-site survey is to assemble the equipment that may be required to obtain preliminary data such as:

1. A 10°-to-650°C (50°-to-1200°F) dial thermometer, 30-cm (12-in.) stem.
2. Velocity meter (velometer, Pitot tube, or anemometer).
3. A 15-m (50-ft) tape measure.
4. Set of basic shop tools.
5. Polaroid type camera.
6. Gas absorption colorimetric indicator tubes for SO₂, CO, NO_x, HC, etc.
7. Survey data forms.
8. Safety equipment (hardhats, safety shoes, goggles, etc.).

1.2 Process Information

One plant employee should be designated as the personal contact for monitoring personnel. This person should understand the process thoroughly and must have authority to obtain information and to elicit the cooperation of other plant personnel. A member of the staff of the plant manager or the plant engineer is often an appropriate contact.

The on-site survey is greatly facilitated by use of a survey form that lists the process parameters. Figures 1.1 and 1.2 are example forms for use in the presurvey of combustion and incineration sources. These forms are general guides; in many cases, additional information will be available and should be noted for possible future use.

When possible, the normal operation of a process should be determined during the survey. If a process varies with time over a defined cycle, monitoring personnel should determine the variation in emission parameters during the cycle as a basis for deciding whether to sample during part of a cycle, during an entire cycle, or during several cycles. If the process involves steady-state operation, the level of operation to be sampled should be determined. The applicable control regulations may indicate the process operating conditions required for emissions tests. Most regulations require sampling at rated capacity. Any seasonal variations in

process conditions should be noted, as should variations in feed stream composition or control device operation.

1.2.1 Stack Information - The sampling site and the number of traverse points designated will affect the quality of the sample extracted. Site selection should be simple for new installations, since in most states one of the requirements for obtaining a permit to construct is the installation of an acceptable sampling site. For new and existing installations, acceptability of the sampling procedure is generally determined by the distances from the nearest upstream and downstream disturbances (obstruction or change in direction) to gas flow. The minimum requirements for an acceptable sampling procedure are in Method 1, and are summarized herein.

In addition to flow considerations, accessibility and safety are important. Clearance for the probe and sampling apparatus, availability of electricity, exposure to weather or excessive heat, presence of toxic or explosive gases, and other safety factors must be considered in selecting a site.

Detailed information is needed regarding the gas stream parameters at the sampling site, especially in the sampling of atypical processes. Figure 1.3 lists the stack data needed to determine the required probe lengths and any change in sampling equipment. Most of the data can be obtained or checked from plant blueprints or engineering drawings, material-balance calculations, process instrumentation readings, or from comparable data obtained for similar processes. When no data can be obtained from these or other sources, exit gas parameters may be determined by inserting a velocity probe (Pitot tube, anemometer, or velometer) and a thermometer into the duct at or near the test site to determine approximate velocity and temperature. Color-change-type gas indicator tubes and a squeeze bulb sampler can be used to determine approximate concentrations of a wide variety of gases, and are useful if estimates based on process parameters cannot be made. These can also be used for ambient air sampling to determine any potential employee exposure problems.

1.2.2 Location of Sampling Points - As mentioned earlier, emission tests

Type of Heat Exchanger

Primary

Standby

Coal fired

☐☐

Oil fired

☐☐

Gas fired

☐☐

If multiple fired, check appropriate boxes

Rated input capacity _____ Btu/h

Maximum operating rate _____ Btu/h

Rated steam output _____ lb/h @ _____ Btu/lb steam

Maximum steam output _____ lb/h @ _____ Btu/lb steam

Furnace volume, width _____ ft x depth _____ ft x height

Operating schedule _____ h/day _____ days/wk _____ wk/yr

Coal FiringType of firing ☐ Grate

Type _____

☐ Spreader stoker☐ Pulverized coal☐ Dry bottom☐ Wet Bottom☐ Cyclone

Fly ash reinjection

Yes

No

Soot blowing

Continuous

☐☐

Intermittent

☐☐

Time interval between blowing _____ min

Duration _____ min

Outside coal storage

☐ Yes☐ No

Maximum amount stored outside _____ tons

Outside storage sprayed

☐ Yes☐ No

Coal consumption

Range

Average

Ash

_____ % to _____ %

_____ %

Sulfur

_____ % to _____ %

_____ %

Btu/lb as fired

_____ to _____

Fuel consumption records kept

☐ Yes☐ No

For stoker system,

Coal size _____

For pulverized coal and cyclone system,

Firing method

☐ Front wall☐ Tangential☐ Front wall - rear wall☐ Other☐ All wall

Type _____

Oil Firing

Firing method

☐ Front wall☐ Tangential☐ Front wall - rear wall☐ Cyclone☐ All wall☐ Other

Type _____

Type of fuel

☐ No. 1☐ No. 4☐ No. 6☐ No. 2☐ No. 5☐ Other

Type _____

Figure 1.1. Example of a presurvey data form for fossil fuel-fired steam generators.

Facility name _____
 Facility address _____
 Name of plant contact _____
 Source code number _____
 Unit designation _____
 Design charge rate _____
 Actual charge rate _____
 Inspection date _____

A. Pre-entry Observations

Time _____

Stack plume (use EPA plume observation procedures)

Opacity regulation ☐ In compliance ☐ Not in compliance

Weight scales ☐ Operating ☐ Not operating

Trucks weighed and recorded before dump ☐ Yes ☐ No

Trucks weighed and recorded after dump ☐ Yes ☐ No

B. Control Equipment

1) Electrostatic precipitator

Section					
Primary current, A					
Primary voltage, V					
Secondary current, mA					
Secondary voltage, kV					
Spark rate, spk/min					

2) Scrubber

Module					
Liquid flow, gal/min					
Pressure across scrubber, in. H ₂ O					

3) Fabric filter

Compartment	
Pressure drop across fabric filter, in. H ₂ O	

Figure 1.2. Example of a presurvey data form for municipal incinerators.

Additional observations :

C. <u>Control Panel</u>		Time _____
Secondary chamber temperature	_____	°F
APC device entry temperature	_____	°F
Underfire air draft	_____	in. H ₂ O
Overfire air draft	_____	in. H ₂ O
O ₂ analyzer	_____ %	
CO ₂ analyzer	_____ %	
CO analyzer	_____ %	
Grate speed	_____	(indicate units)
Refuse measuring sensors	_____	(indicate units)
D. <u>Incinerator</u>		Time _____
Charge cranes	<input type="checkbox"/> Satisfactory	<input type="checkbox"/> Unsatisfactory
Furnace grates (if visible)	<input type="checkbox"/> Satisfactory	<input type="checkbox"/> Unsatisfactory
Residue removal system (including quenching)	<input type="checkbox"/> Satisfactory	<input type="checkbox"/> Unsatisfactory
E. <u>Records</u>		
Temperature charts (dated and filed by incineratory personnel)		
Secondary chamber	<input type="checkbox"/> Satisfactory	<input type="checkbox"/> Unsatisfactory
APC device entry gas	<input type="checkbox"/> Satisfactory	<input type="checkbox"/> Unsatisfactory
Hours of operation	_____	
Charging rate, T/h	_____	
Daily collection, T/day	_____	

Figure 1.2. (continued)

are based on the assumption that the sample obtained at a given point is representative of the concentration at that point. Therefore, a system in which concentrations are nonuniform with respect to the stack cross-sectional area will require more sampling points than will a system with uniform concentrations. Usually, gaseous concentrations are fairly uniform across a duct's cross section, and a single sampling point is sufficient. To obtain representative gas velocities and particulate concentrations, traversing of the duct cross-sectional area is required, as described in the Reference Methods 1 and 2.

Figure 1.4 can be used as a basis for determining the number of sampling points required for representative sampling of a given system for particulate and nonparticulate emissions. First, measure the distances (in duct diameters) from the sampling port to the nearest upstream and downstream disturbances, and determine the corresponding number of traverse points for each distance (Figure 1.4). Select

either the higher of the two numbers of traverse points or a greater even value. For round ducts, select a number that is a multiple of four, and place half of these points along each of two diameters that are at right angles to each other. The exact sample point locations for round ducts can then be determined by using the percentage of stack diameter from the duct's inside wall to the traverse point, as shown in Table 1.1. Duct diameters should be checked along two directions. If the two measurements are similar, use an average value. If they are not similar, use each separate diameter in determining point locations. Figure 1.5 may be used for calculating the distances to each traverse point by multiplying the percentage from Table 1.1 by the stack diameter. The total distance to the point from the outside of the stack or port is obtained by adding the port length and stack wall thickness to the calculated point location. No sampling point should be either <1 in. from an inner wall for stacks >24 in. in diameter, or <0.5 in. (or a distance

equal to the sampling nozzle diameter from the wall) in stacks <24 in. in diameter.

For rectangular ducts, an equivalent diameter is calculated from the following equation to determine the distance to disturbances in terms of duct diameters:

Equivalent diameter =

$$2 \left[\frac{\text{length} \times \text{width}}{\text{length} + \text{width}} \right]$$

The minimum number of traverse points is then determined in the same manner as it is for circular stacks, with the use of Figure 1.4. The rectangular cross section is then divided into equal rectangular areas, according to the values in Table 1.2. Studies referenced in Method 1 show that velocity measurement data quality is not significantly increased by traversing 48 points versus 24 points for acceptable flow conditions. The studies also show that four traverse points along a line

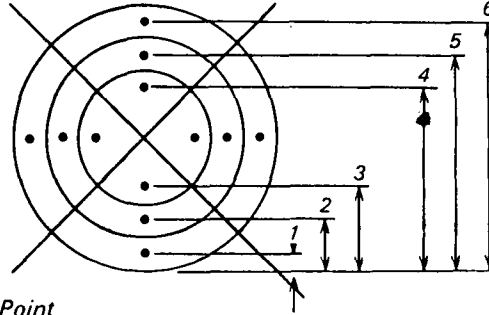
Stack (Vent) Number _____		
Parameter	Value	Comments
Process vented		
Platform height, ft		
Platform width, ft		
Platform length, ft		
Inside diameter, in. at port		
Wall thickness, in. at port		
Material of construction		
Ports: a. Existing		
b. Size opening		
c. Distance from platform		
Straight distance before ports, ft		
Type of restriction before ports		
Straight distance after ports, ft		
Type of restriction after ports		
Environment at sampling site		
Work space area		
Ambient temperature, °F		
Average Pitot reading, in. H ₂ O and range in Δp		
Stack gas velocity, ft/min		
Stack gas flow, ft ³ /min		
Moisture, % by volume		
Stack gas temperature, °F		
Particulate loading, gr/scf		
Particle size		
Gases present		
Stack Pressure, in. H ₂ O		
Water sprays prior to site		
Dilution air prior to site		
Elevator to site?		
Available electricity and distance, ft		

Figure 1.3. Stack and gas stream data requirements.

Table 1.1. Location of Traverse Points in Circular Stacks

Example Showing Circular Stack Cross Section Divided Into 12 Equal Areas With Location of Traverse Points Indicated.

Traverse point	Distance, % of diameter
1	4.4
2	14.6
3	29.6
4	70.4
5	85.4
6	95.6



Percent of Stack Diameter from Inside Wall to Traverse Point

Traverse point number on a diameter ^a	Number of traverse points on a diameter ^b											
	2	4	6	8	10	12	14	16	18	20	22	24
1	14.6	6.7	4.4	3.2	2.6	2.1	1.8	1.6	1.4	1.3	1.1	1.1
2	85.4	25.0	14.6	10.5	8.2	6.7	5.7	4.9	4.4	3.9	3.5	3.2
3		75.0	29.6	19.4	14.6	11.8	9.9	8.5	7.5	6.7	6.0	5.5
4		93.3	70.4	32.3	22.6	17.7	14.6	12.5	10.9	9.7	8.7	7.9
5			85.4	67.7	34.2	25.0	20.1	16.9	14.6	12.9	11.6	10.5
6			95.6	80.6	65.8	35.6	26.9	22.0	18.8	16.5	14.6	13.2
7				89.5	77.4	64.4	36.6	28.3	23.6	20.4	18.0	16.1
8				96.8	85.4	75.0	63.4	37.5	29.6	25.0	21.8	19.4
9					91.8	82.3	73.1	62.5	38.2	30.6	26.2	23.0
10					97.4	88.2	79.9	71.7	61.8	38.8	31.5	27.2
11						93.3	85.4	78.0	70.4	61.2	39.3	32.3
12						97.9	90.1	83.1	76.4	69.4	60.7	39.8
13							94.3	87.5	81.2	75.0	68.5	60.2
14							98.2	91.5	85.4	79.6	73.8	67.7
15								95.1	89.1	83.5	78.2	72.8
16								98.4	92.5	87.1	82.0	77.0
17									95.6	90.3	85.4	80.6
18									98.6	93.3	88.4	83.9
19										96.1	91.3	86.8
20										98.7	94.0	89.5
21											96.5	92.1
22											98.9	94.5
23												96.8
24												98.9

^aPoints numbered from outside wall toward opposite wall.^bThe total number of points along two diameters would be twice the number along a single diameter.

generally are representative of that traverse line. These two determinations allowed EPA to reduce the number of traverse points required for velocity measurement (as shown in Figure 1.4) and to require a more even matrix arrangement of sample points in a square or rectangular duct (as shown in Table 1.2). For small ducts requiring many points, a slot may have to be cut into one side of each duct with a sliding port to accommodate all of the points. The sampling points should be located at the center of each equal area, according to Figure 1.6. Many studies have been conducted on the Pitot tube and Method 1. See References 1 through 14.

The calculation and marking of sampling points on the probe or Pitot

tube are very critical. If marked incorrectly, the sample probe may hit the opposite stack wall, and the emission results will probably be nonrepresentative.

1.2.3 Cyclonic Gas Flow - Location of a suitable sampling site for velocity measurement or for particulate and mist determinations requires that the gas flow be essentially parallel to the stack walls. If there is a possibility of cyclonic or nonparallel flow as determined by observation of the duct system, checks with a Pitot tube and draft gauge (see Section 3.1, Method 2) should be made as follows:

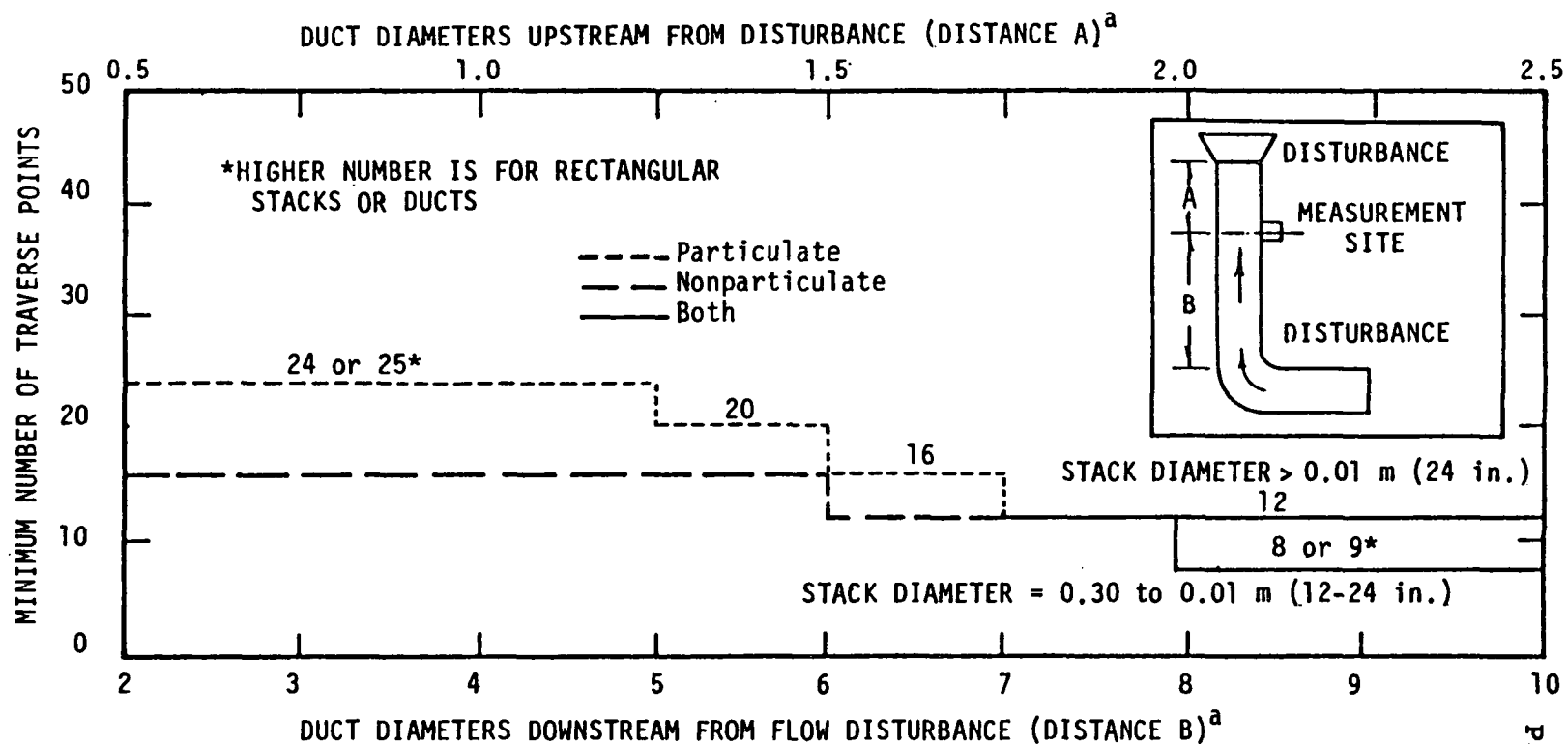
1. Connect an acceptable type-S Pitot tube to a manometer, and leak check as described in Section 3.1,

Table 1.2. Layout of Cross-Sectional Subareas in Rectangular Ducts

Number of traverse points ^a	Subarea layout matrix
9	3 x 3
12	4 x 3
16	4 x 4
20	5 x 4
25	5 x 5
30	6 x 5
36	6 x 6
42	7 x 6
49	7 x 7

^aFrom Figure 1.4.

Revision based on the August 30, 1983 Federal Register (48 FR 45034)



^aFrom point of any type of disturbance (bend, expansion, contraction, etc.)

Figure 1.4. Minimum number of traverse points for velocity (Particulate and Nonparticulate) traverse.

Method 2. Carefully zero the manometer and insert the Pitot tube so that the planes of the face openings are perpendicular to the stack area cross-sectional plane — that is, parallel to the expected gas flow. The Pitot tube is thus 90° from its usual position.

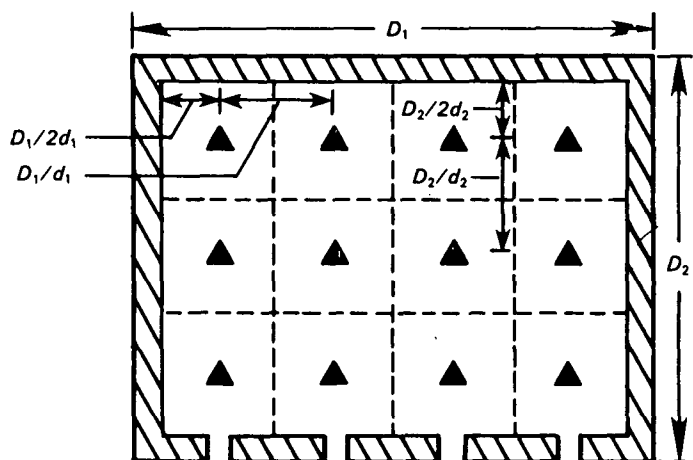
2. Traverse the stack area by measuring the velocity head at each sampling point with the Pitot tube in this position. Keep the sampling port opening sealed with a rag or sponge while traversing. Temperature need not be measured at this time.
3. When the gas flow is exactly parallel to the stack walls and therefore parallel to the Pitot tube face openings, no reading will be obtained on the manometer. If a reading is obtained, rotate the Pitot tube around its longitudinal axis until a zero reading is indicated on the manometer.

4. Record the angle of rotation (starting with 0° in the Pitot tube's initial position), required to obtain a zero manometer reading. Record data on the Method 2 gas velocity and volume data form (Figure 1.7).
5. Obtain an arithmetic average of the angles of rotation at each traverse point, including angles of 0° (Figure 1.7). If the average angle of rotation is $\leq 10^\circ$, the gas flow conditions at the sampling site are acceptable. If the average angle is $> 10^\circ$, the flow conditions are not acceptable; another test site must be found, the flow pattern must be modified by installing flow straighteners or consult the Administrator.

To facilitate measurement of Pitot tube rotation, a number of devices can be made, depending on the ingenuity of the user. Fabrication of a protractor that will fit over the sampling port along with a movable indicating arm clamped to the Pitot tube will provide a measurement of

the angle of rotation. A level indicator (available at most hardware stores) calibrated in 5-degree increments can also be mounted on the Pitot tube and used to measure rotation.

The preferred device is a degree indicating level (available at most hardware stores) with 1° increments which can be mounted on the end of the Pitot tube (Figure 1.8). Its alignment with the head of the Pitot tube can be checked by one of two methods. (1) The use of two indicating levels, one at the front and one at the end or (2) by placing the Pitot on a stable surface then place the indicating level at the front and then the end and compare readings. The readings do not have to be the same. The differential, using the front as the reference, or true value can be subtracted or added to the corresponding angular determinations of stack flow.



where:

▲ = sampling point

d_1 = number of areas across flue width

d_2 = number of areas across flue perpendicular to width

Figure 1.6. Example showing rectangular stack cross section divided into twelve equal areas, with a traverse point at the centroid of each area.

References

1. 40 CFR 60, July 1, 1978.
2. Determination of the Optional Number of Traverse Points: An Analysis of Method 1 Criteria. Final Report, EPA Contract No. 68-01-3172. Entropy Environmentalists, Inc., April 1977.
3. Hansen, H.A., R.I. Davis, et al. Particulate Sampling Strategies for Large Power Plants Including Nonuniform Flow. EPA-600/2-76-120, June 1976.
4. Smith, Franklin, Denny E. Wagoner, et al. Guidelines for Development of a Quality Assurance Program: Volume I - Determination of Stack Gas Velocity and Volumetric Flow Rate (Type-S Pitot Tube). EPA-650/4-74-005-a, February 1974.
5. Source Sampling Reference Manual - Supplemental Training Material for Technical Workshop on Evaluating Performance Tests. EPA, Division of Stationary Source Enforcement, January 1977.
6. Stack Sampling Technical Information: A Collection of Monographs and Papers (Vols. II, IV). EPA-450/2-78-042-b,d, October 1978.
7. Standards of Performance for New Stationary Sources - A Compilation. EPA Contract No. 68-01-4147. PEDCo Environmental, Inc., Cincinnati, OH, November 1977.
8. Williams, J.C., III and F.R. DeJarnette. A Study on the Accuracy of Type-S Pitot Tube. EPA-600/4-77-030, June 1977.
9. Folsom, R. G. Review of the Pitot Tube. Trans. ASME, 78, 1447-1459, 1956.
10. Ower, E. and F. C. Johansen. Design of Pitot-Static Tubes. R and M, No. 981, British A.R.C., 1925.
11. Merriam, K. F., and E. R. Spaulding. Comparative Tests of Pitot Static Tubes. NACA TN 546, 1935.
12. Vollaro, R. F. Use of Type-S Pitot Tubes for the Measurement of Low Velocities. U.S. Environmental Protection Agency, Research Triangle Park, N.C. In-house Report, January 19, 1977.
13. Vollaro, R. F. A Survey of Geometric and Aerodynamic Factors Which Can Affect Type-S Pitot Tube Accuracy. U.S. Environmental Protection Agency, Research Triangle Park, N.C., In-house Report, February 17, 1978.
14. Leland, B. J., J. L. Hall, A. W. Joensen, and J. M. Carroll. Correction of S-Type Pitot-Static Tube Coefficients When Used for Isokinetic Sampling from Stationary Sources. ES&T, 11, 694-700, 1977.

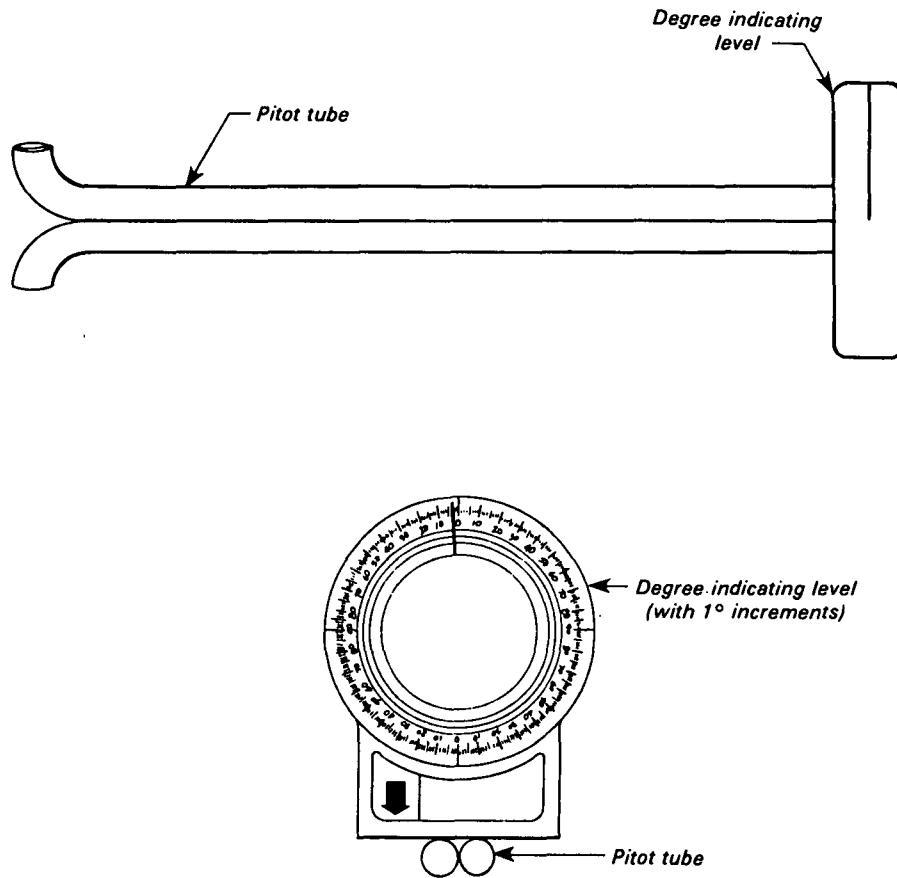


Figure 1.8. Angle determination with a degree indicating level.

2.0 General Factors Involved In Stationary Source Testing

It is essential to the production of valid test data that the emissions measurement program be performed by qualified personnel using proper test equipment. Although the sampling team chief need not be a professional engineer, the chief must be specially trained in source sampling and must be experienced in field test procedures. If the sampling results are used in legal proceedings, the team chief may be called as a witness. Monitoring of a single sampling station usually requires two persons; monitoring of two stations usually requires a minimum of three. In all cases, there should be an adequate staff to perform the level of sampling required.

Similarly, valid emission tests require the use of appropriate and properly functioning test equipment, which consists basically of process-measuring devices such as scales for weighing fuel or raw materials and orifices and gauges for measuring material flows and temperatures. Process-weight regulations may require the use of scales which can be properly serviced and calibrated only by trained personnel. The scale manufacturer usually provides this service. A stamp affixed to the scale by the service crew should note the date of calibration or inspection.

Sampling equipment, such as flow meters and gauges, must be properly calibrated and maintained. As standard practice, the monitoring team should check and record the dates of calibration or servicing. Gas-sampling equipment that requires maintenance and calibration includes the Pitot tube, manometers, thermometers, flow meters, and dry gas meters. Because calibration and maintenance of these instruments is subject to close scrutiny in legal proceedings, written records are required.

Emphasis is placed upon these standard practices as means of ensuring the validity of results. Deviations from standard procedures must be kept to a minimum and applied only when they are absolutely necessary to obtain representative samples. For compliance testing, deviations from standard procedures may be used only with approval of the regulatory agency. Any changes in methodology must be based on sound engineering judgment and must be thoroughly documented.

The following procedures merit particular attention.

1. Locating the sampling site,

2. Determining the number of sampling points in the duct,
3. Using recommended sampling equipment and calibration methods,
4. Determining gas velocities,
5. Maintaining isokinetic sampling conditions for particulates,
6. Handling the sample and maintaining records, and
7. Sample analysis.

The remainder of this section describes procedures for stack sampling; source sampling tools and equipment; identification and handling of samples; laboratory analysis; use of the sampling data; and preparation of reports.

2.1 Source Sampling Tools and Equipment

The needs for specific tools and equipment will vary from test to test. A listing of the most frequently used tools and equipment given below is to serve as a checklist; this equipment is useful, but not mandatory.

1. *Equipment transportation*
 - a. Lightweight handtruck to transport cases.
 - b. A 1.2-cm (0.5 in.) continuous filament nylon rope with a snatch block for raising and lowering equipment on stacks and roofs.
 - c. Tarpaulin or plastic to protect equipment in case of rain; sash cord 0.63 cm (1/4 in.) for securing equipment and tarpaulin.
 - d. One strong metal or wooden box for transporting small items up and down the stack.
2. *Safety equipment*
 - a. First-aid kit.
 - b. Safety harness with nylon and steel lanyards and large throat snaphooks for use with lanyards for hooking over guardrails or safety lines on stacks.
 - c. Earplugs, H₂O, and quick-energy food.
 - d. A fail-safe hook for use with harness when climbing ladders having safety cables.
 - e. Hardhats with chinstraps and winter liners; gas masks, safety glasses, and/or safety goggles.
 - f. Protective clothing including suits for both hot and cold weather, both asbestos and leather gloves, and steel-toed shoes.
 - g. Steel cable 0.5 cm (3/16 in.) cable clips, and turnbuckles for installing a safety line or for securing equipment to the stack structure.

3. Tools and spare parts

- a. Electric and power equipment:
 - (1) Circular saw,
 - (2) Variable voltage transformer,
 - (3) Variable speed electrical drill and bits,
 - (4) Ammeter-voltmeter-ohmmeter (VOM),
 - (5) Extension cords (light, #14 Awg; 2 @ 25 ft, 2 @ 50 ft),
 - (6) Two 3-wire electric adapters,
 - (7) 3-wire electric triple taps,
 - (8) Thermocouple extension wire,
 - (9) Thermocouple plugs,
 - (10) Fuses,
 - (11) Electric wire,
 - (12) Jigsaw, and
 - (13) Small space heater for cold weather.
- b. Tools:
 - (1) Tool boxes (1 large, 1 small),
 - (2) Screwdriver sets (1 flat blade, 1 Philips), and
 - (3) Two C-clamps (6 in., 3 in.).
- c. Wrenches:
 - (1) Open-end set (1/4 in. - 1 in.),
 - (2) Adjustable (12 in., 6 in.),
 - (3) A chain wrench,
 - (4) A 12-in. pipe wrench, and
 - (5) An Allen wrench set.
- d. Miscellaneous:
 - (1) Silicone sealer,
 - (2) Silicone vacuum grease,
 - (3) Pump oil,
 - (4) Manometers (gauge oil),
 - (5) Antiseize compound, e.g., high temperature graphite
 - (6) Pipe fittings,
 - (7) Dry cell batteries,
 - (8) Flashlight,
 - (9) Valves,
 - (10) Thermometers (dial, 6 in. - 36 in., a remote-reading type),
 - (11) Vacuum gauge,
 - (12) Short SS-tubing (1/4 in., 3/8 in., 1/2 in.),
 - (13) Heavy duty wire (telephone type),
 - (14) Adjustable packing gland,
 - (15) Nails,
 - (16) Spare swagelocks,
 - (17) Hammer,
 - (18) Hanging lamp, and
 - (19) Two-by-four's.

4. Data recording

- a. Data forms or data notebook.
- b. Carbon paper.
- c. Slide rule or electronic calculator.
- d. Psychrometric charts.

- e. Combustion nomographs (Reference 1).
- f. Pencils and pens.

2.2 Standard Data Forms

Recorded test data are part of the physical evidence in legal proceedings. Standardized forms are used to ensure that all required information is obtained. Example forms for use in the field, in the laboratory, and for calculations are included in later sections. The field form used when taking the sample identifies the process tested; date and time; location of test station; sampling personnel; and the person who records the data. Ink should always be used to record the data. In the event of error, the data-taker crosses through the erroneous value with a single line, records the correct value above it, and initials the change.

2.3 Identification of Sampling Materials

All samples must be marked to ensure positive identification throughout the test and analysis procedures. The legal rules of evidence require systematic identification of samples at all points in their processing. Valid testimony requires that a laboratory analyst be able to relate the analytical data to a specific sample by number. Analysts also must provide positive identification of filters. All identifying marks on the filters should be made before weighing. The filters should be serially numbered to ensure their unique identification. The ink used for marking must be indelible and unaffected by gases, temperatures, or other conditions to which it is subjected. If any agency specifies another method of identification, that method must be positive and must not impair the capacity of the filter to function.

Finally, the monitoring personnel must provide unique identification for each container to preclude the possibility of interchange. The number of the container is recorded on the field form and on the analysis data form so that it is associated with the sample throughout testing and analysis. See Section 3.0.3 for further details concerning the uses of source samples as evidence.

2.4 Reference

Smith, Walter S., and D. James Groves. *Stack Sampling Nomographs for Field Estimations*. Entropy Environmentalists, Inc., Research Triangle Park, NC.

3.0 Chain-of-Custody Procedure For Source Sampling

As part of the overall quality assurance activities associated with the collection and analysis of source samples, particular attention should be directed to the handling of the sample and the analysis report.

Source test results, or possibly even the sample itself, may be used to prove the compliance status of a facility. However, test results and samples will not be admitted as evidence unless it can be shown that they accurately represent the conditions that prevailed at the time the test was conducted. This requires that:

1. the sample be collected properly,
2. the sample be handled properly,
3. the sample be analyzed in accordance with documented test procedure, and
4. the test report be prepared completely and accurately and then filed in a secure place.

Failure to comply with these requirements may void the results of a test or, at least, diminish the credibility of the test report.

3.1 Sample Collection

Proper sampling requires the use of the correct method, the equipment designated by the method, and competent personnel. Prior to the test date, the tester should determine that the proposed test methods comply with the appropriate testing regulations; in some instances, it may be necessary to deviate from the proposed methods. For example, the only reasonable sample site may be too close to an elbow or a duct obstruction. In such cases, the tester should make an engineering analysis of the use of the test site and then proceed only after obtaining the approval of the regulatory authority. This determination should be recorded in the field notes. An after-the-fact site analysis may suffice in many instances, but good quality assurance techniques dictate that this analysis be made prior to spending the many man-hours required to extract the sample. Once the test method is selected, preparations for the test should be made according to documented guidelines.

3.1.1 Preparations When conducting the test, it is necessary that the sample be extracted in a manner to ensure that it represents the actual conditions at the time of the test. This means that the process is operating in its mode specified by the applicable

control regulation, the extracted sample typifies the stack gas conditions, and the instruments used in the sampling are properly calibrated and maintained.

Because the results of source tests are being used increasingly as proof of compliance, the pretest preparation and posttest scrutiny are becoming more sophisticated. Thus, steps need to be taken prior to the actual test to ensure the integrity of the test data.

In many cases, reagents or filters are prepared prior to sampling and become an integral part of the sample itself. A record should list the date, the person by whom it was prepared, and the location of these items at all times from preparation until actual use for sampling. Since these items become a part of the sample itself, it is necessary that their integrity be maintained from preparation through analysis. For example, a bulk quantity of solution may be prepared and transported to the field where the specified amount is used in accordance with the test method. The bulk solution ultimately becomes an integral part of several samples during the sampling process. For this reason, one member of the sampling crew generally serves as sample custodian and should be responsible for entering information on sample preparation items in the field notebook. However, as long as proper records are kept, more than one individual may serve in this capacity. This serves as a written record for the sampling crew and also fulfills chain-of-custody procedures.

3.1.2 Sample Handling - Once the sample is procured it should be handled in such a way as to ensure that there is no contamination and that the sample analyzed is actually the sample taken under the conditions reported. For example, each sample should be kept in a secure place between the time it is extracted and the time it is analyzed. If further analysis may be required, the sample should be returned to a secure place. It is always best to keep a sample secure up to the time it is discarded. These security measures should be documented by a written record signed by the handlers of the sample.

Identification - Care should be taken to mark the samples to ensure positive identification throughout the test and analysis procedures. The evidence used in legal proceedings requires positive procedures for identification of samples used in analyses as the basis for future

evidence. An admission that the laboratory analyst could not be positive whether sample No. 6 or sample No. 9 was analyzed could destroy the validity of the entire test report.

Positive identification also should be provided for the filters used in any specific test before taring. If ink is used for marking, it must be indelible and unaffected by the gases and temperatures to which it will be subjected. Other methods of identification can be used, if they provide a positive means of identification and do not impair the function of the filter.

Finally, each container should have a unique identification to preclude the possibility of interchange. Grease pencils may be used for this purpose. A better method, however, is to affix an adhesive-backed label to the container. The number of the container should be recorded on the analysis data form. Figure 3.1 shows how a standardized identification sticker can be used for each of the four containers needed to collect a sample for EPA Test Method 5.

Contamination and Tampering - To reduce the possibility of invalidating the results, all components of the sample should be carefully removed from the sampling train and placed in nonreactive containers. The best method of sealing depends on the container. Place containers in a place of limited access (i.e., locked van or locked sample box). This will preclude accidental opening of the container and should be a sufficient safeguard if all other aspects of the chain-of-custody procedure are observed. However, if there is any possibility of temporary access to the samples by unauthorized personnel, the sample jars and containers should be sealed with a self-adhesive sticker that has been signed and numbered by the test supervisor or other responsible person. This sticker should adhere firmly to ensure that it cannot be removed without destruction. The samples should then be delivered to the laboratory for analysis. It is recommended that this be done on the same day that the sample is taken. If this is impractical, all of the samples should be placed in a carrying case or other place of limited access (preferably locked) for protection from breakage, contamination, and loss.

In transporting the sample to the laboratory, it is important that precautions be taken to eliminate the possibility

Container No. A-4
 Plant ABC Corp. City Podunk
 Site Exit Kiln Stack Pollutant Part.
 Date 11-18-77 Run No. 2
☒ Front half Front filter no. _____
 Back half Back filter no. _____
 Rinse Acetone
 Volume: Initial N.A. Final 300 ml.
 Cleanup by J. Doe Field Chief N. Graves

Remarks

Probe rinsings

Container No. A-5
 Plant ABC Corp. City Podunk
 Site Exit Kiln Stack Pollutant Part.
 Date 11-18-77 Run No. 2
 Front half Front filter no. _____
☒ Back half Back filter no. _____
 Rinse Acetone Blank
 Volume: Initial N.A. Final N.A.
 Cleanup by J. Doe Field Chief N. Graves

Remarks

Acetone blank

Container No. F-6
 Plant ABC Corp. City Podunk
 Site ESP Outlet Pollutant Part.
 Date 11-18-77 Run No. 2
 Front half ☒ Front filter no. 14757
 Back half Back filter no. _____
 Rinse N.A.
 Volume: Initial N.A. Final N.A.
 Cleanup by J. Doe Field Chief N. Graves

Remarks

Filter

Container No. S-7
 Plant ABC Corp. City Podunk
 Site ESP Outlet Pollutant Part.
 Date 11-18-77 Run No. 2
 Front half Front filter no. _____
 Back half Back filter no. _____
 Rinse Silica Gel
 Volume: Initial N.A. Final N.A.
 Cleanup by J. Doe Field Chief N. Graves

Remarks 132 GM TARE

Silica gel

Figure 3.1. Typical labels used for samples collected for a source test of particulate matter using EPA Test Method 5.

of tampering, accidental destruction, and physical and/or chemical damage to the sample. This practical consideration should be dealt with on a case-by-case basis. For example, samples obtained from a rock crusher are nonreactive but those from an asphalt saturator may be reactive, and gaseous samples may decay or react.

The person who has custody of the samples should be able to testify that no one tampered with them. Any handling of samples by unauthorized persons can result in contamination. For example, a curious person with a cigarette in his mouth may open a sample; the smallest ash dropping into the container could make a significant difference in the analysis. Security should be continuous. If the samples are put in a truck, lock it. In the laboratory, the samples should be kept in a secure place.

To ensure that none of the sample is lost in transport, mark all liquid levels on the side of the container with a grease pencil. Thus any major losses that occur will be readily ascertainable.

Chain-of-Custody - The chain-of-custody is perhaps the most critical part of the test procedure. The chain-of-custody is necessary to make a *prima facie* showing of the representativeness of the sample. Without it, one cannot be sure that the sample analyzed was the same as the one purported to be taken at a particular time. The samples should be handled only by persons associated in some way with the test. A general rule to follow is "the fewer hands the better," even though a sealed sample may pass through a number of hands without affecting its integrity. Ideally, all sample containers should be transported from the site to the vehicle and from the vehicle to the laboratory by the same person.

It is generally impractical for the analyst to perform the field test. For this reason, each person should remember from whom the sample was received and to whom it was delivered. This requirement is best satisfied by having each recipient sign the data form for the sample or set of samples. Figure 3.2 shows a form for particulate samples which may be used to establish the chain-of-custody from the test site to the laboratory. This form is designed for tests performed by EPA Method 5. Note that the silica gel was weighed in the field. If for some reason this is not done, the silica gel must be returned with the other containers, and an appropriate notation made under "Remarks." Figure 3.3 shows another form which may be used. A form of this type should accompany the samples at all times from the field to the laboratory. All

persons who handle the samples should sign the form. It is important to realize that the chain-of-custody procedures do not stop with the sample analysis. If the sample must be kept for future analysis, it should be kept in a secure storage area. Figures 3.2 and 3.3 reflect this.

3.2 Sample Analysis

For source samples to provide useful information, laboratory analyses should meet the following requirements:

1. Equipment should be adequate for proper analysis;
2. Personnel should be qualified to make analysis;
3. Analysis procedures should be in accordance with accepted good practice; and
4. Records should be complete and accurate.

The first three requirements are discussed elsewhere in this Handbook and need no further elaboration.

Complete and accurate records generally take the form of a laboratory notebook. Where practical, standard preprinted forms should be used. Do not discard these records, since it is possible that they will be needed in the future to substantiate the final report. Figures 3.4 and 3.5 are examples of standardized forms that can be used in the laboratory. Note that the entries on these forms must agree with those shown on the container labels (Figure 3.1) and on the chain-of-custody receipt form (Figures 3.2 and 3.3).

3.3 Field Notes

Manual recording of data is required for source tests. Standardized forms should be utilized to ensure that all necessary data are obtained. These forms should be designed to clearly identify the process tested, the date and time, the test station location, the sampling personnel, and the person who recorded the data. During the actual test period, the meter readings, temperature readings, and other pertinent data should be recorded in the spaces immediately upon observation. These data determine the accuracy of the test and should not be erased or altered. Any error should be crossed out with a single line; the corrected value should be recorded above the crossed-out number.

Do not discard the original field records even if they become soiled. For neatness, the field data may be transcribed or copied for inclusion in the final report, but the originals should be kept on file. Copies are not normally admissible as evidence, but since the records may be subpoenaed, it is important that all field notes be legible.

3.4 The Report as Evidence

In addition to samples and field records, the report of the analysis itself may serve as material evidence. Just as the procedures and data leading up to the final report are subject to the rules of evidence, so is the report itself. Written documents, generally speaking, are considered hearsay and are not admissible as evidence without a proper foundation. A proper foundation consists of testimonies from all persons having anything to do with the major portions of the test and analysis. Thus the chief of the field team, the cleanup man, all persons having custody of the samples, and the laboratory analyst would be required to lay the foundation for introduction of the test report as evidence.

Legal rules recognize that a record of events is the result of input from many persons who have no reason to lie and that introduction of all these persons as witnesses is onerous. These rules recognize the complexity and mobility of our society and are relatively liberal. Indeed, in many cases the trial judge will require the parties to verify the authenticity of source test reports during the pretrial proceedings. However, the party against whom the report is offered still has the right, with reasonable cause, to cross-examine the test participants. In this area, the trial judge may exercise discretion.

The relaxed attitude toward reports of experiments made by persons in the regular course of activity greatly simplifies the introduction of the report as evidence. Only the custodian of the report (usually the supervisor or the test team) need testify.

To ensure compliance with legal rules all test reports should be filed in a secure place by a custodian having this responsibility. Although the field notes and calculations are not generally included in the summary report, this material may be required at a future date to bolster the acceptability and credibility of the report as evidence in an enforcement proceeding. Therefore, the full report — including all original notes and calculation forms — should be kept in the file. Signed receipts for all samples should also be filed with the test data.

The original of a document is the best evidence and a copy is not normally admissible as evidence. Microfilm, snap-out carbon copies, and similar contemporary business methods of producing copies are acceptable in many jurisdictions if the unavailability of the original course is adequately explained and if the copy was made in the ordinary course of business.

In summary, although all the original calculations and test data need not be included in the final report, they should be kept in the files. It is a good rule to file all reports together in a secure place.

Plant ABC Corp., Podunk, Ohio Sample date 11-17-77
 Sample location Kiln Exit Stack Run number 2
 Sample recovery by John Doe Recovery date 11-18-77
 Filter number(s) 14757

Moisture

Impingers		Silica gel	
Final volume (wt)	<u>380</u> ml (g)	Final wt.	<u>268</u> g <u>—</u> g
Initial volume (wt.)	<u>300</u> ml (g)	Initial wt.	<u>250</u> g <u>—</u> g
Net volume (wt)	<u>80</u> ml (g)	Net wt.	<u>18</u> g <u>—</u> g
Total moisture <u>98</u> g			
Color of silica gel <u>pink and blue</u>			
Description of impinger water <u>cloudy</u>			

Recovered Sample

Filter container number F-6 Sealed ✓
 Description of particulate on filter _____

 Acetone rinse container number A-4 Liquid level marked ✓
 Acetone blank container number A-5 Liquid level marked ✓
 Samples stored and locked N/A
 Remarks transported directly to lab

 Date of laboratory custody 11-18-77
 Laboratory personnel taking custody Jim Smith
 Remarks _____

Figure 3.2. Chain-of-custody receipt form for source sample.

Plant ABC Corp, Podunk, OH

Sample number	Number of container	Description of samples			
2	A-4 A-5 F-6	Acetone Rinse Acetone Blank Filter # 14757			

Person responsible for samples				Time	Date
J. Doe				4:30 PM	11-18-77

Sample number	Relinquished by	Received by	Time	Date	Reason for change of custody
2	J. Doe	Jim Smith	5:00 PM	11-18-77	Put in sample locker
	Jim Smith	W. Frank	10:15 A.M.	11-20-77	Run analysis
	W. Frank	Jim Smith	4:30 P.M.	11-20-77	Put in sample locker

Figure 3.3. Chain-of-custody receipt form - general form.

Plant ABC Corp, Podunk, Ohio Run number 2
 Sample location Kiln Exit Stack
 Density of acetone (ρ_a) 0.790 g/ml

Sample type	Container number	Liquid level marked	Container sealed
Acetone blank	A-5	✓	✓
Acetone rinse	A-4	✓	✓
Filter(s)	F-6		✓

Acetone rinse volume (V_{aw}) 300 ml
 Acetone blank residue concentration (C_a) 2.1×10^{-3} mg/g
 $W_a = C_a V_{aw} = (2.1 \times 10^{-3}) (300) (0.790) =$ 0.5 mg
 Date and time of wt. 11-20-77; 9:00 A.M. Gross wt. 5210.8 mg
 Date and time of wt. 11-21-77; 8:25 AM Gross wt. 5210.6 mg
 Average gross wt. 5210.7 mg
 Tare wt. 5108.6 mg
 Less acetone blank wt. (W_a) 0.5 mg
 Weight of particulate in acetone rinse 101.6 mg
 Filter number(s) 14757
 Date and time of wt. 11-20-77; 9:10 A.M. Gross wt. 652.8 mg
 Date and time of wt. 11-21-77; 8:15 A.M. Gross wt. 652.6 mg
 Average gross wt. 652.7 mg
 Tare wt. 450.0 mg
 Weight of particulate on filter(s) 202.7 mg
 Weight of particulate in acetone rinse 101.6 mg
 Total weight of particulate 304.3 mg

Remarks _____

Signature of analyst W. Frank
 Signature of reviewer Jim Smith

Figure 3.4. Standard form for laboratory analysis of sample (EPA Test Method 5).

Plant ABC Corp., Podunk, Ohio Blank number A-5
Sample location Kila Exit Stack
Liquid level at mark ✓ Container sealed ✓
Density of acetone (pa) 0.790 mg/ml
Acetone blank volume (Va) 300 ml
Date and time of wt. 11-20-77; 8:15 A.M. Gross wt. 5080.6 mg
Date and time of wt. 11-20-77; 3:20 P.M. Gross wt. 5080.6 mg
Average gross wt. 5080.7 mg
Tare wt. 5080.2 mg
Weight of blank (ma) 0.5 mg

$$Ca = \frac{ma}{Va \text{ pa}} = \frac{(0.5)}{(300)(0.790)} = \underline{0.0021} \text{ mg/g}$$

Remarks _____

Signature of Analyst W. Frank

Signature of reviewer Jin Smith

Figure 3.5. Standard form for laboratory analysis of acetone blank.

3.0.4. PROCEDURE FOR NBS-TRACEABLE CERTIFICATION OF COMPRESSED
GAS WORKING STANDARDS USED FOR CALIBRATION AND
AUDIT OF CONTINUOUS SOURCE EMISSION MONITORS
(Revised Traceability Protocol No. 1)

CONTENTS

<u>Subsection</u>	<u>Title</u>	<u>Pages</u>
3.0.4.0	General Information	1 to 8
3.0.4.1	<u>Procedure G1</u> : Assay and Certification of a Compressed Gas Standard Without Dilution	G1-1 to G1-5
3.0.4.2	References	

4.0 GENERAL INFORMATION

4.0.1 Purpose and Scope of the Procedure

Section 3.0.4 describes a procedure for assaying the concentration of gaseous pollutant concentration standards and certifying that the assay concentrations are traceable to an authoritative reference concentration standard. This procedure is recommended for certifying the local working concentration standards required by the pollutant monitoring regulations of 40 CFR Part 60^{1,2} for the calibration and audit of continuous source emission monitors. The procedure covers certification of compressed gas (cylinder) standards for CO, CO₂, NO, NO₂, and SO₂ (Procedure G1).

4.0.2 Reference Standards

Part 60 of the monitoring regulations^{1,2} require that working standards used for calibration and audit of continuous source emission monitors be traceable to either a National Bureau of Standards (NBS) gaseous Standard Reference Material (SRM) or a NBS/EPA-approved Certified Reference Material (CRM)³. Accordingly, the reference standard used for assaying and certifying a working standard for these purposes must be an SRM, a CRM, or a suitable intermediate standard (see the next paragraph). SRM cylinder gas standards available from NBS are listed in Table 7.2 at the end of subsection 4.0. A current list of CRM cylinder gases and CRM vendors is available from the Quality Assurance Division (MD-77), Environmental Monitoring Systems Laboratory, U. S. EPA, Research Triangle Park, NC 27711.

The EPA regulations define a "traceable" standard as one which "...has been compared and certified, either directly or via not more than one intermediate standard, to a primary standard such as a...NBS [gaseous] SRM or...CRM"^{4,5}. Certification of a working standard directly to an SRM or CRM primary standard is, of course, preferred and recommended because of the lower error. However, an intermediate reference standard is permitted, if necessary. In particular, a Gas Manufacturer's Intermediate Standard (see subsection 4.0.2.1) that has been referenced directly to an SRM or a CRM according to Procedure G1 is an acceptable intermediate standard and could be used as the reference standard on that basis. However, purchasers of com-

mercial gas standards referenced to an intermediate standard such as a GMIS should be aware that, according to the above definition, such a standard would have to be used directly for calibration or audit. Since a second intermediate standard is not permitted, such a standard could not be used as a reference standard to certify other standards.

4.0.2.1 Gas Manufacturer's Intermediate Standard (GMIS). A GMIS is a compressed (cylinder) gas standard that has been assayed with direct reference to an SRM or CRM and certified according to Procedure G1, and also meets the following requirements:

1. A candidate GMIS must be assayed a minimum of three (3) times, uniformly spaced over a three (3) month period.
2. Each of the three (or more) assays must be within 1.0 percent of the mean of the three (or more) assays.
3. The difference between the last assay and the first assay must not exceed 1.5 percent of the mean of the three (or more) assays.
4. The GMIS must be recertified every three months, and the reassay must be within 1.5 percent of the previous certified assay. The recertified concentration of the GMIS is the mean of the previous certified concentration and the reassay concentration.

4.0.2.2 Recertification of Reference Standards. Recertification requirements for SRMs and CRMs are specified by NBS and NBS/EPA, respectively. See 4.0.2.1 for GMIS recertification requirements.

4.0.3 Using the Procedure

The assay/certification procedure described here is carefully designed to minimize both systematic and random errors in the assay process. Therefore, the procedure should be carried out as closely as possible to the way it is described. Similarly, the assay apparatus has been specifically designed to minimize errors and should be configured as closely as possible to the design specified. Good laboratory practice should be observed in the selection of inert materials (e.g. Teflon, stainless steel, or glass, if possible) and clean, non-contaminating components for use in portions of the apparatus in contact with the candidate or reference gas concentrations.

4.0.4 Certification Documentation

Each assay/certification must be documented in a written certification report signed by the analyst and containing at least the following information:

1. Identification number (cylinder number).
2. Certified concentration of the standard, in ppm or mole percent.
3. Balance gas in the standard mixture.

4. Cylinder pressure at certification.
5. Date of the assay/certification.
6. Certification expiration date (see 4.0.6.3).
7. Identification of the reference standard used: SRM number, cylinder number, and concentration for an SRM; cylinder number and concentration for a CRM or GMIS.
8. Statement that the assay/certification was performed according to this Section 3.0.4.
9. Identification of the laboratory where the standard was certified and the analyst who performed the certification.
10. Identification of the gas analyzer used for the certification, including the make, model, serial number, the measurement principle, and the date of the last multipoint calibration.
11. All analyzer readings used during the assay/certification and the calculations used to obtain the reported certified value.
12. Chronological record of all certifications for the standard.

Certification concentrations should be reported to 3 significant digits. Certification documentation should be maintained for at least 3 years.

4.0.5 Certification Label

A label or tag bearing the information described in items 1 through 9 of subsection 4.0.4 must be attached to each certified gas cylinder.

4.0.6 Assay/Certification of Compressed Gas (Cylinder) Standards

4.0.6.1 Aging of newly-prepared gas standards. Freshly prepared gas standard concentrations and newly filled gas cylinders must be aged before being assayed and certified. SO₂ concentrations contained in steel cylinders must be aged at least 15 days; other standards must be aged at least 4 days.

4.0.6.2 Stability test for reactive gas standards. Reactive gas standards, including nitric oxide (NO), nitrogen dioxide (NO₂), sulfur dioxide (SO₂), and carbon monoxide (CO), that have not been previously certified must be tested for stability as follows: Reassay the concentration at least 7 days after the first assay and compare the two assays. If the second assay differs from the first assay by 1.5% or less, the cylinder may be considered stable, and the mean of the two assays should be reported as the certified concentration. Otherwise, age the cylinder for a week or more and repeat the test, using the second and third assays as if they were the first and second assays. Cylinders that are not stable may not be sold and/or used for calibration or audit purposes.

4.0.6.3 Recertification of compressed gas standards. Compressed gas standards must be recertified according to this Section 3.0.4 within the time limits specified in Table 7.1^{3,6,7}. The reassay concentration must be within 5% of the previous certified concentration. If not, the cylinder must be retested for stability (subsection 4.0.6.2). The certified concentration of a recertified standard should be reported as the mean of all assays, unless a clear trend or substantial change suggests that previous assays are no longer valid.

Table 7.1 Recertification limits for compressed gas standards.

Pollutant	Balance gas	Concentration range	Maximum months until recertification for cylinder material:	
			Al or SS	other
Carbon monoxide	N ₂ or air	≥ 5 ppm	18	6
Nitric oxide	N ₂	≥ 10 ppm	18	6
Sulfur dioxide	N ₂	≥ 10 ppm	18	6
Nitrogen dioxide	N ₂ or air	≥ 10 ppm	6	6
Carbon dioxide	N ₂ or air	≥ 300 ppm	18	18
Oxygen	N ₂	≥ 2 percent	18	18
Sulfur dioxide and carbon dioxide	N ₂	≥ 200 ppm SO ₂ , ≥ 10 percent CO ₂	18	6
Propane	N ₂ or air	≥ 5 ppm	18	6
Others not specifically listed			6	6

4.0.6.4 Minimum cylinder pressure. No compressed gas cylinder standard should be used when its gas pressure is below 700 kPa (100 psi), as indicated by the cylinder pressure gauge.

4.0.6.5 Assay/certification of multi-component compressed gas standards. Procedure G1 may be used to assay and certify individual components of multi-component gas standards, provided that none of the components other than the component being assayed cause a detectable response on the analyzer.

4.0.7 Analyzer Calibration

4.0.7.1 Basic analyzer calibration requirements. The assay procedure described in this Section 3.0.4 employs a direct ratio referencing technique that inherently corrects for minor analyzer calibration variations (drift) and DOES NOT depend on the absolute accuracy of the analyzer calibration. What is required of the analyzer is as follows: 1) it must have a linear response to the pollutant of interest (see subsection 4.0.7.5), 2) it must have good resolution and low noise, 3) its response calibration must be reasonably stable during the assay/certification process, and 4) all assay concentration measurements must fall within the calibrated response range of the analyzer.

4.0.7.2 Analyzer multipoint calibration. The gas analyzer used for the assay/certification must have had a multipoint calibration within 3 months of its use when used with this procedure. This calibration is not used to quantitatively interpret analyzer readings during the assay/certification of the candidate gas because a more accurate, direct ratio comparison of the candidate concentration to the reference standard concentration is used. However, this multipoint calibration is necessary to establish the calibrated range of the analyzer and its response linearity.

The multipoint calibration should consist of analyzer responses to at least 5 concentrations, including zero, approximately evenly spaced over the concentration range. Analyzer response units may be volts, millivolts, percent of scale, or other measurable analyzer response units. The upper range limit of the calibrated range is determined by the highest calibration point used. If the analyzer has a choice of concentration ranges, the optimum range for the procedure should be selected and calibrated. Plot the calibration points and compute the linear regression slope and intercept. See subsection 4.0.7.5 for linearity requirements and the use of a mathematical transformation, if needed. The intercept should be less than 1 percent of the upper concentration range limit, and the correlation coefficient (r) should be at least 0.999.

4.0.7.3 Zero and span check and adjustment. On each day that the analyzer will be used for assay/certification, its response calibration must be checked with a zero and at least one span concentration near the upper concentration range limit. If necessary, the zero and span controls of the analyzer should be adjusted so that the analyzer's response (i.e. calibration slope) is within about ± 5 percent of the response indicated by the most recent multipoint calibration. If a zero or span adjustment is made, allow the analyzer to stabilize for at least an hour or more before beginning the assay procedure, since some analyzers drift for a period of time following zero or span adjustment. If the analyzer is not in continuous operation, turn it on and allow it to stabilize for at least 12 hours before the zero and span check.

4.0.7.4 Pollutant standard for multipoint calibration and zero and span adjustment. The pollutant standard or standards used for multipoint calibration or zero and span checks or adjustments must be obtained from a compressed gas standard certified traceable to an NBS SRM or a NBS/EPA CRM according to Procedure G1 of this Section 3.0.4. This standard need not be the same as the reference standard used in the assay/certification. The zero gas must meet the requirements in subsection 4.0.8.

4.0.7.5 Linearity of analyzer response. The direct ratio assay technique used in Procedure G1 requires that the analyzer have a linear response to concentration. Linearity is determined by comparing the quantitative difference between a smoothly-drawn calibration curve based on all calibration points and a straight line drawn between zero and an upper reference point (see Figure 1). This difference is measured in concentration units, parallel to the concentration axis, from a point on the calibration curve to the corresponding point for the same response on the straight line.

For the general linearity requirement, the straight line is drawn between zero and the highest calibration point (Figure 1a). Linearity is then acceptable when no point on the smooth calibration curve deviates from the straight line by more than 1.5 percent of the value of the highest calibration concentration. An alternative linearity requirement is defined on the basis of the actual reference and candidate concentrations to be used for the assay. In this case, the reference and candidate concentrations are plotted on the calibration curve, and the straight line is drawn from zero to the reference concentration and extrapolated, if necessary, beyond the candidate concentration (Figure 1b). The deviation of the smooth calibration curve from the straight line at the candidate concentration point then must not exceed 0.8 percent of the value of the reference concentration. This latter specification may allow the use of an analyzer having greater nonlinearity when the reference and candidate concentrations are nearly the same.

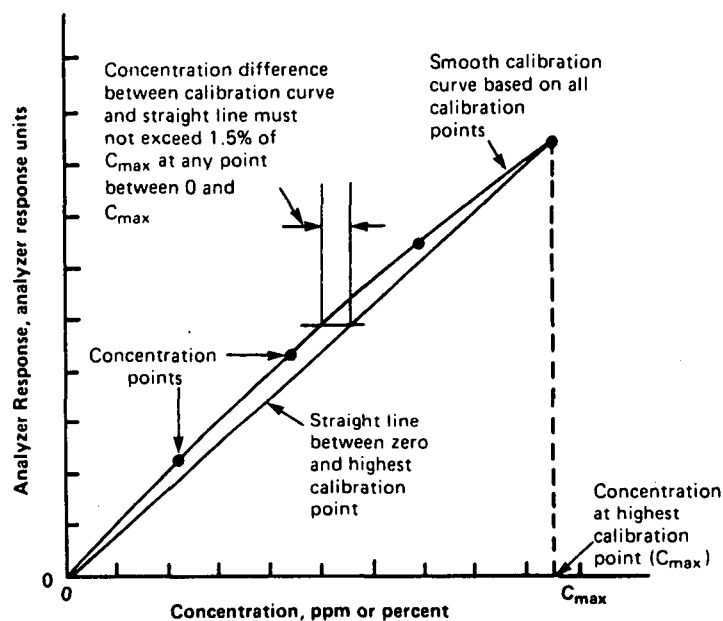
For analyzers having an inherently non-linear response, the response can usually be linearized with a simple mathematical transformation of the response values, such as $R' = \text{square root}(R)$ or $R' = \log(R)$, where R' is the transformed response value and R is the actual analyzer response value. Using the transformed response values, the multipoint calibration should meet one of the above linearity requirements as well as the requirements for intercept and correlation coefficient given in subsection 4.0.7.2.

4.0.8 Zero Gas

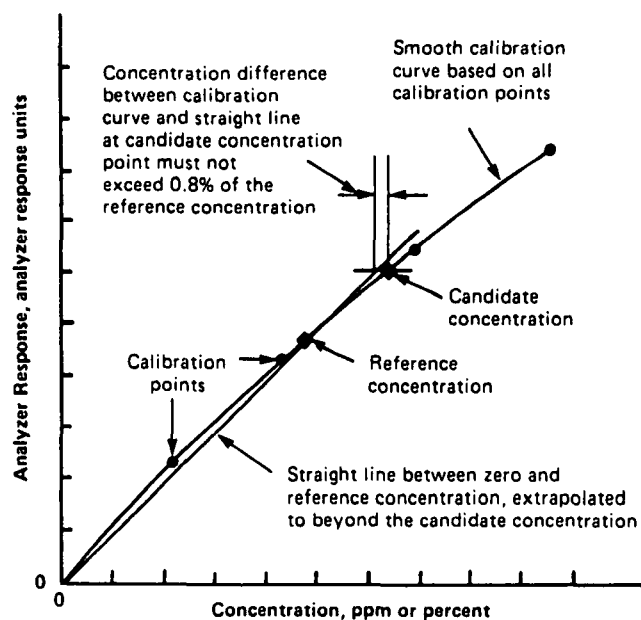
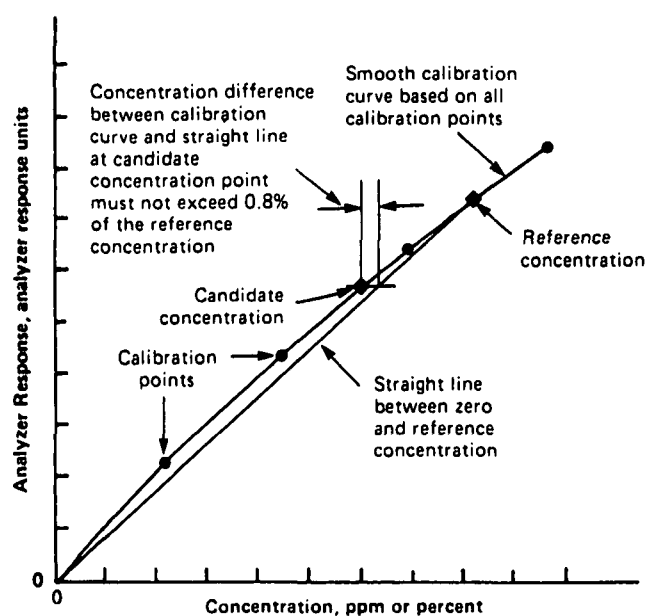
Zero gas used for dilution of any candidate or reference standard should be clean, dry, zero-grade air or nitrogen containing a concentration of the pollutant of interest equivalent to less than 0.5 percent of the analyzer's upper range limit concentration. The zero gas also should contain no contaminant that causes a detectable response on the analyzer or that suppresses or enhances the analyzer's response to the pollutant. The oxygen content of zero air should be the same as that of ambient air.

4.0.9 Accuracy Assessment of Commercially Available Standards

Periodically, the USEPA will assess the accuracy of commercially available compressed gas standards that have been assayed and certified according to this Section 3.0.4. Accuracy will be assessed by EPA audit analysis of representative actual commercial standards obtained via an anonymous agent. The accuracy audit results, identifying the actual gas manufacturers or vendors, will be published as public information.



a) General linearity requirement



b) Alternative linearity requirement

Figure 1. Illustration of linearity requirements.

Table 7.2. NBS SRM reference gases.

SRM number	Type	Nominal concentration		SRM number	Type	Nominal concentration	
2627	NO/N ₂	5	ppm	1693	SO ₂ /N ₂	50	ppm
2628	NO/N ₂	10	ppm	1694	SO ₂ /N ₂	100	ppm
2629	NO/N ₂	20	ppm	1661a	SO ₂ /N ₂	500	ppm
1683b	NO/N ₂	50	ppm	1662a	SO ₂ /N ₂	1000	ppm
1684b	NO/N ₂	100	ppm	1663a	SO ₂ /N ₂	1500	ppm
1685b	NO/N ₂	250	ppm	1664a	SO ₂ /N ₂	2500	ppm
1686b	NO/N ₂	500	ppm	1696	SO ₂ /N ₂	3500	ppm
1687b	NO/N ₂	1000	ppm				
2630	NO/N ₂	1500	ppm	1670	CO ₂ /Air	330	ppm
2631	NO/N ₂	3000	ppm	1671	CO ₂ /Air	340	ppm
				1672	CO ₂ /Air	350	ppm
2653	NO ₂ /Air	250	ppm				
2654	NO ₂ /Air	500	ppm	2632	CO ₂ /N ₂	300	ppm
2655	NO ₂ /Air	1000	ppm	2633	CO ₂ /N ₂	400	ppm
2656	NO ₂ /Air	2500	ppm	2634	CO ₂ /N ₂	800	ppm
				2619a	CO ₂ /N ₂	0.5	percent
2612a	CO/Air	10	ppm	2620a	CO ₂ /N ₂	1.0	percent
2613a	CO/Air	20	ppm	2621a	CO ₂ /N ₂	1.5	percent
2614a	CO/Air	45	ppm	2622a	CO ₂ /N ₂	2.0	percent
				2623a	CO ₂ /N ₂	2.5	percent
1677c	CO/N ₂	10	ppm	2624a	CO ₂ /N ₂	3.0	percent
2635	CO/N ₂	25	ppm	2625a	CO ₂ /N ₂	3.5	percent
1678c	CO/N ₂	50	ppm	2626a	CO ₂ /N ₂	4.0	percent
1679c	CO/N ₂	100	ppm	1674b	CO ₂ /N ₂	7.0	percent
2636	CO/N ₂	250	ppm	1675b	CO ₂ /N ₂	14.0	percent
1680c	CO/N ₂	500	ppm				
1681c	CO/N ₂	1000	ppm	1665b	C ₃ H ₈ /Air	3	ppm
2637	CO/N ₂	2500	ppm	1666b	C ₃ H ₈ /Air	10	ppm
2638	CO/N ₂	5000	ppm	1667b	C ₃ H ₈ /Air	50	ppm
2639	CO/N ₂	1	percent	1668b	C ₃ H ₈ /Air	100	ppm
2640	CO/N ₂	2	percent	1669b	C ₃ H ₈ /Air	500	ppm
2641	CO/N ₂	4	percent				
2642	CO/N ₂	8	percent	2643	C ₃ H ₈ /N ₂	100	ppm
				2644	C ₃ H ₈ /N ₂	250	ppm
2657	O ₂ /N ₂	2	percent	2645	C ₃ H ₈ /N ₂	500	ppm
2658	O ₂ /N ₂	10	percent	2646	C ₃ H ₈ /N ₂	1000	ppm
2659	O ₂ /N ₂	21	percent	2647	C ₃ H ₈ /N ₂	2500	ppm
				2648	C ₃ H ₈ /N ₂	5000	ppm
				2649	C ₃ H ₈ /N ₂	1	percent
				2650	C ₃ H ₈ /N ₂	2	percent

NBS-SRM cylinders contain approximately 870 liters of gas at STP.

For availability, contact: Office of Standard Reference Materials
Chemistry Building, Room B311
NBS, Gaithersburg, Maryland 20899
(301) 975-6776. (FTS 879-6776)

4.1 PROCEDURE G1: ASSAY AND CERTIFICATION OF A COMPRESSED GAS STANDARD WITHOUT DILUTION

4.1.1 Applicability

This procedure may be used to assay the concentration of a candidate compressed gas (cylinder) pollutant standard, based on the concentration of a compressed gas (cylinder) reference standard of the same pollutant compound, and certify that the assayed concentration thus established for the candidate standard is traceable to the reference standard. The procedure employs a pollutant gas analyzer to compare the candidate and reference gas concentrations by direct measurement--without dilution of either gas--to minimize assay error.

4.1.2 Limitations

1. The concentration of the candidate gas standard must be between 0.3 and 1.3 times the concentration of the reference gas standard.
2. The analyzer must have a calibrated range capable of directly measuring both the candidate and the reference gas concentrations.
3. The analyzer's response (or transformed response) must be linear with respect to concentration.
4. The balance gas in both the candidate and reference standards must be identical, unless it can be shown that the analyzer is insensitive to any difference in the balance gases.
5. A source of clean, dry zero gas is required.

4.1.3 Assay Apparatus

Figure G1 illustrates the relatively simple assay apparatus. The configuration is designed to allow convenient routing of the zero gas and undiluted samples of the reference gas and candidate gases, in turn, to the analyzer for measurement, as selected by three-way valves V1 and V2. Pressure regulators and needle valves (V3 and V4) control the individual gas flows. The pollutant concentrations are delivered to the analyzer via a vented tee, which discharges excess flow and insures that the assay concentrations sampled by the analyzer are always at a fixed (atmospheric) pressure. A small, uncalibrated rotameter monitors the vent flow to verify that the total gas flow rate exceeds the sample flow rate demand of the analyzer so that no room air is admitted through the vent. Valves V1 and V2 could be replaced by a single four-way valve (with 3 inputs and 1 output) or by manually moving the output connection to each of the gases as needed. See also subsection 4.0.3.

4.1.4 Analyzer

See subsection 4.0.7.1. The pollutant gas analyzer must have a linear response function and a calibrated range capable of measuring the full concentration of both the candidate and the reference gas standards directly, without dilution. It must

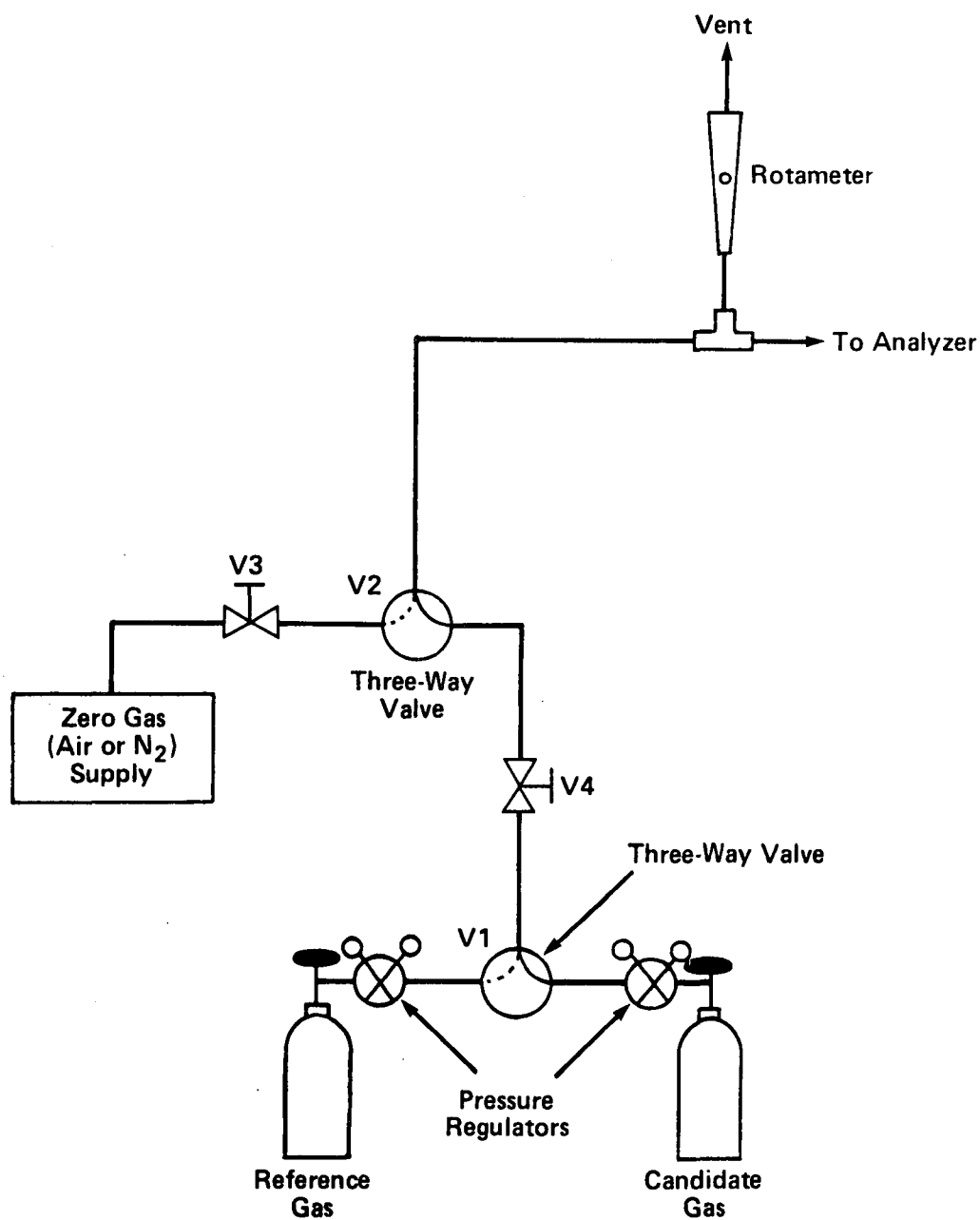


Figure G1. Suggested assay apparatus for Procedure G1.

have good resolution (readability), good precision, a stable response, and low output signal noise. In addition, the analyzer must have good specificity for the pollutant of interest so that it has no detectable response to any contaminant that may be contained in either the candidate or reference gas. If the candidate and reference gases contain dissimilar balance gases (air versus nitrogen or different proportions of oxygen in the balance air, for example), the analyzer must be proven to be insensitive to the two different balance gases. This may be accomplished by showing no difference in analyzer response when measuring pollutant concentrations diluted with identical flow rates of the two balance gases.

The analyzer should be connected to a suitable, precision chart recorder or other data acquisition device to facilitate graphical observation and documentation of the analyzer responses obtained during the assay.

4.1.5 Analyzer Calibration

4.1.5.1 Multipoint calibration. See subsections 4.0.7.2 and 4.0.7.4.

4.1.5.2 Calibration range. The calibrated range of the analyzer must include both the candidate and reference gas concentrations, such that the higher concentration does not exceed 97 percent of the upper range limit, and the lower concentration is not below 25 percent of the upper range limit (assuming a lower range limit of zero). Within these limits, select a calibrated analyzer range that will produce the highest analyzer responses.

4.1.5.3 Linearity. The direct ratio assay technique used in this procedure requires that the analyzer have a linear response to concentration (see subsection 4.0.7.5). High-concentration-range analyzers of the type that are required for this procedure may not be inherently linear, but they usually have a predictable, non-linear response characteristic that can be mathematically transformed to produce a sufficiently linear response characteristic suitable for use in this procedure. Any such response transformation should be verified by using it for the multipoint calibration. Caution should be exercised in using a transformed response curve because physical zero or span adjustments to the analyzer may produce unexpected effects on the transformed characteristic.

4.1.5.4 Zero and span adjustment. See subsections 4.0.7.3 and 4.0.7.4. Prior to carrying out the assay/certification procedure, check the calibration of the analyzer and, if necessary, adjust the analyzer's zero and span controls to re-establish the response characteristic determined at the most recent multipoint calibration. Allow the analyzer to stabilize for an hour or more after any zero or span adjustment. If there is any doubt that a transformed response characteristic is still linear following a zero or span adjustment, verify linearity with a multipoint calibration (subsection 4.0.7.2) using at least 3 known pollutant concentrations, including zero.

4.1.6 Assay Gases

4.1.6.1 Candidate gas standard. See subsections 4.0.6 and 4.1.2.

4.1.6.2 Reference gas standard. See subsections 4.0.2, 4.1.2, and 4.0.6.4. Select a reference standard such that the concentration of the candidate gas is not

more than 30 percent above nor less than 70 percent below the concentration of the standard.

4.1.6.3 Zero gas. See subsection 4.0.8. The zero gas should match the balance gas used in the cylinder concentrations.

4.1.7 Assay Procedure

1. Verify that the assay apparatus is properly configured, as described in subsection 4.1.3 and shown in Figure G1.

2. Verify that the linearity of the analyzer has been checked within the last 3 months (see subsections 4.0.7.2, 4.0.7.5, and 4.1.4), that the zero and span are adjusted correctly (subsection 4.0.7.3), that the candidate and reference gas concentrations are within 25 and 97 percent of the upper range limit of the calibrated measurement range of the analyzer, and that the analyzer is operating stably.

3. Adjust the flow rates of the three gases (reference, candidate, and zero) to approximately the same value that will provide enough flow for the analyzer and sufficient excess to assure that no ambient air will be drawn into the vent.

4. Conduct a triad of measurements with the analyzer. Each triad consists of a measurement of the zero gas concentration, a measurement of the reference gas concentration, and a measurement of the candidate gas concentration. Use valves V1 and V2 to select each of the three concentrations for measurement. For each measurement, allow ample time for the analyzer to achieve a stable response reading. Record the stable analyzer response for each measurement, using the same response units (volt, millivolts, percent of scale, etc.) used for the multipoint calibration and any transformation of the response readings necessary for linearity. Do not translate the response readings to concentration values via the calibration curve (see the footnote following Equation G1). Do not make any zero, span, or other physical adjustments to the analyzer during the triad of measurements.

5. Conduct at least 2 additional measurement triads, similar to step 4 above. However, for these subsequent triads, change the order of the three measurements (e.g. measure reference gas, zero gas, candidate gas for the second triad and zero gas, candidate gas, reference gas for the third triad, etc.).

6. If any one or more of the measurements of a triad is invalid or abnormal for any reason, discard all three measurements of the triad and repeat the triad.

7. For each triad of measurements, calculate the assay concentration of the candidate gas as follows:

$$C_C = C_R \frac{R_C - R_Z}{R_R - R_Z} \quad \text{Equation G1}$$

where: C_C = Assay concentration of the candidate gas standard, ppm or percent;
 C_R = Concentration of the reference gas standard, ppm or percent;
 R_C = Stable response reading of the analyzer for the candidate gas, analyzer response units;*
 R_Z = Stable response reading of the analyzer for the zero gas, analyzer response units;*
 R_R = Stable response reading of the analyzer for the reference gas, analyzer response units.*

*Analyzer response units are the units used to express the direct response readings of the analyzer, such as volts, millivolts, percent of scale, etc. DO NOT convert these direct response readings to concentration units with the multipoint calibration curve or otherwise adjust these readings except for transformation necessary to achieve response linearity.

8. Calculate the mean of the 3 (or more) valid assays. Calculate the percent difference of each assay from the mean. If any one of the assay values differs from the mean by more than 1.5%, discard that assay value and conduct another triad of measurements to obtain another assay value. When at least 3 assay values all agree within 1.5% of their mean, report the mean value as the certified concentration of the candidate gas standard. For newly-prepared reactive standards, a reassay at least 7 days later is required to check the stability of the standard; see subsection 4.0.6.2.

4.1.8 Stability Test for Newly-Prepared Standards

See subsections 4.0.6.1 and 4.0.6.2.

4.1.9 Certification Documentation

See subsections 4.0.4 and 4.0.5.

4.1.10 Recertification Requirements

See subsections 4.0.6.3 and 4.0.6.4.

4.2 References.

1. Code of Federal Regulations, Title 40, Part 60, "Standards of Performance for New Stationary Sources," Appendix A, Method 20 (1982).
2. Standards of Performance for New Stationary Sources; Quality Assurance Requirements for Gaseous Continuous Emission Monitoring Systems Used for Compliance Determination, promulgated in the Federal Register, June 4, 1987, pp. 21003-21010.
3. "A Procedure for Establishing Traceability of Gas Mixtures to Certain National Bureau of Standards Standard Reference Materials. EPA-600/7-81-010. Joint publication by NBS and EPA, May 1981. Available from the U.S. Environmental Protection Agency, Environmental Monitoring Systems Laboratory (MD-77), Research Triangle Park, NC 27711.
4. Code of Federal Regulations, Title 40, Part 50, "National Ambient Air Quality Measurement Methodology".
5. Code of Federal Regulations, Title 40, Part 58, "Ambient Air Quality Surveillance," Appendixes A and B.
6. Shores, R. C. and F. Smith, "Stability Evaluation of Sulfur Dioxide, Nitric Oxide, and Carbon Monoxide Gases in Cylinders. NTIS No. PB 85-122646. Available from the National Technical Information Service, 5285 Port Royal Road, Springfield, VA 22161.
7. Method 6A and 6B, "Determination of Sulfur Dioxide, Moisture, and Carbon Dioxide Emissions from Fossil Fuel Combustion Sources," Quality Assurance Handbook for Air Pollution Measurement Systems, Volume III, Section 3.13.8, July 1986. Available from the U.S. Environmental Protection Agency, Center for Environmental Research Information, Cincinnati, OH 45268.
8. "List of Designated Reference and Equivalent Methods." Current edition available from the U.S. Environmental Protection Agency, Environmental Monitoring Systems Laboratory, Quality Assurance Division (MD-77), Research Triangle Park, NC 27711.

United States
Environmental Protection
Agency

Environmental Monitoring Systems
Laboratory
Research Triangle Park NC 27711

Research and Development



Section 3.5

Method 6—Determination of Sulfur Dioxide Emissions from Stationary Sources

Outline

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Method Description		
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4. On-Site Measurements	3.5.4	7
5. Postsampling Operations	3.5.5	7
6. Calculations	3.5.6	2
7. Maintenance	3.5.7	1
8. Auditing Procedure	3.5.8	3
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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 mg SO₂/m³ (2.12 x 10⁻⁷ lb SO₂/ft³). Although no upper limit has been established, tests have shown

that concentrations as high as 80,000 mg SO₂/m³ can be collected efficiently in two midjet impingers, each containing 15 ml of 3% hydrogen peroxide and the sampling rate is 1.0 L/min for 20 min. Based on theoretical calculations, the upper concentration limit in a 20-L sample is about 93,300 mg SO₂/m³ 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 SO₂ 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 midjet 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 $\times 10^{-6}$ 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 SO_2/m^3 (17.6, 35.2, and 52.8 $\times 10^{-6}$ lb SO_2/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 midjet impingers and midjet bubblers with sample rates of about 1 liter per minute (l/min). If the tester opts to use the standard-sized impingers, the Method 8 description (Section 3.7) should be used as the reference for equipment calibration, sample setup, leak check, operation, and sample recovery. The only exceptions are that glass wool may be put in the U-tube between the isopropanol and peroxide impinger as an option to the filter, the sampling is to be conducted at a constant rate of about 0.02 scm/min (0.75 scfm) ($\Delta H@$, orifice pressure differential that gives 0.75 scfm of air at 70°F at 29.92 in. Hg); and the isopropanol need not be analyzed.

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

1. Procurement of Equipment

Section 3.5.1 (Procurement of Apparatus and Supplies) gives the specifications, criteria, and design features of the equipment and material required to perform Method 6 tests with the midjet 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 midjet 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 midjet 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 SO₂ 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 SO₂ 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 SO₂ 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)*

<i>Apparatus check</i>	<i>Acceptable</i>		<i>Quantity required</i>	<i>Ready</i>		<i>Loaded and packed</i>	
	<i>Yes</i>	<i>No</i>		<i>Yes</i>	<i>No</i>	<i>Yes</i>	<i>No</i>
<i>Probe</i>							
<i>Type liner</i>							
<i>Glass _____</i>							
<i>Stainless</i>							
<i>steel _____</i>							
<i>Other _____</i>							
<i>Heated properly</i>							
<i>Leak checked on</i>							
<i>sampling train</i>							
<i>Filter</i>							
<i>Glass wool</i>							
<i>Other _____</i>							
<i>Glassware</i>							
<i>Midget bubbler</i>							
<i>Midget impinger</i>							
<i>Size _____</i>							
<i>Type _____</i>							
<i>Meter System</i>							
<i>Leak-free pumps*</i>							
<i>Rate meter*</i>							
<i>Dry gas meter*</i>							
<i>Reagents</i>							
<i>Distilled water</i>							
<i>H₂O₂, 30%</i>							
<i>Isopropanol, 100%*</i>							
<i>Silica gel</i>							
<i>Other</i>							
<i>Barometer</i>							
<i>Drying tube</i>							

**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% 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? _____

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 $Y_1 =$ _____ $Y_2 =$ _____ ($\pm 5\%$ 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 $Y_1 =$ _____

Posttest check $Y_1 =$ _____ (within $\pm 10\%$ of pretest factor)

Recalibration recommended? _____ yes _____ no

If performed, recalibration factor $Y_1 =$ _____

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 midjet 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 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 SO₂.

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 ±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 ±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 ±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 m³/min (0.1 ft³/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.) H₂O.
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.

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.

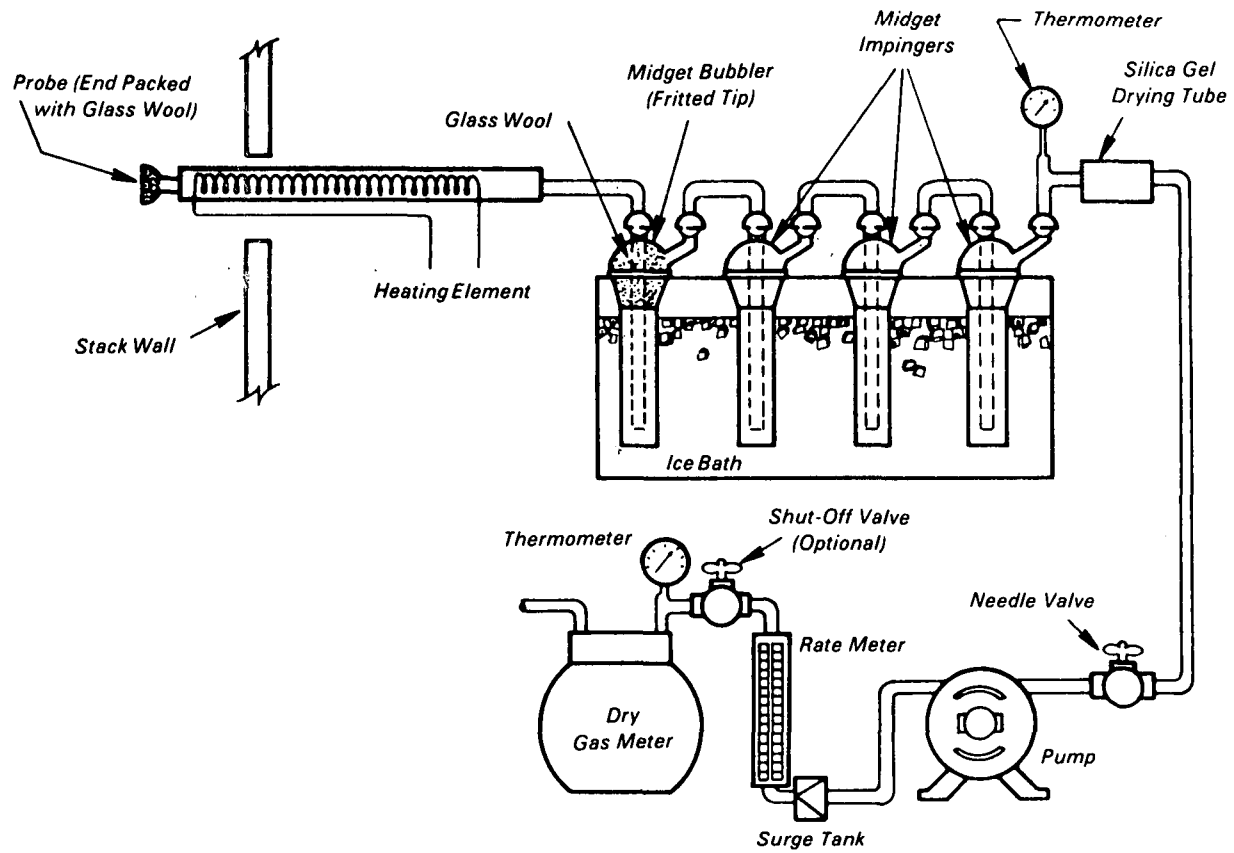
Thorin Indicator - Use reagent grade or certified ACS 1-(o-arsonophenylazo)-2-naphthol-3, 6-disulfonic acid, disodium salt. Dissolve 0.20 g in 100 ml of deionized distilled water.

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 $0.0100\text{N} \pm 0.0002\text{N}$ 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.

Figure 1.1. SO₂ sampling train.

Procurement Log

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.

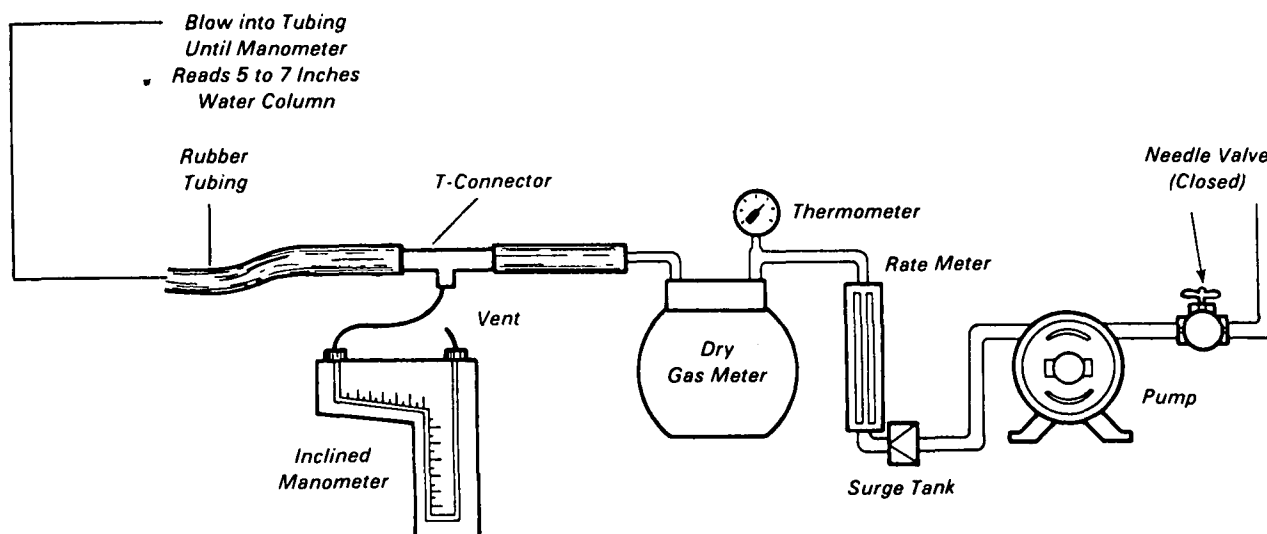


Figure 1.3. Meter box leak check.

Table 1.1. Activity Matrix for Procurement of Apparatus and Supplies

Apparatus and supplies	Acceptance limits	Frequency and method of measurement	Action if requirements are not met
Sampling			
Sampling probe with heating system	Capable of maintaining 100°C (212°F) exit air at flow rate of 1.0 L/min	Visually check and run heating system checkout	Repair or return to supplier
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° 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

Table 1.1. (continued)

<i>Apparatus and supplies</i>	<i>Acceptance limits</i>	<i>Frequency and method of measurement</i>	<i>Action if requirements are not met</i>
<i>Barometer</i>	<i>Capable of measuring atmospheric pressure to within ± 2.5 mm (0.1 in.) Hg calibrate</i>	<i>Check against mercury-in-glass barometer or equivalent (Sec. 3.5.2)</i>	<i>Determine correction factor, or reject if difference is more than ± 2.5</i>
<i>Vacuum gauge</i>	<i>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</i>	<i>Check against U-tube mercury manometer upon receipt</i>	<i>Adjust or return to supplier</i>
Sample Recovery			
<i>Wash bottles</i>	<i>Polyethylene or glass, 500 ml</i>	<i>Visually check for damage upon receipt</i>	<i>Replace or return to supplier</i>
<i>Storage bottles</i>	<i>Polyethylene, 100 ml</i>	<i>Visually check for damage upon receipt, and be sure that caps seal properly</i>	<i>As above</i>
Analysis Glassware			
<i>Pipettes, volumetric flasks, burettes, and graduated cylinder</i>	<i>Glass, Class A</i>	<i>Upon receipt, check for stock number, cracks, breaks, and manufacturer flaws</i>	<i>As above</i>
Reagents			
<i>Distilled water</i>	<i>Must conform to ASTM-D1193-74, Type 3</i>	<i>Check each lot or specify type when ordering</i>	<i>As above</i>
<i>Isopropanol</i>	<i>100% isopropanol, reagent grade or certified ACS with no peroxide impurities</i>	<i>Upon receipt, check each lot for peroxide impurities with a spectrophotometer</i>	<i>Redistill or pass through alumina column, or replace</i>
<i>Hydrogen peroxide</i>	<i>30% H_2O_2 reagent grade or certified ACS</i>	<i>Upon receipt, check label for grade or certification</i>	<i>Replace or return to manufacturer</i>
<i>Potassium iodide solution</i>	<i>Potassium iodide, reagent grade or certified ACS</i>	<i>As above</i>	<i>As above</i>
<i>Thorin indicator</i>	<i>1-(o-arsonophenylazo)-2-naphthol-3, 6-disulfonic acid disodium salt, reagent grade or certified ACS</i>	<i>As above</i>	<i>As above</i>
<i>Barium perchlorate solution</i>	<i>Barium perchlorate trihydrate ($Ba(ClO_4)_2 \cdot 3H_2O$), reagent grade or certified ACS</i>	<i>As above</i>	<i>As above</i>
<i>Sulfuric acid solution</i>	<i>Sulfuric acid, 0.0100N $\pm 0.0002N$</i>	<i>Have certified by manufacturer or standardize against 0.0100N NaOH that has been standardized against potassium acid phthalate (primary standard grade)</i>	<i>As above</i>

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.
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 cm^3/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).

$$Y_i = \frac{V_w \left(P_m + \frac{D_m}{13.6} \right) (t_d + 460)}{V_d P_m (t_w + 460)}$$

Equation 2-1

where

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

V_w = volume measured by wet test meter, m^3 (ft^3),

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

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

t_d = average temperature of dry gas meter, $^{\circ}C$ ($^{\circ}F$),

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 $\pm 1^{\circ}C$ ($2^{\circ}F$) at both points. If the difference is greater than $\pm 1^{\circ}C$ ($2^{\circ}F$), 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 $\pm 2^{\circ}C$ ($4^{\circ}F$) 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 $50^{\circ}C$ (104° to $122^{\circ}F$). 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 $3^{\circ}C$ ($5.4^{\circ}F$) at both points (steps 1 and 2 above) or if the temperature differentials at both points are within $\pm 3^{\circ}C$ ($5.4^{\circ}F$) 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 $\pm 6^{\circ}C$ ($10.8^{\circ}F$) 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).

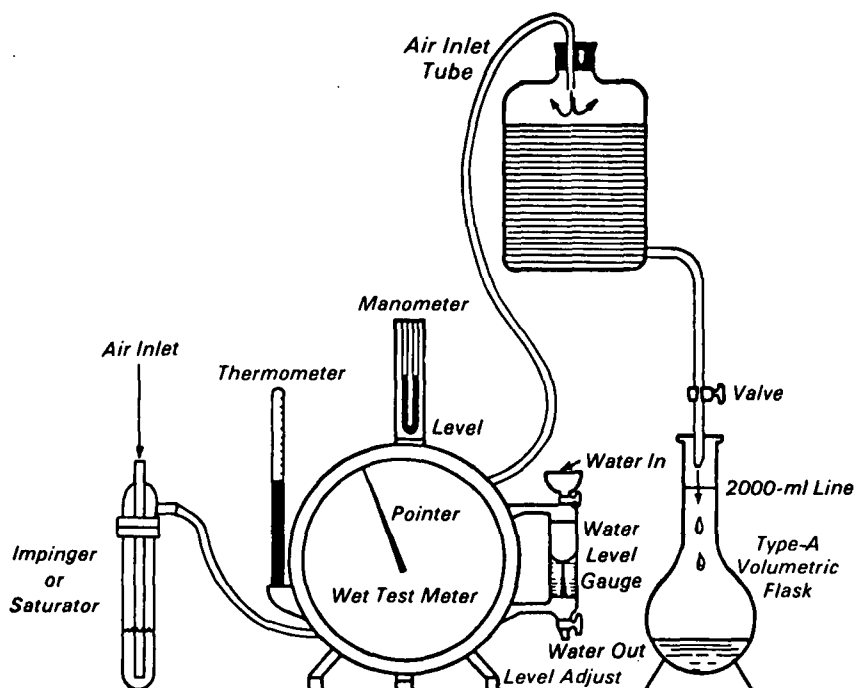


Figure 2.1. Calibration check apparatus for wet test meter.

Wet Test Meter Calibration Log

Wet test meter serial number 43-246 Date 1/27/77Range of wet test meter flow rate 0-120 l/minVolume of test flask $V_s =$ 2.00 lSatisfactory leak check? yesAmbient 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 = $100 (V_m - V_s) / V_s =$ _____ ($\pm 1\%$).Johnny Bench Signature of calibration person

Figure 2.2. Wet test meter calibration log.

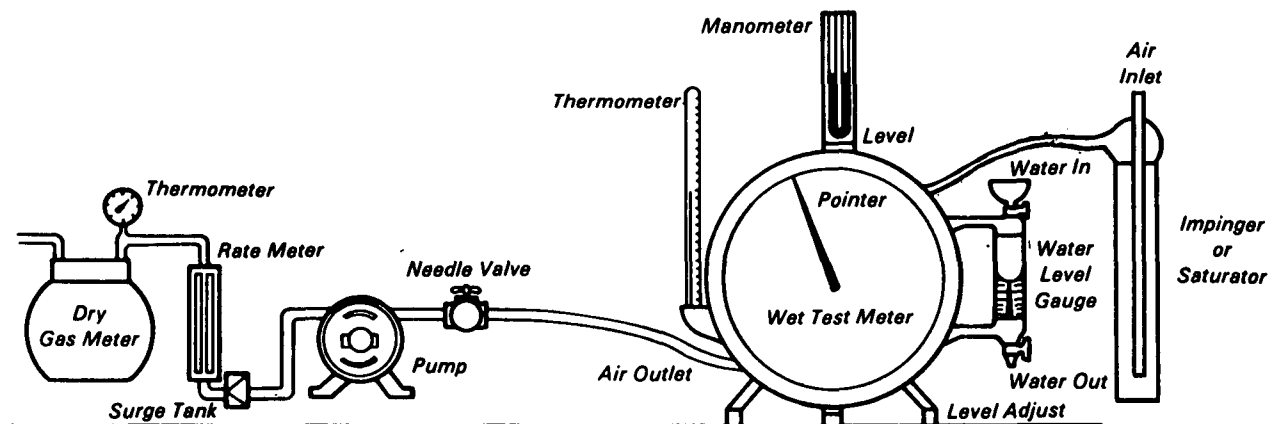


Figure 2.3. Sample meter system calibration setup.

Date 1-25-78 Calibrated by J. J. Jones Meter box number JJ-1
 Barometer pressure, $P_m =$ 29.41 in. Hg Wet test meter number 101-A
 Meter temperature correction factor NA °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), °F	Dry test meter				(Y_1) , ^c
			Initial	Final			Outlet gas temp (t_{d_0}), °F	Average gas temp (t_d), °F	Time of run (θ), min	Average ratio (Y_d), ^e	
0.25	0.035	1.058	725.613	726.672	72	80	79	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 a negative number.

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

^cThe average of t_{d_1} and t_{d_0} if using two thermometers; the actual reading if using one thermometer.

^dThe time it takes to complete the calibration run.

^eWith Y defined as the average ratio of volumes for the wet test and the dry test meters, $Y_1 = Y \pm 0.02 Y$ for calibration and $Y_1 = Y \pm 0.05 Y$ for the posttest checks, thus,

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

^fWith Y defined as the average ratio of volumetric measurements by wet test meter to rotameter, tolerance $Y_1 = 1 \pm 0.05$ for calibration and $Y \pm 0.1$ for posttest checks.

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

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

Date 1-25-78 Calibrated by J.J. Jones Meter box number JJ-1
 Barometer pressure, $P_m =$ 748 mm Hg Wet test meter number 101-A
 Meter temperature correction factor NA °C

Wet test meter pressure drop (D_m), ^a mm H ₂ O	Rota-meter setting (R_d), 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), °C	Dry test meter				(Y_1) , ^c
			Initial	Final			Outlet gas temp (t_{d_0}), °C	Average gas temp (t_d), °C	Time of run (θ), min	Average ratio (Y_d), ^e	
6.4	1.0	29.958	105.631	135.618	22	27	26	26.5	30	1.015	1.02
6.4	1.0	29.987	140.362	170.377	22	28	27	27.5	30	1.019	1.02
6.4	1.0	30.043	181.619	211.634	22	29	27	28.5	30	1.018	1.03

^a D_m expressed as negative number.

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

^cThe average of t_{d_1} and t_{d_0} if using two thermometers; the actual reading if using one thermometer.

^dThe time it takes to complete the calibration run.

^eWith Y defined as the average ratio of volumes for the wet test and the dry test meters, $Y_1 = Y \pm 0.02 Y$ for calibration and $Y_1 = Y \pm 0.05 Y$ for the posttest checks, thus,

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

^fWith Y defined as the average ratio of volumetric measurements by wet test meter to rotameter, tolerance $Y_1 = 1 \pm 0.05$ for calibration and $Y \pm 0.1$ for posttest checks.

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

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

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 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 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.

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).

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

*Most significant items/parameters to be checked.

Figure 3.1. Pretest preparations.

Table 3.1. Activity for Presampling Operations

<i>Operation</i>	<i>Acceptance limits</i>	<i>Frequency and method of measurement</i>	<i>Action if requirements are not met</i>
Apparatus			
<i>Probe</i>	1. <i>Probe liner free of contaminants</i> 2. <i>Probe leak free at 250 mm (10 in.) Hg</i> 3. <i>No moisture condensation</i>	1. <i>Clean probe internally by brushing with tap water, then deionized distilled water, then acetone; allow to dry in air before test</i> 2. <i>Visual check before test</i> 3. <i>Check out heating system initially and when moisture appears during testing</i>	1. <i>Retrace cleaning procedure and assembly</i> 2. <i>Replace</i> 3. <i>Repair or replace</i>
<i>Midget bubbler, midget impinger, and glass connectors</i>	<i>Clean and free of breaks, cracks, etc.</i>	<i>Clean with detergent, tap water, and then with deionized distilled water</i>	<i>Repair or discard</i>
<i>Flow control valve and rotameter</i>	<i>Clean and without sign of erratic behavior (ball not moving freely)</i>	<i>Clean prior to each field trip or upon erratic behavior</i>	<i>Repair or return to manufacturer</i>
<i>Vacuum pump</i>	<i>Maintain sampling rate of about 1 L/min up to 250 mm (10 in.) Hg</i>	<i>Service every 3 mo or upon erratic behavior; check oiler jars every 10th test</i>	<i>As above</i>
<i>Dry gas meter</i>	<i>Clean and within $\pm 2\%$ of calibration factor</i>	<i>Calibrate according to Sec. 3.5.2; check for excess oil if oiler is used</i>	<i>As above</i>
Reagents			
<i>Sampling</i>	<i>Requires all ACS grade reagents</i>	<i>Prepare fresh daily and store in sealed containers</i>	<i>Prepare new reagent</i>
<i>Sample recovery</i>	<i>Requires deionized distilled water on site</i>	<i>Use water and reagent grade isopropanol to clean midget bubbler after test and before sampling</i>	<i>Prepare new reagent</i>
Package Equipment for Shipment			
<i>Probe</i>	<i>Protect with polyethylene foam</i>	<i>Prior to each shipment</i>	<i>Repack</i>
<i>Midget bubbler, impingers, connectors, and assorted glassware</i>	<i>Pack in rigid containers with polyethylene foam</i>	<i>As above</i>	<i>As above</i>
<i>Drying tubes, volumetric glassware</i>	<i>Sturdy container lined with foam</i>	<i>As above</i>	<i>As above</i>
<i>Meter box</i>	<i>Meter box case and/or container to protect components; pack spare meter box and oil</i>	<i>As above</i>	<i>As above</i>
<i>Wash bottles and storage containers</i>	<i>Pack in rigid foam-lined container</i>	<i>As above</i>	<i>As above</i>

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_n should be between 0.9 and 1.1; if not, the meter box has lost its rate or volume calibration. The tester can still use the meter box, but the data should not be released for decision making until a posttest recalibration has been made. If the dry gas meter calibration factor did change, the dry gas meter volumes may have to be corrected. Record the test identification number on the sampling data form, Figure 4.1.

4.3 Sampling

The on-site sampling includes the following steps:

1. Preparation and/or addition of the absorbing reagents to the midjet 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 midjet bubbler or into a graduated impinger bottle. Do not use the pipette or graduated cylinder that was used to add the hydrogen peroxide solution. 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 midjet impingers; leave the final midjet impinger dry.
3. Pack glass wool into the top of the midjet bubbler to prevent sulfuric acid mist from entering the midjet 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 cm^3/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 $\leq 2\%$ of the average sampling rate is acceptable. *Note* - Carefully release the probe inlet

plug before turning off the pump. It is suggested (but not mandatory) that the pump be leak checked separately, either prior to or after the sampling run. If prior to the run, the pump leak check shall precede the leak check of the sampling train. If after, the pump leak check shall follow the train leak check. To leak check the pump, proceed as follows: Disconnect the drying tube from the probe impinger assembly. Place a vacuum gauge at the inlet to either the drying tube or the pump. Pull a vacuum of 250 mm (10 in.) Hg. Plug or pinch off the outlet of the flow meter and then turn off the pump. The vacuum should remain stable for at least 30 s.

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

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

1. Record the initial dry gas meter readings, barometer reading, and other data as indicated in Figure 4.1. Double check the dry gas meter reading and be sure that no hydrogen peroxide has been allowed to back up and wet the glass wool.
2. Position the tip of the probe at the sampling point, connect the probe to the bubbler, and start the pump. *Warning* - If the stack is under a negative pressure of >50 mm (2 in.) H_2O 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 midget 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 SO₂ 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 H₂O₂. Analysis of the isopropanol may be useful in detecting cleanup or sampling errors. Cap off the midget impinger section with the use of polyethylene or equivalent caps before transport to the cleanup area. 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% H₂O₂) 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 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.

Plant name ACME POWER PLANT City Anywhere, U.S.A.
 Sample location Boiler No. 3 Date 8/10/77
 Operator Joe Smith Sample number 50-1
 Barometric pressure, mm Hg 758 Probe length m 1.5
 Probe material Glass Probe heater setting 250°F
 Meter box number VS-1 Meter calibration factor (Y) 1.01
 Ambient temperature, °C 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	Sample flow rate setting, L/min	Sample volume metered (ΔV_m), L	Percent deviation ^a , %	Dry gas meter temp, °C	Impinger temp, °C
0	1100	120.20	—	—	—	—	—
5	1105	125.30	1.0	5.1	2	27	19
10	1101	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_m avg 5.0	Avg dev 1.6	Avg 29	Max temp 20

^aPercent deviation = $\frac{\Delta V_m - \Delta V_m \text{ avg}}{\Delta V \text{ avg}_m} 100$.

Figure 4.1. Field sampling data form for SO₂.

Plant	<u>Acme Power Plant</u>	City	<u>Anywhere</u>
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"/>	Front solution <input type="checkbox"/>	
Back rinse <input type="checkbox"/>	Back filter <input type="checkbox"/>	Back solution <input checked="" type="checkbox"/>	
Solution	<u>H₂O₂</u>	Level marked <input checked="" type="checkbox"/>	
Volume: Initial	<u>30m L</u>	Final	<u><100mL</u>
Cleanup by	<u>WGD</u>		
			Remarks

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 ml

Signature of field sample trustee Joe Smith

Laboratory Data Checks

Lab person with direct responsibility for recovered samples D. Jones

Date recovered samples received 8/11/77

Analyst D. Jones

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

Remarks _____

Signature of lab sample trustee Debbie Jones

Figure 4.3. Sample recovery and integrity data.

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

<i>Activity</i>	<i>Acceptance limits</i>	<i>Frequency and method of measurement</i>	<i>Action if requirements are not met</i>
<i>Preparation and/or addition of absorbing reagents</i>	<i>Add 15 ml of 80% isopropanol to midget bubbler and 15 ml of 3% H₂O₂ to first two midget impingers</i>	<i>Prepare 3% H₂O₂ fresh daily; use pipette or graduated cylinder to add solutions</i>	<i>Reassemble collection system</i>
<i>Assembling the sampling train</i>	<ol style="list-style-type: none"> <i>1. Assemble to specifications in Fig. 1.1</i> <i>2. A leakage rate $\leq 2\%$ of the average sampling rate</i> 	<ol style="list-style-type: none"> <i>1. Before each sampling</i> <i>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</i> 	<ol style="list-style-type: none"> <i>1. Reassemble</i> <i>2. Correct the leak</i>
<i>Sampling (constant rate)</i>	<ol style="list-style-type: none"> <i>1. Within $\pm 10\%$ of a constant rate</i> <i>2. Minimum acceptable time is 20 min and volume is 20 L corrected to STP or as specified by regulation</i> <i>3. Less than 2% leakage rate at 250 mm (10 in.) Hg</i> <i>4. Purge remaining SO₂ from isopropanol</i> 	<ol style="list-style-type: none"> <i>1. Calculate % deviation for each sample using equation in Fig. 4.1</i> <i>2. Make a quick calculation prior to completion and an exact calculation after</i> <i>3. Leak check after sample run (mandatory); use same procedure as above</i> <i>4. Drain ice and purge 15 min with clean air at the sample</i> 	<ol style="list-style-type: none"> <i>1. Repeat the sampling, or obtain acceptance from a representative of the Administrator</i> <i>2. As above</i> <i>3. As above</i> <i>4. As above</i>
<i>Sample logistics (data) and packing of equipment</i>	<ol style="list-style-type: none"> <i>1. All data are recorded correctly</i> <i>2. All equipment examined for damage and labeled for shipment</i> <i>3. All sample containers properly labeled and packaged</i> 	<ol style="list-style-type: none"> <i>1. Visually check upon completion of each run and before packing</i> <i>2. As above</i> <i>3. Visually check upon completion of test</i> 	<ol style="list-style-type: none"> <i>1. Complete the data form</i> <i>2. Redo test if damage occurred during testing</i> <i>3. Correct when possible</i>

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% 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

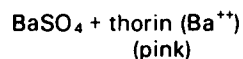
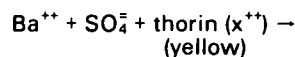
run. The lesser calibration factor will give the lower gas volume.

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 (BaSO₄) 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 KMnO₄ 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 ±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 H₂SO₄ to ±0.002N 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 H₂SO₄ may be prepared in the following manner:

- Prepare 0.5N H_2SO_4 by adding approximately 1500 ml of distilled water to a 2-L volumetric flask.
- Cautiously add 28 ml of concentrated sulfuric acid and mix.
- Cool if necessary.
- Dilute to 2 L with distilled water.
- 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 .
- 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:

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

- 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.
- 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.

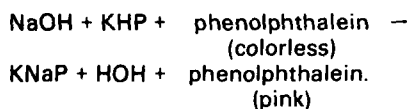
$$N_{\text{NaOH}} = \frac{\text{mg KHP}}{\text{ml titrant} \times 204.23}$$

where

N_{NaOH} = calculated normality of sodium hydroxide,
 mg KHP = weight of the phthalate, mg, and
 ml titrant = volume of sodium hydroxide titrant, ml

Equation 5-2

The chemical reaction for this standardization is shown in Equation 5-3. The sodium hydroxide is added to the potassium hydrogen phthalate and colorless phenolphthalein solution until there is an excess of diluted hydroxyl ions which causes the phenolphthalein solution to change to a pink color.



Equation 5-3

5.2.3 Standardization of Sulfuric Acid - To standardize sulfuric acid, proceed as follows:

- Pipette 25 ml of the H_2SO_4 into each of three 250-ml Erlenmeyer flasks.
- Add 25 ml of deionized distilled water to each.
- Add two drops of phenolphthalein indicator, and titrate with the standardized NaOH solution to a persistent pink endpoint, using a white background.
- Titrate a blank of 25 ml of deionized distilled water, using the same technique as step 3. The normality will be the average of the three independent values calculated using the following equation:

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

Equation 5-4

where

$N_{\text{H}_2\text{SO}_4}$ = calculated normality of sulfuric acid,
 ml $\text{NaOH}_{\text{acid}}$ = volume of titrant used for H_2SO_4 , ml,
 ml $\text{NaOH}_{\text{blank}}$ = volume of titrant used for blank, ml, and
 N_{NaOH} = normality of sodium hydroxide.

5.2.4 Standardization of Barium Perchlorate (0.0100N) - To standardize barium perchlorate, proceed as follows:

- Pipette 25 ml of sulfuric acid standard (0.0100N) into each of three 250-ml Erlenmeyer flasks.
- Add 100 ml of reagent grade isopropanol and two to four drops of thiorin indicator, and titrate to a pink endpoint using 0.0100N barium perchlorate. Perform all thiorin titrations against a white background to facilitate the detection of the pink endpoint color.
- 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.
- Use the endpoint of the blank or the endpoint of the first titration as a visual comparator for the succeeding titrations.
- Record data on analytical data form, Figure 5.2. The normality of the barium perchlorate will be the average of the three independent values calculated using Equation 5-5.

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

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

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

where

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

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

V_{soln_i} = initial sample volume placed in storage container, ml, and

V_{soln_f} = final sample volume removed from storage container, ml.

6. Both the corrected and uncorrected values should be submitted in the test report to the Agency.

Proceed with the analysis as follows:

1. Transfer the contents of the sample bottle to a 100-ml volumetric flask (V_{soln}), and dilute to the mark with deionized distilled water.
2. Pipette a 20-ml aliquot (V_a) of this solution into a 250-ml Erlenmeyer flask, and add 80 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.

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 $Y_t =$ 1.03

Posttest check $Y_t =$ 1.05 (within $\pm 10\%$ of pretest factor)

Recalibration recommended? ☐ yes ☒ no

If performed, recalibration factor $Y_t =$ _____

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.

Plant Acme Power Plant Date 8/12/77
 Sample location Boiler No. 3 Analyst Debbie Jones
 Volume and normality of barium perchlorate
 1 24.52 ml 0.01019 N
 2 24.50 ml 0.01020 N
 3 24.50 ml 0.01020 N } 0.0102 N, avg

Sample number	Sample identification number	Total sample volume (V_{soln}), ml	Sample aliquot volume (V_a), ^a ml	Volume of titrant (V_t), ^b ml		
				1st titration	2nd titration	Average
1	<u>50-1</u>	<u>100</u>	<u>20</u>	<u>11.31</u>	<u>11.29</u>	<u>11.30</u>
2						
3						
4						
5						
6						
Blank		<u>N/A</u>		<u>0</u>	<u>0</u>	$V_{\text{tb}} = 0$

^aVolume for the blank must be the same as that of the sample aliquot.

^b1st titration = 0.99 to 1.01 or $|1\text{st titration} - 2\text{nd titration}| \leq 0.2$ ml.

2nd titration

Signature of analyst

Signature of reviewer or supervisor

Figure 5.2. Sulfur dioxide analytical data form.

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	Titration volume, ^a ml			
		1st	2nd	3rd	Avg
<u>1</u>	<u>0930</u>	<u>25.0</u>	<u>25.0</u>		<u>25.0</u>

^aTwo titrant volumes must agree within 0.2 ml.

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

25.0 ml \times 0.010 N = 0.250

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

Does value agree? yes no

Signature of analyst

Signature of reviewer

Figure 5.3. Control sample analytical data form.

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.

Table 5.1. Activity Matrix for Postsampling Operations

<i>Activity</i>	<i>Acceptance limits</i>	<i>Frequency and method of measurement</i>	<i>Action if requirements are not met</i>
Sampling Apparatus			
<i>Dry gas meter</i>	<i>Within $\pm 5\%$ of pretest calibration factor</i>	<i>Make two independent runs after each field test</i>	<i>Recalibrate and use calibration factor that gives lower sample volume</i>
<i>Rate meter</i>	<i>Within $\pm 10\%$ of desired flow rate (recommended)</i>	<i>Make two independent runs during the check of the rate meter</i>	<i>Recalibrate</i>
<i>Meter thermometer</i>	<i>Within $\pm 6^\circ\text{C}$ (10.8°F) at ambient temperature</i>	<i>Compare with ASTM mercury-in-glass thermometer after each field test</i>	<i>Recalibrate and use higher temperature value for calculations</i>
<i>Barometer</i>	<i>Within ± 5.0 mm (0.2 in.) Hg at ambient pressure</i>	<i>Compare with mercury-in-glass barometer after each field test</i>	<i>Recalibrate and use lower barometric value for calculations</i>
Analysis			
<i>Reagents</i>	<i>Prepare according to requirements detailed in Subsec. 5.2</i>	<i>Prepare and/or standardize within 24 h of sample analysis</i>	<i>Prepare new solutions and/or re-standardize</i>
<i>Control sample</i>	<i>Titants differ by ≤ 0.2 ml; analytical results within $\pm 5\%$ of stated value</i>	<i>Before and after analysis of field samples</i>	<i>Prepare new solutions and/or re-standardize</i>
<i>Sample analysis</i>	<i>Titrant volumes differ by $\leq 1\%$ or ≤ 0.2 ml, whichever is greater</i>	<i>Titrate until two or more sample aliquots agree within 1% or 0.2 ml, whichever is greater; review all analytical data</i>	<i>Void sample if any two titrations do not meet criterion</i>

6.0 Calculations

Calculation errors due to procedural or mathematical mistakes can be a part of total system error. Therefore, it is recommended that each set of calculations be repeated or spotchecked, preferably by a team member other than the one who performed the original calculations. If a difference greater than typical round-off error is detected, the calculations should be checked step-by-step until the source of error is found and corrected. A computer program is advantageous in reducing calculation errors. If a standardized computer program is used, the original data entry should be included in the printout to be checked; if differences are observed, a new computer run should be made. Table 6.1 at the end of this section summarizes the quality assurance activities for calculations.

Calculations should be carried out to at least one extra decimal figure beyond that of the acquired data and should be rounded off after final calculation to two significant digits for each run or sample. All rounding off of numbers should be performed in accordance with the ASTM 380-76 procedures. All calculations should then be recorded on a calculation form such as the ones in Figures 6.1A 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 -

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

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

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

Equation 6-2

where

$K_2 = 32.03$ mg/meq for metric units, or
 $= 7.061 \times 10^{-5}$ lb/meq for English 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

Sample Volume^a

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

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

Equation 6-1

SO₂ Concentration

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

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

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

Equation 6-2

^aCalculation 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 $V_{m(\text{std})} = \underline{\hspace{1cm}} \text{ ft}^3$.

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

Sample Volume^a

$$V_m = \underline{20.000} \text{ l} \times 0.001 = \underline{0.0200} \text{ m}^3$$

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

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

Equation 6-1

SO₂ Concentration

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

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

$$C_{\text{SO}_2} = 32.03 \frac{N(V_t - V_{tb})(V_{\text{soln}}/V_a)}{V_{m(\text{std})}} = \underline{942.0} \text{ mg/dscm}$$

Equation 6-2

^aCalculation 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 $V_{m(\text{std})} = \underline{\hspace{1cm}} \text{ m}^3$.

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

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

<i>Apparatus</i>	<i>Acceptance limits</i>	<i>Frequency and method of measurements</i>	<i>Action if requirements are not met</i>
<i>Routine maintenance</i>	<i>No erratic behavior</i>	<i>Routine maintenance performed quarterly; disassemble and clean yearly</i>	<i>Replace parts as needed</i>
<i>Fiber vane pump</i>	<i>In-line oiler free of leaks</i>	<i>Periodically check oiler jar; remove head and change fiber vanes</i>	<i>Replace as needed</i>
<i>Diaphragm pump</i>	<i>Leak-free valves functioning properly</i>	<i>Clean valves during yearly disassembly</i>	<i>Replace when leaking or malfunctioning</i>
<i>Dry gas meter</i>	<i>No excess oil, corrosion, or erratic rotation of the dial</i>	<i>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</i>	<i>Replace parts as needed or replace meter</i>
<i>Rotameter</i>	<i>Clean and no erratic behavior</i>	<i>Clean every 3 mo or whenever ball does not move freely</i>	<i>Replace</i>
<i>Sample train</i>	<i>No damage</i>	<i>Visually check every 3 mo; completely disassemble and clean or replace yearly</i>	<i>If failure noted, use another entire meter box, sample box, or umbilical cord</i>

8.0 AUDITING PROCEDURE

An audit is an independent assessment of data quality. Independence is achieved if the individual(s) performing the audit and their standards and equipment are different from the regular field crew and their standards and equipment. In the case of a compliance test, the required performance audit will be conducted by the responsible enforcement agency. Routine quality assurance checks by a field team are necessary in generation of good quality data, but they are not part of the auditing procedure. Table 8.1 at the end of this section summarizes the quality assurance functions for auditing.

Based on the results of collaborative tests^{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 for both Methods.

It is suggested that a systems audit be conducted as specified by the quality assurance coordinator, in addition to these performance audits. The two performance audits and the systems audit are described in detail in Subsections 8.1 and 8.2, respectively.

8.1 Performance Audits

Performance audits are generally made to quantitatively evaluate the quality of data produced by the total measurement system (sample collection, sample analysis, and data processing). It is recommended that these audits be performed by the responsible control agency once during every enforcement source test. A source test for enforcement comprises a series of runs at one source. No performance audit is recommended at this time for the sampling phase. The performance audit of the analytical phase is subdivided into two steps: (1) a pretest audit which is optional, and (2) an audit during the field sampling and/or analysis phase which is required.

8.1.1 Pretest Audit of Analytical Phase Using Aqueous Ammonium Sulfate (Optional) - The pretest audit described in this section can be used to determine the proficiency of the analyst and the standardization of solutions in the Method 6 analysis and should be performed at the discretion of the agency auditor, the laboratory supervisor, source test company, or quality assurance officer. The analytical phase of Method 6 can be audited with the use of aqueous ammonium sulfate samples provided to the testing laboratory before the enforcement source test. Aqueous ammonium sulfate samples may be prepared by the procedure described in Section 3.5.5 on control sample preparation.

The pretest audit provides the opportunity for the testing laboratory to check the accuracy of its analytical procedure. This audit is especially recommended for a laboratory with little or no experience with the Method 6 analysis procedure described in this Handbook.

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

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

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

where:

C_d = Determined audit sample concentration, mg/dsm³.

C_a = Actual audit sample concentration, mg/dsm³.

8.1.2 Audit of Analytical Phase of the Field Test (Required) - As stated in 40 CFR 60, Section 3.3.6 (49 FR 26522, 06/27/84), the testing laboratory should provide the responsible agency/organization requesting the performance test with a notification of the intent to test 30 days prior to the enforcement source test. The responsible agency obtains the audit samples from the appropriate EPA Regional Quality Assurance Coordinator shown in Table 5.1 of Section 3.0.5 of this Handbook. The responsible agency then provides the testing laboratory with two audit samples to be analyzed along with the field samples from the enforcement source test. The purpose of this audit is to assess the data quality at the time of the analysis.

The two audit samples and the compliance samples should be concurrently analyzed in the same manner to evaluate the technique of the analyst and the standards preparation. (Note: It is recommended that known quality control samples be analyzed

prior to the compliance and audit sample analysis to optimize the system accuracy and precision. One source of these samples has been listed above.) The same analyst, analytical reagents, and analytical system shall be used both for compliance samples and the EPA audit samples; if this condition is met, auditing of subsequent compliance analyses for the same enforcement agency within 30 days may not be required. An audit sample set may not be used to validate different sets of compliance samples under the jurisdiction of different enforcement agencies, unless prior arrangements are made with both enforcement agencies.

Calculate the concentrations in mg/dsm^3 using the specified sample volume in the audit instructions. (Note: Indication of acceptable results may be obtained immediately by reporting the audit results in mg/dsm^3 and compliance results in total $\text{mg NO}_2/\text{sample}$ by telephone to the responsible enforcement agency.) Include the results of both audit samples, their identification numbers, and the analyst's name with the results of the compliance determination samples in appropriate reports to the EPA regional office or the appropriate enforcement agency. Include this information with subsequent compliance analyses for the same enforcement agency during the 30-day period.

The concentration of the audit samples obtained by the analyst shall agree within 5-percent of the actual concentrations. If the 5-percent specification is not met, reanalyze the compliance samples and audit samples, and include initial and reanalysis values in the test report (see Note in first paragraph of this section).

Failure to meet the 5-percent specification may require retests until the audit problems are resolved. However, if the audit results do not affect the compliance or noncompliance status of the affected facility, the Administrator may waive the reanalysis requirement, further audits, or retests and accept the results of the compliance test. While steps are being taken to resolve audit analysis problems, the Administrator may also choose to use the data to determine the compliance or noncompliance status of the affected facility.

8.1.3 Audit of Data Processing - Calculation errors are prevalent in Method 6.3, 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 appear in the field), and by requesting that the data calculation be completed and that the results be returned to the agency/organization. This audit is useful in

checking both computer programs and manual methods of data processing.

8.2 Systems Audit

A systems audit is an on-site qualitative inspection and review of the total measurement system (sample collection, sample analysis, data processing, etc.). Initially, a systems audit is recommended for each enforcement source test, defined here as a series of three runs at one source. After the test team gains experience with the method, the frequency of audit may be reduced--for example, to once for every four tests.

The auditor should have extensive background experience in source sampling, specifically with the measurement system being audited. The functions of the auditor are summarized below:

1. Inform the testing team of the results of pretest audits, specifying any area(s) that need special attention or improvement.
2. Observe procedures and techniques of the field team during sample collection.
3. Check/verify records of apparatus calibration checks and quality control used in the laboratory analysis of control samples from previous source tests, where applicable.
4. Record the results of the audit and forward them with comments to the team management so that appropriate corrective action may be initiated.

While on site, the auditor observes the source test team's overall performance, including the following specific operations:

1. Setting up and leak testing the sampling train.
2. Preparing and adding the absorbing solution to the impingers.
3. Purging the sampling train.

Figure 8.1 is a suggested checklist for the auditor.

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

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 sulfate solution	Measured RE of the pretest audit samples should be less than $\pm 5\%$ for both audit results (optional)	<u>Frequency:</u> As considered necessary by the testing firm <u>Method:</u> Measure reference samples and compare with true value	Review operating techniques
	Measured RE for audit during test should be less than $\pm 5\%$ for both audit results (required)	<u>Frequency:</u> Once during every enforcement source test (required) <u>Method:</u> Measure audit samples and compare with true samples	Review operating technique and repeat both the audit and field sample analyses
Data processing errors (recommended)	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
System audit (recommended)	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 and 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 ($2.12 \times 10^{-7} \text{ lb/ft}^3$). Although no upper limit has been established, tests have shown that concentrations as high as 80,000 mg/m^3 of SO_2 can be collected efficiently in two midjet impingers, each containing 15 milliliters of 3 percent hydrogen peroxide, at a rate of 1.0 Lpm for 20 minutes. Based on theoretical calculations, the upper concentration limit in a 20-liter sample is about 93,300 mg/m^3 .

Possible interferents 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 interferents.

Free ammonia interferes by reacting with SO_2 to form particulate sulfite 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 midjet 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 8.

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 midjet 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 midjet impingers. The bubbler and midjet 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 midjet impinger may be used in place of the midjet 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 surge 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

*40 CFR 60, July 1, 1978

(dial thermometer, or equivalent) capable of measuring temperature to within 3°C (5.4°F).

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

2.1.12 Vacuum Gauge and Rotameter. At least 760 mm Hg (30 in. Hg) gauge and 0-40 cc/min rotameter, 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 1000-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 352 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 352 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, 3 Percent. Dilute 30 percent hydrogen peroxide 1:9 (v/v) with deionized, distilled water (30 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-arsonophenylazo)-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 1.95 g of barium perchlorate trihydrate $[\text{Ba}(\text{ClO}_4)_2 \cdot 3\text{H}_2\text{O}]$ 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 midjet bubbler and 15 ml of 3 percent hydrogen peroxide into each of the first two midjet impingers. Leave the final midjet 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:

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.

Other leak-check procedures may be used, subject to the approval of the Administrator, U.S. Environmental Protection Agency.

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 or use procedures acceptable to the Administrator to adjust the sample volume for the leakage. 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 midget impinger with 15 ml of 3 percent H₂O₂. The tester may opt to simply use ambient air, without purification.

4.2 Sample Recovery. Disconnect the impingers after purging. Discard the contents of the midget bubbler. Pour the contents of the midget impingers into a leak-free polyethylene bottle for shipment. Rinse the three midget 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 thiorin 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 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.

Next, calibrate the metering system (at the sampling flow rate specified 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, Y (wet test meter calibration volume divided by the dry gas meter volume, both volumes adjusted to the same reference temperature and pressure), for each run, and average the results. If any Y value deviates by more than 2 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 Posttest 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_{SO₂} = 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_{soln} = Total volume of solution in which the sulfur dioxide sample is contained, 100 ml.

V_t = Volume of barium perchlorate titrant used for the sample, ml (average of replicate titrations).

V_{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 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

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

6.3 Sulfur Dioxide Concentration

$$C_{\text{SO}_2} = K_2 \frac{(V_t - V_{tb}) N \left(\frac{V_{\text{soln}}}{V_a} \right)}{V_{m(\text{std})}}$$

Equation 6-2

where

$K_2 = 32.03 \text{ mg/meq.}$ for metric units.
 $= 7.061 \times 10^{-6} \text{ lb/meq.}$ for English units.

7. Bibliography

1. Atmospheric Emissions from Sulfuric Acid Manufacturing Processes. U.S. DHEW, PHS, Division of Air Pollution. Public Health Service Publication No. 999-AP-13. Cincinnati, Ohio. 1965.
2. Corbett, P.F. The Determination of SO_2 and SO_3 in Flue Gases. Journal of the Institute of Fuel. 24: 237-243. 1961.
3. Matty, R.E. and E.K. Diehl. Measuring Flue-Gas SO_2 and SO_3 . Power. 101: 94-97. November 1957.
4. Patton, W.F. and J.A. Brink, Jr. New Equipment and Techniques for Sampling Chemical Process Gases. J. Air Pollution Control Association. 13: 162. 1963.
5. Rom, J.J. Maintenance, Calibration, and Operation of Isokinetic Source-Sampling Equipment. Office of Air Programs, Environmental Protection Agency. Research Triangle Park, N.C. APTD-0576. March 1972.
6. Hamil, H.F. and D.E. Camann. Collaborative Study of Method for the Determination of Sulfur Dioxide Emissions from Stationary Sources (Fossil-Fuel Fired Steam Generators). Environmental Protection Agency, Research Triangle Park, N.C. EPA-650/4-74-024. December 1973.
7. Annual Book of ASTM Standards. Part 31; Water, Atmospheric Analysis. American Society for Testing and Materials. Philadelphia, Pa. 1974. pp. 40-42.
8. Knoll, J.E. and M.R. Midgett. The Application of EPA Method 6 to High Sulfur Dioxide Concentrations. Environmental Protection Agency. Research Triangle Park, N.C. EPA-600/4-76-038. July 1976.

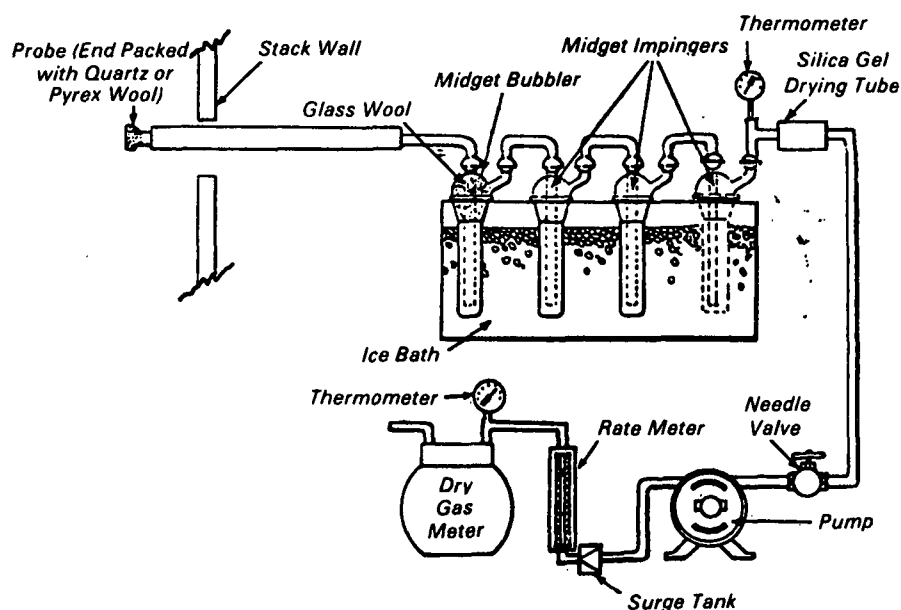


Figure 6-1. SO_2 sampling train.

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 D. 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., D. E. Camann, and R. 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, R. A., D. E. Camann, and H. 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, F., and C. Nelson, Jr. Guidelines for Development of a Quality Assurance Program. EPA-R4-73-028d. August 1973.
9. Fuerst, R. G. Improved Temperature Stability of Sulfur Dioxide Samples Collected by the Federal Reference Method. EPA-600/4-78-018, April 1978.
10. Knoll, J. E., and M.R. Midgett. The Application of EPA Method 6 to High Sulfur Dioxide Concentrations. EPA-600/4-76-038. July 1976.
11. Osborne, M. C., and M. R. Midgett. 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 D. E. Wagoner. 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 Inter-laboratory 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.

<i>Form</i>	<i>Title</i>
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
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

<i>Item description</i>	<i>Qty.</i>	<i>Purchase order number</i>	<i>Vendor</i>	<i>Date</i>		<i>Cost</i>	<i>Disposition</i>	<i>Comments</i>
				<i>Ord.</i>	<i>Rec.</i>			

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						

^aMust 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 _____ °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), °F	Dry test meter					(Y_i) , ¹
			Initial	Final		Inlet gas temp (t_{d1}), °F	Outlet gas temp (t_{d0}), °F	Average gas temp (t_d), ^c °F	Time of run (θ), ^d min	Average ratio (Y), ^e	

^a D_m expressed as a negative number.

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

^cThe average of t_{d1} and t_{d0} if using two thermometers; the actual reading if using one thermometer.

^dThe time it takes to complete the calibration run.

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

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

¹With Y , defined as the average ratio of volumetric measurement by wet test meter to rotameter. Tolerance $Y_i = 1 \pm 0.05$ for calibration and $Y \pm 0.1$ for posttest checks

$$Y_{i1} = \frac{V_w(t_d + 460^\circ F)(P_m + (D_m/13.6))(60)}{\theta(t_w + 460^\circ F)(P_m)(0.035)} \quad (\text{Eq. 3}) \quad Y_i = \frac{Y_1 + Y_2 + Y_3}{3} \quad (\text{Eq. 4})$$

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_w), 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					(Y), ^c
			Initial	Final		Inlet gas temp (t_{di}), °C	Outlet gas temp (t_{do}), °C	Average gas temp (t_d), ^c °C	Time of run (θ), ^d min	Average ratio (Y), ^e	

^a D_m expressed as a negative number.

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

^cThe average of t_{di} and t_{do} if using two thermometers; the actual reading if using one thermometer.

^dThe time it takes to complete the calibration run.

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

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

^fWith Y, defined as the average ratio of volumetric measurement by wet test meter to rotameter. Tolerance $Y_i = 1 \pm 0.05$ for calibration and $Y_i = 1 \pm 0.1$ for posttest checks

$$Y_i = \frac{V_w(t_d + 273^\circ\text{F})[P_m + (D_m/13.6)]}{\theta(t_w + 273^\circ\text{C})(P_m)(0.035)} \quad (\text{Eq. 3}) \quad Y_i = \frac{Y_1 + Y_2 + Y_3}{3} \quad (\text{Eq. 4})$$

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

$$^a \text{Percent deviation} = \frac{(\Delta V_m - \Delta V_m \text{ avg})}{\Delta V \text{ avg}_m} 100.$$

Sample Label

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

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Sample Recovery and Integrity Data

Plant _____ Sample location _____

Field Data Checks

Sample recovery personnel _____

Person with direct responsibility for recovered samples _____

<i>Sample number</i>	<i>Sample identification number</i>	<i>Date of recovery</i>	<i>Liquid level marked</i>	<i>Stored in locked container</i>
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 _____

<i>Sample number</i>	<i>Sample identification number</i>	<i>Date of analysis</i>	<i>Liquid at marked level</i>	<i>Sample identified</i>
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 perchlorate 1 _____ ml _____ N

2 _____ ml _____ N _____ N, avg

3 _____ ml _____ N

Sample number	Sample identification number	Total sample volume (V_{soln}), ml	Sample aliquot volume (V_{al}), ^a ml	Volume of titrant (V_t), ^b ml		
				1st titration	2nd titration	Average
1						
2						
3						
4						
5						
6						
Blank		N/A				$V_{\text{tb}} =$

^aVolume for the blank must be the same as that of the sample aliquot.^b1st titration = 0.99 to 1.01 or $|1\text{st titration} - 2\text{nd titration}| \leq 0.2\text{ ml}$.
2nd titration

Signature of analyst _____

Signature of reviewer or supervisor _____

Control Sample Analytical Data Form

Plant _____ Date analyzed _____

Analyst _____ N Ba(ClO₄)₂ _____

Weight of ammonium sulfate is 1.3214 g? _____

Dissolved in 2 L of distilled water? _____

Titration of blank _____ ml Ba(ClO₄)₂ (must be < 0.5-ml)

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

^aTwo titrant volumes must agree within 0.2 ml

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

$$\text{_____ ml} \times \text{_____ N} = \text{_____}$$

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

Does value agree? _____ yes _____ no

Signature of analyst_____
Signature of reviewer

*Sulfur Dioxide Calculation Form
(English units)*

Sample Volume^a

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

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

Equation 6-1

SO₂ Concentration

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

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

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

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 $V_{m(\text{std})} = \text{---} \cdot \text{---} \text{ ft}^3$.*

*Sulfur Dioxide Calculation Form
(metric units)*

Sample Volume^a

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

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

$$V_{m(\text{std})} = 0.3858 \frac{K}{mm Hg} \frac{Y V_m P_{\text{bar}}}{T_m} = \text{---} \cdot \text{---} m^3 \quad \text{Equation 6-1}$$

SO₂ Concentration

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

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

$$C_{\text{SO}_2} = 32.03 \frac{N (V_t - V_{tb}) (V_{\text{soln}}/V_a)}{V_{m(\text{std})}} = \text{---} \cdot \text{---} mg/dscm \quad \text{Equation 6-2}$$

^aCalculation 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 $V_{m(\text{std})} = \text{---} \cdot \text{---} m^3$.

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 adsorbing 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

United States
Environmental Protection
Agency

Environmental Monitoring Systems
Laboratory
Research Triangle Park NC 27711

Research and Development



Section 3.6

Method 7—Determination of Nitrogen Oxide Emissions from Stationary Sources

Outline

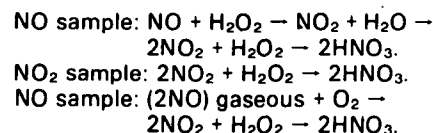
Section	Document	Number of Pages
Summary	3.6	2
Method Highlights	3.6	7
Method Description		
1. Procurement of Apparatus and Supplies	3.6.1	5
2. Calibration of Apparatus	3.6.2	5
3. Presampling Operations	3.6.3	5
4. On-site Measurements	3.6.4	8
5. Postsampling Operations	3.6.5	5
6. Calculations	3.6.6	4
7. Maintenance	3.6.7	1
8. Auditing Procedure	3.6.8	4
9. Recommended Standards for Establishing Traceability	3.6.9	1
10. Reference Method	3.6.10	5
11. References	3.6.11	1
12. Data Forms	3.6.12	13

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 (NO₂). The applicable regulation should be consulted to determine any additional requirements (i.e., velocity traverse or O₂ 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 ammonium 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 potassium 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.

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.

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)*

	<i>Acceptable</i>		<i>Quantity required</i>	<i>Ready</i>		<i>Loaded and packed</i>	
	<i>Yes</i>	<i>No</i>		<i>Yes</i>	<i>No</i>	<i>Yes</i>	<i>No</i>
<i>Apparatus check</i>							
<i>Probe</i> <i>Glass liner clean</i> <i>Heated properly</i> <i>Leak checked</i>							
<i>Collection Flask</i> <i>Clean</i> <i>Leak checked</i> <i>Temperature gauge</i>							
<i>Evacuation System</i> <i>Leak-free pumps</i> <i>Manifold and tubing</i> <i>U-tube manometer</i> <i>Barometer</i>							
<i>Reagents</i> <i>Distilled water</i> <i>Absorbing solution*</i> <i>Sodium hydroxide, 1N</i> <i>pH paper</i>							
<i>Sample Recovery</i> <i>Dropper or burette</i> <i>Sample bottles</i> <i>Pipette, 25 ml</i>							

**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 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.*

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 steel or Teflon[®] 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. 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.

[®]Trade name.

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 s.

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 - 5S 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 per 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 (transferal) 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, polymethylpentene 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 H_2O 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 KNO₃ solution - Dissolve exactly 2.198 g of dried potassium nitrate (KNO₃) 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 H₂O 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.

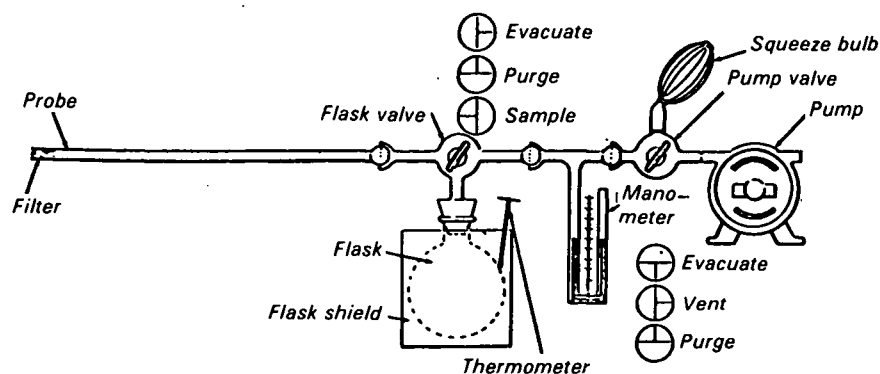


Figure 1.1. Evacuated flask sampling train.

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

Table 1.1 (continued)

<i>Apparatus/ reagents</i>	<i>Acceptance limits</i>	<i>Frequency and method of measurement</i>	<i>Action if requirements are not met</i>
<i>Stopcock grease</i>	<i>High vacuum, high temperature chloro- fluorocarbon grease</i>	<i>As above</i>	<i>As above</i>
<i>Barometer (or consult local weather station)</i>	<i>Capable of reading atmospheric pressure to ± 2.5 mm Hg</i>	<i>Visually check; calibrate against mercury-in-glass barometer</i>	<i>As above</i>
<i>Storage bottle</i>	<i>Polyethylene, 100-ml, or greater capacity, screw cap</i>	<i>Visually check upon receipt</i>	<i>Return to supplier and note in pro- curement log</i>
<i>Wash bottle</i>	<i>Polyethylene or glass</i>	<i>Visually check label upon receipt</i>	<i>As above</i>
<i>Glass stirring rod</i>	<i>As Above</i>	<i>As above</i>	<i>As above</i>
<i>pH paper</i>	<i>Sensitive in pH range 7-14</i>	<i>As above</i>	<i>Return to supplier</i>
<i>Volumetric flasks</i>	<i>50-, 100-, 1000-ml glass (Class A)</i>	<i>As above</i>	<i>As above</i>
<i>Evaporating dishes</i>	<i>Porcelain evaporating dishes or polymethyl- pentene beakers</i>	<i>As above</i>	<i>Discard when the bottoms become etched</i>
<i>Steam bath</i>	<i>Evaporate the sample solution at a low controlled temperature</i>	<i>As above</i>	<i>Return to supplier</i>
<i>Polyethylene policeman</i>	<i>Polyethylene stirring rod</i>	<i>As above</i>	<i>As above</i>
<i>Graduated cylinders</i>	<i>50, 100 ml (Class A) with 1-ml divisions</i>	<i>As above</i>	<i>As above</i>
<i>Spectrophotometer</i>	<i>Capable of measuring absorbance at 410 nm (such as Bausch & Lomb Spectronic 70)</i>	<i>Upon receipt, either check wavelength with filters or ensure optimum wavelength is between 400 and 415 nm</i>	<i>Adjust, re- calibrate as per manu- facturer's instructions, and note in procurement log</i>
<i>Dropping pipette or dropper</i>	<i>Able to add reagents dropwise</i>	<i>Visually check upon receipt</i>	<i>Return to supplier</i>
<i>Sulfuric acid</i>	<i>Concentrated, ACS reagent grade</i>	<i>Visually check upon receipt; check speci- fications</i>	<i>As above</i>
<i>Hydrogen peroxide</i>	<i>30% aqueous solution, ACS reagent grade</i>	<i>As above</i>	<i>As above</i>
<i>Sodium hydroxide</i>	<i>ACS reagent grade pellets</i>	<i>Visually check upon receipt; check speci- fications</i>	<i>Return to supplier</i>
<i>Sulfuric acid</i>	<i>Fuming, 15-18% free sulfur trioxide</i>	<i>As above</i>	<i>As above</i>
<i>Phenol</i>	<i>White solid, ACS reagent grade</i>	<i>As above</i>	<i>As above</i>
<i>Potassium nitrate</i>	<i>ACS reagent grade</i>	<i>As above</i>	<i>As above</i>

Procurement Log

<i>Item description</i>	<i>Qty.</i>	<i>Purchase order number</i>	<i>Vendor</i>	<i>Date</i>		<i>Cost</i>	<i>Dispo- sition</i>	<i>Comments</i>
				<i>Ord.</i>	<i>Rec.</i>			
<i>Spectrophotometer</i>	<i>1</i>	<i>1035</i>	<i>Bausch + Lomb</i>	<i>2-11-77</i>	<i>2-14-77</i>	<i>\$2500.</i>	<i>OK</i>	

Figure 1.2. Example of a procurement log.

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 μ g 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 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.
2. Compare readings after the bath stabilizes.
3. 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.

Spectrophotometer number PEI-2 Date 2/10/77
 Calibrated by B. PLUMMER Reviewed by T. SEAYER

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	.792
413	.811	.028	.783
414	.806	.015	.791
415	.785	.009	.776
416	.777	.000	.777

^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 408 nm.

If the maximum actual absorbance occurs at the spectrophotometer setting of ≤399 or ≥416 nm, the spectrophotometer must be repaired or recalibrated.

Figure 2.1. Optimum wavelength determination data form.

Table 2.1. Activity Matrix for Calibration of Equipment

<i>Apparatus</i>	<i>Acceptance limits</i>	<i>Frequency and method of measurement</i>	<i>Action if requirements are not met</i>
<i>Collection flask</i>	<i>Measure volume within ± 10 ml</i>	<i>On receipt, measure with graduated cylinder</i>	<i>Recalibrate</i>
<i>Spectrophotometer</i>	<ol style="list-style-type: none"> <i>1. Calibrate wavelength scale^a</i> <i>2. Determine optimum wavelength within 399 to 416 nm^a</i> 	<ol style="list-style-type: none"> <i>1. Upon receipt and every 6 mo, use glass filters or light source</i> <i>2. Upon receipt and every 6 mo scan between 400 and 415 nm with 200 mg NO₂ standard solution</i> 	<ol style="list-style-type: none"> <i>1. Return to manufacturer for repair</i> <i>2. As above</i>
<i>Barometer</i>	<i>Reading agrees within ± 2.5 mm (0.1 in.) Hg of mercury-in-glass barometer</i>	<i>Upon receipt and before each field test</i>	<i>Repair or return</i>
<i>Thermometer</i>	<i>Reading agrees within $\pm 1^{\circ}\text{C}$ (2°F) of mercury-in-glass thermometer</i>	<i>As above</i>	<i>As above</i>
<i>Vacuum gauge (mechanical only)</i>	<i>Reading agrees within ± 2.5 mm (0.1 in.) Hg of mercury U-tube manometer</i>	<i>As above</i>	<i>As above</i>
<i>Analytical balance</i>	<i>Weight within ± 2 mg of standard weights (Class S)</i>	<i>Use standard weight before preparation of working solution</i>	<i>Repair or return to manufacturer</i>

^aThe 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 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 decahydronaphthalene ($C_{10}H_{18}$), 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 μ g 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. X 15 in. X 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.

Date 2-15-77 Calibrated by B. Plummer

Flask Volume

Flask volume 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 solution*	✓		1 liter	✓		✓	
Sodium hydroxide, 1 N	✓		1 liter	✓		✓	
pH paper	✓		1 pkq.	✓		✓	
<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.

Table 3.1 Activity Matrix for Presampling Preparation

<i>Characteristic</i>	<i>Acceptance limits</i>	<i>Frequency and method of measurement</i>	<i>Action if requirements are not met</i>
Apparatus Check			
<i>Probe</i>	<ol style="list-style-type: none"> 1. Clean; glass liner inert to oxides of nitrogen 2. Heating properly if equipped with heating system 3. Leak free 	<ol style="list-style-type: none"> 1. Before each test 2. As above 3. Pressure <380 mm (15 in.) Hg 	Must be replaced
<i>Collection flask</i>	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
<i>Evacuation system</i>	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
Absorbing Reagents			
<i>Sulfuric acid, concentrated</i>	2.8 ml/L	Prepare fresh absorbing solution weekly; use graduated pipette	Make up new solution
<i>Hydrogen peroxide, 3%</i>	6 ml/L	As above	As above
Sample Recovery Reagents			
<i>Sodium hydroxide</i>	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
<i>Water</i>	Deionized distilled to ASTM specifications D11 93-82, Type 3		Prepare fresh for each analysis period
Analytical Reagent			
<i>Potassium nitrate</i>	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
<i>Phenoldisulfonic acid solution</i>	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

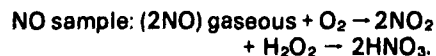
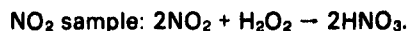
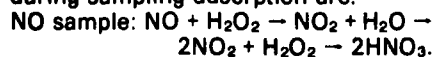
A sample is taken as follows:

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_f), 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 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 complete (≥ 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.
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 4.2A or 4.2B.

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).

Nitrogen Oxide Field Data Form
(English units)

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).

Nitrogen Oxide Field Data Form
(metric units)

Plant Acme Power Plant City Acme, Ohio
 Sample location ESP Outlet Boiler #1 Date 2/29/77
 Operator P. Rose Barometric 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).

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}) 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 _i	Leg B _i	P _i ^a	°F (t _i)	°R (T _i) ^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	✓	✓	✓

$$^a P_i = P_{\text{bar}} - (A_i + B_i)$$

$$^b T_i = t_i + 460^\circ\text{F}$$

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).

NO_x Sample Recovery and Integrity Data Form
(metric 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 _i	Leg B _i	P _i ^a	°C (t _i)	K (T _i) ^b				
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	✓	✓	✓

$$^a P_i = P_{\text{bar}} - (A_i + B_i).$$

$$^b T_i = t_i + 230^\circ\text{C}.$$

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).

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?* 0.11 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

<i>Characteristic</i>	<i>Acceptance limits</i>	<i>Frequency and method of measurement</i>	<i>Action if requirements are not met</i>
<i>Apparatus assembly</i>	<i>Assemble using Fig. 1.1; no leakage</i>	<i>Before sample collection, visually and physically inspect all connections</i>	<i>Check for leaks; repair system; re-pair test</i>
<i>Operational check</i>	<i>Maximum vacuum of 75 mm (3 in.) Hg absolute pressure</i>	<i>Before sample collection, use Hg-filled U-tube manometer</i>	<i>Check system for leaks; check vacuum pump</i>
	<i>Leakage rate ≤ 10 mm (0.4 in.) Hg/min</i>	<i>As above</i>	<i>Check all joints and valves for source of leakage</i>
<i>Sample recovery</i>	<i>Shake flask for 5 min</i> <i>Let flask set for a minimum of 16 h</i> <i>Shake flask for 2 min</i> <i>Determine flask pressure and temperature</i> <i>Adjust pH of sample to 9-12 with NaOH</i> <i>Mark sample level on container</i> <i>Record data on data form (Fig. 4.2)</i>	<i>During each sample collection, use manometer, centigrade thermometer, and pH paper</i>	<i>Reject sample, rerun test</i>
<i>Sample logistics</i>	<i>Properly label all containers, etc.</i>	<i>Visually check each sample</i>	<i>Complete the labeling</i>
	<i>Record all data on field data forms (Fig. 4.1 and Fig. 4.2)</i>	<i>As above</i>	<i>Complete the data records</i>

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 (V_{soln}), 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 ($V_{\text{soln}_f} < V_{\text{soln}_i}$), correct the sample volume (V_{soln}) by using Equation 5-1.

$$V_{\text{soln}}' = V_{\text{soln}} \left(\frac{V_{\text{soln}_i}}{V_{\text{soln}_f}} \right)$$

Equation 5-1

where

- V_{soln} = sample volume to be used for the calculations, ml,
 V_{soln} = total volume of solution in which the NO_x 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 A₄ (the absorbance of the 400 µg NO₂ 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 NO₂.
 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 ±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 ±15% for intralaboratory control samples is recommended based on the control limit of ±20% for interlaboratory audit results discussed in Section 3.6.8.
 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).

Standard Solution and Control Sample
Analytical Data Form

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

^aOD = (μg)/ K_c ; i.e., SI calculated absorbance = 100/ K_c .

$$K_c = 100 \left[\frac{A_1 + 2A_2 + 3A_3 + 4A_4}{A_1^2 + A_2^2 + A_3^2 + A_4^2} \right] = \underline{525}$$

^bAbsorbance comparison errors:

$$\% = 100 \times \left[\frac{(\text{measured absorbance, OD}) - (\text{calculated absorbance, OD})}{\text{calculated absorbance, OD}} \right]$$

^cAverage of absolute values.

Figure 5.1. Standard solution and control sample analytical data form.

NO_x Laboratory 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. Seaver
Calibration factor (K_c) 528 Date of review 3/5/77

Sample number	Sample absorbance, A	Dilution factor, F	Total mass of NO _x as 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.

ReagentsPhenoldisulfonic acid stored in dark stoppered bottle? ☒Sulfuric acid, concentrated, 95% minimum assay reagent grade? ☒Ammonium hydroxide, concentrated reagent grade? ☒Sample PreparationHas liquid level noticeably changed?* No

Original volume _____

Corrected volume _____

AnalysisSpectrophotometer calibrated?* ☒Setting for maximum absorbance of standard 408 nmControl sample prepared?* ☒Any solids in sample removed through Whatman No. 41 filter paper? N/AAbsorbance 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 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 NO₂, 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 NO₂ 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 (°R).
- T_i = Initial absolute temperature of flask, K (°R).

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

where

$$K_2 = 10^3 \frac{\text{mg/m}^3}{\mu\text{g/ml}} \text{ for metric units, or}$$

$$K_2 = 6.243 \times 10^{-5} \frac{\text{lb/scf}}{\mu\text{g/ml}} \text{ for English units.}$$

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°R)) by using the following equation.

$$V_{sc} = \frac{T_{std}(V_f - V_a)}{P_{std}} \left(\frac{P_f}{T_f} - \frac{P_i}{T_i} \right)$$

$$= K_1 (V_f - 25 \text{ ml}) \left(\frac{P_f}{T_f} - \frac{P_i}{T_i} \right)$$

Equation 6-1

where

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

$$K_1 = 17.64 \frac{^\circ\text{R}}{\text{in. Hg}} \text{ for English units.}$$

6.2.2 Total μg of NO₂ Per Sample - Calculate the total μg of NO₂ per sample by using Equation 6-2.

$$m = 2 K_c A F$$

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.

$$C = K_2 \left[\frac{m}{V_{sc}} \right]$$

Equation 6-3

*Nitrogen Oxide Calculation Form
(English units)*

Sample Volume

$$V_1 = \underline{2013} \text{ ml}, P_1 = \underline{27.64} \text{ in. Hg}, T_1 = \underline{533} ^\circ R$$

$$P_2 = \underline{0.59} \text{ in. Hg}, T_2 = \underline{532} ^\circ R$$

$$V_{sc} = 17.64 (V_1 - 25) \left[\frac{P_1}{T_1} - \frac{P_2}{T_2} \right] = \underline{1780} \text{ ml} \quad \text{Equation 6-1}$$

Total $\mu\text{g NO}_2$ Per Sample

$$K_c = \underline{528}, A = \underline{0.243} \text{ OD}, F = \underline{1.00} \quad \text{Equation 6-2}$$

$$m = 2K_c AF = \underline{785} \mu\text{g of NO}_2$$

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).

*Nitrogen Oxide Calculation Form
(metric units)*

Sample Volume

$$V_i = \underline{2013} \text{ ml}, P_i = \underline{702.0} \text{ mm Hg}, T_i = \underline{295.2} \text{ K}$$

$$P_i = \underline{17.0} \text{ mm Hg}, T_i = \underline{295.5} \text{ K}$$

$$V_{sc} = 0.3858 (V_i - 25) \left[\frac{P_i}{T_i} - \frac{P_i}{T_i} \right] = \underline{1775} \text{ ml} \quad \text{Equation 6-1}$$

Total $\mu\text{g NO}_2$ Per Sample

$$K_c = \underline{528} \text{ A} = \underline{0.743} \text{ OD}, F = \underline{1.00}$$

$$m = 2K_c AF = \underline{784} \text{ } \mu\text{g of NO}_2 \quad \text{Equation 6-2}$$

Sample Concentration

$$C = 10^3 \left[\frac{m}{V_{sc}} \right] = \underline{0.442} \times 10^3 \text{ mg/dscm.} \quad \text{Equation 6-3}$$

Figure 6.1B. Nitrogen oxide calculation form (metric units).

Table 6.1 Activity Matrix for Calculations

<i>Characteristic</i>	<i>Acceptance limits</i>	<i>Frequency and method of measurement</i>	<i>Action if requirements are not met</i>
<i>Sample volume calculation</i>	<i>All data available; calculations correct within round-off error</i>	<i>For each sample, examine the data form</i>	<i>Complete the data or void the sample</i>
<i>Sample mass calculation</i>	<i>As above</i>	<i>As above</i>	<i>As above</i>
<i>Sample concentration</i>	<i>As above</i>	<i>As above</i>	<i>As above</i>
<i>Calculation check</i>	<i>Original and check calculations agree within round-off error</i>	<i>For each sample, perform independent calculation using data on Figs. 4.1, 4.2, and 4.3</i>	<i>Check and correct all data</i>
<i>Document and report results</i>	<i>All data available; calculations correct within round-off error</i>	<i>For each sample, examine the data form</i>	<i>Complete the data or void the sample</i>

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

<i>Apparatus</i>	<i>Acceptance limits</i>	<i>Frequency and method of measurement</i>	<i>Action if requirements are not met</i>
<i>Routine maintenance</i>	<i>Proper functioning</i>	<i>Perform routine maintenance quarterly; disassemble and clean yearly</i>	<i>Replace parts as needed</i>
<i>Fiber vane pump</i>	<i>Oil translucent pump leakless and capable of pulling a vacuum of less than 75 mm (3 in.) Hg absolute pressure</i>	<i>Check oiler jar periodically; remove head and change fiber vanes</i>	<i>Replace as needed</i>
<i>Diaphragm pump</i>	<i>Leak free, valves functioning properly, and capable of pulling a vacuum of <75 mm (3 in.) Hg absolute pressure</i>	<i>Clean valves during disassembly; replace diaphragm as needed</i>	<i>Replace when leaking or malfunctioning</i>
<i>Shipping container</i>	<i>Protect equipment from damage</i>	<i>Inspect quarterly; repair as needed</i>	<i>Replace</i>

8.0 AUDITING PROCEDURE

An audit is an independent assessment of data quality. Independence is achieved if the individual(s) performing the audit and their standards and equipment are different from the regular field crew and their standards and equipment. In the case of a compliance test, the required performance audits will be conducted by the responsible enforcement agency. Routine quality assurance checks by a field team are necessary in generation of good quality data, but they are not part of the auditing procedure. Table 8.1 at the end of this section summarizes the quality assurance functions for auditing.

Based on the results of collaborative tests^{2,3,4} of Method 7, two specific performance audits are recommended:

1. Audit of the analytical phase of Method 7.
2. Audit of data processing for both Methods.

It is suggested that a systems audit be conducted as specified by the quality assurance coordinator, in addition to these performance audits. The two performance audits and the systems audit are described in detail in Subsections 8.1 and 8.2, respectively.

8.1 Performance Audits

Performance audits are generally made to quantitatively evaluate the quality of data produced by the total measurement system (sample collection, sample analysis, and data processing). It is recommended that these audits be performed by the responsible control agency once during every enforcement source test. A source test for enforcement comprises a series of runs at one source. No performance audit is recommended at this time for the sampling phase. The performance audit of the analytical phase is subdivided into two steps: (1) a pretest audit which is optional, and (2) an audit during the field sampling and/or analysis phase which is required.

8.1.1 Pretest Audit of Analytical Phase Using Aqueous Ammonium Sulfate (Optional) - The pretest audit described in this section can be used to determine the proficiency of the analyst and the standardization of solutions in the Method 7 analysis and should be performed at the discretion of the agency auditor, the laboratory supervisor, source test company, or quality assurance officer. The analytical phase of Method 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 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 7 analysis procedure described in this Handbook.

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

The accuracy for each of two samples should be within 10 percent of true value. The relative error (RE) is a measure of the bias of the analytical phase of Method 7. Calculate RE using Equation 8-1.

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

where:

C_d = Determined audit sample concentration, mg/dsm³.

C_a = Actual audit sample concentration, mg/dsm³.

8.1.2 Audit of Analytical Phase of the Field Test (Required) - As stated in 40 CFR 60, Section 3.3.9 (49 FR 26522, 06/27/84), the testing laboratory should provide the responsible agency/organization requesting the performance test with a notification of the intent to test 30 days prior to the enforcement source test. The responsible agency obtains the audit samples from the appropriate EPA Regional Quality Assurance Coordinator shown in Table 5.1 of Section 3.0.5 of this Handbook. The responsible agency then provides the testing laboratory with two audit samples to be analyzed along with the field samples from the enforcement source test. The purpose of this audit is to assess the data quality at the time of the analysis.

The two audit samples and the compliance samples should be

concurrently analyzed in the same manner to evaluate the technique of the analyst and the standards preparation. (Note: It is recommended that known quality control samples be analyzed prior to the compliance and audit sample analysis to optimize the system accuracy and precision. One source of these samples has been listed above.) The same analyst, analytical reagents, and analytical system shall be used both for compliance samples and the EPA audit samples; if this condition is met, auditing of subsequent compliance analyses for the same enforcement agency within 30 days may not be required. An audit sample set may not be used to validate different sets of compliance samples under the jurisdiction of different enforcement agencies, unless prior arrangements are made with both enforcement agencies.

Calculate the concentrations in mg/dsm^3 using the specified sample volume in the audit instructions. (Note: Indication of acceptable results may be obtained immediately by reporting the audit results in mg/dsm^3 and compliance results in total $\text{mg NO}_2/\text{sample}$ by telephone to the responsible enforcement agency.) Include the results of both audit samples, their identification numbers, and the analyst's name with the results of the compliance determination samples in appropriate reports to the EPA regional office or the appropriate enforcement agency. Include this information with subsequent compliance analyses for the same enforcement agency during the 30-day period.

The concentration of the audit samples obtained by the analyst shall agree within 10-percent of the actual concentrations. If the 10-percent specification is not met, reanalyze the compliance samples and audit samples, and include initial and reanalysis values in the test report (see Note in first paragraph of this section).

Failure to meet the 10-percent specification may require retests until the audit problems are resolved. However, if the audit results do not affect the compliance or noncompliance status of the affected facility, the Administrator may waive the reanalysis requirement, further audits, or retests and accept the results of the compliance test. While steps are being taken to resolve audit analysis problems, the Administrator may also choose to use the data to determine the compliance or noncompliance status of the affected facility.

8.1.3 Audit of Data Processing - Calculation errors are prevalent in Method 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 appear in the field), and by requesting that the data calculation be completed and that the results be

returned to the agency/organization. This audit is useful in checking both computer programs and manual methods of data processing.

8.2 Systems Audit

A systems audit is an on-site qualitative inspection and review of the total measurement system (sample collection, sample analysis, data processing, etc.). Initially, a systems audit is recommended for each enforcement source test, defined here as a series of three runs at one source. After the test team gains experience with the method, the frequency of audit may be reduced--for example, to once for every four tests.

The auditor should have extensive background experience in source sampling, specifically with the measurement system being audited. The functions of the auditor are summarized below:

1. Inform the testing team of the results of pretest audits, specifying any area(s) that need special attention or improvement.
2. Observe procedures and techniques of the field team during sample collection.
3. Check/verify records of apparatus calibration checks and quality control used in the laboratory analysis of control samples from previous source tests, where applicable.
4. Record the results of the audit and forward them with comments to the team management so that appropriate corrective action may be initiated.

While on site, the auditor observes the source test team's overall performance, including the following specific operations:

1. Setting up and leak testing the sampling train.
2. Preparing the absorbing solution and adding it to the collection flasks.
3. Collecting the sample.
4. Sample absorption, recovery, and preparation for shipment.
5. The spectrophotometer calibration should be checked for every series of analyses. The calculated concentration values should not differ from the actual concentrations by more than 7 percent for three of the four standards.

Figure 8.1 is a suggested checklist for the auditor.

Yes	No	Comment	
			<u>Presampling preparation</u>
—	—	—	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
			<u>On-site measurements</u>
—	—	—	5. Leak testing of sampling train
—	—	—	6. Preparation and pipetting of absorbing solution into sampling flask
			<u>Postsampling</u> (Analysis and Calculation)
—	—	—	7. Control sample analysis
—	—	—	8. Sample aliquotting techniques
—	—	—	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 (+ 7 percent for 3 of 4 standards) d. Wavelength and absorbance, including blanks e. Check for calibration of instrument wavelength (once every six months)
—	—	—	11. Audit results (+ 10%)
			a. Use of computer program b. Independent check of calculations
<u>Comments</u>			

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	Measured RE of the pretest audit samples should be less than $\pm 10\%$ for both audit results (optional)	<u>Frequency:</u> As considered necessary by the testing firm <u>Method:</u> Measure reference samples and compare their true value	Review operating technique and/or calibration curve check
	Measured RE of the audit samples should be less than $\pm 10\%$ for both audit samples (required)	<u>Frequency:</u> Once during every enforcement source test* (required) <u>Method:</u> Measure audit samples and compare their true values	Review operating technique and/or calibration curve check and repeat the analysis of the audit and field samples
Data processing errors (recommended)	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 (recommended)	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 NO₂) 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 ± 5 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.

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 (25 to 125°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 25-5S 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. 45006 (shallow-form, 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 (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 and each standard), 100 ml (one for each sample and each standard, and one for the working standard KNO₃ 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.

*40 CFR 60, July 1, 1978

³Mention of trade names or specific products does not constitute endorsement by the Environmental Protection Agency.

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 2.8 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 at 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 2.198 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. Procedures

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_f) 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 pressures 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_f) 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 (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. 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 3 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 A_4 , the absorbance of the 400 $\mu\text{g NO}_2$ 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 ± 10 ml. Record this volume on the flask.

5.2 Spectrophotometer Calibration.

5.2.1 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 $\mu\text{g NO}_2$ 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. 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.

5.2.2 Determination of Spectrophotometer Calibration Factor K_c . Add 0.0 ml, 2 ml, 4 ml, 6 ml, and 8 ml of the KNO_3 working standard solution (1 ml = 100 $\mu\text{g NO}_2$) 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 between 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. 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- $\mu\text{g NO}_2$ standard

A_2 = Absorbance of the 200- $\mu\text{g NO}_2$ standard

A_3 = Absorbance of the 300- $\mu\text{g NO}_2$ standard

A_4 = Absorbance of the 400- $\mu\text{g NO}_2$ standard

5.3 Barometer. Calibrate against a mercury barometer.

5.4 Temperature Gauge. Calibrate dial 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, $^{\circ}\text{K}$ ($^{\circ}\text{R}$).

T_i = Initial absolute temperature of flask, $^{\circ}\text{K}$ ($^{\circ}\text{R}$).

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

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.

$$V_{sc} = \frac{T_{std}}{P_{std}} (V_f - V_a) \left[\frac{P_f}{T_f} - \frac{P_i}{T_i} \right]$$

$$= K_1 (V_f - 25 \text{ ml}) \left[\frac{P_f}{T_f} - \frac{P_i}{T_i} \right]$$

Equation 7-2

where:

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

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

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.

$$C = K_2 \frac{m}{V_{sc}}$$

Equation 7-4

where

$$K_2 = 10^3 \frac{\text{mg}/\text{m}^3}{\mu\text{g}/\text{ml}} \text{ for metric units}$$

$$= 6.243 \times 10^{-5} \frac{\text{lb}/\text{scf}}{\mu\text{g}/\text{ml units}} \text{ for English units}$$

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-1606-60, p. 725-729.
3. Jacob, M.B. The Chemical Analysis of Air Pollutants. New York, Interscience Publishers, Inc. 1960. Vol. 10, p. 351-356.
4. 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. Dept. of Interior. R.I. 3687. February 1943.
5. Hamil, H.F. and D.E. Camann. 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. Hamil, 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.

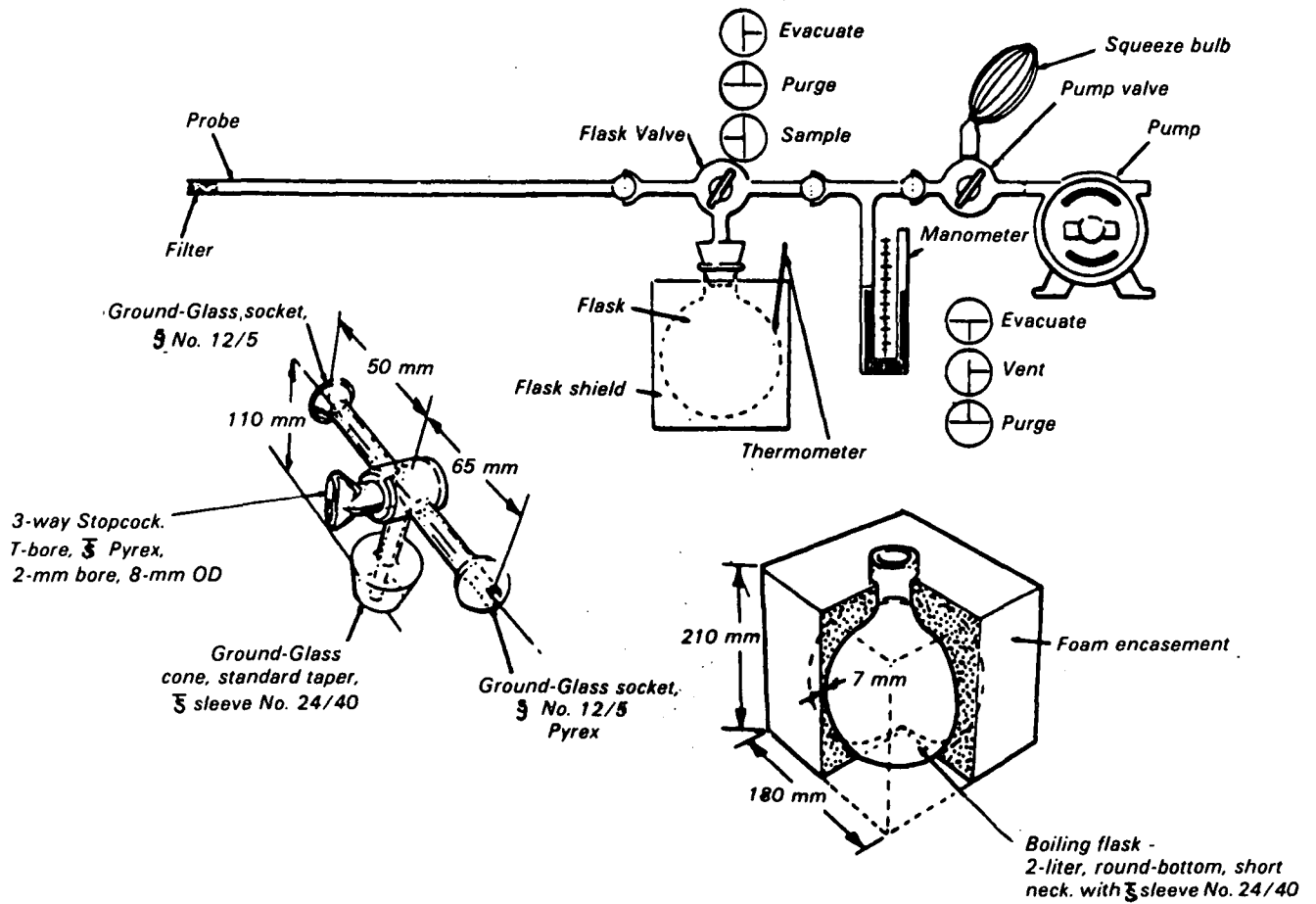


Figure 7-1. Sampling train, flask valve, and flask.

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.
10. Hamil, H.F. and D.E. Camann. Collaborative Study of Methods for the Determination of Nitrogen of Nitrogen Oxide Emissions from Stationary Sources (Fossil Fuel Fired Steam Generators). Southwest Research Institute report for EPA, Research Triangle Park, N.C. October 5, 1973.
11. Hamil, H.F. and R.E. Thomas. Collaborative Study of Methods for the Determination of Nitrogen Oxide Emissions from Stationary Sources (Nitric Acid Plants). Southwest Research Institute report for EPA, Research Triangle Park, N.C. May 8, 1974.
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, 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 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.

<i>Form</i>	<i>Title</i>
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 Analyt- ical Data Form
5.2	NO _x Laboratory Data Form
5.3 (MH)	Posttest Operations
6.1A and 6.1B	Nitrogen Oxide Calcu- lation Form (English and metric units)
8.1	Method 7 Checklist to be Used by Auditors

Procurement Log

<i>Item description</i>	<i>Qty.</i>	<i>Purchase order number</i>	<i>Vendor</i>	<i>Date</i>		<i>Cost</i>	<i>Dispo- sition</i>	<i>Comments</i>
				<i>Ord.</i>	<i>Rec.</i>			

Optimum Wavelength Determination Data Form

Spectrophotometer number _____ Date _____

Calibrated by _____ Reviewed by _____

<i>Spectrophotometer setting, nm</i>	<i>Absorbance of standard OD^a</i>	<i>Absorbance of blank OD^b</i>	<i>Actual absorbance of OD^c</i>
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 the spectrophotometer setting of ≤399 or ≥416 nm, the spectrophotometer must be repaired or recalibrated.

**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 $T_i = t_i + 460^\circ\text{F}.$

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5

Section 3.6.12

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 ₁	Leg B ₁	P ₁ ^a	°F (t ₁)	°R (T ₁) ^b				

^a $P_1 = P_{\text{bar}} - (A_1 + B_1)$

^b $T_1 = t_1 + 460^\circ\text{F}$

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 _____

Quality Assurance Handbook M7-4.2A

*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-h	pH adjusted 9 to 12	Liquid Level marked	Samples stored in locked container
	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 $T_i = t_i + 273^\circ\text{C}.$

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

$$K_c = 100 \left[\frac{A_1 + 2A_2 + 3A_3 + 4A_4}{A_1^2 + A_2^2 + A_3^2 + A_4^2} \right] = \underline{\hspace{2cm}}$$

^a Calculated absorbance: $OD = (\mu\text{g})/K_c$ 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* _____

<i>Sample number</i>	<i>Sample absorbance, A</i>	<i>Dilution factor, F</i>	<i>Total mass of NO_x as NO₂ in sample, m (μg)</i>

$m = 2 K_c A F$, 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

$$V_i = \underline{\hspace{1cm}} \text{ ml}, P_i = \underline{\hspace{1cm}} \text{ in. Hg}, T_i = \underline{\hspace{1cm}} ^\circ R$$

$$P_i = \underline{\hspace{1cm}} \text{ in. Hg}, T_i = \underline{\hspace{1cm}} ^\circ R$$

$$V_{sc} = 17.64 (V_i - 25) \left[\frac{P_i}{T_i} - \frac{P_i}{T_i} \right] = \underline{\hspace{1cm}} \text{ ml} \quad \text{Equation 6-1}$$

Total $\mu\text{g NO}_2$ Per Sample

$$K_c = \underline{\hspace{1cm}}, A = \underline{\hspace{1cm}} \text{ OD}, F = \underline{\hspace{1cm}}$$

$$m = 2K_c AF = \underline{\hspace{1cm}} \mu\text{g of NO}_2$$

Equation 6-2

Sample Concentration

$$C = 6.243 \times 10^{-5} \left[\frac{m}{V_{sc}} \right] = \underline{\hspace{1cm}} \times 10^{-5} \text{ lb/dscf}$$

*Nitrogen Oxide Calculation Form
(metric units)*

Sample Volume

$$V_1 = ______ \cdot \text{ml}, P_1 = ______ \cdot \text{mm Hg}, T_1 = ______ \cdot \text{K}$$

$$P_2 = ______ \cdot \text{mm Hg}, T_2 = ______ \cdot \text{K}$$

$$V_{sc} = 0.3858 (V_1 - 25) \left[\frac{P_1}{T_1} - \frac{P_2}{T_2} \right] = ______ \cdot \text{ml} \quad \text{Equation 6-1}$$

Total $\mu\text{g NO}_2$ Per Sample

$$K_c = ______ \cdot A = ______ \cdot \text{OD}, F = ______ \cdot$$

$$m = 2K_c AF = ______ \cdot \mu\text{g of NO}_2 \quad \text{Equation 6-2}$$

Sample Concentration

$$C = 10^3 \left[\frac{m}{V_{sc}} \right] = ______ \cdot 10^3 \text{ mg/dscm.} \quad \text{Equation 6-3}$$

*Method 7 Checklist to be Used by Auditors
Presampling Preparation*

<i>Yes</i>	<i>No</i>	
_____	_____	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 <ul style="list-style-type: none"> 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 <ul style="list-style-type: none"> a. Use of computer program b. Independent check of calculations

Comments

United States
Environmental Protection
Agency

Environmental Monitoring Systems
Laboratory
Research Triangle Park NC 27711

Research and Development



Section 3.7

Method 8—Determination of Sulfuric Acid Mist and Sulfur Dioxide Emissions from Stationary Sources

Outline

Section	Documentation	Number of Pages
Summary	3.7	2
Method Highlights	3.7	7
Method Description		
1. Procurement of Apparatus and Supplies	3.7.1	7
2. Calibration of Apparatus	3.7.2	10
3. Presampling Operations	3.7.3	4
4. On-Site Measurements	3.7.4	10
5. Postsampling Operations	3.7.5	9
6. Calculations	3.7.6	6
7. Maintenance	3.7.7	2
8. Auditing Procedure	3.7.8	3
9. Recommended Standards for Establishing Traceability	3.7.9	1
10. Reference Method	3.7.10	5
11. References	3.7.11	1
12. Data Forms	3.7.12	17

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 interferents 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 these 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 $1 \text{ ft}^3/\text{min}$. The most common error results when hydrogen peroxide solution is allowed to back up, 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 posttest 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 (within ± 2.5 mm (0.1 in.) Hg of mercury-in-glass barometer)? ____ yes ____ no.

*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	
Probe						
Type glass liner						
Borosilicate _____						
Quartz _____						
Heated						
Leak checked						
Nozzle						
Glass _____						
Stainless steel _____						
Other _____						
Pitot Tube						
Types _____						
Other _____						
Properly attached _____						
Modifications _____						
C _p _____						
Differential Pressure Gauge						
Inclined manometer _____						
Other _____						
Filter Holder						
Borosilicate glass						
Glass frit						
Gasket						
Silicone _____						
Teflon _____						
Viton _____						
Condenser						
Impingers						
Greenburg-Smith						
Modified Greenburg-Smith						
Impinger Temperature Sensor						
Thermometer _____						
Other _____						
Calibrated _____						

Pretest Preparations
(Method 8, Figure 3.1)
 (continued)

Apparatus check	Acceptable		Quantity required	Ready		Loaded and packed
	Yes	No		Yes	No	
Other						
Barometer						
Mercury _____						
Aneroid _____						
Other _____						
Calibrated* _____						
Stack Temperature Sensor						
Type _____						
Calibrated* _____						
Reagents						
Distilled water						
Hydrogen peroxide						
(30%)						
Isopropanol (80%)						
(changed for						
peroxides)						
Silica gel						
Meter System						
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 $Y_1 =$ _____ $Y_2 =$ _____ ($\pm 5\%$ of pretest factor)*

Recalibration required? _____ yes _____ no

If yes, recalibration factor $Y =$ _____ (within $\pm 2\%$ 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 $\pm 6^\circ\text{C}$ (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 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.

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.

Determination of filterable particulate matter simultaneously with sulfuric acid mist (and with SO₃ and SO₂) 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 m³/min (0.75 ft³/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 SO₂, and then each must be analyzed separately. These extra absorbers must not contain more than 1% of the total H₂SO₄ or SO₂.

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 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.

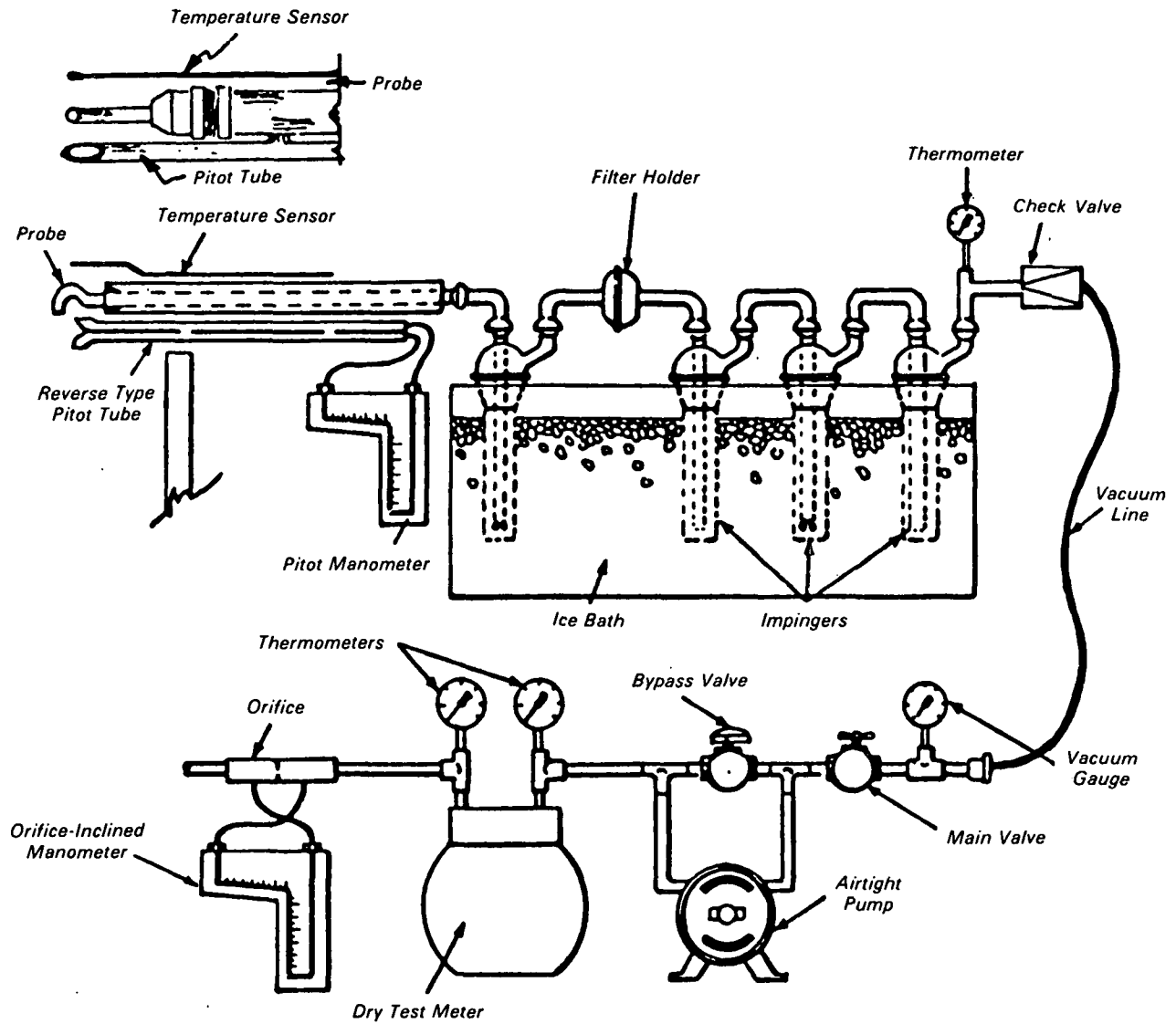


Figure 1.1. Schematic of Method 8 sampling train.

Procurement Log

Item description	Qty.	Purchase order number	Vendor	Date		Cost	Disposition	Comments
				Ord.	Rec.			
(1) Meter Box w/Fiber Yane Pump, Magna- helic Gauges	1	77A25	ARC Technology	12/23/76	1/28/77	\$5,600	Calibrated Ready for Use	Calibrated 2/4/77 by G.L.S.

Figure 1.2. Example of a procurement log.

Table 1.1 Activity Matrix for Procurement of Apparatus & Supplies

<i>Apparatus</i>	<i>Acceptance limits</i>	<i>Frequency and method of measurement</i>	<i>Action if requirements are not met</i>
<i>Sampling probe with heating system</i>	<i>Capable of 100°C (212°F) exit air at flow rate of 20 L/min</i>	<i>Visually check; run heating system checkout</i>	<i>Repair, return to supplier, or reject</i>
<i>Probe nozzle</i>	<i>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)</i>	<i>Visually check before each test; use a micrometer to measure ID before field use after each repair</i>	<i>Reshape and sharpen, return to the supplier, or reject</i>
<i>Pitot tube</i>	<i>Type-S (Meth. 2, Sec. 3.1.2); attached to probe with impact (high pressure) opening plane even with or above nozzle entry plane</i>	<i>Calibrate according to Meth. 2, Sec. 3.1.2</i>	<i>Repair or return to supplier</i>
<i>Differential pressure gauge (manometer)</i>	<i>Criteria in Meth. 2, Sec. 3.1.2; agree within 5% of gauge-oil manometer used to calibrate</i>	<i>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.)H₂O</i>	<i>As above</i>
<i>Vacuum gauge</i>	<i>0-760 mm Hg range; ± 25 mm (1 in.) Hg accuracy at 380 mm (15 in.) Hg</i>	<i>Check against a mercury U-tube manometer upon receipt</i>	<i>Adjust or return to supplier</i>
<i>Vacuum pump</i>	<i>Capable of maintaining a flow rate of 0.03-0.05 m³/min (1-1.7 ft³/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</i>	<i>Check upon receipt for leaks and capacity</i>	<i>Repair or return to supplier</i>
<i>Orifice meter</i>	<i>$\Delta H@$ of 46.74 \pm 6.35 mm (1.84 \pm 0.25 in.) (recommended)</i>	<i>Visually check upon receipt for damage; calibrate against wet test meter</i>	<i>Repair, if possible; otherwise, return to supplier</i>
<i>Impingers</i>	<i>Standard stock glass; pressure drop across impingers not excessive (Sec. 3.7.1)</i>	<i>Visually check upon receipt; check pressure drop (Sec. 3.7.1)</i>	<i>Return to supplier</i>
<i>Filter holder</i>	<i>Leak free</i>	<i>Visually check before use</i>	<i>As above</i>
<i>Filters</i>	<i>Glass fiber without organic binder designed to remove 99.95% ($\leq 0.05\%$ penetration) of 0.3-μm dioctyl phthalate smoke particles</i>	<i>Manufacturer's guarantee that filters meet ASTM standard method D2986-71; observe under light for defects</i>	<i>Return to supplier and replace</i>

Table 1.1 (continued)		Frequency and method of measurement	Action if requirements are not met
Apparatus	Acceptance limits		
<i>Dry gas meter</i>	<i>Capable of measuring total volume with accuracy of $\pm 2\%$ at flow rate of $0.02 \text{ m}^3/\text{min}$ ($0.75 \text{ ft}^3/\text{min}$)</i>	<i>Check for damage upon receipt; calibrate against wet test meter (Sec. 3.7.2)</i>	<i>Reject if damaged, behaves erratically, or cannot be properly adjusted</i>
<i>Wet test meter</i>	<i>Capable of measuring total volume with accuracy of $\pm 1\%$</i>	<i>Upon assembly, leak check all connections and check calibration by a liquid displacement method</i>	<i>As above</i>
<i>Thermometers</i>	<i>Within $\pm 1^\circ\text{C}$ (2°F) of value in range of 0°C to 25°C (32°F to 67°F) for impinger thermometer; $\pm 3^\circ\text{C}$ (6°F) of true value in range of 0°C to 90°C (32°F to 194°F) for dry gas meter thermometers</i>	<i>Check each thermometer upon receipt for damage--i.e., dents or bent stem; calibrate (Sec. 3.7.2)</i>	<i>Reject if unable to calibrate</i>
<i>Barometer</i>	<i>Capable of measuring atmospheric pressure to within 2.5 mm (0.1 in.) Hg</i>	<i>Check against a mercury-in-glass barometer or equivalent; calibrate (Sec. 3.7.2)</i>	<i>Determine correction factor, or reject if difference in the readings exceeds $\pm 2.5 \text{ mm}$ (0.1 in.) Hg</i>
Sample Recovery			
<i>Wash bottles</i>	<i>Polyethylene or glass, 500 ml</i>	<i>Visually check for damage upon receipt</i>	<i>Replace or return to supplier</i>
<i>Storage bottles</i>	<i>Polyethylene, 1000 ml and 100 ml</i>	<i>Visually check for damage upon receipt; be sure caps make proper seals</i>	<i>As above</i>
<i>Graduated cylinders</i>	<i>Glass (Class A), 250 ml and 1000 ml</i>	<i>Visually check upon receipt</i>	<i>As above</i>
<i>Trip balance</i>	<i>500-g capacity, $\pm 0.5 \text{ g}$; needed to weigh silica gel only if moisture measurement desired</i>	<i>Check with standard weights up to 500 g</i>	<i>Adjust or return to supplier</i>
Analysis Glassware			
<i>Pipettes, volumetric flasks, burette, and graduated cylinder</i>	<i>Glass (Class A)</i>	<i>Upon receipt, check for stock number, cracks, breaks, and manufacturer's flaws</i>	<i>As above</i>
Reagents			
<i>Distilled water</i>	<i>ASTM-D1193-74, Type 3</i>	<i>Check each lot or specify type when ordering</i>	<i>As above</i>
<i>Isopropanol</i>	<i>100% isopropanol, reagent grade or certified ACS with no peroxide impurities; absorbance ≤ 0.1 at 352 nm on spectrophotometer</i>	<i>Upon receipt, check each lot for peroxide impurities with a spectrophotometer</i>	<i>Redistill, pass through alumina column, or replace</i>

Table 1.1 (continued)

<i>Apparatus</i>	<i>Acceptance limits</i>	<i>Frequency and method of measurement</i>	<i>Action if requirements are not met</i>
<i>Hydrogen peroxide</i>	<i>30% H₂O₂, reagent grade or certified ACS</i>	<i>Upon receipt, check label for grade or certification</i>	<i>Replace or return to</i>
<i>Potassium iodide</i>	<i>KI reagent grade or certified ACS</i>	<i>As above</i>	<i>As above</i>
<i>Thorin indicator</i>	<i>1-[o-arsonophenylazo]-2-naphthol-3,6 disulfonic acid disodium salt, reagent grade or certified ACS</i>	<i>Upon receipt, check label for grade or certification</i>	<i>As above</i>
<i>Barium perchlorate trihydrate solution</i>	<i>Ba(ClO₄)₂ · 3H₂O, reagent grade or certified ACS</i>	<i>As above</i>	<i>As above</i>
<i>Sulfuric acid solution</i>	<i>H₂SO₄, 0.0100N ±0.0002N</i>	<i>Certified by manufacturer, or standardize against 0.0100N NaOH previously standardized against potassium acid phthalate (primary standard grade)</i>	<i>As above</i>

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 ($>3\text{L}/\text{rev}$), 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 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.
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:

$$\Delta H@ = \frac{\Delta H@_1 + \Delta H@_2 + \Delta H@_3 + \Delta H@_4 + \Delta H@_5 + \Delta H@_6}{6}$$

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 $\pm 6^\circ C$ ($10.8^\circ F$) 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 mercury-in-glass thermometer that meets ASTM E-1 No. 3C or 3F 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 $\pm 1^\circ C$ ($2^\circ F$) at both points. If the difference is greater than $\pm 1^\circ C$ ($2^\circ F$), 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 $\pm 2^\circ C$ ($4^\circ F$) 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. 3C or 3F specifications:

1. Place the dial type or equivalent thermometer and the mercury-in-glass thermometer in a hot water bath, 40° to $50^\circ C$ (105° to $122^\circ F$). 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 $\pm 3^\circ C$ ($5.4^\circ F$) at both points or (2) the temperature differentials at both points are within $\pm 3^\circ C$ ($5.4^\circ F$) and the temperature differential is taped to the thermometer and recorded on the pretest sampling checks form (Figure 2.5).
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 $\pm 6^\circ C$ ($10.8^\circ F$) 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 minus 2.5 mm Hg per 30 m (minus 0.1 in. per 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.

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.

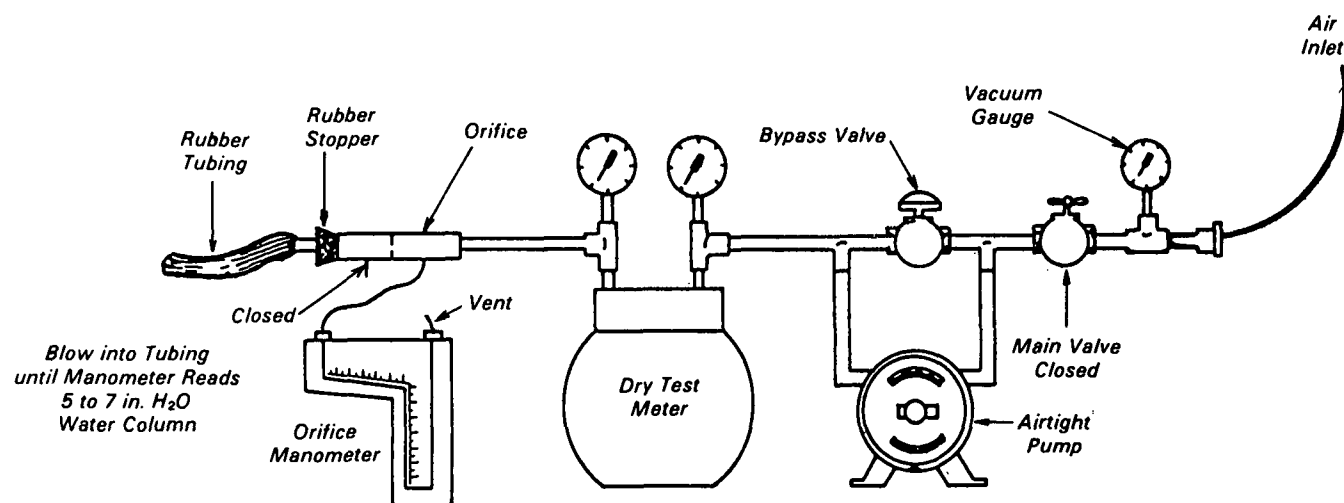


Figure 2.1. Positive leak check of metering system.

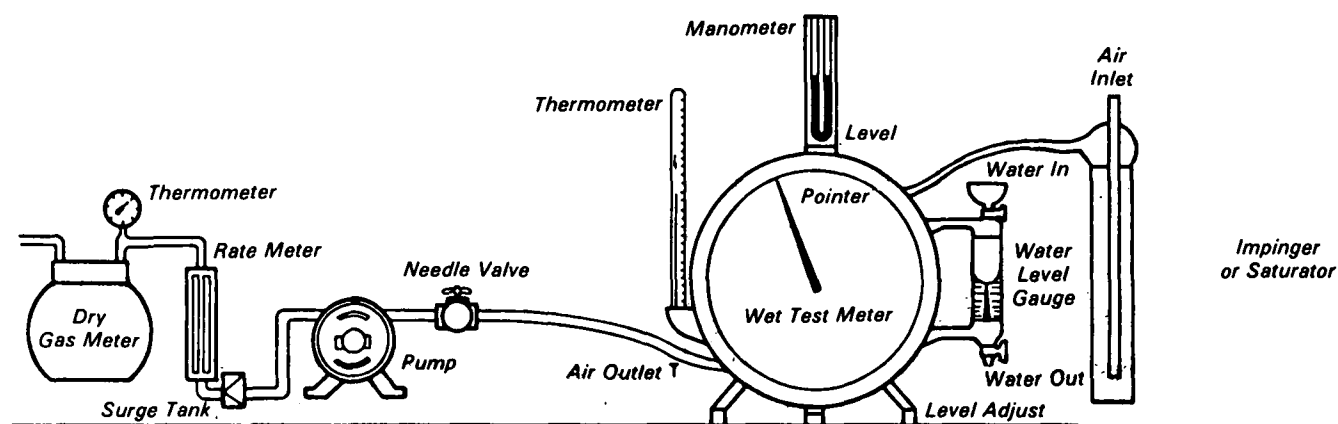


Figure 2.2. Sample meter system calibration setup.

Date 8/10/78Meter box number FM-2Barometric 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 (t _d), ^a °F			
0.5	5	130.000 135.140	71.5 71.5	91 98	82 85	89	12.47 60	1.004	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	$\frac{5(29.64)(549)}{5.14(29.67)(931.5)}$	$\frac{(0.0317)(0.5)}{(29.64)(549)} \left[\frac{(531.5)(12.78)}{5} \right]^2$
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 .**Nomenclature:** V_w = Gas volume passing through the wet test meter, ft³. V_d = Gas volume passing through the dry test meter, ft³. t_w = Temperature of the gas in the wet test meter, °F. t_{di} = Temperature of the inlet gas of the dry test meter, °F. t_{do} = 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 t_{di} and t_{do} , °C. ΔH = Pressure differential across orifice, mm H₂O. 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 m³ of air at standard conditions for each calibration run, mm H₂O. Tolerance $\Delta H@_i = \Delta H \pm 3.8$ mm H₂O (recommended). Θ = Time of each calibration run, min. P_b = Barometric pressure, mm Hg.**Figure 2.3A.** Dry gas meter calibration data (English units).

Date 4/10/78 Meter box number FM-2
 Barometric pressure, $P_b =$ 736 mm Hg. Calibrated by WDG

Orifice manometer setting (ΔH), mm H ₂ O	Gas volume ^a		Temperature ^a				Time (Θ), min	Y _i	$\Delta H@_i$
	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 (t _d), ^a °C			
10	0.15	25.0320 24.8800	18 18	20 19	18 17	18	10 49/ 60	.986	23
25	0.15								
40	0.30								
50	0.30								
75	0.30								
100	0.30								
Average									

ΔH	$\frac{\Delta H}{13.6}$	$Y_i = \frac{V_w P_b (t_d + 273)}{\Delta H_i V_d (P_b + 13.6) (t_w + 273)}$	$\Delta H@_i = \frac{0.00117 \Delta H}{P_b (t_d + 273)} \left[\frac{(t_w + 273) \Theta}{V_w} \right]^2$
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		

^aIf there is only one thermometer on the dry gas meter, record it under t_d .

Nomenclature:

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 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. 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 m³ of air at standard conditions for each calibration run, mm H₂O. Tolerance $\Delta H@_i = \Delta H@ \pm 3.8$ mm H₂O (recommended).

Θ = Time of each calibration run, min.

P_b = Barometric pressure, mm Hg.

Figure 2.3B. Dry gas meter calibration data (metric units).

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 ₂ O	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	$Y_i = \frac{V_w P_b (t_d + 460)}{V_d \left[P_b + \frac{\Delta H}{13.6} \right] (t_w + 460)}$
			Wet test meter (t_w), °F	Dry gas meter						
				Inlet (t_{d_i}), °F	Outlet (t_{d_o}), °F	Average (t_d), ^a °F				
1.41	10	886.544 876.321	72	83	75	79	13.35	3	0.987	$\frac{10(28.72)(79+460)}{10.223(28.72+1.41/13.6)(72+460)}$
	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 of 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 in 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.

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

Date 9/13/78 Test numbers ABI-3 Plant Acme Power Plant
 Barometric pressure, P_b = 730 mm Hg Meter box number FM-7 Pretest Y 0.993
 Dry gas meter number FM-7

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	$Y_i = \frac{V_w P_b (t_d + 273)}{V_d \left[P_b + \frac{\Delta H}{13.6} \right] (t_w + 273)}$
			Wet test meter (t_w), °C	Dry gas meter						
				Inlet (t_{d_i}), °C	Outlet (t_{d_o}), °C	Average (t_d) ^a , °C				
36	0.30	20.1742 19.8730	21	23.5	21.5	22.5	13.50	75	0.990	$\frac{0.30(730)(21.5+273)}{0.3012(730+\frac{75}{13.6})(21+273)}$
										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, 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 in 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.

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

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 $\pm 1^\circ\text{C}$ (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 (within ± 2.5 mm (0.1 in.) Hg of mercury-in-glass barometer)? ☒ yes
☐ no.

*Most significant items/parameters to be checked.

Figure 2.5. Pretest sampling checks.

Table 2.1. Activity Matrix for Calibration of Equipment

<i>Apparatus</i>	<i>Acceptance limits</i>	<i>Frequency and method of measurement</i>	<i>Action if requirements are not met</i>
<i>Wet test meter</i>	<i>Capacity of at least 3.4 m³/h (120 ft³/h) and an accuracy within $\pm 1.0\%$</i>	<i>Calibrate initially and then yearly by the liquid displacement technique</i>	<i>Adjust until specifications are met, or return to manufacturer</i>
<i>Dry gas meter</i>	<i>$Y_i = Y \pm 0.02 Y$ at a flow rate of 0.02-0.03 m³/min (0.66-1)</i>	<i>Calibrate vs. wet test meter initially, and when the posttest check is not within $Y \pm 0.05 Y$</i>	<i>Repair or replace and then recalibrate</i>
<i>Thermometers</i>	<i>Impinger thermometer $\pm 1^\circ\text{C}$ (2°F); dry gas meter thermometer within $\pm 3^\circ\text{C}$ (5.4°F) over range</i>	<i>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</i>	<i>Adjust; determine a constant correction factor; or reject</i>
<i>Barometer</i>	<i>± 2.5 mm (0.1 in.) Hg of mercury-in-glass barometer</i>	<i>Calibrate initially using mercury-in-glass barometer, and check before and after each field test</i>	<i>Adjust to agree with certified barometer</i>
<i>Probe nozzle</i>	<i>Average of three ID measurements of nozzle; difference between high and low not to exceed 0.1 mm (0.004 in.), $\alpha \leq 30^\circ$</i>	<i>Use a micrometer to measure to the nearest 0.025 mm (0.001 in.)</i>	<i>Recalibrate, reshape, and sharpen when nozzles are nicked, dented, or corroded</i>
<i>Trip balance</i>	<i>Standard weights measured within ≤ 0.5 g of stated value</i>	<i>Balance calibration verified when first purchased, any time moved or subjected to rough handling, and during routine operations when cannot weigh within ≤ 0.5 g</i>	<i>Manufacturer should recalibrate or adjust</i>
<i>Type-S Pitot tube</i>	<i>Initially calibrated according to Sec. 2 of Method 2, and tube tips undamaged</i>	<i>Visually check before each field test</i>	<i>Repair or replace</i>

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).

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 (H₂O₂, 3%) is prepared by diluting 100 ml of 30% H₂O₂ to 1 L (1000 ml) with deionized distilled water. The 3% H₂O₂ 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.

Apparatus check	Acceptable		Quantity required	Ready		Loaded and packed
	Yes	No		Yes	No	
<u>Probe</u>			4-6 'eff	✓		✓
Type glass liner						
Borosilicate _____	✓					
Quartz _____						
Heated	✓					
Leak checked	✓					
<u>Nozzle</u>			3 sets	✓		✓
Glass _____						
Stainless steel _____	✓					
Other _____						
<u>Pitot Tube</u>			4-6 'eff	✓		✓
Type _____	✓		"5"			
Other _____						
Properly attached _____	✓					
Modifications _____						
C _p _____	.84					
<u>Differential Pressure Gauge</u>						
Inclined manometer _____	✓		0-0.25	✓		✓
Other _____						
<u>Filter Holder</u>			5	✓		✓
Borosilicate glass	✓					
Glass frit	✓					
Gasket						
Silicone _____	✓					
Teflon _____						
Viton _____						
<u>Condenser</u>						
Impingers						
Greenburg-Smith	✓		6	✓		✓
Modified	✓		14	✓		✓
Greenburg-Smith						
<u>Impinger Temperature Sensor</u>			4			✓
Thermometer _____	✓			✓		✓
Other _____				✓		✓
Calibrated _____	✓					

Figure 3.1. Example of a pretest preparation checklist.

Apparatus check	Acceptable		Quantity required	Ready		Loaded and packed
	Yes	No		Yes	No	
<u>Other</u>						
<u>Barometer</u>						
Mercury _____						
Aneroid _____	✓		1	✓		✓
Other _____						
Calibrated* _____						
<u>Stack Temperature Sensor</u>						
Type _____	✓		2	✓		✓
Calibrated* _____	✓					
<u>Reagents</u>						
Distilled water	✓		3 gal	✓		✓
Hydrogen peroxide	✓		2 pt	✓		✓
(30%)						
Isopropanol (80%)			1 gal	✓		✓
(checked for	✓					
peroxides)	✓		5#	✓		✓
Silica gel						
<u>Meter System</u>			2			
Pump leak free*	✓			✓		✓
Orifice meter*	✓			✓		✓
Dry gas meter*	✓			✓		✓

* Most significant items/parameters to be checked.

Figure 3.1. (continued)

Table 3.1. Activity Matrix for Presampling Operations

<i>Operation</i>	<i>Acceptance limits</i>	<i>Frequency and method of measurement</i>	<i>Action if requirements are not met</i>
Apparatus			
<i>Probe</i>	<ol style="list-style-type: none"> 1. Probe liner should be free of contaminants and constructed of borosilicate glass, or quartz, or the equivalent (no metal liners) 2. Probe must be leak free at 380 mm (15 in.) Hg 3. Probe must prevent condensation of moisture 	<ol style="list-style-type: none"> 1. Clean probe internally by brushing with tap deionized distilled water, then acetone; allow to dry in air before test 2. Visually check before test 3. Check out heating system initially and when moisture cannot be prevented during testing (Sec. 3.7.1) 	<ol style="list-style-type: none"> 1. Retrace cleaning procedure and assembly 2. Replace 3. Repair or replace
<i>Impingers, filter holders, and glass connectors</i>	Clean, free of breaks, cracks, leaks, etc.	Clean with detergent and tap water, then deionized distilled water	Repair or discard
<i>Pump</i>	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
<i>Dry gas meter</i>	±2% of calibration factor and clean	Calibrate according to Sec. 3.7.2, and check for excess oil	As above
Reagents and Equipment			
<i>Sampling</i>	All reagents must be certified ACS or reagent grade	Prepare fresh daily and store in sealed containers	Prepare new reagent
<i>Sample recovery</i>	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
Package Equipment for Shipment			
<i>Probe</i>	Pack in rigid container and protect with polyethylene foam	Pack prior to each shipment	Repack
<i>Impingers, connectors, and assorted glassware</i>	Pack in rigid containers and protect with polyethylene foam	Pack prior to each shipment	Repack
<i>Pump</i>	Sturdy case lined with polyethylene foam material or as part of meter box	As above	As above
<i>Meter box</i>	Meter box case and/or additional material to protect train components; pack spare meter box	As above	As above
<i>Wash bottles and storage containers</i>	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:

$$\text{Maximum } \Delta H \leq \frac{1.09 P_m M \Delta H@}{T_m}$$

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 m³/min (1.0 ft³/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°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 380mm (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

m³/min (0.02 ft³/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.
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 $\pm 10\%$ 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 laboratory 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 SO₃) 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 SO₂ is captured in the second and third impingers and in all connecting glassware. To recover the SO₂ sample:

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% H₂O₂) 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.
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.

Method 8 Field Test Data Form

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 EM-16
 Meter $\Delta H@$ 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 _s), °C (°F)	Velocity head (ΔP_s), 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	156.511	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.

Plant	<u>Sulfuric Acid Plant</u>	City	<u>Acidville, U.S.A.</u>
Site	<u>Unit 1 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>		
		Remarks	

Figure 4.2. Example of a sample label.

Sample Recovery and Integrity Data

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.

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

$\Delta H@$ 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

<i>Apparatus</i>	<i>Acceptance limits</i>	<i>Frequency and method of measurement</i>	<i>Action if requirements are not met</i>
Sampling			
<i>Preparation and/or addition of absorbing reagents to collection system</i>	<i>100 ml of 80% isopropanol to first impinger and 100 ml of 3% H₂O₂ to each of the second and third impingers</i>	<i>Prepare H₂O₂ and 80% isopropanol fresh daily; use pipette or graduated cylinder to add solutions</i>	<i>Reassemble collection system</i>
Filter			
<i>Filter</i>	<i>Properly centered; no breaks, damage, or contamination during loading</i>	<i>Use tweezers or surgical gloves to load</i>	<i>Discard filter and reload</i>
Assembling sampling train			
	<ol style="list-style-type: none"> 1. Assemble to specifications in Fig. 1.1 2. Leakage rate <4% or 0.00057 m³/min (0.02 ft³/min) 	<ol style="list-style-type: none"> 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 	<ol style="list-style-type: none"> 1. Reassemble 2. Correct leak
Sampling (iso-kinetically)			
	<ol style="list-style-type: none"> 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 should not exceed 0.03 m³/min (1.0 ft³/min) 4. Minimum number of points sampled, as specified by Meth. 1 5. Leakage rate not to exceed 0.00057 m³/min (0.02 ft³/min) or 4% of average sampling rate; apply correction to sample volume if rate is exceeded 6. Purge remaining SO₂ from isopropanol 	<ol style="list-style-type: none"> 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 4. Check before the first test run by measuring duct and sampling site location 5. Leak check after each test run or before equipment replacement during a run at maximum vacuum occurring during the run (mandatory) 6. Drain ice, and purge with clean air for 15 min 	<ol style="list-style-type: none"> 1. Repeat sample or obtain acceptance from a representative of the Administrator 2. As above 3. As above 4. As above 5. Correct sample volume or repeat sample 6. Repeat sample
Sample recovery	<i>Noncontaminated sample</i>	<i>Transfer sample to labeled polyethylene container after each test run. Mark level of solution in the container</i>	<i>Repeat sample</i>

Table 4.1. (continued)

<i>Apparatus</i>	<i>Acceptance limits</i>	<i>Frequency and method of measurement</i>	<i>Action if requirements are not met</i>
<i>Sample logistics (data) and packing of equipment</i>	<i>1. All data recorded correctly</i>	<i>1. Upon the completion of each sample and before packing for shipment</i>	<i>1. Complete data</i>
	<i>2. All equipment examined for damage and labeled for shipment</i>	<i>2. As above</i>	<i>2. Repeat sampling if damage occurred during testing</i>
	<i>3. All sample containers properly labeled and packaged</i>	<i>3. Visually check up on completion of each sample</i>	<i>3. Correct when possible</i>

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.

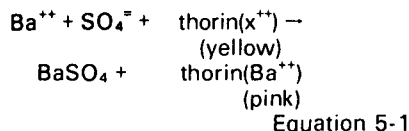
The posttest check of the dry gas meter is described in Section 3.7.2. If the posttest dry gas meter calibration factor (Y) is within 5% of the initial calibration factor, the initial calibration is used for calculations; if it deviates by >5%, recalibrate the metering system (as shown in Section 3.7.2) and use for the calculations the calibration factor (initial or recalibrated) 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 (BaSO₄) 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 (SO₄⁼) in solution to form a highly insoluble barium sulfate (BaSO₄) precipitate. After the Ba⁺⁺ has reacted with all SO₄⁼, 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 SO₃) and the SO₂ samples.

Water - Deionized distilled water to conform to ASTM specification D1193-74, Type 3. At the option of the analyst, the KMnO₄ test for oxidizable organic matter may be omitted when high concentrations of organic matter are not expected to be present. *Note* - It is imperative that the distilled water meet the ASTM specifications since SO₄⁼ 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 SO₄⁼ concentration). This added SO₄⁼ concentration would result in an erroneous standardization of the Ba(ClO₄)₂ titration, which directly measures SO₄⁼ 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 (Ba(ClO₄)₂ · 3H₂O) in 200 ml of deionized distilled water and dilute to 1 L with isopropanol. Alternatively, 1.22 g of barium chloride dihydrate (BaCl₂ · 2H₂O) may be used instead of the trihydrate. Standardize as in the subsection below with H₂SO₄. *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 ±0.0002N H₂SO₄ against 0.0100N NaOH that has been standardized against potassium acid phthalate (primary standard grade), as described in the subsection below.

The 0.01N H₂SO₄ may be prepared in the following manner:

- Prepare 0.5N H₂SO₄ by adding approximately 1500 ml of deionized distilled water into a 2 L volumetric flask.
- Cautiously add 28 ml of concentrated H₂SO₄ and mix. Cool, if necessary.
- Dilute to 2 L with deionized distilled water.
- Prepare 0.01N H₂SO₄ by adding approximately 800 ml of deionized distilled water to a 1 L volumetric flask.
- Add 20.0 ml of the 0.5N H₂SO₄.
- Dilute to the 1 L with distilled water and mix thoroughly. *Note* -

It is recommended that 0.1N sulfuric acid be purchased. Pipette 10.0 ml of H₂SO₄ (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 Sub-section 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°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. 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.

$$N_{\text{NaOH}} = \frac{\text{mg KHP}}{\text{ml titrant} \times 204.23}$$

Equation 5-1

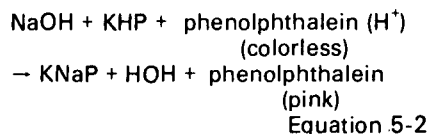
where

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 H₂SO₄, proceed as follows:

1. Pipette 25 ml of H₂SO₄ 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.

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

Equation 5-3

where

$N_{\text{H}_2\text{SO}_4}$ = calculated normality of H₂SO₄, N,

ml NaOH_{H₂SO₄} = volume of NaOH titrant used for H₂SO₄, ml,

ml NaOH_{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(ClO₄)₂, proceed as follows:

1. Pipette 25 ml of standard 0.0100N H₂SO₄ 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(ClO₄)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 SO₄²⁻. 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(ClO₄)₂ will be the average of the three independent values calculated using Equation 5-4.

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

Equation 5-4

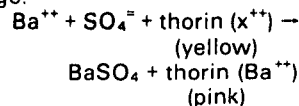
where

$N_{\text{Ba(ClO}_4)_2}$ = calculated normality of Ba(ClO₄)₂, N,

$N_{\text{H}_2\text{SO}_4}$ = normality of standard H₂SO₄, N, and

ml Ba(ClO₄)₂ = volume of Ba(ClO₄)₂ required to titrate H₂SO₄, ml.

The chemical reaction for this standardization is shown in Equation 5-5. The Ba⁺⁺ reacts preferentially with SO₄²⁻ in solution to form a highly insoluble BaSO₄ precipitate. When the Ba⁺⁺ has reacted with all of the SO₄²⁻, 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 Ba(ClO₄)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 H₂SO₄ 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 Ba(ClO₄)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 ((NH₄)₂SO₄) 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 (NH₄)₂SO₄.
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 (NH₄)₂SO₄.
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 Ba(ClO₄)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 Ba(ClO₄)₂ to a faint pink endpoint, using the blank endpoint that persists for at least 30s. 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 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 ±5% of the stated value, the technique is considered 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 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:

1. Mark the new volume level of the sample.
2. Transfer the sample to a 250-ml or 1-L (whichever is appropriate), volumetric flask (V_{soln}).
3. Put water in the sample storage container to the initial sample mark, and measure the initial sample volume (V_{soln}).
4. Put water in the sample storage container to the mark of the transferred sample, and measure the final volume (V_{soln}).
5. Use Equation 5-6 to correct the sample volume (V_{soln}) if the final volume (V_{soln}) is >50% of the initial volume.

$$V_{\text{soln}}' = V_{\text{soln}} \left[\frac{V_{\text{soln}}}{V_{\text{soln}}} \right]$$

Equation 5-6

where

V_{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} = initial sample volume placed in sample storage container, ml, and

V_{soln} = 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 SO₃) 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 Ba(ClO₄)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 at V_i 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 Ba(ClO₄)₂ solution from evaporation at all times.

Sulfur dioxide analysis - Proceed with the SO₂ 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.

Meter Box Number FM-1

Dry Gas Meter

Pretest calibration factor $Y =$ 0.986

Posttest check $Y_1 =$ 0.987 $Y_2 =$ _____ ($\pm 5\%$ of pretest factor)*

Recalibration required? _____ yes ☒ no

If yes, recalibration factor $Y =$ _____ (within $\pm 2\%$ of average)

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 $\pm 6^\circ\text{C}$ (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 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.

Method 8 Analytical Data Form

Plant Sulfuric Acid Plant Date 9/22/78Sample location Unit 1 Acidville Analyst R. KuntzVolume and normality of
barium perchlorate1. 25.0 ml Ba (ClO₄)₂
2. 25.0 ml Ba (ClO₄)₂
Blank 0.0 ml Ba (ClO₄)₂N = 0.010

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 V_{tb}^* - Volume of barium perchlorate
titrant used for blank, ml $\frac{1\text{st titration}}{2\text{nd titration}} = 0.99 \text{ to } 1.01 \text{ or } |1\text{st titration} - 2\text{nd titration}| \leq 0.2 \text{ ml}$

Run 1	Run 2	Run 3
250		
100		
19.0		
19.1		
19.05		
0.0		
0.0		
0.0		

Sulfur Dioxide 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 V_{tb}^* - Volume of barium perchlorate
titrant used for blank, ml $\frac{1\text{st titration}}{2\text{nd titration}} = 0.99 \text{ to } 1.01 \text{ or } |1\text{st titration} - 2\text{nd titration}| \leq 0.2 \text{ ml}$ Signature of analyst Ronda KuntzSignature of reviewer or supervisor Craig Caldwell

* Volume of blank and sample titrated should be the same; otherwise a volume correction must be made.

Control Sample Analytical Data Form

Plant Sulfuric Acid Plant Date analyzed 9/22/78
 Analyst R. Kuntz $N_{Ba}(ClO_4)_2$ 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 $Ba(ClO_4)_2$
 (must be less than the 0.5 ml titrant)

Control Sample Number	Time of Analysis 24 h	Titrant volume, ml			
		1st	2nd	3rd	Ave
<u>1</u>	<u>0930</u>	<u>25.0</u>	<u>25.0</u>		<u>25.0</u>

(Two consecutive volumes must agree within 0.2 ml)

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

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

(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.

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.

Table 5.1. Activity Matrix for Postsampling Operations

<i>Apparatus</i>	<i>Acceptance limits</i>	<i>Frequency and method of measurement</i>	<i>Action if requirements are not met</i>
Sampling Apparatus			
<i>Dry gas meter</i>	<i>Within $\pm 5\%$ of pretest calibration factor</i>	<i>Make three runs at one intermediate orifice setting and at highest vacuum of test (Sec. 3.7.2)</i>	<i>Recalibrate and use calibration factor that gives lower sample</i>
<i>Meter thermometer</i>	<i>Within $\pm 6^\circ\text{C}$ (10.8°F) at ambient temperature</i>	<i>Compare with mercury-in-glass thermometer after each test</i>	<i>Recalibrate and use higher temperature for calculations</i>
<i>Barometer</i>	<i>Within ± 5.0 mm (0.2 in.) Hg at ambient pressure</i>	<i>Compare with mercury-in-glass barometer after each test</i>	<i>Recalibrate and use lower barometric values for calculations</i>
Analysis			
<i>Reagents</i>	<i>Prepare according to Sec. 3.7.5</i>	<i>Prepare and/or standardize within 24 h of analysis</i>	<i>Prepare new solutions and/or re-standardize</i>
<i>Control sample</i>	<i>Titriments differ by ≤ 0.2 ml; analytical results within $\pm 5\%$ of stated value</i>	<i>Before and after analysis of field samples</i>	<i>Prepare new solutions and/or re-standardize</i>
<i>Sample analysis</i>	<i>Titriments differ by $\leq 1\%$ or 0.2 ml, whichever is greater</i>	<i>Titrate until two or more aliquots agree within 1% or 0.2 ml, whichever is greater; review all analytical data</i>	<i>Void sample if any two consecutive titriments do not meet criterion</i>

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.

6.0 Calculations

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 1000 ml, 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).

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

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

Equation 6-1

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.

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 SO_3) Concentration -

$$C_{H_2SO_4} = K_2 \left[\frac{N (V_t - V_{tb}) \left[\frac{V_{soln}}{V_a} \right]}{V_{m(std)}} \right]$$

Equation 6-2

where

$K_2 = 0.04904$ g/meq for metric units, or
 $= 1.081 \times 10^{-4}$ lb/meq for English units.

6.2.4 Sulfur Dioxide Concentration -

$$C_{SO_2} = K_3 \left[\frac{N (V_t - V_{tb}) \left[\frac{V_{soln}}{V_a} \right]}{V_{m(std)}} \right]$$

Equation 6-3

where

$K_3 = 0.03203$ g/meq for metric units, or
 $= 7.061 \times 10^{-5}$ lb/meq for English units.

6.2.5 Isokinetic Variation (I) in Raw Data -

$$I = \frac{T_s \left\{ K_4 V_{tc} + \left[\frac{V V_m}{T_m} \right] \left[P_{bar} + \frac{\Delta H}{13.6} \right] \right\}}{60 \Theta V_s P_s A_n} \times 100$$

Equation 6-4

where

$K_4 = 0.003464$ mm Hg-m³/ml-K for metric units, or
 $= 0.002676$ in. Hg-ft³/ml-°R for English units.

6.2.6 Isokinetic Variation (I) in Intermediate Values -

$$I = \frac{\left[\frac{T_s V_{m(std)} P_{std}}{T_{std} 60 \Theta V_s P_s A_n [1 - B_{ws}]} \right] 100}{K_5 \frac{T_s V_{m(std)}}{\Theta V_s P_s A_n [1 - B_{ws}]}}$$

Equation 6-5

where

$K_5 = 4.320$ for metric units, or
 $= 0.09450$ 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

*Sulfuric Acid Mist (Including SO₃) Calculation Form
(English units)*

Sample Volume

$$V_m = 45.080 \text{ ft}^3, T_m = 542.6 \text{ } ^\circ\text{R}, P_{\text{bar}} = 29.96 \text{ in. Hg}$$

$$Y = 1.016, \Delta H = 1.89 \text{ in. H}_2\text{O}$$

$$V_{\text{mstd}} = 17.64 V_m Y \left[\frac{P_{\text{bar}} + (\Delta H/13.6)}{T_m} \right] = 44.82 \text{ ft}^3$$

Equation 6-1

Sulfuric Acid Mist (Including SO₃) Concentrations

$$N = 0.100 \text{ g-eg/L}, V_t = 19.05 \text{ ml}, V_{\text{tb}} = 0.02 \text{ ml}$$

$$V_{\text{soln}} = 250.0 \text{ ml}, V_a = 100.0 \text{ ml}, V_{\text{mstd}} = 44.82 \text{ ft}^3$$

$$C_{\text{H}_2\text{SO}_4} = 1.081 \times 10^{-4} \left\{ \frac{N (V_t - V_{\text{tb}}) \left(\frac{V_{\text{soln}}}{V_a} \right)}{V_{\text{mstd}}} \right\} = 0.115 \times 10^{-4} \text{ lb/dscf}$$

Equation 6-2

Figure 6.1A. Sulfuric acid mist (including SO₃) calculation form (English units).

*Sulfuric Acid Mist (Including SO₃) Calculation Form
(metric units)*

Sample Volume

$$V_m = \underline{1.276} \text{ m}^3, T_m = \underline{301.1} \text{ K}, P_{\text{bar}} = \underline{761.0} \text{ mm Hg}$$

$$Y = \underline{1.016}, \Delta H = \underline{48.0} \text{ mm H}_2\text{O}$$

$$V_{\text{mstd}} = 0.3858 V_m Y \left[\frac{P_{\text{bar}} + (\Delta H/13.6)}{T_m} \right] = \underline{1.270} \text{ m}^3$$

Equation 6-1

Sulfuric Acid Mist (Including SO₃) Concentrations

$$N = \underline{.0100} \text{ g-eg/L}, V_t = \underline{19.05} \text{ ml}, V_{\text{tb}} = \underline{0.02} \text{ ml}$$

$$V_{\text{soln}} = \underline{250.} \text{ ml}, V_a = \underline{100.0} \text{ ml}, V_{\text{mstd}} = \underline{1.270} \text{ m}^3$$

$$C_{\text{H}_2\text{SO}_4} = 0.04904 \left[\frac{N (V_t - V_{\text{tb}}) \left(\frac{V_{\text{soln}}}{V_a} \right)}{V_{\text{mstd}}} \right] = \underline{.01837} \text{ g/dscm}$$

Equation 6-2

Figure 6.1B. Sulfuric acid mist (including SO₃) calculation form (metric units).

*Sulfur Dioxide Calculation Form
(English units)*

Sample Volume

$$V_m = \underline{45.080} \text{ ft}^3, T_m = \underline{542.6} \text{ }^\circ\text{R}, P_{\text{bar}} = \underline{29.96} \text{ in. Hg}$$

$$Y = \underline{1.016}, \Delta H = \underline{1.89} \text{ in. H}_2\text{O}$$

$$V_{\text{mstd}} = 17.64 V_m Y \left[\frac{P_{\text{bar}} + (\Delta H / 13.6)}{T_m} \right] = \underline{44.82} \text{ ft}^3$$

Equation 6-1

Sulfuric Acid Mist (Including SO₃) Concentrations

$$N = \underline{.0100} \text{ g-eg/L}, V_t = \underline{11.34} \text{ ml}, V_{\text{tb}} = \underline{0.02} \text{ ml}$$

$$V_{\text{soln}} = \underline{1000.0} \text{ ml}, V_a = \underline{10.0} \text{ ml},$$

$$C_{\text{SO}_2} = 7.061 \times 10^{-5} \left[\frac{N (V_t - V_{\text{tb}}) \left(\frac{V_{\text{soln}}}{V_a} \right)}{V_{\text{mstd}}} \right] = \underline{0.177} \times 10^{-4} \text{ lb/dscf}$$

Equation 6-2

Figure 6.2A. Sulfur dioxide calculation form (English units).

*Sulfur Dioxide Calculation Form
(metric units)*

Sample Volume

$$V_m = 1.276 \text{ m}^3, T_m = 301.1 \text{ K}, P_{\text{bar}} = 761.0 \text{ mm Hg}$$

$$Y = 1.016, \Delta H = 48.0 \text{ mm H}_2\text{O}$$

$$V_{\text{mstd}} = 0.3858 V_m Y \left[\frac{P_{\text{bar}} + (\Delta H / 13.6)}{T_m} \right] = 1.270 \text{ m}^3$$

Equation 6-1

SO₂ Concentration

$$N = 0.100 \text{ g-eg/L}, V_t = 11.34 \text{ ml}, V_{\text{tb}} = 0.02 \text{ ml}$$

$$V_{\text{soln}} = 1000. \text{ ml}, V_a = 10.0 \text{ ml},$$

$$C_{\text{SO}_2} = 3.203 \times 10^{-2} \left[\frac{N (V_t - V_{\text{tb}}) \left(\frac{V_{\text{soln}}}{V_a} \right)}{V_{\text{mstd}}} \right] = 0.286 \text{ g/dscm}$$

Equation 6-2

Figure 6.2B. Sulfur dioxide calculation form (metric units).

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

<i>Apparatus</i>	<i>Acceptance limits</i>	<i>Frequency and method of measurement</i>	<i>Action if requirements are not met</i>
<i>Routine maintenance</i>	<i>No erratic behavior</i>	<i>Routine maintenance quarterly. Disassemble and clean yearly</i>	<i>Replace parts as needed</i>
<i>Fiber vane pump</i>	<i>In-line oiler free of leaks</i>	<i>Periodic check of oiler jar; remove head and change fiber vanes</i>	<i>Replace as needed</i>
<i>Diaphragm pump</i>	<i>Leak-free valves functioning properly</i>	<i>Clean valves during yearly disassembly</i>	<i>Replace when leaking or malfunctioning</i>
<i>Dry gas meter</i>	<i>No excess oil, corrosion, or erratic rotation of the dial</i>	<i>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</i>	<i>Replace parts as needed, or replace meter</i>
<i>Inclined manometer</i>	<i>No discoloration or visible matter in the fluid</i>	<i>Check periodically during yearly disassembly</i>	<i>Replace parts as needed</i>
<i>Sample train</i>	<i>No damage</i>	<i>Visually check every 3 mo and completely disassemble and clean or replace yearly</i>	<i>If failure noted, use another entire control console, sample box, or umbilical cord</i>
<i>Nozzle</i>	<i>No dents, corrosion, or other damage</i>	<i>Visually check before and after each test run</i>	<i>Use another nozzle or clean out, sharpen, and recalibrate</i>

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 test⁶ 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.

$$\%A = \frac{C_{SO_2}(M) - C_{SO_2}(A)}{C_{SO_2}(A)} \times 100$$

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

Audit date	Known audit concentration, mg SO ₂ /dscm	90th percentile for %A, %
5/78	686	4.1
10/78	572	6.4

1500 to 2500 mg SO₂/dscm

Audit date	Known audit concentration, mg SO ₂ /dscm	90th percentile for %A, %
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.

Table 8.1. Activity Matrix for Auditing Procedure

<i>Audit</i>	<i>Acceptance limits</i>	<i>Frequency and method of measurement</i>	<i>Action if requirements are not met</i>
<i>Analytical phase of Method 8 using aqueous ammonium sulfate</i>	<i>The measured value of the pretest audit sample should be less than the 90th percentile value, 7%</i>	<i>Once during every enforcement source test, measure reference samples and compare with their true values</i>	<i>Review operating technique</i>
<i>Data-processing errors</i>	<i>The original and check calculations should agree within round-off error</i>	<i>Once during every enforcement source test, perform independent calculations, starting with recorded data</i>	<i>Check and correct all data for the source test</i>
<i>Systems audit—observance of technique</i>	<i>Operation technique described in this section of the Handbook</i>	<i>Once during every enforcement test until experience gained; then every fourth test. Observation of technique, assisted by audit checklist, Fig. 8.1</i>	<i>Explain to team its deviations from recommended techniques, and note on Fig. 8.1</i>

Method 8 Checklist To Be Used By Auditors

Yes	No	Comment	
		<u>OK</u>	Presampling Preparation
			1. Knowledge of process conditions
✓			2. Calibration of pertinent equipment, in particular, the dry gas meter, prior to each field test
✓			On-site Measurements
✓			3. Leak-testing of sampling train after sample run
✓			4. Preparation and addition of absorbing solutions to impingers
		<u>OK</u>	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
		<u>*</u>	8. Maintaining the probe at a given temperature
<u>**</u>			Postsampling
			9. Control sample analysis - accuracy and precision
		<u>OK</u>	10. Sample aliquotting techniques
		<u>OK</u>	11. Titration technique, particularly endpoint precision
✓			12. Use of detection blanks in correcting field sample results
		<u>OK</u>	13. Calculation procedure/check
		<u>OK</u>	14. Calibration checks
		<u>OK</u>	15. Standard barium perchlorate solution
General Comments			
* probe shorted out during run 3 but sampling was allowed to continue			
** first set of audit samples were acceptable			

Figure 8.1. Method 8 checklist to be used by auditors.

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-thorin 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 (0.03×10^{-7} pounds/cubic foot) for sulfur trioxide and 1.2 mg/m^3 ($0.74 \times 10^{-7} \text{ lb/ft}^3$) 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 m^3 (35.3 ft^3) gas sample is about $12,500 \text{ mg/m}^3$ ($7.7 \times 10^{-4} \text{ lb/ft}^3$). The upper limit can be extended by increasing the quantity of peroxide solution in the impingers.

Possible 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, U.S. EPA are required.

Filterable particulate matter may be determined along with SO_3 and SO_2 (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; H_2SO_4 acid mist is not determined separately.

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-0581. Changes from the APTD-0581 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 unstricted 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.

2.2.1 Wash Bottles. Polyethylene or glass, 500 ml (two).

2.2.2 Graduated Cylinders. 250 ml, 1 liter. (Volumetric flasks may also be used.)

2.2.3 Storage Bottles. Leak-free polyethylene bottles, 1000 ml size (two for each sampling run).

2.2.4 Trip Balance. 500-gram capacity, to measure to $\pm 0.5 \text{ g}$ (necessary only if a moisture content analysis is to be done).

2.3 Analysis.

2.3.1 Pipettes. Volumetric 25 ml, 100 ml.

2.3.2 Burette. 50 ml.

2.3.3 Erlenmeyer Flask. 250 ml. (one for each sample blank and standard).

2.3.4 Graduated Cylinder. 100 ml.

2.3.5 Trip Balance. 500 g capacity, to measure to $\pm 0.5 \text{ g}$.

2.3.6 Dropping Bottle. To add indicator solution, 125-ml size.

3. Reagents

Unless otherwise indicated, all reagents are to conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, where such speci-

*CFR 60, July 1978.

cations are available. Otherwise, use the best available grade.

3.1 Sampling.

3.1.1 Filters. Same as Method 5, Section 3.1.1.

3.1.2 Silica Gel. Same as Method 5, Section 3.1.2.

3.1.3 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.

3.1.4 Isopropanol, 80 Percent. Mix 800 ml of isopropanol with 200 ml of deionized, distilled water.

Note - Experience has shown that only ACS grade isopropanol is satisfactory. Tests have shown that isopropanol obtained from commercial sources occasionally has peroxide impurities that will cause erroneously high sulfuric acid mist measurement. Use the following test for detecting peroxides in each lot of isopropanol: Shake 10 ml of the 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 on a spectrophotometer at 352 nanometers. If the absorbance exceeds 0.1, the isopropanol shall not be used. 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 is readily available from commercial sources; therefore, rejection of contaminated lots may be more efficient than following the peroxide removal procedure.

3.1.5 Hydrogen Peroxide, 3 Percent. Dilute 100 ml of 30 percent hydrogen peroxide to 1 liter with deionized, distilled water. Prepare fresh daily.

3.1.6 Crushed Ice.

3.2 Sample Recovery.

3.2.1 Water. Same as 3.1.3.

3.2.2 Isopropanol, 80 Percent. Same as 3.1.4.

3.3 Analysis.

3.3.1 Water. Same as 3.1.3.

3.3.2 Isopropanol, 100 Percent.

3.3.3 Thorin Indicator. 1-(o-arsonophenylazo)-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 (0.0100 Normal). Dissolve 1.95 g of 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 liter with isopropanol; 1.22 g of barium chloride dihydrate ($\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$) may be used instead of the barium perchlorate. Standardize with sulfuric acid as in Section 5.2. This solution must be protected against evaporation at all times.

3.3.5 Sulfuric Acid Standard (0.0100 N). Purchase or standardize to ± 0.0002 N against 0.0100 N NaOH that has previously been standardized against primary standard potassium acid phthalate.

4. Procedure

4.1 Sampling.

4.1.1 Pretest Preparation. Follow the procedure outlined in Method 5, Section 4.1.1; filters should be inspected, but need not be desiccated, weighed, or identified. If the effluent gas can be considered dry, i.e., moisture free, the silica gel need not be weighed.

4.1.2 Preliminary Determinations. Follow the procedure outlined in Method 5, Section 4.1.2.

4.1.3 Preparation of Collection Train. Follow the procedure outlined in Method 5, Section 4.1.3 (except for the second paragraph and other obviously inapplicable parts) and use Figure 8-1 instead of Figure 5-1. Replace the second paragraph with: Place 100 ml of 80 percent isopropanol in the first impinger, 100 ml of 3 percent hydrogen peroxide in both the second and third impingers; retain a portion of each reagent for use as a blank solution. Place about 200 g of silica gel in the fourth impinger.

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 m^3/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 posttest (mandatory) leak-check as in Section 4.1.4.3 of Method 5 (with appropriate modification) and record the leak rate. If the posttest 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. At the option of the tester, ambient air (without cleaning) may be used.

4.1.6 Calculation of Percent Iso-kinetic. 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 thiorin 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 40 ml of isopropanol, 2 to 4 drops of thiorin 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 thiorin 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_n = Cross-sectional area of nozzle, m^3 (ft^3).

B_{ws} = Water vapor in the gas stream, proportion by volume.

CH_{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 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), $^{\circ}K$ ($^{\circ}R$).

T_s = Average absolute stack gas temperature (see Figure 8-2), $^{\circ}K$ ($^{\circ}R$).

T_{std} = Standard absolute temperature, 293 $^{\circ}K$ (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 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, dscm (dscf).

V_{ts} = 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_t = Volume of barium perchlorate 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 = 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 5-2 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). Calculate 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 SO₃) concentration.

$$C_{H_2SO_4} = K_2 \frac{N(V_t - V_u) \left(\frac{V_{soln}}{V_a} \right)}{V_{m(std)}}$$

Equation 8-2

where

$K_2 = 0.04904$ g/milliequivalent for metric units.

$= 1.081 \times 10^{-4}$ lb/meq for English units.

6.6 Sulfur dioxide concentration.

$$C_{SO_2} = K_3 \frac{N(V_t - V_{tb}) \left(\frac{V_{soln}}{V_a} \right)}{V_{m(std)}}$$

Equation 8-3

where

$K_3 = 0.03203$ g/meq for metric units
 $= 7.061 \times 10^{-5}$ lb/meq for English units.

6.7 Isokinetic Variation.

6.7.1 Calculation from raw data.

$$I = \frac{100 T_s [K_4 V_{ic} + (B_m Y / T_m) (P_{bar} + \Delta H / 13.6)]}{60 \theta v_s P_s A_n} \quad \text{Equation 8-4}$$

where:

$K_4 = 0.003464$ mm Hg-m³/ml-°K for metric units.

$= 0.002676$ in. Hg-ft³/ml-°R for English units.

6.7.2 Calculation from intermediate values.

$$I = \frac{T_s V_{m(std)} P_{std} 100}{T_{std} V_s \theta A_n P_s 60 (1 - B_{ws})}$$

$$= K_5 \frac{T_s V_{m(std)}}{P_a V_s A_n \theta (1 - B_{ws})} \quad \text{Equation 8-5}$$

where

$K_5 = 4.320$ for metric units.

$= 0.09450$ for English units.

6.5 Acceptable Results. If 90 percent $\leq I \leq 110$ 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 judgements. Otherwise, reject the results and repeat the test.

7. Bibliography

1. Atmospheric Emissions from Sulfuric Acid Manufacturing Processes. U.S. DHEW, PHS, Division of Air Pollution. Public

Health Service Publication No. 999-AP-13. Cincinnati, Ohio. 1965.

2. Corbett, P.F. The Determination of SO₂ and SO₃ in Flue Gases. Journal of the Institute of Fuel. 24:237-243. 1961.
3. Martin, R. M. Construction Details of Isokinetic Source Sampling Equipment. Environmental Protection Agency. Research Triangle Park, N.C. Air Pollution Control Office Publication No. APTD-0581. April 1971.
4. Patton, W.F. and J.A. Brink, Jr. New Equipment and Techniques for Sampling Chemical Process Gases. Journal of Air Pollution Control Association. 13:162. 1963.
5. Rom, J.J. Maintenance, Calibration, and Operation of Isokinetic Source-Sampling Equipment. Office of Air Programs, Environmental Protection Agency. Research Triangle Park, N.C. APTD-0576. March 1972.
6. Hamil, H.F. and D.E. Camann. Collaborative Study of Method for Determination of Sulfur Dioxide Emissions from Stationary Sources (Fossil Fuel-Fired Steam Generators). Environmental Protection Agency. Research Triangle Park, N.C. EPA-650/4-74-024. December 1973.
7. Annual Book of ASTM Standards. Part 31; Water, Atmospheric Analysis. pp. 40-42. American Society for Testing and Materials. Philadelphia, Pa. 1974.

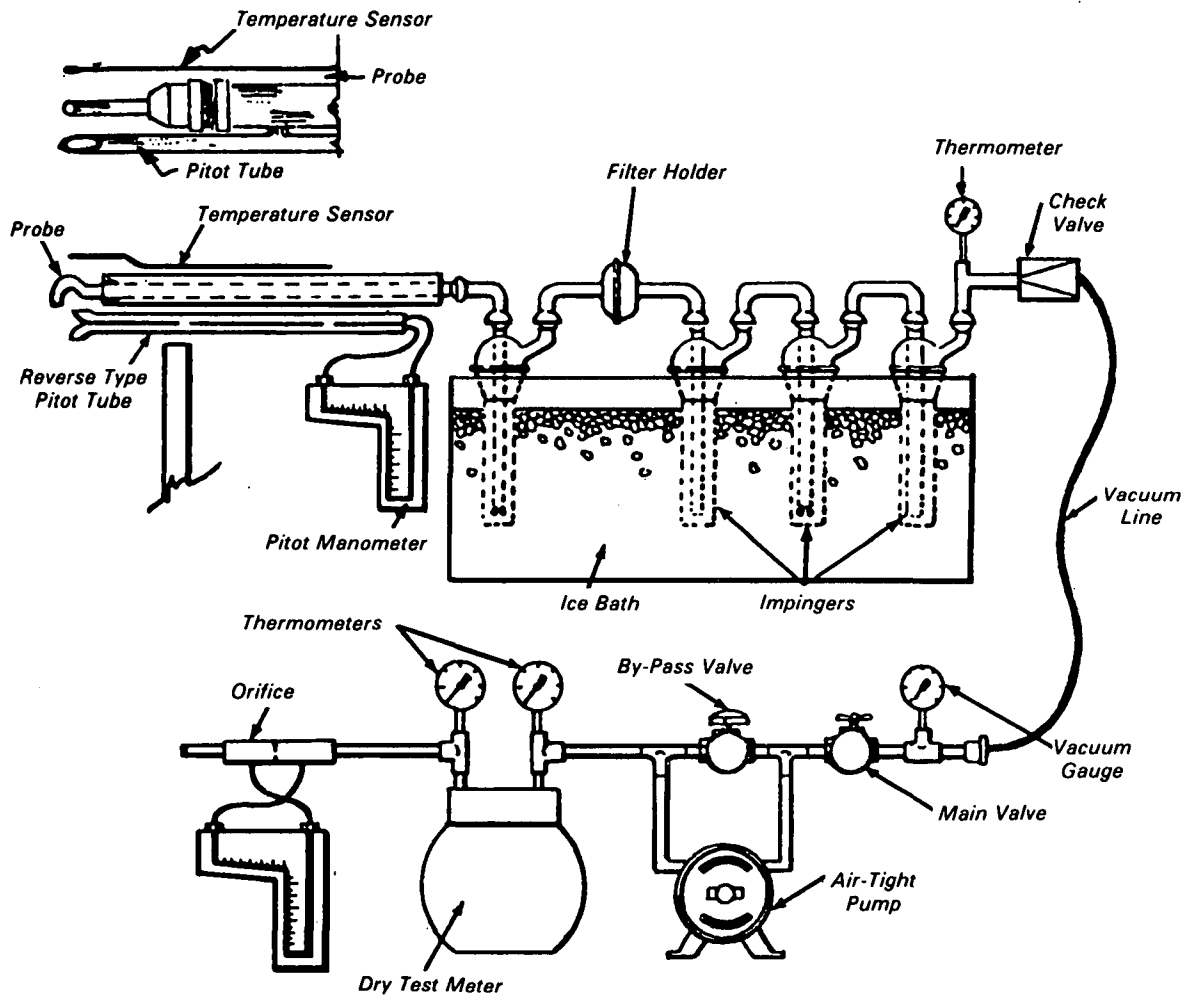
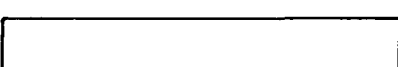


Figure 8.1. Sulfuric acid mist sampling train.

Plant _____ Location _____ Operator _____ Date _____ Run No. _____ Sample box no. _____ Meter box no. _____ Meter $\Delta H@$ _____ C factor _____ Pitot tube coefficient, C_p _____	 Schematic of stack cross section	Static pressure mm Hg (in. Hg) _____ Ambient temperature _____ Barometric pressure _____ Assumed moisture, % _____ Probe length, m (ft) _____ Nozzle identification no. _____ Average calibrated nozzle diameter, cm (in.) _____ Probe heater setting _____ Leak rate, m ³ /min, (cfm) _____ Probe liner material _____ Filter no. _____
---	--	---

Traverse Number	Sampling Time (Θ), min	Vacuum mm Hg (in. Hg)	Stack Temperature (T_s), °C (°F)	Velocity Head (ΔP_s), 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)	
.Total							Avg.	Avg	
Average							Avg		

Figure 8.2. *Field data.*

11.0 References

1. Buchanan, J.W., and D.E. Wagoner. Guidelines for Development of a Quality Assurance Program: Volume VII - Determination of Sulfuric Acid Mist and Sulfur Dioxide Emissions from Stationary Sources. EPA-650/4-74-005-g. Environmental Protection Agency, Research Triangle Park, N.C., March 1976.
2. Hamil, H. F., D. E. Camann, and R. E. Thomas. Collaborative Study of Method for the Determination of Sulfuric Acid Mist and Sulfur Dioxide Emissions from Stationary Sources. EPA-650/4-75-003, Environmental Protection Agency, Research Triangle Park, N.C. 1974.
3. Driscoll, J., J. Becker, and R. Herbert. Validation of Improved Chemical Methods for Sulfur Oxide Measurements from Stationary Sources. EPA-R2-72-105. National Environmental Research Center, Research Triangle Park, N.C.
4. Martin, R. M. Construction Details of Isokinetic Source Sampling Equipment. Publication No. APTD-0581. Air Pollution Control Office, Environmental Protection Agency, Research Triangle Park, N.C. 1971.
5. Rom, J.J. Maintenance, Calibration, and Operation of Isokinetic Source Sampling Equipment. Publication No. APTD-0576. Office of Air Programs, Environmental Protection Agency, Research Triangle Park, N.C. 1972.
6. Fuerst, R.G., R.L. Denny, and M.R. Midgett. A Summary of Interlaboratory Source Performance Surveys for EPA Reference Methods 6 and 7 - 1977. Available from U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory (MD-77), Research Triangle Park, N.C. 27711.
7. Fuerst, R.G. and M.R. Midgett. A Summary of Interlaboratory Source Performance Surveys for EPA Reference Methods 6 and 7 - 1978. Report in preparation by U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory (MD-77), Research Triangle Park, N.C. 27711.

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.

<i>Form</i>	<i>Title</i>
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 Calib- ration 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 Analy- tical Data Form
5.4 (MH)	Posttest Operations
6.1A and 6.1B	Sulfuric Acid Mist Calculation Form (Eng- lish and metric units)
6.2A and 6.2B	Sulfur Dioxide Calcul- ation Form (English and metric units)
8.1	Method 8 Checklist to be Used by Auditors

Procurement Log

<i>Item description</i>	<i>Qty.</i>	<i>Purchase order number</i>	<i>Vendor</i>	<i>Date</i>		<i>Cost</i>	<i>Dispo- sition</i>	<i>Comments</i>
				<i>Ord.</i>	<i>Rec.</i>			

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_2O	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), $^{\circ}F$	Dry gas meter					
				Inlet (t_{d1}), $^{\circ}F$	Outlet (t_{d2}), $^{\circ}F$				Average (t_d), ^a $^{\circ}F$
0.5	5								
1.0	5								
1.5	10								
2.0	10								
3.0	10								
4.0	10								
Average									

ΔH	$\frac{\Delta H}{13.6}$	$Y_i = \frac{V_w P_b (t_d + 460)}{V_d (P_b + 13.6) (t_w + 460)}$	$\Delta H@_i = \frac{0.0317 \Delta H}{P_b (t_d + 460)} \left[\frac{(t_w + 460) \Theta}{V_w} \right]^2$
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, $^{\circ}F$. t_{d1} = Temperature of the inlet gas of the dry test meter, $^{\circ}F$. t_{d2} = 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 t_{d1} and t_{d2} , $^{\circ}F$. ΔH = Pressure differential across orifice, in. H_2O . Y_i = Ratio of accuracy of wet test meter to dry test meter for each run. 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. $\Delta H@_i$ = Orifice pressure differential at each flow rate that gives $0.75 ft^3/min$ 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 $0.75 ft^3/min$ 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 (t_d), ^a °C			
10	0.15								
25	0.15								
40	0.30								
50	0.30								
75	0.30								
100	0.30								
Average									

ΔH	$\frac{\Delta H}{13.6}$	$Y_i = \frac{V_w P_b (t_d + 273)}{V_d (P_b + \frac{\Delta H}{13.6}) (t_w + 273)}$	$\Delta H@_i = \frac{0.00117 \Delta H}{P_b (t_d + 273)} \left[\frac{(t_w \times 273) \Theta}{V_w} \right]^2$
10	0.7		
25	1.8		
40	2.94		
50	3.68		
75	5.51		
100	7.35		

^aIf 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 t_{d_o} and t_{d_i} , $^{\circ}C$.

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.

$\Delta H@_i$ = 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).

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 ₂ O	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 = $\frac{V_w P_b (t_d + 460)}{V_d \left[P_b + \frac{\Delta H}{13.6} \right] (t_w + 460)}$
			Wet test meter (t_w), °F	Dry gas meter						
				Inlet (t_{d_i}), °F	Outlet (t_{d_o}), °F	Average (t_d), ^a °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, ft³.

V_d = Gas volume passing through the dry test meter, ft³.

t_w = Temperature of the gas of the wet test meter, °F.

t_{d_i} = Temperature of the inlet gas of the dry test meter, °F.

t_{d_o} = Temperature of the outlet gas of the dry test meter, °F.

t_d = Average temperature of the gas in the dry test meter, obtained by the average 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 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	$Y_i =$ $\frac{V_w P_b (t_d + 273)}{V_d P_b + \frac{\Delta H}{13.6} (t_w + 273)}$
			Wet test meter (t_w), °C	Dry gas meter						
				Inlet (t_{d_i}), °C	Outlet (t_{d_o}), °C	Average (t_d) ^a , °C				
0.30										
0.30										
0.30										
										$Y =$

^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.

Nozzle Calibration

Date _____

Calibrated by _____

Nozzle identification number	D_1 , mm (in.)	D_2 , mm (in.)	D_3 , mm (in.)	ΔD , mm (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.)
 Δ = 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 .

Section 3.7.12

8

5-01-79

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

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 perchlorate1. _____ ml Ba (ClO₄)₂
2. _____ ml Ba (ClO₄)₂
Blank _____ ml Ba (ClO₄)₂

N = _____

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

 $\frac{\text{1st titration}}{\text{2nd titration}} = 0.99 \text{ to } 1.01$ or $|1\text{st titration} - 2\text{nd titration}| \leq 0.2 \text{ ml}$

Run 1	Run 2	Run 3

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

 $\frac{\text{1st titration}}{\text{2nd titration}} = 0.99 \text{ to } 1.01$ or $|1\text{st titration} - 2\text{nd titration}| \leq 0.2 \text{ ml}$

Run 1	Run 2	Run 3

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.

Sulfuric Acid Mist (Including SO₃) Calculation Form
(English units)

Sample Volume

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

$$Y = \underline{\hspace{1cm}} \cdot \underline{\hspace{1cm}}, \Delta H = \underline{\hspace{1cm}} \cdot \underline{\hspace{1cm}} \text{ in. } H_2O$$

$$V_{mstd} = 17.64 V_m Y \left[\frac{P_{bar} + (\Delta H / 13.6)}{T_m} \right] = \text{---} \cdot \text{---} \text{ ft}^3 \quad \text{Equation 6-1}$$

Sulfuric Acid Mist (Including SO₂) Concentrations

$N =$ _____ $g\text{-eq/L}$, $V_i =$ _____ ml , $V_{ib} =$ _____ ml

$V_{\text{soln}} = \underline{\hspace{1cm}} \text{ ml}$, $V_a = \underline{\hspace{1cm}} \text{ ml}$, $V_{\text{std}} = \underline{\hspace{1cm}} \text{ ft}^3$

$$C_{H_2SO_4} = 1.081 \times 10^{-4} \left\{ \frac{N(V_t - V_{td}) \left(\frac{V_{soln}}{V_a} \right)}{V_{mstd}} \right\} = \text{---} \times 10^{-4} \text{ lb/dscf} \quad \text{Equation 6-2}$$

Sulfuric Acid Mist (Including SO₃) Calculation Form
(metric units)

Sample Volume

$V_m = \text{---} \cdot \text{---} \text{---} m^3, T_m = \text{---} \cdot \text{---} K, P_{\text{bar}} = \text{---} \cdot \text{---} mm \text{ Hg}$

$$Y = \underline{\hspace{1cm}} \cdot \underline{\hspace{1cm}}, \Delta H = \underline{\hspace{1cm}} \cdot \underline{\hspace{1cm}} \text{ mm H}_2\text{O}$$

$$V_{\text{mstd}} = 17.64 V_m Y \left[\frac{P_{\text{bar}} + (\Delta H/13.6)}{T_m} \right] = \text{---} \text{---} \text{---} m^3 \quad \text{Equation 6-1}$$

Sulfuric Acid Mist (Including SO₃) Concentrations

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

$$V_{\text{soln}} = \text{---} \text{ ml}, V_{\text{a}} = \text{---} \text{ ml}, V_{\text{mstd}} = \text{---} \text{ m}^3$$

$$C_{H_2SO_4} = 0.04904 \left[\frac{N(V_1 - V_{1b}) \frac{V_{soln}}{V_a}}{V_{mstd}} \right] = \text{--- g/dscm} \quad \text{Equation 6-2}$$

*Sulfur Dioxide Calculation Form
(English units)*

Sample Volume

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

$$Y = ______, \Delta H = ______ \text{ in. H}_2\text{O}$$

$$V_{\text{mstd}} = 17.64 V_m Y \left[\frac{P_{\text{bar}} + (\Delta H/13.6)}{T_m} \right] = ______ \text{ ft}^3 \quad \text{Equation 6-1}$$

Sulfuric Acid Mist (Including SO₃) Concentrations

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

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

$$C_{\text{SO}_2} = 7.061 \times 10^{-5} \left[\frac{N (V_t - V_{\text{tb}}) \left(\frac{V_{\text{soln}}}{V_a} \right)}{V_{\text{mstd}}} \right] = ______ \times 10^{-4} \text{ lb/dscf} \quad \text{Equation 6-2}$$

*Sulfur Dioxide Calculation Form
(metric units)*

Sample Volume

$V_m = __\cdot______ m^3$, $T_m = _____\cdot______ K$, $P_{bar} = _____\cdot______ mm\ Hg$

$Y = __\cdot______$, $\Delta H = _____\cdot______ mm\ H_2O$

$$V_{mstd} = 0.3858 V_m Y \left[\frac{P_{bar} + (\Delta H/13.6)}{T_m} \right] = __\cdot______ m^3$$

Equation 6-1

SO₂ Concentration

$N = __\cdot______ g\text{-}eq/L$, $V_t = _____\cdot______ ml$, $V_{tb} = _____\cdot______ ml$

$V_{soln} = _____\cdot______ ml$, $V_a = _____\cdot______ ml$

$$C_{SO_2} = 3.203 \times 10^{-2} \left[\frac{N (V_t - V_{tb}) \left(\frac{V_{soln}}{V_a} \right)}{V_{mstd}} \right] = __\cdot______ g/dscm$$

Equation 6-2

Method 8 Checklist To Be Used By Auditors

<i>Yes</i>	<i>No</i>	<i>Comment</i>	
_____	_____	_____	<i>Presampling Preparation</i>
_____	_____	_____	1. <i>Knowledge of process conditions</i>
_____	_____	_____	2. <i>Calibration of pertinent equipment in particular, the dry gas meter, prior to each field test</i>
			<i>On-site Measurements</i>
_____	_____	_____	3. <i>Leak-testing of sampling train after sample run</i>
_____	_____	_____	4. <i>Preparation and addition of absorbing solutions to impingers</i>
_____	_____	_____	5. <i>Isokinetic sampling</i>
_____	_____	_____	6. <i>Purging of the sampling train and rinsing of the impingers and connecting tubes to recover the sample.</i>
_____	_____	_____	7. <i>Recording of pertinent process condition during sample collection</i>
_____	_____	_____	8. <i>Maintaining the probe at a given temperature</i>
			<i>Postsampling</i>
_____	_____	_____	9. <i>Control sample analysis - accuracy and precision</i>
_____	_____	_____	10. <i>Sample aliquotting techniques</i>
_____	_____	_____	11. <i>Titration technique, particularly endpoint precision</i>
_____	_____	_____	12. <i>Use of detection blanks in correcting field sample results</i>
_____	_____	_____	13. <i>Calculation procedure/check</i>
_____	_____	_____	14. <i>Calibration checks</i>
_____	_____	_____	15. <i>Standard barium perchlorate solution</i>
			<i>General Comments</i>