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Environmental Monitoring Series

GUIDELINES FOR DEVELOPMENT OF A QUALITY ASSURANCE PROGRAM: VOLUME VII - DETERMINATION OF SULFURIC ACID MIST AND SULFUR DIOXIDE EMISSIONS FROM STATIONARY SOURCES

Office of Research and Development
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ABSTRACT

Guidelines for the quality control of stack gas analysis for sulfuric acid mist and sulfur dioxide emissions by the Federal reference method are presented. These include:

1. Good operating practices;
2. Directions on how to assess performance and to qualify data;
3. Directions on how to identify trouble and to improve data quality;
4. Directions to permit design of auditing activities.

The document is not a research report. It is designed for use by operating personnel.

This work was submitted in partial fulfillment of contract Durham 68-02-1234 by Research Triangle Institute under the Sponsorship of the Environmental Protection Agency. Work was completed as of November, 1975.

TABLE OF CONTENTS

SECTION			PAGE
I		INTRODUCTION	1
II		OPERATIONS MANUAL	5
	2.0	GENERAL	5
	2.1	APPARATUS SELECTION AND REQUIREMENTS	11
	2.2	PRESAMPLING PREPARATION	15
	2.3	ON-SITE MEASUREMENTS	29
	2.4	POST-SAMPLING OPERATIONS (BASE LABORATORY)	39
III		MANUAL FOR FIELD TEAM SUPERVISOR	43
	3.0	GENERAL	43
	3.1	ASSESSMENT OF DATA QUALITY (INTRATEAM)	45
	3.2	SUGGESTED PERFORMANCE CRITERIA	47
	3.3	COLLECTION AND ANALYSIS OF INFORMATION TO IDENTIFY TROUBLE	49
IV		MANUAL FOR MANAGER OF GROUPS OF FIELD TEAMS	57
	4.0	GENERAL	57
	4.1	FUNCTIONAL ANALYSIS OF THE TEST METHOD	61
	4.2	ACTION OPTIONS	73
	4.3	PROCEDURES FOR PERFORMING A QUALITY AUDIT	81
	4.4	DATA QUALITY ASSESSMENT	85
V		REFERENCES	97
APPENDIX A		METHOD 8	99
APPENDIX B		ILLUSTRATED AUDIT PROCEDURES AND CALCULATIONS	111
APPENDIX C		GLOSSARY OF SYMBOLS	115
APPENDIX D		GLOSSARY OF TERMS	117

LIST OF ILLUSTRATIONS

FIGURE NO.		PAGE
1	Sequence of operations to be performed.	6
2	Wet test meter calibration data.	21
3	Sample control chart for standardized barium perchlorate solution.	55
4	Sample control chart for range of duplicate measurements.	55
5	Summary of data quality assurance program.	60
6	Added cost versus data quality (CV) for selected action options, for SO_3/H_2SO_4 data.	77
7	Added cost versus data quality (CV_b) for selection action options for SO_3/H_2SO_4 data.	78
8	Example illustrating $p < 0.10$ and satisfactory data quality.	89
9	Example illustrating $p > 0.10$ and unsatisfactory data quality.	89
10	Flow chart of the audit level selection process.	92
11	Average cost versus audit level (n).	95
8-1	Sulfur acid mist sampling train.	100
8-2	Field data.	107

LIST OF TABLES

TABLE NO.		PAGE
1	Suggested performance criteria	47
2	Assumed means and coefficients of variations of variables in influencing emissions rate determinations for SO_2	63
3	Variance analysis for $V_{m_{std}}$	67
4	Variance analysis for C_{SO_2}	67
5	Variance analysis for Q_s	68
6	Variance analysis for reproducibility of ER	69
7	Assumed within - laboratory, between - laboratory, and laboratory bias components of variability for given action options	75
8	Computation of mean difference, $\bar{d}$, and standard deviation of differences, s_d	90
9	Sample plan constants, k for P {not detecting a lot with proportion p outside limits L and U} $\leq$ 0.1	91

SECTION I INTRODUCTION

This document presents guidelines for developing a quality assurance program for Method 8, Determination of Sulfuric Acid Mist and Sulfur Dioxide Emissions from Stationary Sources. This method was initially published by the Environmental Protection Agency in the Federal Register,* and is reproduced as appendix A of this report for convenience of reference.

This document is divided into four sections:

Section I, Introduction. The introduction lists the overall objectives of a quality assurance program and delineates the program components necessary to accomplish the given objectives.

Section II, Operations Manual. This manual sets forth recommended operating procedures to insure the collection of data of high quality, and instructions for performing quality control checks designed to give an indication or warning that invalid data or data of poor quality are being collected, allowing for corrective action to be taken before future measurements are made.

Section III, Manual for Field Team Supervisor. This manual contains directions for assessing data quality on an intralaboratory basis and for collecting the information necessary to detect and/or identify trouble.

Section IV, Manual for Managers of Groups of Field Teams. This manual presents information relative to the test method (a functional analysis) to identify the important operations variables and factors, and statistical properties of and procedures for carrying out auditing procedures for an independent assessment of data quality.

The objectives of this quality assurance program for Method 8 are to:

1. Minimize systematic errors (biases) and maintain precision within acceptable limits in the measurement process,
2. Provide routine indications for operating purposes of satisfactory performance of personnel and/or equipment,
3. Provide for prompt detection and correction of conditions that contributes to the collection of poor quality data, and
4. Collect and supply information necessary to describe the quality of the data.

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*Reference to be supplied in final version of document.

To accomplish the above objectives, a quality assurance program must contain the following components:

1. Recommended operating procedures,
2. Routine training of personnel and evaluation of performance of personnel and equipment,
3. Routine monitoring of the variables and parameters that may have a significant effect on data quality,
4. Development of statements and evidence to qualify data and detect defects, and
5. Action strategies to increase the level of precision/accuracy in the reported data.

Component (2) above will be treated in the final report of this contract. All other components are treated in this document.

Implementation of a properly designed quality assurance program should enable measurement teams to achieve and maintain an acceptable level of precision and accuracy in their stack gas composition measurements. It will also allow a team to report an estimate of the precision of its measurements for each source emissions test.

Variability in emission data derived from multiple tests conducted at different times includes components of variation from:

1. Process conditions,
2. Equipment and personnel variation in field procedures, and
3. Equipment and personnel variation in the laboratory.

In many instances time variations in source output may be the most significant factor in the total variability. The deviation resulting from this component of variation is minimized by knowing the time characteristics of the source output and sampling over the complete output cycle.

Quality assurance guidelines for Method 8 as presented here are designed to insure the collection of data of acceptable quality by prevention, detection, and quantification of equipment and personnel variations in both the field and the laboratory through:

1. Recommended operating procedures as a preventive measure,
2. Quality control checks for rapid detection of undesirable performance, and

3. A quality audit to independently verify the quality of the data.

The scope of this document has been purposely limited to that of a field and laboratory document. Additional background information is contained in the final report under this contract.

SECTION II OPERATIONS MANUAL

2.0 GENERAL

This manual sets forth recommended procedures for the measurement of sulfuric acid mist and sulfur dioxide emissions from stationary sources according to Method 8 (ref. 1). (Method 8 is reproduced from the Federal Register and included as appendix A of this document.) Quality control procedures and checks designed to give an indication or warning that invalid data or data of poor quality are being collected are written as part of the operating procedures and are to be performed by the operator on a routine basis. In addition, the performance of special quality control procedures and/or checks as presented by the supervisor may be required of the operator on certain occasions. The precision and/or validity of data obtained from this method depends upon equipment performance and the proficiency with which the operator performs his various tasks. From equipment calibration through on-site measurements, calculations, and data reporting, this method is susceptible to a variety of errors. Detailed instructions are given for minimizing or controlling equipment error and procedures designed to minimize personnel errors are recommended. Before using this document, the operator should study Method 8 as written in appendix A in detail. In addition, one is advised to read the Operations Manuals of the quality assurance documents for Methods 2, 3, 4, and 6.

The sequence of operations to be performed is given in figure 1. Two columns are used. The columns are numbered 1 through 22. Quality checkpoints in the measurement process for which appropriate quality control limits are assigned are represented by blocks enclosed by heavy lines. Other checkpoints involve go/no-go checks, and subjective judgments by the operator with proper guidelines for decisionmaking are spelled out in the procedures.

The precision/accuracy of data obtained from this method depends upon equipment performance and the proficiency and conscientiousness with which the field team members carry out their various tasks. Deviations from the recommended operational procedure may result in the collection of invalid or poor quality data.

PRESAMPLING PREPARATION

1. SELECT THE EQUIPMENT APPROPRIATE FOR THE PROCESS (SOURCE) TO BE TESTED. CHECK THE EQUIPMENT FOR PROPER OPERATION.

2. CALIBRATE TYPE-S PITOT TUBE, NOZZLE DIAMETER, PROBE TEMPERATURE, DRY GAS METER(S), AND ORIFICE

3. PACK EQUIPMENT IN A MANNER TO PRECLUDE BREAKAGE OR DAMAGE DURING HANDLING AND SHIPMENT.

ON-SITE SO_2 MEASUREMENT

4. TRANSPORT EQUIPMENT FROM FLOOR LEVEL TO THE SAMPLING SITE BY THE BEST MEANS AVAILABLE.

5. ASSEMBLE THE EQUIPMENT ON-SITE AND PERFORM AN OPERATIONAL CHECK (EVALUATION OF THE SYSTEM).

6. DETERMINE THE TRAVERSE POINTS (SAMPLE POINTS) ACCORDING TO METHOD 1.

7. DETERMINE THE INSIDE AREA OF STACK BY (1) MEASURING THE DIAMETER OR (2) MEASURING THE CIRCUMFERENCE AND CORRECTING FOR WALL THICKNESS.*

8. PERFORM THE VELOCITY TRAVERSE OF THE STACK GAS USING THE QUALITY ASSURANCE DOCUMENT FOR METHOD 2.

9. DETERMINE THE MOISTURE CONTENT OF THE STACK GAS USING THE QUALITY ASSURANCE DOCUMENT FOR METHOD 4 (IF APPLICABLE TO SOURCE).

*If the stack is rectangular, simple multiply two adjacent sides together.

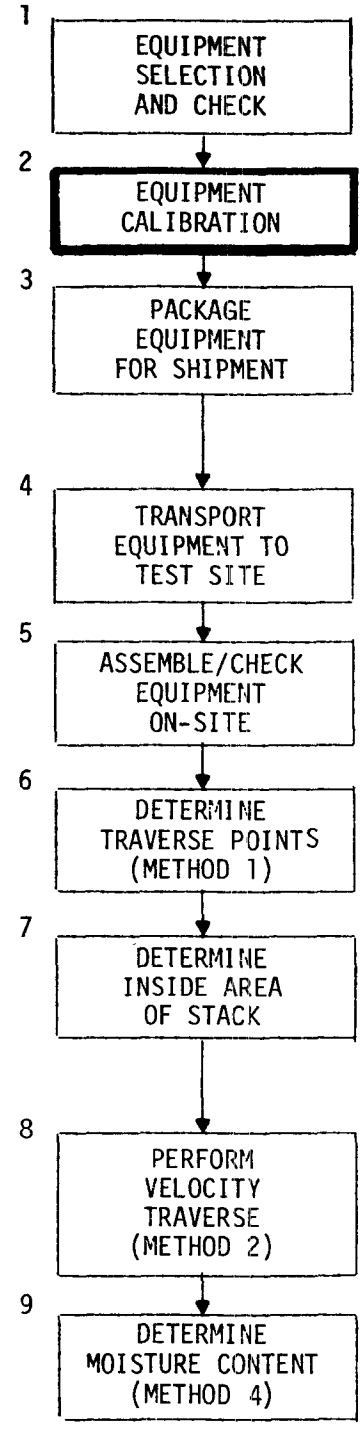

Figure 1. Sequence of operations to be performed.

10. DETERMINE THE MOLECULAR WEIGHT OF THE STACK GAS (WET BASIS) USING THE QUALITY ASSURANCE DOCUMENT FOR METHOD 3 AND THE RESULTS OF STEP 9 ABOVE

11. DETERMINE THE VOLUMETRIC FLOW RATE OF THE SOURCE USING THE QUALITY ASSURANCE DOCUMENT FOR METHOD 2.

12. SET NOMOGRAPH UTILIZING THE PRELIMINARY STACK GAS PARAMETERS

13. PREPARE ABSORBING REAGENTS AND ADD 100 ml 80-PERCENT ISOPROPANOL (FIRST IMPINGER) AND 100 ml OF 3-PERCENT H_2O_2 (SECOND AND THIRD IMPINGERS).

14. SET UP SAMPLING TRAIN AND LEAK CHECK SYSTEM

15. PERFORM SAMPLE COLLECTION (ISOKINETIC) ACCORDING TO THE PROCEDURE GIVEN IN SUBSECTION 2.3.3.

16. PERFORM LEAK CHECK AT END OF TEST.

17. QUANTITATIVELY RECOVER IMPINGER SOLUTIONS.

18. VISUALLY INSPECT EQUIPMENT FOR DAMAGE AFTER ALL MEASUREMENTS HAVE BEEN MADE AND RECORDED.

19. PACK EQUIPMENT AND SAMPLES FOR SHIPMENT BACK TO THE BASE LABORATORY.

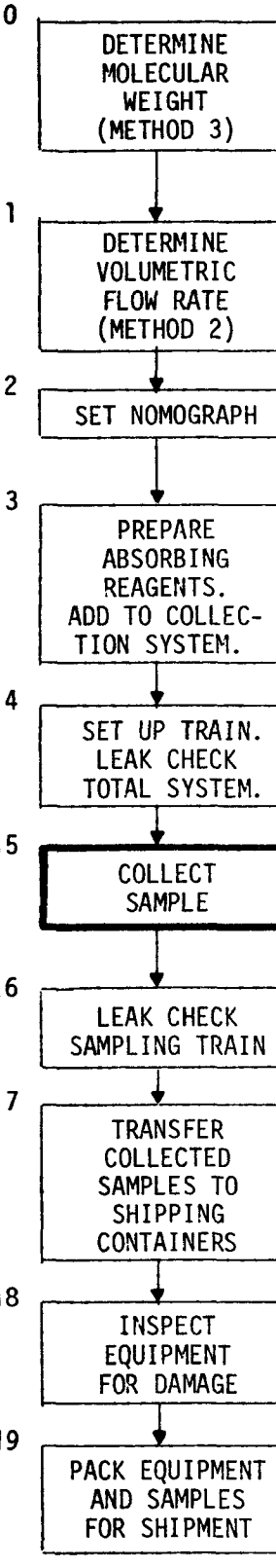

Figure 1. Sequence of operations to be performed (continued).

POST-SAMPLING OPERATIONS

20. PERFORM POST CALIBRATION AND ANALYSIS OF SAMPLES FOR SULFURIC ACID AND SULFUR DIOXIDE

21. PERFORM CALCULATIONS UTILIZING ALL FIELD AND CALIBRATION DATA.

22. FORWARD DATA WITH PERTINENT REMARKS CONCERNING QUALITY CHECKS FOR FURTHER INTERNAL REVIEW OR TO USER.

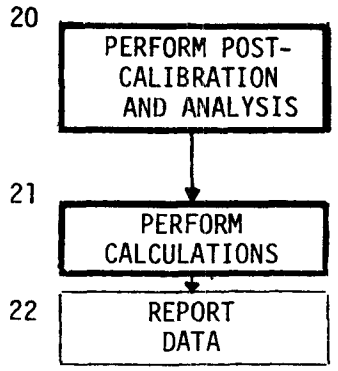

Figure 1. Sequence of operations to be performed (continued).

For discussion purposes, the measurement process is divided into four phases. They are:

1. Apparatus selection and requirements,
2. Presampling preparation,
3. On-site measurements, and
4. Post-sampling operations.

It is assumed that all apparatus is selected to satisfy the reference method specifications and that the manufacturer's recommendations will be followed when using a particular item of equipment (e.g., barometer, thermocouple, or differential pressure gauge).

The presampling preparation phase consists of a preliminary site visit (optional), equipment inspection and calibration, and the packing of equipment for transporting to the test site area. Unpacking and assembly of equipment, preliminary velocity traverse, determination of gas composition (molecular weight), moisture determination, particulate sampling, data recording and inspection, and packing the equipment for shipment back to the home laboratory are included in the on-site measurement phase. Post-sampling operations include calibration checks, analysis, calculations, and data reporting. Each phase is discussed separately.

2.1 APPARATUS SELECTION AND REQUIREMENTS

2.1.1 Sampling.

The sampling system consists of a heated probe, pitot tube, collection system, leak-free pump, dry test meter, and temperature monitoring system.

2.1.1.1 Probe. A glass probe (borosilicate glass) with electrical heating to prevent condensation during sampling is used. The glass liner should be protected with an outer sheath of stainless steel. The probe should have the heating capability to maintain the stack gas temperature at $\geq$175° C (ref. 2). The high-temperature (>425° C) probes may be fabricated from quartz. Stack gas should be cooled to about 300° to 375° C to minimize the changes in sample concentration in contact with the sample probe.

2.1.1.2 Nozzle. A stainless steel nozzle with a sharp, tapered leading edge is specified by the reference method. A set of three nozzles, approximately 0.6, 1, and 1.3 cm (1/4, 3/8, and 1/2 inch) in diameter will usually suffice for most stack sampling applications. It is recommended that for certain situations, such as high stack gas velocities or extreme moisture or stack temperature, that one also have nozzles 0.5 and 1.6 cm (3/16 and 5/8 inch) in diameter (ref. 3). These sizes are not stock items but are available by special order.

2.1.1.3 Pitot Tube and Differential Pressure Gauge and Stack Gas Temperature Monitoring System. A Type-S or equivalent pitot tube attached to the probe is required to monitor stack gas velocity. A differential pressure gauge, such as an inclined manometer, and sufficient connecting lines are required. A temperature measuring device attached or capable of being attached to the pitot tube is required for monitoring stack temperature.

2.1.1.4 Filter Holder. A pyrex glass filter holder is specified by the reference method. The filter support media should be a glass frit. The glass frit should always be cleaned before sampling according to the manufacturer's recommendations. A standard cleaning procedure is not applicable to all filter supports due to the variation in construction materials. A filter holder should be durable, easy to load, and leak free in normal applications. The design of the filter holder must be such that the filter material is not torn as the filter is tightened and the only flow through the holder is through the filter.

2.1.1.5 Filter Media. A glass-fiber media filter designed to remove 99.7 percent of the particulates larger than 0.3 μm (dioctylphthalate test) should be used. The filter must be chemically inert.

2.1.1.6 Barometer. A calibrated barometer (shock-mounted spring system) for measuring the barometric pressure should be used. An alternate is to obtain the uncorrected barometric pressure from a nearby weather station.

2.1.1.7 Impingers and Container. Four impingers are connected in series with inert joints. The first, third, and fourth impingers are of the Greenburg-Smith design, modified by replacing the tip with a 1/2-inch ID glass tube extending to 1/2 inch from the bottom of the flask. The second impinger is of the Greenburg-Smith design with the standard tip. Upon purchase of a new Greenburg-Smith impinger, fill the inner impinger tube with water. If the water does not drain through the orifice in at least 6 to 8 seconds, the impinger tip should be replaced or enlarged. This is required to prevent an excessive pressure drop in the sampling system. The fourth impinger is required (charged with silica gel) to remove moisture and to protect the vacuum pump and dry test meter. The reference method requires that the condensate trap be used to keep the effluent gas temperature to 20° C or less. Ice containers are available in commercial trains or can be fabricated from closed-pore styrofoam material. The efficiency of the ice bath can be increased by the addition of salt.

2.1.1.8 Metering System. The metering system includes a vacuum gauge, leak-free pump, thermometers capable of measuring temperatures to within 3° C, dry gas meter with 2 percent accuracy, and related equipment to facilitate the taking of isokinetic source samples. Individual items of equipment are:

1. The vacuum gauge for measuring sampling stream pressure serves a twofold purpose: (1) a leak check of the sampling train at 38 cm of mercury and (2) an indication (by vacuum increase) of the buildup of particulate matter on the filter media. The leak check is performed at 38 cm of mercury because water starts to boil at higher vacuums and will tend to saturate the silica gel (desiccant).
2. A leak-free vacuum pump is required for the sampling train described in the reference method. At this time there are

two commonly used vacuum pumps: (1) a modified sliding fiber vane pump and (2) a diaphragm pump. The vacuum pump must not bias the recorded sample volume (refs. 4,5).

3. A calibrated dry test meter with a temperature measuring system to determine the average temperature of the gas flowing through the meter and the total sample volume, respectively, is required.
4. A calibrated orifice meter is used to monitor the sample flow rate.
5. A dual inclined manometer or its equivalent is used to measure the velocity head, ΔP, in the source duct and the pressure drop, ΔH, across the calibrated orifice meter. Maintenance instructions for an inclined manometer are contained in section 2.1.1.1B of the Quality Assurance Document for Method 2. The differential pressure system must have an accuracy of $\pm$ 1.0 percent for any given reading.
6. A reproducible heating system is required to maintain the probe at a temperature which prevents condensation prior to the collection system (impinger).
7. A temperature measuring system is required to monitor the stack gas temperature and the effluent gas temperature as they exit from the last impinger.

2.1.2 Sample Recovery.

2.1.2.1 Glass Wash Bottles. Two or more glass wash bottles are needed for quantitative recovery of collected samples.

2.1.2.2 Glass Sample Storage Containers. Two 1-ℓ glass sample bottles are required for each collected sample plus two glass containers to retain blanks for each absorbing solution utilized in testing.

2.1.2.3 Graduated Cylinders. Two graduated cylinders (glass), 250 mℓ and 1,000 mℓ, are required for sample recovery.

2.1.3 Analysis.

2.1.3.1 Pipettes. Several pipettes (volumetric, Class A), including 25 mℓ and 100 mℓ, are required.

2.1.3.2 Burette. A 50-mℓ standard burette is required for filtrations.

2.1.3.3 Erlenmeyer Flasks. Several 250-mℓ Erlenmeyer flasks are required for filtration vessels.

2.1.3.4 Graduated Cylinder. One 100-mℓ graduated cylinder is needed for additions of isopropanol.

2.1.3.5 Balance. One trip or top-loading balance with 300-g capacity and an accuracy of ± 0.05 g is required.

2.1.3.6 Dropping Bottle. One bottle (eye dropper) to add indicator solution is required. This bottle (if needed for storage) should be of polyethylene, since the indicator tends to deteriorate if stored in glass (ref. 3).

2.2 PRESAMPLING PREPARATION

2.2.1 Preliminary Site Visit (Optional).

The primary objective of a preliminary site visit is to gather information to design and implement an efficient source test. Prior preparation will result in the prevention of unwarranted loss of time, unnecessary expenses, and injury to test and/or plant personnel. A test plan developed from a thorough set of parameters will result in more precise and accurate results. Test experience and a complete repertoire of equipment may allow dropping the preliminary site visit.

2.2.1.1 Process (Background Data on Process and Controls). It is recommended that the testers, before a preliminary site visit is made or before performing tests, become familiar with the operation of the plant (source). Data from similar operations that have been tested should be reviewed if they are available. Background data on stack gas species should be noted for further consideration of the final analytical results.

2.2.1.2 Sampling Site Preparedness. Each facility tested should provide an individual who understands the plant process and who has the authority to make decisions concerning plant operation to work with the team. This would include decisions concerning whether the plant would be operated at normal load conditions or at a rated capacity. If the source is cyclic in nature, information must be made available as to the timing of the sequence and the duration of the cycle. This individual or individuals will supervise installation of ports, sampling platform, and electrical power. If the above installations are already in existence, they must be examined for their suitability for obtaining a valid test and for meeting minimum safety standards. If ports have to be installed, specify 8- or 10-cm ports with plugs. Port locations should be based upon Method 1 of the Federal Register (ref. 1). Port locations must be based upon existing technical knowledge and sound judgment. An electrical service should be available at the sampling area with 115-volt and 20-amp service.

2.2.1.3 Stack Gas Conditions. The following should be determined on the initial site survey, either by measurement or estimation:

$T_{s_{avg}}$ = average stack gas temperature

P_s = the static pressure (positive or negative),

ΔP_{avg} = the average velocity heads,

% H_2O = moisture content,

M_s = gas constituent concentration.

The above parameters can be roughly determined using an inclined manometer (0 to 12 cm), a Type-S pitot tube manual thermometer, or thermocouple attached to the pitot tube with potentiometric readout device. The moisture content (approximate) can be determined with a wet bulb/dry bulb (acid gases $\geq$10 ppm SO_3 will result in high results) technique or by condensation (Method 4) and the gaseous constituents by hand-held indicator kits. Nomographs are useful in checking and estimating preliminary data required (ref. 6).

2.2.1.4 Method and Equipment for Transporting Apparatus to Test Site. The preliminary site visit (or correspondence) should include a logical plan developed by the plant personnel and the tester on how the equipment can best be transported to the sampling site. A presampling area must be designated in which absorbing solution can be prepared and added to the collection system. In addition to the above, it is recommended, when permitted, that pictures be taken of the hoisting area and sampling area (ports, sampling platform) so that any further discussion will be clarified.

2.2.2 Apparatus Check and Calibration.

2.2.2.1 Sampling Train. The design specifications of the H_2SO_4/SO_2 train used by EPA are given in appendix A of this document (figure 8-1). Commercial models of this system are available. Each individual or fabricated train must be in compliance with the specifications in the reference method. Each individual train must be examined to see if it is in compliance with the specifications in APTD-0581 or its equivalent (ref. 7). In addition, the Office of Air Programs Publication No. APTD-0576, "Maintenance, Calibration, and Operations of Isokinetic Source-Sampling Equipment" is a valuable reference (ref. 8).

2.2.2.2 Probe. Check the probe in the following manner:

1. Disassemble probe and check for breakage of inner liner or damage to other parts of probe.
2. Clean all metal parts with acetone.
3. Reassemble probe, clean inner liner with brush with the following solvents: tap water, D.I. water, and acetone. In extreme cases, the glass liner can be cleaned with stronger cleaning reagents.
4. Check to see if probe will heat to required temperature ($\geq$175° C). The probe temperature can be profiled with a remote reading thermometer or by a thermocouple with readout device.
5. The probe should be sealed on the nozzle side and checked for leaks at a vacuum of 38 cm of mercury.
6. Cover open ends of probe with serum caps or equivalent.

At temperatures greater than 125° C or if asbestos string has been used as a gasket between the glass probe and the union holding the nozzle to the probe and probe sheath, there exists the probability of leakage. Most stacks have a negative pressure; therefore, a leak would introduce diluent air into the system and result in a low bias. This problem can be eliminated by:

1. sealing the sheath from the outside air with a rubber stopper or its equivalent (ref. 7), and
2. drilling a 0.3-cm (1/8-inch) hole in the sheath on the opposite side of the pitot tube just behind the nut.

This modification also prevents "out" gases from deterioration of the probe from contaminating the stack sample (ref. 9).

2.2.2.3 Nozzle. Upon the purchase of each new nozzle, measure the inside diameter to the nearest 0.0025 cm using a micrometer. Make 10 individual measurements using different diameters each time, and calculate an average diameter. The range (i.e., the difference in smallest and largest values) of the 10 measurements should not exceed 0.0125 cm. Number the nozzle, and record the number and diameter of the nozzle to the nearest 0.0025 cm in the laboratory calibration log book. The diameter of the nozzle should be visually checked before each field test. Nozzles should have a sharp knife edge and be made of thin-walled tubing.

2.2.2.4 Type-S Pitot Tube Against a Standard Pitot Tube. The Type-S pitot tube should be calibrated against a standard pitot tube (or an NBS-calibrated Type-S pitot tube) as recommended in the Quality Assurance Document for Method 2. The Type-S pitot tube coefficient varies from one tube to another, as a function of air velocity for the same pitot tube and according to its proximity to the sampling probe and/or temperature sensor. For these reasons, it is important to calibrate the Type-S tube over the velocity range that is expected in the field operation and to orient the tube, probe, and temperature sensor as shown in figure 8-1 of appendix A. For a detailed description and discussion of the calibration procedure, see the Quality Assurance Document for Method 2 (Determination of Stack Gas Velocity and Volumetric Flow Rate).

2.2.2.5 Stack Gas Temperature Measuring Device. A temperature measuring device attachable to a pitot tube* and capable of measuring the stack gas temperature to within 1.5 percent of the minimum absolute stack gas temperature is required. A high-quality mercury bulb thermometer calibrated at ice water and boiling water (corrected for local pressure) temperatures and readable to the nearest 0.1° C is an acceptable laboratory standard for calibration of temperature measuring devices. The calibration procedure is contained in section 2.1.2.2 of the Quality Assurance Document for Method 2.

2.2.2.6 Dry Gas Meter and Orifice Meter. An initial check should be made of the sampling train to check for proper operation of the pump, dry test meter, vacuum gauge, and dry test meter thermometer(s). After the meter system components have been checked, the vacuum system should be leak tested. This is done by plugging the inlet side of the metering system, pulling a vacuum of 60 cm of mercury, and observing the dry test meter. If the leakage exceeds 1.5×10^{-4} m^3/min, the leak(s) must be found and minimized until the above specification is satisfied.

The dry gas meter should be calibrated before and after each field trip. The after-calibration for one test serves as the before-calibration for the next test. Calibration is performed by making simultaneous total volume

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*See figure 8-1, appendix A, for spacial arrangement of temperature probe relative to pitot tube orifice.

measurements with a calibrated wet test meter and the dry gas meter in the meter box. The wet test meter should be calibrated periodically against a primary standard. The wet test meter must be of the proper capacity and accuracy. For commercial sampling trains the wet test meter capacity must be at least 0.03 m^3/revolution with a ± 1 percent accuracy. The wet test meter must be of the proper capacity; otherwise, at the higher flow rates the linkage in the wet test meter will slip, producing an erratic correlation with the volume recorded by the dry test meter. A dry test meter is unacceptable as a calibration standard due to the inability to check for valve float in the dry test meter. The recommended calibration procedures are as follows:

1. Check the sampling system (dry test meter) for valve float in the following manner (ref. 10).
   a. Operate the sampling system at orifice readings between 0.1 and 12 cm of water. Initially operate the system at 0.02 m^3/min for 10 minutes before taking data.
   b. Take data through the above range ≈0.003 and 0.03 m^3/min, once with the bypass closed and once with it completely open. Time each setting for 1 minute. Record the ΔH setting (orifice reading) and the initial and final volume on the dry test meter.
   c. Calculate ΔH@ from the two sets of data:

$$\Delta H@ = \frac{K^{*} \Delta H}{V^2} .$$

   Plot two curves (one with the bypass valve opened and the other with it closed) of ΔH@ vs. the volume (V) recorded by the dry test meter. If the values are floating, the two curves will not coincide. Ideally, the curves should coincide and be horizontal over the whole range; in practice, the curve will probably have a slight slope. This initial check for valve float is performed only once upon building or purchasing a sampling train. This must be repeated

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* K = 0.56 in English units and 4.49×10^{-4} in metric units.

whenever a new pump is installed in the system. Valve float, if present, must be corrected.

2. Determination of $\Delta H@$ and γ is as follows:

   a. The wet test meter is placed upstream of the sampling system with its outlet connected to the inlet (sample umbilical connection) of the meter box (ref. 4). These connections must be leak free.

   b. Operate the pump for 15 minutes to warm up the pump and wet the surface of the wet test meter ($\approx 0.02\ m^3/min$).

   c. Collect and record as shown in figure 2 the calibration data by setting ΔH on the orifice manometer and letting a given volume of air pass through the wet test meter (the larger the volume, the greater the accuracy). Repeat the above procedures until the data are collected. Always have the bypass valve opened. A stop watch or laboratory timer is used to record the elapsed time (Θ) of the calibration. The symbols in figure 2 are:

      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_2 = 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

      Θ = Time of calibration run, minutes

      ΔH = Orifice manometer setting, with a resultant orifice meter pressure drop in cm of H_2O

Date _____ Calibration by ___ Wet test meter No. _____

Barometric pressure, P_b = _____ cm Hg Wet test meter capacity _____

Dry gas meter No. _____ Date of wet test meter calibration _____

Orifice manometer setting, ΔH, (cm H_2O)	Gas volume wet test meter V_w, m^3	Gas volume dry gas meter V_d, m^3	Temperature				Time Θ, min.	γ	ΔH@
			Wet test	Dry gas meter					
			Meter t_w, °C	Inlet t_{di}, °C	Outlet t_{do}, °C	Average t_d, °C			
0.25	0.075								
0.50	0.075								
0.75	0.075								
1.25	0.150								
2.5	0.150								
3.75	0.3								
5.0	0.3								
6.25	0.3								
7.5	0.3								
10.0	0.3								
15.0	0.3								
20.0	0.3								
							Average		

Calculations

ΔH	$\frac{\Delta H}{13.6}$	γ $\frac{V_w P_b (t_d + 273)}{V_d P_b + \frac{\Delta H}{13.6}(t_w + 273)}$	ΔH@ $\frac{0.0012\ \Delta H}{P_b (t_d + 273)} \left[\frac{(t_w + 273)\ \Theta}{V_w}\right]^2$
0.25	0.0184		
0.30	0.0368		
0.75	0.0552		
1.25	0.0920		
2.5	0.1840		
3.75	0.2760		
5.0	0.3680		
6.25	0.4600		
7.5	0.5520		
10.0	0.7360		
15.0	1.1040		

Figure 2. Wet test meter calibration data.

γ = Ratio of accuracy of wet test meter to dry test meter. Tolerance = ± 0.02

$\Delta H@$ = Orifice pressure differential that gives 0.02 m^3/min of air at 20°C and 76 cm of mercury, in cm of H_2O. Tolerance = ± 0.40.

d. Calculate γ and $\Delta H@$ for each orifice manometer setting and record on the calibration sheet as depicted in figure 2. Plot curves of γ and $\Delta H@$ versus ΔH (orifice manometer setting in cm of H_2O). The value of γ should be 1.0 ± 0.02. Adjust the linkage of the dry test meter (if needed) as directed by the manufacturer until this tolerance is obtained. The value of $\Delta H@$ should be 4.7 ± 0.7 with a variability of ± 0.40 over the range of 1.25 to 20 cm of water across the orifice. If this is not obtained, adjust the orifice opening or replace the orifice as directed in "Construction Details of Isokinetic Source Sampling Equipment" (ref. 5) and recalibrate.

2.2.2.7 Pump. The vacuum pump should be serviced as recommended by the manufacturer every 3 months or upon resultant erratic operations. Additional pump oil, if applicable, should be available for field work.

2.2.3 Reagents and Miscellaneous Equipment.

2.2.3.1 Sampling. The first impinger reagent, which consists of 80 percent isopropanol*, is prepared by mixing 800 mℓ alcohol with 200 mℓ of deionized, distilled water. The second and third impinger absorbing reagent (hydrogen peroxide, 3 percent) is prepared by diluting 100 mℓ of 30-percent hydrogen peroxide to 1 ℓ with deionized, distilled water. Preweighed containers with 250 g silica gel (indicating type 6-16 mesh, dried at 175° C) are required for sampling (one per test).

2.2.3.2 Sample Recovery. Deionized, distilled water will be required on site for quantitative transfer of impinger solutions to storage containers.

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*The isopropanol must be peroxide free, to avoid oxidation of SO_2 and high values for acid mist (ref. 27).

2.2.3.3 Source Sampling Tools and Equipment. The need for specific tools and equipment will vary from test to test. A listing of the most frequently used tools and equipment is given below.

1. Equipment Transportation
   a. Lightweight hand truck that can be used to transport cases and be converted to a four-wheel cart for supporting the meter box control unit;
   b. A 1.3-cm (1/2-inch) continuous filament nylon rope with large boat snap and snatch block for raising and lowering equipment on stacks and roofs;
   c. Tarpaulin or plastic to protect equipment in case of rain; sash cord (0.6 cm) for securing equipment and tarpaulin;
   d. A canvas bucket is useful for transporting small items. up and down the stack.
2. Safety Equipment
   a. Safety harness with nylon and steel lanyards, large throat snap hooks for use with lanyards for hooking over guardrails or safety line on stack;
   b. A fail-safe climbing hook for use with climbing harness when climbing ladders having a safety cable;
   c. Hard hats with chin straps and winter liners, gas masks, safety glass and/or safety goggles;
   d. Protective clothing including the following: appropriate suits for both heat and cold, gloves (both asbestos and cloth), and steel-toed shoes;
   e. Steel cable (0.5 cm) with thimbles, cable clips and turn buckles; these are required for installing a safety line or securing equipment to the stack structure.
3. Tools and Spare Parts
   a. Electrical and Power Equipment
      1. Circular saw
      2. Variable voltage transformer
      3. Variable speed electrical drill and bits

4. Ammeter-voltmeter-ohmeter (VOM)
5. Extension cords - light (#14 Avg) 2 x 25
6. Two or three wire electrical adapters
7. Three wire electrical
8. Thermocouple extension wire
9. Thermocouple plugs
10. Fuses
11. Electrical wire

b. Tools
1. Tool boxes (one large and one small)
2. Screwdrivers
   one set flat blade
   one set Philips
3. C-clamps (two), 15 cm and 7.5 cm

c. Wrenches
1. Open-end set, 1/4 inch to 1 inch
2. Adjustables (12 inch and 6 inch)
3. One chain wrench
4. One 12-inch pipe wrench
5. One Allen wrench set

d. Miscellaneous
1. Silicone sealer
2. Silicone vacuum grease
3. Pump oil
4. Manometers (gauge oil)
5. Antiseize compound
6. Pipe fittings
7. Dry cell batteries
8. Flashlight
9. Valves
10. Thermometers (Dial, 15 to 90 cm) and a remote reading thermometer (stack)
11. Vacuum gauge
12. SS tubing (0.6, 0.9, 1.2 cm), short lengths
13. Heavy-duty wire (telephone type)
14. Adjustable packing gland.

2.2.3.4 Data Recording. Pack one large briefcase with at least the following:

1. Nomograph for maintaining isokinetic conditions
2. Data sheets or data notebook
3. Carbon paper
4. Slide rule or electronic calculator
5. Psychrometric charts
6. Combustion nomographs (refs. 3,9)
7. Pencils, pens
8. Calibration data, $\Delta H@$, etc.

2.2.4 Package Equipment for Shipment.

This aspect of any source testing method in terms of logistics, time of sampling, and quality of data is very dependent 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 with the assumption that it will receive severe treatment during shipping and field operation. One major consideration in shipping cases is the construction materials. Durable containers are the most cost effective.

2.2.4.1 Type-S Pitot Tube and Probe. Pack the pitot tube and probe in a case protected by polyethylene or other suitable packing material. An ideal container is a wood case or equivalent (lined with foam) in which separate compartments are cut to hold the individual devices. It is also recommended that inserts for the individual nozzles be provided. The case should have handles that can withstand hoisting and be rigid enough to prevent bending or twisting of the devices during shipping and handling.

2.2.4.2 Differential Pressure Gauge (Dual Inclined Manometer). Always close all valves on the pressure gauge. Pack it in a suitable case for shipment. Spare parts, such as O-rings and gauge oil should also be packed.

2.2.4.3 Stack Temperature Measuring Device. The temperature measuring device (thermocouple, thermistor, remote reading thermometer, etc.) should be protected from breakage, i.e., placed in a tube or a suitable shipping container. If the device is an integral part of the pitot tube, it can be shipped in the Type-S pitot tube shipping case.

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

2.2.4.5 Pitot Tube Lines and Sample Line (Umbilical). All pitot lines and sample lines should be coiled to use the smallest amount of space. The ends should be connected together and sealed to prevent dust and dirt from impairing their operation. For shipment all lines should be stored in a case (footlocker) for protection and portability.

2.2.4.6 Glassware (Impingers, U-Joints, etc). A word of caution is needed in the use of glassware. It is expensive and fragile, but with sensible handling and packing, its failure rate and resultant costs are minimal. Generally, breakage of glassware occurs during packing and movement to the sampling facility. It is recommended that glass impingers be packed in a suitable case (approximate dimensions 50 cm x 50 cm x 50 cm) with a three-tiered layer of foam in which holes are cut to hold the glass bottom of the shipping case (ref. 10). A separate case lined with foam, with layers of 6-cm foam, can be used to carry the rest of the individual glass joints, filter holders, and preweighed filters. One major point to consider in shipping cases is the construction materials. Durable containers, although more expensive to build, are the most cost effective. A poorly constructed shipping case of cheap material will quickly deteriorate.

2.2.4.7 Metering System (Meter Box Assembly). A standard (commercial) unit including pump, vacuum gauge, dry test meter, inclined manometer, etc., is contained in one meter box. This meter box should be placed in a shipping container lined with a cushion material such as polyurethane. If the vacuum pump is not integral to the meter box, it should be packed in a shipping container unless its housing is sufficient for travel. Additional pump oil should be packed with the pump if oil is required for its operation.

2.2.4.8 Sample and Sample Recovery. All glass wash bottles or glass storage containers should be packed with cushion material at the top and bottom of the case with some form of dividers to separate the components. One shipping case can contain the preweighed silica gel, glass wash bottles, and graduated

cylinders. A water container and ice chest can be shipped as is. It is recommended in certain cases that these two items be purchased on site. A rule of thumb in source testing is "when possible, always carry a spare."

2.3 ON-SITE MEASUREMENTS

The on-site measurement activities include transporting the equipment to the test site, unpacking and assembling the equipment, making duct measurements and traverse points, 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 data recording.

2.3.1 Transport of Equipment to the Sampling Site.

The most efficient means of transporting or moving the equipment from floor level to the sampling site is decided during the preliminary site visit (or prior correspondence). Care should 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 reagents, charging the impingers, sample recovery, and documentation.

2.3.2 Preliminary Measurements and Setup.

2.3.2.1 Duct Measurement. Measure the duct and determine the number of traverse points by Method 1 or check traverse points as determined from preliminary site visit (ref. 1).

2.3.2.2 Sample Box Logistics. Once the sampling points are selected and the probe has been marked with either a china marker or heat-bonding fiberglass tape, the most efficient setup for the sample box must be determined. A poor choice will create a back-breaking and time-consuming sampling experience. Several systems exist for sampling ranging from duo rails to monorails in which the sampling box slides on a rolling track. Each individual sampling situation will dictate the system of the sample box support. It is recommended that one modify his sampling box to allow at least two alternate methods of support.

2.3.2.3 Stack Gas Moisture Content. Determine the moisture content of the stack gases by Method 4 or its equivalent (ref. 3). 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 the sampling for the moisture content used in final calculations.

2.3.2.4 Molecular Weight of Stack Gas. Determine the dry molecular weight of the gas stream by Method 3. It is recommended that the sample be of the integrated type for two reasons: (1) the possibility of a more representative sample and (2) the convenience of taking the sample at the stack and being able to transport the sampling bag to a more suitable area for Orsat analysis.

2.3.2.5 Stack Temperature and Velocity Heads. Set up and level dual inclined manometer and determine the minimum and maximum velocity head (ΔP) and the stack temperature (T_s). This is done most efficiently with a Type-S pitot tube with a temperature sensing device attached. The ΔP's are determined with an inclined manometer by drawing the pitot tube across the stack diameter in two directions (90° traverses). This must be done in order to pick the correct nozzle size and to set the nomograph. Incorrect selection of nozzle size and/or setting of the nomograph may result in one not being able to reach the isokinetic rate, thereby voiding the sample. Determine the static pressure as directed in the Quality Assurance Document for Method 2.

2.3.3 Sampling.

The on-site sampling includes final selection of proper nozzle size, setting the nomograph, loading the filter media into the filter holder, preparation and assembly of the sampling train, initial leak test, inserting the probe into the stack, sealing the port, sampling isokinetically while traversing, recording data, and a final leak check of the sampling system. Sampling is the foundation of source testing. The most critical problems in testing result from poor or incorrect sampling. The analytical technique (laboratory) can never correct for errors made in the field either by poor judgment or instrument failure. If the initial site survey, apparatus check and calibration, and preliminary measurement and setup on site have been implemented properly, the testing should go smoothly with a minimal amount of effort.

2.3.3.1 Preliminary Setting of the Nomograph. The setup of the nomograph using the parameters obtained in section 2.3.2 is given in detail in APTD-0576 (ref. 8). The section pertaining to nomographs is reproduced in appendix B for convenience of reference. A reference table is included in the appendix for checking the nomograph for correct design.

2.3.3.2 Select Nozzle Size. After the nozzle size and appropriate probe length have been selected, insert the nozzle in the probe sheath union and tighten the union. Do not use wrenches; finger-tight is sufficient in most cases. Uncontrolled pressure upon tightening the union will result in a broken or cracked inner liner. The above precautions only apply to a glass probe. Keep the ball joint and nozzle tip protected from dust and dirt with a serum cap or equivalent. The presence of excess particulates in analytical filtration can cause an interference.

Caution: If the coefficient, C_p, of the Type-S pitot tube being used is outside the range of 0.85 ± 0.02, compute the ratio $(C_p/0.85)^2$ and multiply this constant by the correction factor, C, obtained from the nomograph. Use this new "C" factor in setting the nomograph for isokinetic sampling (see appendix B for further discussion).

2.3.3.3 Preparation and/or Addition of Absorbing Reagent to Collection System. If preparation of absorbing reagent is necessary on site (all reagents should be prepared fresh daily), follow directions as given in section 2.2.3.1 of this document. Place 100 mℓ (measured with a graduated cylinder) of 80% isopropanol in the first impinger, 100 mℓ of 3% hydrogen peroxide in both the second and third impingers, and approximately 250 g of silica gel in the fourth impinger. The silica gel can be preweighed if a moisture determination is applicable. The first and third impingers are of the Greenburg-Smith design with standard tip. The second and fourth are of the Greenburg-Smith design with 1.25 cm (1/2-inch) I.D. glass tube extending to 1.25 cm (1/2 inch) from the bottom of the impingers.

2.3.3.4 Assembling Sampling Train. Assemble the glass impinger train as follows:

1. Load the filter, making certain that the filter is centered correctly in the holder with the sample sides toward the probe. The filter should be tightened until the two halves are secure. Overtightening the two halves can break the filter holder or tear the filter.

2. Seal the inlet of the filter holder and leak check at $\geq$38 cm of Hg vacuum. The filter should be leak free.
3. Place the impingers and filter into the sample box and assemble the sampling train.
4. A very light coat of silicone lubricant should be applied to assure a leak-free system.

   Note: Apply the lubricant in a manner to minimize or prevent contact with the sample.

2.3.3.5 Leak Check. Leak check the sampling train by plugging the inlet to the first impinger, turning on the vacuum pump, and opening the valve system until the vacuum in the system reaches 38 cm of mercury. A leakage rate not in excess of 0.005 m^3/min at 38 cm of mercury is acceptable. To release the pressure in the system, do not turn off the pump until the following sequence has been completed:

1. Slowly release the pressure in the system by carefully opening (twisting) the glass ball in the inlet of the filter holder.
2. Shut the coarse valve (main vacuum valve).
3. When the vacuum gauge reads zero vacuum, remove the glass ball and shut down the pump.

2.3.3.6 Installation of Probe. Mount the probe in the sampling box and connect the probe to the inlet of the first impinger and leak check in the following manner:

1. Seal the inlet of the probe nozzle with a serum cap.
2. Turn on vacuum pump.
3. Open the valve system and adjust the vacuum to 38 cm of mercury.
4. Check the leak rate on the dry gas meter. A leakage rate not in excess of 0.0005 m^3/min at 38 cm of mercury is acceptable.
5. After completion of the leak check, release the pressure as follows:
   a. Slowly release vacuum by carefully opening (squeezing) the serum cap until the system

pressure is back to ambient (monitor with built-in vacuum gauge);

b. Turn valve system off (coarse valve);

c. Turn off the vacuum pump.

Note: Operations 2.3.3.5 and 2.3.3.6 can be combined, thereby requiring only one initial leak check.

2.3.3.7 Taking of Sample. Turn the probe heater to its normal setting to obtain 175° C. The meter box operator should now recheck his setting of the nomograph while the sample box operator checks the ice around the impingers and touches the probe to see if it is heating properly. It is recommended that a thermocouple be mounted next to the glass liner so that the probe temperature can be monitored. One must realize that this probe temperature is just a point measurement of the probe skin temperature. In lieu of this, the operator can use his hand to check if the probe is heating properly.

As soon as the probe temperature is up to 175° C, the test can be performed. During this time period prior to taking of the sample, record the barometric pressure on the data log sheet.

1. Remove the plug or cap from the sampling port and remove the dust (particulates) in the port walls by using a wire brush or its equivalent. Remove the serum cap from the nozzle tip. Record the initial volume of the dry test meter on the data log sheet.
2. If the sample gas is hot, start at the traverse point farthest from the port and draw the probe out as the test continues. Asbestos gloves should be used in handling hot sampling probes and pitot tubes.
3. Attach a proper electrical ground to the probe and sampling system.
4. Insert the probe to the farthest traverse point with the nozzle pointing directly into the gas stream and immediately start the pump and adjust the coarse- and fine-adjust valves until isokinetic conditions are obtained. Note the time and record it on the log sheet.

5. Maintain isokinetic conditions during the entire sampling period. Sample an equal amount of time at each traverse point. The time at each traverse point should be long enough to set the sample rate and record the required data. While sampling, reset the nomograph if:

   a. The temperature in the stack changes more than $\pm$ 15° C for T_s < 550° C or $\pm$ 30° C for T_x > 550° C, or

   b. T_m (average temperature of meter) varies more than $\pm$ 5° C.

   Note: The commercial nomographs are set up assuming the composition of the stack gas is air (Molecular weight ~ 29 $\pm$ 20 percent). An adjustment must be applied when sampling streams other than air.

   Adjust the sampling rate for every point, and maintain the isokinetic rate by continuous observation. Record the meter volume at the end of sampling at each individual traverse point. Take readings at each sampling point at least every 5 minutes (or during sampling period at each traverse point). When significant changes in stack conditions are observed, compensating adjustments in flow rate should be made to maintain isokinetic conditions. Record the traverse point number, stack temperature (T_s), velocity pressure head (ΔP cm of H_2O), ΔH (orifice pressure differential, cm of H_2O), gas temperature at dry gas meter ($T_{m_{in}}$ and $T_{m_{out}}$ or T_{avg}, °C), sample box temperature, condenser temperature, and the probe temperature if the probe has a thermocouple and appropriate readout.

6. When sampling at one traverse point has been completed, move the sampler to the next point as quickly as possible. Close the control valve only when transferring the sampler from one sample port to the other. Exclude the time required to transfer the sampler from one port to another from the total sampling time.

   Note: Movement from port to port is time consuming, and it is recommended that longer probes be employed to allow only

one move during a test if it is a circular stack. Probes up to 10 feet can be managed without too much difficulty provided there is adequate space on the sampling platform.

a. Monitor the vacuum through the system. An indication of particulate buildup on the filter is an increase in vacuum. Excess particulates could cause interference in the wet chemical analysis. Loss in vacuum is an indication of a broken impinger, connector, filter, or possibly a loose connection.

b. Keep the impingers iced down (i.e., monitor the condenser temperature) to hold the temperature below 20° C. Add salt to the ice bath if necessary.

c. Check the line voltage with a voltmeter.

   Caution: Digital temperature systems may read erroneously with a drop in line voltage.

d. Make sure that the dual inclined manometer is level and that the pitot lines and pitot tube are unobstructed. A signal of trouble would be ΔP's not representative of the velocity heads obtained in a preliminary site visit velocity traverse.

e. All data should be recorded on a log sheet as depicted in figure 8-2 of appendix A. In addition, a column can be added for recording the temperature of the probe if so desired and the sample box reading can be changed to condenser exit temperature.

7. At the completion of the test, close the coarse control valve on the meter, remove the probe from the stack, and turn off the pump. Place a serum cap or equivalent over the nozzle tip and leak check the system at 5 cm of mercury vacuum above the operating vacuum during the test. The leak-test vacuum should be no greater than 38 cm of mercury. (Do not boil the water in the impingers.) Follow the same leak-test procedures as outlined in section 2.3.3.6. Seal the end of the nozzle and disconnect the probe. Drain the ice bath and purge the remaining part of the train by drawing clean ambient air through the system for 15 minutes. Disconnect the pitot lines

and umbilical. Protect pitot and umbilical connections with tape or an appropriate equivalent. Record on the data log sheet the leak rate in m^3/min and the vacuum at which the leak check was performed. Check all connectors such as umbilical connect, pitot lines, glass connections, etc., for evidence of malfunctions. Record all abnormalities on the data log sheet. This will not necessarily void the sample but may help to improve the quality of sampling performance.

2.3.4 Sample Recovery.

The reference method requires a quantative transfer of the impinger solutions and filter to suitable storage containers. These transfers should be done in a "laboratory-type" area to prevent contamination of the test samples.

2.3.4.1 Impinger Solution (80% Isopropanol). Recover impinger solution as follows:

1. Transfer the isopropanol solution from the first impinger to a 250 mℓ graduate cylinder.
2. Rinse the probe, first impinger, and all connecting glassware before the filter with 80% isopropanol. Add the rinse solutions to the 250 mℓ graduate.
3. Dilute to 250 mℓ with 80% isopropanol.
4. Add the filter to the solution, mix, and transfer to a suitable storage container.

   Note: Record initial solution volume and total rinse volume.

2.3.4.2 Impinger Solutions (3% Hydrogen Peroxide). Recover the impinger solutions as follows:

1. Transfer the solution from the second and third impingers to a 1,000-mℓ graduated cylinder.
2. Rinse all glassware between the filter and silica gel impinger with deionized, distilled water and add the rinse water to the cylinder.
3. Dilute to a volume of 1,000 mℓ with deionized, distilled water. Transfer the solution to a suitable storage container.

   Note: Record initial total impinger solution volume and total rinse volume.

2.3.5 Sample Logistics (Data) and Packing of Equipment.

The above procedures are followed until the required number of tests are completed. If the glassware (impingers and connectors) are used in the next test, they should be rinsed with distilled water (impingers and connectors) and then with 80% isopropanol (first impinger). New silica gel should be added to the sampling train. The following is recommended at the completion of testing:

1. Check all sample containers for proper labeling (time and date of test, location of testing, number of test, and any pertinent documentation).
2. All data recorded during field testing should be recorded in duplicate by carbon paper or by utilizing data sheets and a field laboratory notebook. One set of data should be mailed to the base laboratory and the other hand carried. This is a recommendation that can prevent a very costly and embarrasing mistake.
3. All sample containers and equipment should be examined for damage, noted in log book, and properly packed for shipment to the base laboratory. All shipping containers should be properly labeled to prevent loss of samples or equipment.

2.4 POST-SAMPLING OPERATIONS (BASE LABORATORY)

2.4.1 Apparatus Check.

2.4.1.1 Type-S Pitot Tube. The Type-S pitot tube is checked according to the Quality Assurance Document for Method 2, Determination of Stack Gas Velocity and Volumetric Flow Rate (ref. 11).

2.4.1.2 Dry Gas Meter and Orifice Meter (Sampling Train). A post check (a post check for one test can serve as the presampling check for the next test) should be made of the sampling train to check for proper operation of the pump, dry test meter, vacuum gauge, and dry test meter thermometers. Leak check the vacuum system. Determine γ and $\Delta H@$ at 0.25, 0.8, 2.5, 5.0, 8.0, and 15.0 cm of water as previously instructed in subsection 2.2.2.6 (2). This is a check on the system for future testing and gives confidence in the data from the previous field test. This is a recommended procedure to improve the data quality and to prevent field sampling under assumed conditions.

2.4.2 Analysis (Base Laboratory).

The requirements for a precise and accurate analysis are an experienced analyst and familiarity with the analytical method; calibration is of the utmost importance, and neglect in this area cannot be accepted. The analytical method is based on the insolubility of barium sulfate ($BaSO_4$) and the formation of a colored complex between barium ions and thorin indicator, [1-(0-arsonophenylazo) -2-naphthol-3, 6-disulfonic acid, disodium salt]. Aliquots from the impinger solution are analyzed by titration with barium perchlorate to the orange-pink endpoint.

2.4.2.1 Reagents (Standardization and Analysis).

1. Water--deionized, distilled.
2. Isopropanol.
3. Thorin indicator: 1-(0-arsonophenylazo)-2-naphthol-3, 6-disulfonic acid, disodium salt (or equivalent). Dissolve 0.20 g in 100 mℓ distilled water.
4. Barium perchlorate: dissolve 1.95 g [$Ba(ClO_4)_2 \cdot 3 H_2O$] in 200 mℓ distilled water and dilute to 1 ℓ with isopropanol. Standardize with sulfuric acid (H_2SO_4).

5. Sulfuric standard (0.01 N): Standardize against 0.01 N NaOH which has been previously standardized against potassium acid phthalate [C_6H_4 (COOH) Cook primary standard].

2.4.2.2 Standardization of Sodium Hydroxide (0.01 N NaOH). Dry the potassium acid phthalate for 1 to 2 hours at 110° C and cool. Accurately weigh about 1 g KHP into each of three 250-mℓ Erlenmeyer flasks and dissolve in 25 to 50 mℓ of distilled, deionized water (preferably freshly boiled and cooled). Add two drops of phenolphthalein indicator and titrate with 0.1 N sodium hydroxide (NaOH) to the first pink color that persists for 30 seconds. The base (NaOH, 0.1 N) can be purchased commercially or prepared from reagent-grade NaOH. The 0.0 1N NaOH is prepared by pipetting 50 mℓ of the standardized solution into a 500 mℓ volumetric flask and diluting to the mark with deionized, distilled water. The final concentration of the base will be the standardized value divided by 10. This solution should be made up fresh for each set of sample titrations.

2.4.2.3 Standardization of Sulfur Acid vs 0.01 N NaOH. The 0.01 N sulfuric acid is standardized by pipetting 25 mℓ of the H_2SO_4 solution into a 250-mℓ Erlenmyer which contains 25 mℓ of water. A blank should be prepared that contains 50 mℓ of distilled, deionized water. Add two drops of phenolphthalein indicator and titrate with the above standardized 0.01 N NaOH until the first permanent pink color that lasts for 30 seconds. All standards should be done in triplicate. At the completion of the titrations, calculate the normality as the mean of the three values obtained. This solution should be made up fresh for each set of sample titrations.

2.4.2.4 Standardization of Barium Perchlorate (0.01 N). Pipette 25 mℓ of sulfuric acid standard (0.01 N) into a 125-mℓ Erlenmeyer flask. Add 100 mℓ of reagent-grade isopropanol and two to four drops of thorin indicator and titrate to a pink endpoint using the 0.01 N barium perchlorate. Run a blank which contains 25 mℓ of deionized, distilled water and 100 mℓ of isopropanol. Standardizations should be done in duplicate. All Thorin titrations should be done against a white background. This will facilitate the detection of the pink endpoint (orange-pink color). (The analyst unfamiliar with this titration should, for practice, carry out titrations on aliquots at low, medium, and high concentrations. Pipette various aliquots of 0.01 N N_2SO_4, add four times this volume of 100% isopropanol and titrate with barium perchlorate to become

familiar with the endpoint.) The presence of particulate matter can make the detection of this endpoint quite difficult (ref. 12). The standardization should be repeated before each set of titrations or every month, whichever is longer.

2.4.2.5 Sample Analysis.

2.5.2.5.1 Isopropanol Solution. Analyze the isopropanol solution as follows:

1. Shake the container holding the isopropanol and filter for 1 minute.
2. Allow the solution to settle for 3 minutes.
3. Pipette a 100-mℓ aliquot of sample into a 250-mℓ Erlenmeyer flask.
4. Add two to four drops of Thorin indicator and titrate the sample with barium perchlorate (previously standardized) to a pink endpoint.
5. Repeat steps 3 and 4 on a second aliquot.

2.4.2.5.2 Hydrogen Peroxide Solution. Analyze the hydrogen peroxide solution as follows:

1. Shake the container holding the contents of the second and third impingers.
2. Pipette a 25-mℓ aliquot of sample into a 250-mℓ Erlenmeyer flask. Add 100 mℓ of isopropanol.
3. Add two to four drops of Thorin indicator and titrate with barium perchlorate to a pink endpoint.

   Note: When Thorin titrations are being carried out, a completely white background is mandatory to distinguish the endpoint.
4. Repeat steps 2 and 3 on a second aliquot.

2.4.2.5.3 Blanks. Titrate all blanks identically as performed on the respective samples. All samples must be corrected for its respective blank.

2.4.3 Calculations.

Calculation errors due to procedural or mathematical mistakes can be a large component of total system error. Therefore, it is recommended that every third set of calculations be repeated or spot checked, preferably by a team member other than the one that performed the original calculations. If a difference greater than a typical roundoff error is detected, the calculations

should be checked step by step until the source of error is found and corrected. A computer program is advantageous in reducing calculation errors. A standardized computer program could be developed to treat all raw field data. If a computer program is used, the original data entry should be checked, and if differences are observed, a new computer run made.

2.4.3.1 Sample Volume. Calculate the sample volume at standard conditions (76 cm of mercury, 20° C) by using equation 8-1 of appendix A. Average the dry gas meter temperatures $\left(T_{m_{in}}\ (°C) \text{ and } T_{m_{out}}\ (°C) \right)$ to obtain the average temperature, T_m (°C), of the gas flowing through the meter during the test. Determine the average orifice pressure drop by totaling the ΔH values at each traverse point and dividing by the total number of traverse points. Orifice pressure readings and the calculated average in cm of water should be rounded to two significant digits (e.g., 0.12 or 1.2).

2.4.3.2 Sulfuric Acid Concentration. Calculate the concentration of sulfuric acid at standard conditions on a dry basis in g/m^3 by using equation 8-2 of appendix A. The volume of V_{soln}/V_a is determined by the total dilution volume of the sample and the aliquot taken for titration.

2.4.3.3 Sulfur Dioxide Concentration. Calculate the concentration of sulfur dioxide at standard conditions on a dry basis in g/m^3 by using equation 8-3 of appendix A.

2.4.3.4 Emission Rates. The emission rates for H_2SO_4 and SO_2 are determined by the equation $ER = Q_s x C_{H_2SO_4(SO_2)}$, where Q_s = volumetric flow rate of the effluent in m^3/hr at standard conditions on a dry basis as determined by the quality control document for Method 2 (ref. 11), and $C_{H_2SO_4(SO_2)}$ = the concentration of sulfuric acid (sulfur dioxide), as determined in subsections 2.4.3.2 and 2.4.3.3, respectively.

SECTION III MANUAL FOR FIELD TEAM SUPERVISOR

3.0 GENERAL

The term "supervisor" as used in this document applies to the individual in charge of a field team. He is directly responsible for the validity and the quality of the field data collected by his team. He may be a member of an organization which performs source sampling under contract to government or industry, a government agency performing source sampling, or an industry performing its own source sampling activities.

It is the responsibility of the supervisor to identify sources of uncertainty or error in the measurement process for specified situations and, if possible, eliminate or minimize them by applying appropriate quality control procedures to assure that the data collected are of acceptable quality. Specific actions and operations required of the supervisor for a viable quality assurance program are summarized in the following listing.

1. Monitor/Control Data Quality
   a. Direct the field team in performing field tests according to the procedures given in the Operations Manual.
   b. Perform or qualify results of the quality control checks (i.e., assure that checks are valid).
   c. Perform necessary calculations and compare quality control checks to suggested performance criteria.
   d. Make corrections or alter operations when suggested performance criteria are exceeded.
   e. Forward qualified data for additional internal review or to user.
2. Routine Operation
   a. Obtain from team members immediate reports of suspicious data or malfunctions. Initiate corrective action or, if necessary, specify special checks to determine the trouble; then take corrective action. Document the corrective action taken.
   b. Examine the team's log books periodically for completeness and adherence to operating procedures.
   c. Approve data sheets, calibration checks, etc., for filing.

3. Evaluation of Operations

   a. Evaluate available alternative(s) for accomplishing a given objective in light of experience and needs.

   b. Evaluate operator training/instructional needs for specific operations.

Consistent with the realization of the objectives of a quality assurance program as given in section I, this section provides the supervisor with brief guidelines and directions for:

1. Collection of information necessary for assessing data quality on an intrateam basis;
2. The use of performance criteria to aid in the collection of data of acceptable precision and accuracy;
3. Isolation, evaluation, and monitoring of major components of system error.

The above three topics will be discussed in the order that they appear in this manual. In subsection 3.1 a method of assessing data quality on an intrateam basis is given. This method involves calculating a sample standard deviation using the six replicate runs required in a field test and calculating 90 percent confidence limits for the average of the six replicates.

Subsection 3.2 presents suggested criteria for judging equipment performance and frequency of calibration.

Directions for collection and analysis of information to identify trouble and subsequently control data quality within acceptable limits are given in the third subsection.

3.1 ASSESSMENT OF DATA QUALITY (INTRATEAM)

Sulfuric acid concentration, $\overline{C}_{H_2SO_4}$*, and sulfur dioxide concentration, $\overline{C}_{SO_2}$, for a particular field test is the average of six replicates for each concentration. Intrateam assessment of data quality as discussed herein provides for an estimate of the precision of the measurements. Precision in this case refers to repeatability, i.e., the within-laboratory variability, and is expressed as a coefficient of variation. This precision statement combines variability due to process changes and random measurement errors. Measurement bias (see subsection 4.1.2 for a discussion of bias) could occur from an error due to sampling train leaks, insufficiently heated sampling probe, or failure to sample proportionally. However, if the operating procedures given in the Operations Manual are followed, the bias should be small in most cases. An independent quality audit which would make possible a bias estimate is suggested and discussed in section IV, the Management Manual.

3.1.1 Calculating Precision of Field Data.

Each field test is comprised of at least three sample runs. Using the sample runs as replicates, a standard deviation can be calculated. This calculated standard deviation is a combined measure of the measurement and process variabilities. The standard deviation is calculated by

$$s\{C\} = \left[\frac{\sum_{i=1}^{6} C_{(i)} - \overline{C}^{\,2}}{5}\right]^{1/2}$$

where $s\{C\}$ = Standard deviation for the six concentrations

$C_{(i)}$ = Concentration for the ith concentration

$\overline{C}$ = Mean concentration

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*Throughout this document, C is used to mean a single concentration determination. The notation $\overline{C}$ is used to represent the result of a field test, and is the average of six replicates. Since concentrations of two chemical species are measured in Method 8, general statements about concentrations C and $\overline{C}$ can be assumed to apply to both sulfuric acid and sulfur dioxide.

and 5 = Number of concentration determinations minus 1, or the number of degrees of freedom.

3.1.2 Reporting Data Quality.

It is recommended that the average measured sulfuric acid and sulfur dioxide concentrations be reported with 90 percent confidence limits. Assuming the values of $\overline{C}$ are normally distributed (this is usually a valid assumption since sample means tend to be normally distributed even for nonnormal parent distributions) and using s{C} as calculated in 3.1.1 above to estimate the standard deviations, confidence limits can be calculated for the true $C_{H_2SO_4}$ and C_{SO_2} values using the Student t-distribution with r - 1 = 5 degrees of freedom. This assumes no bias in the average values. The average measured value with 90 percent confidence limits is reported as:

$$\overline{C} \pm 2.02\ s\{C\}$$

where $\overline{C}$ = The average of six replicates, g/m^3

s{C} = Estimated standard deviation of C based on 6 replicates, g/m^3

2.02 = 95th percentile of the Student t-distribution with 5 degrees of freedom which yields a 90 percent confidence interval.

For example, if for a given field test $\overline{C}$ = 2 g/m^3 and s{C} was calculated to be 0.08 g/m^3, the reported value with 90 percent confidence limits would be

$$2.0\ g/m^3 \pm (2.02)\ (0.08\ g/m^3)$$

or the true concentration, C_t, would be assumed to be in the interval

$$1.84\ g/m^3 \leq C_{(t)} \leq 2.16\ g/m^3\ .$$

The utility of the above statement follows from the fact that if this procedure for computing confidence limits is followed, then 90 percent of the time the true C value will be contained within the given limits (assuming that $\overline{C}$ is not biased).

3.2 SUGGESTED PERFORMANCE CRITERIA

Data assessment as discussed in the previous subsection is based on the premise that all variables are controlled within a given level, thereby guarding against large undetected biases in the measurement process. These levels of suggested performance criteria are the values given in the Operations Manual for determining when equipment and/or personnel variability is out of control. Criteria for judging performance are summarized in table 1.

Table 1. Suggested performance criteria

1.	Suggested criteria for field equipment performance:	
	(a) Dry gas meter:	$0.98 \leq \gamma \leq 1.02$
	(b) Barometer:	$\pm$ 5 mmHg
	(c) Thermometers:	$\pm$ 1° C
	(d) Stack temperature measuring system:	$\pm$ 3° C
	(e) Sampling train leakage:	< 1 percent of sampling flow rate at 250 mmHg
	(f) Probe heating system:	Uniform heating of probe, with a minimum temperature of 175° C at exit end and at a flow rate of 2 ℓ/min at room temperature
2.	Suggested criteria for analytical procedure:	
	(a) Duplicate samples:	$\leq$ 5 percent of mean
	(b) Standard 0.01 N barium perchlorate:	$\leq$ 0.0005 N of mean

3.3 COLLECTION AND ANALYSIS OF INFORMATION TO IDENTIFY TROUBLE

In a quality assurance program, one of the most effective means of preventing trouble is to respond immediately to indications of suspicious data or equipment malfunctions. There are certain visual and operational checks that can be performed while the measurements are being made to help insure the collection of data of good quality. These checks are written as part of the routine operating procedures in section II. In order to effectively apply preventative-type maintenance procedures to the measurement process, the supervisor must know the important variables in the process, know how to monitor the critical variables, and know how to interpret the data obtained from monitoring operations. These subjects are discussed in the following subsections.

3.3.1 Identification of Important Variables.

Determination of the sulfuric acid and sulfur dioxide concentrations requires a sequence of operations and measurements that yields as an end result two numbers that serve to represent the average sulfuric acid and sulfur dioxide emission rates for that field test. There is no way of knowing the accuracy, i.e., the agreement between the measured and true value, for a given field test. However, a knowledge of the important variables and their characteristics allows for the application of quality control procedures to control the effect of each variable at a given level during the field test, thus providing a certain degree of confidence in the validity of the final result.

A functional analysis of this method of measuring sulfuric acid and sulfur dioxide emission rates from a stationary source was made to try to identify important components of system error. Also, results of a collaborative study of Method 8 (ref. 13) showed the following: for sulfuric acid, the precision was proportional to the mean concentration, $\overline{C}_{H_2SO_4}$; for sulfur dioxide, the precision was independent of the mean concentration, $\overline{C}_{SO_2}$. The numerical results were used as an estimate of overall system error, while the individual error components were estimated using engineering judgment in a manner such that their combined variability was consistent with overall system error.

Variability in emissions data derived from multiple restrictions includes components of variation from:

1. Process conditions,
2. Equipment and personnel in field procedures, and
3. Equipment and personnel in the laboratory.

In many instances, time variations in source output may be the most significant factor in the total variability. In order to judge the relative magnitudes of measurement variability and process output variability, process parameters should be monitored throughout the test. Process information is also required if the sulfuric acid and sulfur dioxide emission rates are to be given as a function of fuel input. The exact process data to be obtained are dependent upon the process being tested. In general, all factors which have a bearing on the emissions should be recorded at approximately 15-minute intervals.

It is important to realize that the largest measurement errors can result from poor technique, such as an insufficient purge of the sampling train after sample collection, failure to maintain the probe at a given temperature, or failure to adequately leak check the sampling train. Such deviations from recommended procedures generally cannot be evaluated or corrected. It is important to detect and eliminate such occurrences while the test is in progress. Collaborative test results (ref. 13) indicate that most of the total variability in the method occurs during sample collection rather than the analysis phase.

Sources of variation involving equipment include:

1. The dry gas meter,
2. The sampling probe heater,
3. Sampling train leaks,
4. Impinger solution temperature, and
5. Vacuum pump malfunctions.

These sources of variation are controlled either by a calibration or calibration check before each field test or by special checks immediately before, during, and immediately after the field test.

Assuming good technique, i.e., neglecting the possibility of gross errors due to sampling and/or analysis mistakes, the major error sources of the measurement process are discussed and the effect of each source on the measured mass emission rates is estimated in a functional analysis (subsection 4.1). The relationship of a particular variable or error source to the final measured value should be obtained from this subsection, and a summary of the important parameters is given. Specific subjects to be discussed include:

1. Equipment calibration,
2. Sampling train leaks,
3. Proportional sampling,
4. Sample recovery,
5. Reagent standardization,
6. Sample blanks, and
7. Calculations.

3.3.1.1 Equipment Calibration. Equipment calibration is the crux of any quality assurance program. It is important that the calibration procedure be carried out correctly, that the calibration standards are properly maintained, and that the frequency of calibration is adequate.

The quality assurance document of this series for Method 2 (ref. 14) should be adhered to for calibration of apparatus used in determining the volumetric flow rate of the source being tested.

The dry gas meter, including its temperature measuring device, is calibrated to achieve an acceptable level of accuracy in the sample volume at standard conditions. An error in the sample volume is directly reflected in the concentration measurements and subsequently in the mass emission rates.

3.3.1.2 Sampling Train Leaks. Sampling train leaks result in measured sample volumes larger than the true sample volume. Leaks also introduce errors in the collected H_2SO_4 and SO_2 that cannot be corrected in most cases. Sampling train leaks must be kept sufficiently small so that the resulting error will not significantly increase total system variability.

3.3.1.3 Anisokinetic Sampling. Anisokinetic sampling can occur from error in the calibration constants of the pitot tube, orifice meter, and nozzle diameter. It can also result to a lesser degree, usually from measurement error in the moisture content and molecular weight of the stack gas. Errors from the above sources will not be directly reflected in the percent of isokinetic sampling calculation. Therefore, it is important to determine each parameter as accurately as possible, either through calibrations or careful measurements.

Failure, or in some instances the inability, to make adjustment in the sampling rate as the stack gas velocity varies can result in anisokinetic sampling. Use of a nomograph can be a cause of anisokinetic sampling because

of (1) any inaccuracy in the nomograph, (2) use of preset values for C_p, $\Delta H@$, and M_d (these errors can be eliminated by using actual values and adjusting the correction factor on the nomograph), and (3) operator error in setting the nomograph. The sum of these errors is quantified to a certain extent by the percent of isokinetic sampling calculation.

Deviation from isokinetic sampling cannot be related directly to error in the measurement process (see subsection 4.1). However, failure to maintain isokinetic sampling conditions under otherwise normal operations reflects the lack of alertness and, perhaps even the level of competency, of the field crew.

3.3.1.4 Sample Recovery. Sample recovery, including purging of the sampling train and rinsing of the impingers and connecting tubes to quantitatively recover the sample, can be critical to the precision and accuracy of the measurement.

3.3.1.5 Reagent Standardization. An error in the standardized barium perchlorate solution (subsection 2.4.2.4) is directly reflected in the H_2SO_4 and SO_2 concentrations and mass emission rates.

3.3.1.6 Sample Blanks. The use of blanks is important in correcting the field sample for contaminants contained in the reagents and not part of the collected sample. Also, the routine measurement of blanks should preclude errors due to the use of contaminated reagents.

3.3.1.7 Calculations. Calculations for this method are known to be a major source of error. Some calculations involve several terms and should only be attempted (for the final report) at a desk or work table and preferably with the aid of a calculator or at least a good slide rule. A computer program using raw data as an input is highly recommended for making the final calculations.

As a check, it is recommended that all calculations be independently repeated from raw data.

3.3.2 How to Monitor Important Variables.

In general, if the procedures outlined in the Operations Manual are followed, the major sources of measurement variability will be in control. It is felt, however, that the supervisor should visually check certain parameters

and operations periodically while measurements are being made to insure good operator technique and the proper use of equipment. The parameters and operations to check are the same as those recommended for the auditor as listed in subsection 4.3.2.

Results of the calibration checks for the dry gas meter, rotameter, thermometer, and pitot tube should be checked before each field test. Any item of equipment not satisfying the suggested performance criteria of table 1 should be calibrated or replaced.

Also, actual involvement in or observance of such on-site operations as (1) sampling train leak check before and after sample collection, (2) purging the sampling train after sample collection, and (3) sample recovery should serve as a means of monitoring these important operations.

There appears to be a need for more actual field data on several of the parameters or variables involved in this measurement method in order to better judge their influence on measurement variability. One of the most effective means of identifying and quantifying important sources of variability is through the use of quality control charts. Quality control charts will provide a basis for action with regard to the measurement process; namely, whether the process is satisfactory and should be left alone, or is out of control (or approaching control limits) and action should be taken to find and eliminate the causes of excess variability. The quality control charts can be evaluated after a period of time to determine the range of variation that can be expected for each variable charted under normal operating conditions.

For Method 8, five control charts are recommended as follows:

1. A chart for the successive $BaClO_4$ normality determinations,
2. Range charts for duplicate determinations of both H_2SO_4 and SO_2 concentrations, and
3. Relative range charts for the CV of both $\overline{C}_{SO_2}$ and $\overline{C}_{H_2SO_4}$ as determined from each set of six determinations.

It is good practice to note directly on control charts the reason for out-of-control conditions, if determined, and the corrective actions taken. It is also good practice to maintain control charts in large size, e.g., 8-1/2 x 11 inches or larger and to keep them posted on a wall for viewing by all concerned, rather than have them filed in a notebook.

3.3.2.1 Pitot Tube Calibration Coefficient. A sample control chart for pitot tube calibration checks is given in the quality assurance document of this series for Method 2, Determination of Stack Gas Velocity and Volumetric Flow Rate (type-S pitot tube), page 38 (ref. 14).

3.3.2.2 Control Chart for Normality of Standardized Barium Perchlorate Solution. For a given batch of standardized barium perchlorate, it is assumed that later checks should not deviate more than ± 5 percent from the original value. Using ± 5 percent* as the action limits for checking and preparing new reagents, a control chart for the standardized barium perchlorate solution can be constructed. For this example, an original standardized value of 0.0100 N. is used and the control chart would be as shown in figure 3. It is important to recognize and attempt to determine the reason for trends away from the assumed standard value of 0.01 N.

Each time the barium perchlorate solution is restandardized, that value is plotted on the control chart and connected to the previous plotted value by a straight line.

It is recommended that any time the most current standardization value deviates more than ± 5 percent from the original or the previous value, all reagents used in standardizing the barium perchlorate solution should be checked and/or restandardized. If no problems are detected in these reagents, then a new batch of barium perchlorate should be prepared and standardized.

It is also recommended that the latest standardization value be used in subsequent sample analyses.

3.3.2.3 Control Chart for Duplicate Samples. The within-laboratory standard deviation (σ) for the Method 8 analytical phase is estimated as 0.0035 g/m^3 for SO_2 (ref. 13). If 2 σ is taken as the warning limit magnitude and 3 σ as the action limit magnitude, a control chart can be constructed as in figure 4. The difference for duplicate analyses (to be made on two out of the six samples taken per field test) is calculated as

$$|d| = C_{(1)} - C_{(2)}$$

*This is a suggested initial action limit, which should be tightened if experience indicates that better precision is either possible or necessary for acceptable results.

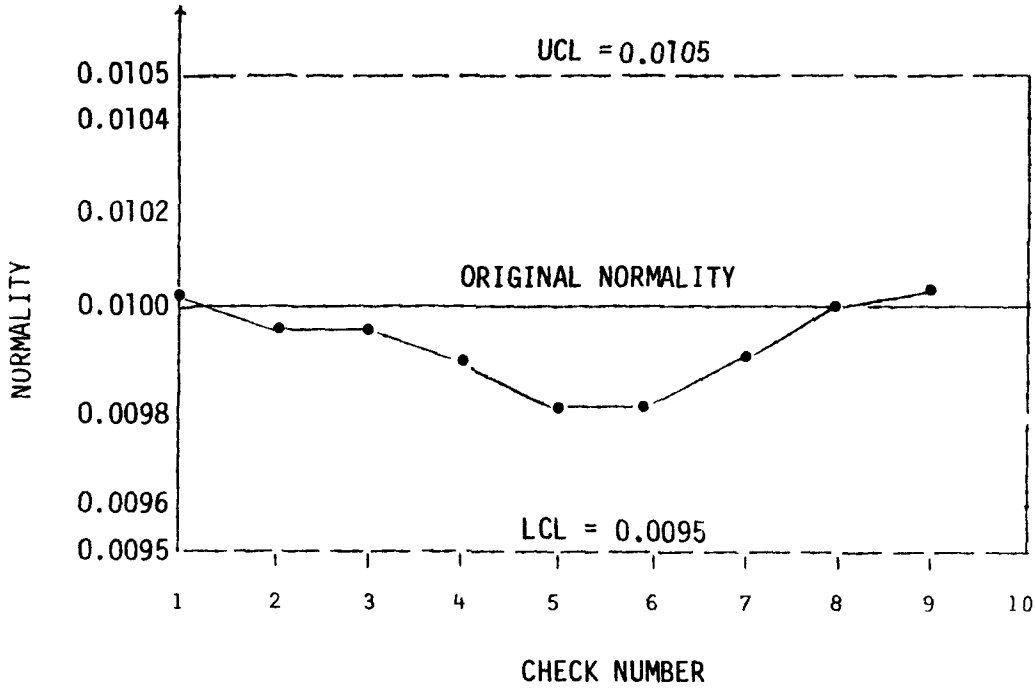

Figure 3. Sample control chart for standardized barium perchlorate solution.

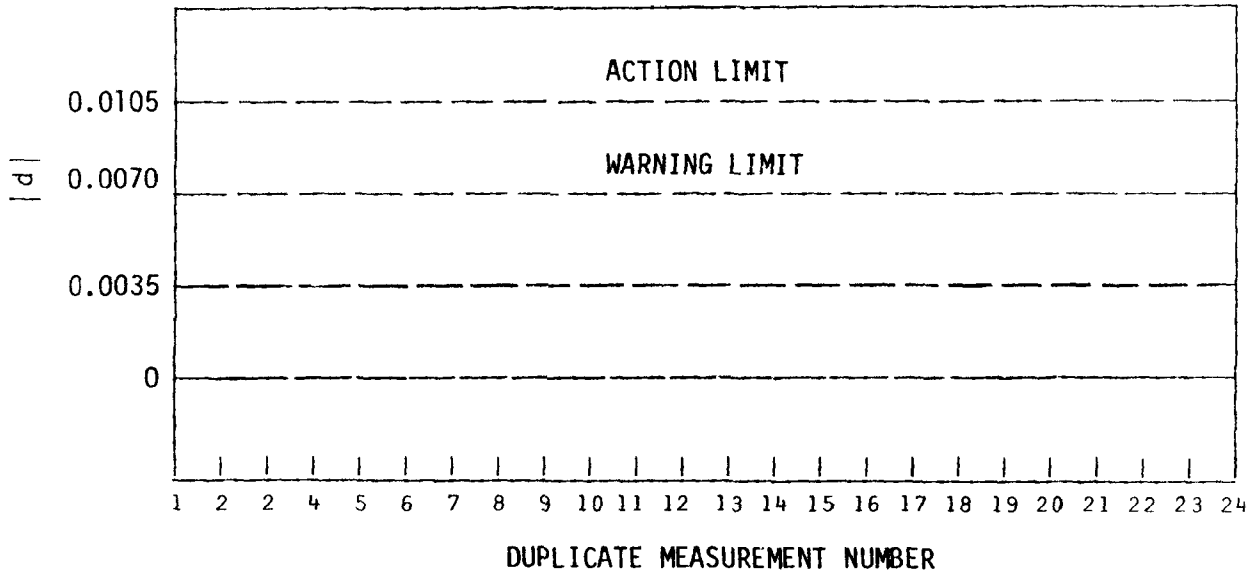

Figure 4. Sample control chart for range of duplicate measurements of SO_2.

where $C_{(1)}$ = Original determination of concentration

$C_{(2)}$ = duplicate determination of concentration.

The magnitude of d (the number obtained, ignoring the sign), symbolized as $|d|$, is plotted each time a duplicate measurement is made. The analysis procedure, reagents, and apparatus should be checked and appropriate action taken any time one of the following criteria is exceeded:

1. One point falls outside the control limit;
2. Two consecutive points fall between the warning limit and control limit;
3. Seven consecutive points fall above the σ line (on figure 4, 0.0035 g/m^3).

When criterion 1 is exceeded, the six samples for that field test should be reanalyzed, after the cause of the excess variability has been located and corrected. Exceeding the second or third criteria will usually indicate poor technique and the need for additional supervision/training.

Separate control charts should be kept for analysis of both sulfuric acid and sulfur dioxide. The control chart for acid mist should plot $|\%d|$ rather than $|d|$, since the precision of acid mist measurements is said to be proportional to the mean concentration level.

It would be desirable to maintain separate control charts for the relative range of CV of both SO_2 and H_2SO_4 for each set of six determinations.

SECTION IV MANUAL FOR MANAGER OF GROUPS OF FIELD TEAMS

4.0 GENERAL

The guidelines for managing quality assurance programs for use with Test Method 8, Determination of Sulfuric Acid Mist and Sulfur Dioxide Emissions from Stationary Sources, are given in this part of the field document. This information is written for the manager of several teams for measuring source emissions and for the appropriate EPA, State, or Federal administrators of these programs. It is emphasized that if the analyst carefully adheres to the operational procedures and checks of section II, then the errors and/or variations in the measured values should be consistent with the performance criteria as suggested. Consequently, the auditing routines given in this section provide a means of determining whether the stack sampling test teams of several organizations, agencies, or companies are following the suggested procedures. The audit function* is primarily one of independently obtaining measurements and performing calculations where this can be done. The purpose of these guidelines is to:

1. Present information relative to the test method (a functional analysis) to identify the important operations and factors;
2. Present a methodology for comparing action options for improving the data quality and selecting the preferred action;
3. Present a data quality audit procedure for use in checking adherence to test methods and validating that performance criteria are being satisfied;
4. Present the statistical properties of the auditing procedure in order that the appropriate plan of action may be selected to yield an acceptable level of risk to be associated with the reported results.

These four purposes will be discussed in the order stated in the sections which follow. The first section will contain a functional analysis of the test method with the objective of identifying the most important factors

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*The independent audit is only one device available to a manager. He may also wish (for example) to make quality control comparisons of field data obtained within and among teams; i.e., to obtain CV and CV_b values from field data.

which affect the quality of the reported data and of estimating the expected variation and bias in the measurements resulting from equipment and operator errors.

Section 4.2 contains several actions for improving the quality of the data; for example, by improved analysis techniques, instrumentation, and/or training programs. Each action is analyzed with respect to its potential improvement in the data quality as measured by its precision. These results are then compared on a cost basis to indicate how to select the preferred action. The cost estimates are used to illustrate the methodology. The manager or supervisor should supply his own cost data and his own actions for consideration. If it is decided not to conduct a data audit, sections 4.1 and 4.2 would still be appropriate as they contain a functional analysis of the reference method and of alternative methods or actions.

There are no absolute standards with which to compare the routinely derived measurements. Furthermore, the taking of completely independent measurements at the same time that the routine data are being collected (e.g., by introducing two sampling probes into the stack and collecting two samples simultaneously) is not considered practical due to the constrained environmental and space conditions under which the data are being collected. Hence, a combination of an on-site system audit, including visual observation of adherence to operating procedures and a quantitative performance quality audit check, is recommended as a dual means of independently checking on the source emissions data.

The third section contains a description of a data quality audit procedure. The most important variables identified in section 4.1 are considered in the audit. The procedure involves the random sampling of n stacks from a lot size of N = 20 stacks (or from the stacks to be tested during a 3-month period, if less than 20) for which one firm is conducting the source emissions tests. For each of the stacks selected, independent measurements will be made of the indicated variables. These measurements will be used in conjunction with the routinely collected data to estimate the quality of the data being collected by the field teams.

The data quality audit procedure is an independent check of data collection and analysis techniques with respect to the important variables. It provides a means of assessing data collected by several teams and/or firms with the

potential of identifying biases/excessive variation in the data collection procedures. A quality audit should not only provide an independent quality check, but also identify the weak points in the measurement process. Thus the auditor, an individual chosen for his background knowledge of the measurement process, will be able to guide field teams in using improved techniques. In addition, the auditor is in a position to identify procedures employed by some field teams which are improvements over the current suggested ones, either in terms of data quality and/or time and cost of performance. The auditor's role will thus be one of aiding the quality control function for all field teams for which he is responsible, utilizing the cross-fertilization of good measurement techniques to improve the quality of the collected and reported data.

The statistical sampling and test procedure recommended is sampling by variables. This procedure is described in section 4.4. It makes maximum use of the data collected, and it is particularly adaptable to the small lot size and consequently the small sample size applications. The same sampling plans can be employed in the quality checks performed by a team or firm in its own operations. The objectives of the sampling and test procedure are to characterize data quality for the user and to identify potential sources of trouble in the data collection process for the purpose of correcting the deficiencies in data quality.

Section 4.4.4 describes how the level of auditing, sample size n, may be determined on the basis of relative cost data and prior information about the data quality. This methodology is described in further detail in the final report on the contract. The cost data and prior information concerning data quality are supplied to illustrate the procedure and these data must be supplied by the manager of groups of field teams depending upon the conditions particular to his responsibility.

Figure 5 provides an overall summary of the several aspects of the data quality assurance program as described in these documents. The flow diagram is subdivided into four areas by solid boundary lines. These areas correspond to specific sections or subsections of the document as indicated in the upper right hand corner of each area. The details are considered in these respective sections of the document and will not be described here.

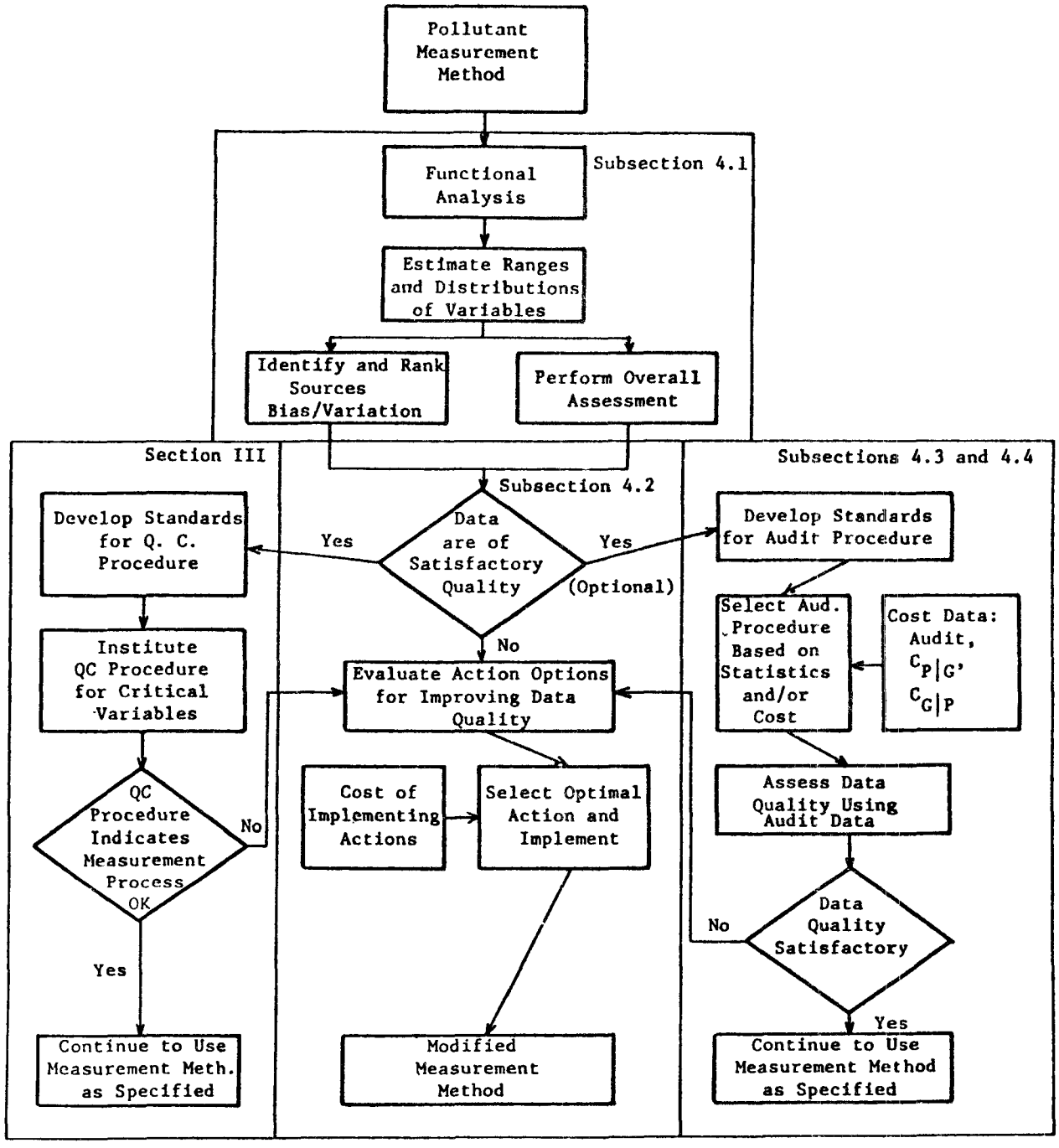

Figure 5. Summary of data quality assurance program.

4.1 FUNCTIONAL ANALYSIS OF THE TEST METHOD

Test Method 8, Determination of Sulfuric Acid and Sulfur Dioxide Emissions from Stationary Sources, is described in the Federal Register and reproduced in appendix A of this document. This method is used to determine the concentrations of sulfuric acid and sulfur dioxide in stack gas. Results from this method combined with the volumetric flow rate as measured by Method 2 yield sulfuric acid and sulfur dioxide emission rates for the source being tested.

A functional analysis of the measurement process is performed to identify and, where possible, quantify important sources of variability. Estimates of the error ranges associated with intermediate measurements are made using published data if available, and engineering judgment if data are not available. Extensive use is made of the results from a collaborative test of the method (ref. 13) for overall variability and for the division of variability due to the sample collection and analysis phases of the process. A variance analysis is performed to show the influence of the intermediate measurements on the measured sulfuric acid and sulfur dioxide concentrations and the emission rates.

The functional analysis is discussed in two parts. First, the governing mathematical relationships are given, and estimated means and coefficients of variation are given for each variable. A variance analysis is then performed, identifying the most critical variables. An approximate model is given for estimating overall variability, using only the most critical variables.

Special symbols and definitions used in the functional analysis include the following:

C = A single determination of (H_2SO_4 or SO_2) concentration at standard conditions, on a dry basis, g/m^3.

$\overline{C}$ = The average concentration of six repetitions, g/m^3.

$CV\{C\}$ = Within-laboratory coefficient of variation (same laboratory, personnel, equipment, and sample), percent.

$CV_b\{C\}$ = Between-laboratory coefficient of variation (variation in simultaneous determinations of C by different laboratories at the same true value of C), percent.

$CV_L\{C\}$ = Laboratory bias coefficient of variation (variability in concentration determinations due to changes in personnel, equipment and procedural details), percent.

$CV\{C\}/\sqrt{6}$ = Repeatability coefficient of variation for concentration determinations based on six replicates, percent.

$\sqrt{CV_L^2\ \{C\} + CV^2\{C\}/6}$ = Reproducibility coefficient of variation for a field test result based on six replicates, percent.
= CV(R)

4.1.1 Variable Evaluation and Error Range Estimates.

The emission rates of sulfuric acid and sulfur dioxide are calculated from measured values by the relationship

$$ER = D\ \frac{N(V_t - V_{tb})\ (V_{soln}\ /\ V_a)}{V_{m(std)}}\ (1 - B_{wo})\ C_p\ (\sqrt{\Delta P})_{avg}\ A_s \left[\frac{P_s}{(T_s)_{avg}\ M_s}\right]^{1/2}$$

where ER = Sulfuric acid or sulfur dioxide emission rate, g/hr

D = 280.1 for SO_2 and 428.9 for H_2SO_4

V_t = Volume of barium perchlorate titrant used for the sample, mℓ

V_{tb} = Volume of barium perchlorate titrant used for the blank, mℓ

V_{soln} = Total solution volume of sulfuric acid or sulfur dioxide, mℓ

V_a = Volume of sample aliquot titrated, mℓ

$V_{m(std)}$ = Volume of gas sample measured by the dry gas meter and corrected to standard conditions, ℓ

B_{wo} = Proportion by volume of water vapor in the stack gas, dimensionless

$(\sqrt{\Delta P})_{avg}$ = Average of the square roots of the velocity pressure head measurements, $(\text{mm of } H_2O)^{1/2}$

A_s = Stack cross sectional area, m^2

P_s = Absolute stack pressure, mm of Hg

$(T_s)_{avg}$ = Average stack gas temperature, ° K

M_s = Stack gas molecular weight on a wet basis, g/g-mole.

Table 2 lists the variables in the equation, with estimated coefficients of variations and mean values to be used in the variance analysis in the following subsections.

Table 2. Assumed means and coefficients of variations of variables in influencing emissions rate determinations for SO_2

Variable	Assumed mean value	Within-laboratory coefficient of variation CV{X} percent	Between-laboratory coefficient of variation $CV_b\{X\}$ percent
$(V_t - V_{tb})$	7 mℓ	3.90	5.50
(V_{soln}/V_a)	5 dimensionless	0.50	1.00
N	0.01 normal	0.10	1.00
V_m	28 ℓ	0.50	1.25
T_m	294° K	0.25	0.50
P_m	760 mm of Hg	0.10	0.30
$(1 - B_{wo})$	0.90	0.15	0.30
C_p	0.85 dimensionless	0.50	1.00
$(\sqrt{\Delta P})_{avg}$	7 (mm of $H_2O)^{1/2}$	0.85	1.70
A_s	0.7 m^2	0.50	1.00
P_s	760 mm of HG	0.20	0.40
$(T_s)_{avg}$	294° K	0.50	1.00
M_s	28.8 g/mole	0.35	0.71

The first four variables in table 2 are the only ones unique to this method. The remaining variables are common to methods 2, 3, and 4 and are discussed in the quality assurance documents of this series dealing with those methods. Estimates of the variance of the first four variables in table 2 [$(V_t - V_{tb})$, (V_{soln}/V_a), N and V_m] are discussed in the following subsections.

4.1.1.1 Volume of Titrant $(V_t - V_{tb})$. The difference in the volumes of titrant used in the sample and the blank, symbolized by $(V_t - V_{tb})$, is a direct measure of the quantity of SO_2 or SO_3/H_2SO_4 absorbed in the sample solution. The component of error or variability of this term attributable to the analysis phase of the measurement method; i.e., the actual volume determinations of V_t and V_{tb}, and the ability to detect the endpoint in the titration, should be relatively small. However, the above term directly reflects the variability due to sample collection. Any difference in the masses of SO_2 and acid mist in a given volume of stack gas and that retained in the absorbing solution after sampling that volume of gas will result in the same percent difference in the volumes of titrant that the sample would have required (had there been no error in sample collection) and the volumes actually required in the analysis.

Differences in the true masses of H_2SO_4 and SO_2 in a given volume of stack gas and the measured value can result from:

1. Incomplete purging of the sampling train after sample collection. This would lead to high H_2SO_4 and low SO_2 values, since SO_2 remaining in the 80% isopropanol solution would oxidize to sulfate;
2. Less than 100 percent collection efficiency of the absorbing solution;
3. Loss of SO_2 due to reactions with particulate matter trapped by the particulate filter (ref. 16);
4. Loss of sample during sample recovery.

There are no data available for estimating the variability of these terms. The coefficients of variation of 3.9 and 5.5 (for within-laboratory and between-laboratory variabilities) as given in table 2 are taken from the Quality Assurance Guidelines document for Method 6, which involves collection and analysis of sulfur dioxide only. Variability in sulfuric acid mist (on a percentage basis) would be much larger, due to the lower concentration of H_2SO_4 relative to SO_2 (ref. 15).

4.1.1.2 Fraction of Total Solution Volume Titrated (V_{soln}/V_a). The sample volume is determined by transferring the contents of the sample bottles (see subsection 2.3.4) into 250-mℓ (H_2SO_4) and 1,000-mℓ (SO_2) graduated cylinders and diluting to volume. Errors due to the graduated cylinders, incomplete transfer, and diluting to volume should be small in most cases. A pipette is used to measure the aliquot, V_a, and (neglecting operator mistakes) should exhibit negligible variability. The estimated coefficients of variations of 0.5 and 1.0 percent (for within-laboratory and between-laboratory, respectively) do not significantly increase the total variability of the measurement method.

4.1.1.3 Normality of Barium Perchlorate Titrant (N). By exercising proper care, the normality of the barium perchlorate titrant should be repeatable to the fourth decimal place. Since the titrant is approximately 0.01 N, the fourth decimal place would be equivalent to 1.0 percent. Coefficients of variation of 0.1 and 1.0 percent are used for this analysis, as shown in table 2. The small value of 0.1 is used for fixed within-laboratory repeatability since the same batch of titrant is used for all samples from a given field test. Hence, there should be little variability. However, the variability between laboratories and for that matter between batches within a laboratory would be expected to be significantly larger. Thus, a CV of 1.0 percent is assumed.

4.1.1.4 Sample Volume (V_m). Variability in the measured sample gas volume at meter conditions can result from

1. Calibration variability (of the dry gas meter),
2. Imprecision of the dry gas meter,
3. Sampling train leaks,
4. Meter reading errors.

The coefficients of variation given in table 2 of 0.50 and 1.25 percent are estimates of what can be expected of a properly trained and motivated field team.

To simplify the variance analysis, the overall equation can be written in terms of concentration and volumetric flow rate. That is,

$$ER = C \times Q_s$$

where the concentration, C, in g/m^3 is given by

$$C = K \frac{N(V_t - V_{tb})\ (V_{soln}/V_a)}{V_{m_{std}}}$$

where K = 32 for SO_2 and 49 for H_2SO_4

and $V_{m_{std}}$, the sample gas volume, ℓ, through the dry gas meter (corrected to standard conditions) is

$$V_{m_{std}} = 0.3868 \frac{V_m P_m}{T_m} .$$

Also, the volumetric flow rate, Q_s, in m^3/hr is given by

$$Q_s = 8.754 \times 10^5 (1 - B_{wo})\ C_p\ (\sqrt{\Delta P})_{avg}\ A_s \left[\frac{P_s}{(T_s)_{avg}\ M_s}\right]^{1/2} .$$

The variance analysis can now be performed in steps. That is, the coefficients of variation are determined for $V_{m_{std}}$, C_{SO_2},* Q_s, then ER,† in that order (tables 3, 4, 5, and 6). An approximate model containing the most important variables is developed. This model should give a reasonable estimate of measurement variability under normal operating conditions.

We have defined that

$$CV_b^2\ \{C_{SO_2}\} = CV_L^2\{C_{SO_2}\} + CV^2\{C_{SO_2}\}$$

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*The analysis is carried to completion with sulfur dioxide, for illustrative purposes. Numbers used are the same as in the Quality Assurance Guidelines document for Method 6.

†Method 6 does not require calculation of the emission rate, ER. It is useful to carry the analysis out (for reproducibility only), to demonstrate the predominance of concentration determination precision in ER precision.

Table 3. Variance analysis for $V_{m_{std}}$

Variable	Assumed $CV_b^2\{X\}$ $(CV_L^2\{X\})$	× Weighting coefficient	= Weighted $CV_b^2\{X\}$ $(CV^2\{X\})$
V_m	1.56 (1.31)	1	1.56 (1.31)
P_m	0.09 (0.08)	1	0.09 (0.08)
T_m	0.25 (0.19)	1	0.25 (0.19)
$V_{m_{std}}$			$CV_b^2\{V_{m_{std}}\}$ = 1.90 (1.58)
			$CV_b\{V_{m_{std}}\}$ = 1.38 (1.26)

Table 4. Variance analysis for C_{SO_2}

Variable	Assumed $CV_b^2\{X\}(CV^2\{X\})$	× Weighting factor	= Weighted $CV_b^2\{X\}$ $(CV^2\{X\})$
N	1.0 (0.01)	1	1.0 (0.01)
$(V_t - V_{tb})$	30.25 (15.21)	1	30.25 (15.21)
(V_{soln}/V_a)	1.00 (0.25)	1	1.00 (0.25)
$V_{m_{std}}$	1.90 (1.58)	1	1.90 (1.58)
C_{SO_2}			$CV_b^2\{C_{SO_2}\}$ = 34.15 (17.1)
			$CV_b\{C_{SO_2}\}$ = 5.8 (4.1)

Table 5. Variance analysis for Q_s

Variable	Assumed $CV_b^2\{X\}$	×	Weighting coefficient[a]	=	Weighted $CV_b^2\{X\}$
$1 - B_{wo}$	0.09		1.23		0.11
C_p	1.00		1.0		1.00
A	1.00		1.0		1.00
P_s	0.16		0.25		0.04
$(\sqrt{\Delta P})_{avg}$	2.89		1.00		2.89
$(T_s)_{avg}$	1.0		0.25		0.250
M_s	0.50		0.25		0.125
Q_s					$CV_b^2\{Q_s\} = 5.42$
					$CV_b\{Q_s\} = 2.33\%$

[a]The weighting coefficient for $1 - B_{wo}$ is $1/(1 - B_{wo})^2$, and assuming B_{wo} to be 0.10, this yields $1/(.9)^2 = 1.23$.

Table 6. Variance analysis for reproducibility of ER

Variable	Assumed $CV^2\{X\}$	×	Weighting Factor	=	Weighted $CV^2\{X\}$
$\bar{C}_{SO_2}$	$CV_L^2\{\bar{C}_{SO_2}\} = 17.1$		1		17.1
	$CV^2\{C_{SO_2}\}/6 = 2.8$		1		2.8
Q_s	5.42		1		5.4
ER					$CV_b^2\{ER\} = 25.3$
					$CV_b\{ER\} = 5.0\%$

and for values in table 2, $CV_L^2\{C_{SO_2}\}$ becomes

$$34.12 = CV_L^2\{C_{SO_2}\} + 17.1,$$

then $$CV_L^2\{C_{SO_2}\} = 17.1$$

and $$CV_L\{C_{SO_2}\} = 4.1 \text{ percent.}$$

The reproducibility coefficient of variation then is taken as

$$\sqrt{CV(R) = CV_L^2\{C_{SO_2}\} = CV^2\{C_{SO_2}\}/6}$$

$$CV(R) = 4.5 \text{ percent}$$

based on six replicates.

The collaborative study of Method 8 (ref. 13) shows that the precision of the SO_2 data is independent of the mean SO_2 concentration level, whereas the precision of the H_2SO_4/SO_3 data is proportional to the mean level. A similar study of Method 6 (ref. 17) indicates that the precision of the SO_2 measurements is proportional to the mean level. The analysis by barium-thorin

titration is identical in both methods, but there are differences in the collection techniques. Method 8 collection is by way of Greenburg-Smith impingers and sampling is isokinetic, whereas Method 6 uses midget impingers and samples proportionally. In any event, any statistical differences (if real) must arise from the collection techniques rather than the analyses. This document takes the position that, in view of the questions raised by the statistics obtained in these two studies, it is not appropriate to undertake a detailed variance analysis of Method 8 without further testing. The numbers used in the foregoing discussion have been lifted from the guidelines document for Method 6 and serve only to illustrate how such an analysis can be carried out.

There is more opportunity for error in the sulfuric acid mist determination, since the concentration range is normally much lower than that for sulfur dioxide. Any SO_2 not purged from the isopropanol impinger tube and filter system may be oxidized to sulfate, with resulting high bias in the SO_3/H_2SO_4 determination. The greater uncertainty in this measurement is reflected in the collaborative study, which (excluding the high values) gives the following coefficients of variation: CV = 58.5 percent, CV_b = 66.1 percent, and CV_L = 30.8 percent. Not excluding the high values yields a CV of 95.8 percent. Prompt analysis of the isopropanol impinger, immediately after thorough system purging, may minimize high bias due to SO_2 oxidation, but in general it is expected that the precision of the mist determination will be quite poor.

4.1.2 Interferences.

4.1.2.1 Cations From Particulates. The poor endpoint visibility of the barium ion-thorin titration is mentioned in subsection 2.4.2.4. A detailed field study (ref. 18) indicates that this problem is due to the presence of interfering cations (sodium and potassium). The intorduction of a fine, neutral pH,* particulate filter in the sampling train greatly sharpens the endpoint.

4.1.2.2 Nitric Oxide. Nitric oxide does not interfere with Method 8 results (ref. 16).

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*A glass fiber filter is not acceptable due to the natural alkalinity of the glass.

4.1.3 Bias Analysis.

The collaborative study of Method 8 (ref. 13) does not attempt to determine bias for the method, but does indicate that the analytical phase (the barium-thorin titration) is accurate. A small negative bias of 1 to 3 percent, falling within the 95 percent confidence interval, was evident.

High SO_3/H_2SO_4 results and corresponding low SO_2 data would indicate failure to purge the system rigorously after sampling. A field evaluation of Method 6 (ref. 19) showed that up to 14 percent of the SO_2 may be retained in the isopropanol bubblers if purging is not carried out. In view of the low H_2SO_4/SO_2 concentration ratios normally sampled, incomplete purging would surely bias the mist results. There seems to be no experimental confirmation of this in the literature.

Subsection 4.1.1.1 indicates other possible reasons for incomplete sample collection, all of which would negatively bias the results. However, there is no way to quantify the loss of sample due to these possibilities.

Assuming reasonable care in following the recommended collection and analysis procedure, results from Method 8 should be unbiased or very slightly negatively biased. Field personnel should be aware of the possibility of introducing a negative bias due to any of the reasons listed in section 4.1.1.1, or because of such problems as sampling train leaks. No evidence is available indicating a positive bias in the method.

4.2 ACTION OPTIONS

Suppose it has been determined as a result of the functional analysis and/or the reported data from the checking and auditing schemes, that the data quality is not consistent with suggested standards or with the user requirements. Poor data quality may result from (1) a lack of adherence to the control procedures given in section II--Operations Manual, or (2) the need for an improved method or instrumentation for taking the measurements. It is assumed in this section that (2) applies, that is, the data quality needs to be improved beyond that attainable by following the operational procedures given for the reference method.

The selection of possible actions for improving the data quality can best be made by those familiar with the measurement process. For each action, the variance analysis can be performed to estimate the variance, standard deviation, and coefficient of variation of the pertinent measurement(s). In some cases it is difficult to estimate the reduction in specific variances that are required to estimate the precisions of the pertinent measurements. In such cases, an experimental study should be made of the more promising actions based on preliminary estimates of precision/bias and the costs of implementing each action.

In order to illustrate the methodology, three actions and appropriate combinations thereof are suggested. Variance and cost estimates are made for each action, resulting in estimates of the overall precision of each action. The actions are as follows:*

A0: Reference Method

A1: Photometric endpoint detection (cost is $800/20 field tests**)

A2: Crew training workshop (cost is $1,000/20 field tests)

A3: Calculations by standard computer program (cost is $200/20 tests)

A4: (A1 + A3): Improved endpoint detection plus calculations by computer (total cost of $1,000/20 tests).

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*Actions presented here are same as those outlined in the corresponding quality assurance document for Method 6, in view of the similarity of Methods 6 and 8.

**Equipment costs are amortized over 5 years, at 20 tests per year, and allowance is made for the continuing cost of supplies and labor.

The costs given for each action are additional costs above that of the reference method. The assumptions made concerning the reduction in the variances (or improved precisions) are given in the following for each action.

A0: Reference Method. The functional analysis (section 4.1.3) does not anticipate a bias in Method 8, and provided the procedures (both field and laboratory) stipulated in the method are rigorously adhered to, unbiased results should be obtained. The collaborative study (ref. 13) indicates that the sulfuric acid mist data has precision proportional to the mean and thus expressed as a percent of the mean. The SO_2 data precision, on the other hand, is independent of the mean and expressed in absolute units of grams/cubic meter. If the high (outlying) values are excluded, the results for H_2SO_4 and SO_2 are as follows:

SO_3/H_2SO_4 $\quad CV = 58.5,\ CV_b = 66.1,\ CV_L = 30.8$

SO_2 $\quad \sigma = 0.106 \quad \sigma_b = 0.114 \quad \sigma_L = 0.044.$

For convenience it is assumed that these estimates of precision will be affected in a corresponding way; i.e., if a given strategy improves CV for mist determination, it will also improve σ for SO_2 and by a proportional amount. Given the strategies suggested, this is a reasonable assumption. Other possible strategies, especially if concerned with certain areas of the sample collection phase, might have differing effects on the quality of acid mist and SO_2 data.

Table 7 gives assumed effects of A1, A2, A3, and A4 on the precision of Method 8. The within-laboratory, between-laboratory and laboratory bias components of variability are symbolized as P, P_b, and P_L and apply to both SO_3/H_2SO_4 and SO_2. These symbols (i.e., P, P_b, and P_L) represent CV, CV_b, and CV_L, respectively for acid mist variability and σ, σ_b, and σ_L respectively for SO_2 variability.

A1: Photometric Endpoint Detection. A major problem associated with Method 8 is the poor visibility of the thorin titration endpoint. Photometric endpoint detection could greatly improve precision by eliminating visual estimation of endpoint color and intensity. Unless the photometric technique became highly standardized, however, there

Table 7. Assumed within-laboratory, between-laboratory, and laboratory bias components of variability for given action options.

		P	P_b	P_L	Added cost per 20 field tests
A0	Reference	P	$(P_b)_R$	$(P_L)_R$	0
A1	Photometric endpoint detection	$0.8\ P_R$	$0.9\ (P_b)_R$	$0.99\ (P_L)_R$	$ 800
A2	Crew training workshop	$0.8\ P_R$	$0.8\ (P_b)_R$	$0.8\ (P_L)_R$	$1,000
A3	Calculations by standard computer program	$1.0\ P_R$	$0.89\ (P_b)_R$	$0.8\ (P_L)_R$	$ 200
A4	(A1 + A3)	$0.78\ P_R$	$0.80\ (P_b)_R$	$0.79\ (P_L)_R$	$1,000

would remain differences in technique among various laboratories, so that the improvement in P_b is assumed not as great, and thus P_L is virtually unchanged.

A2: Crew Training Workshop. From discussing this method with experienced field testers, it is felt that the method requires an operator who understands the system and its capability. Early detection of out-of-control conditions by the operator can substantially improve data quality. It is assumed here that crew training could affect all sources of variability, and therefore an improvement in all three measures of variability is shown. A 1-week course a year, or special on-the-job training, is estimated to cost approximately $1,000 per 20 field tests.

A3: Calculations by Computer. This recommended option serves a twofold purpose:

1. It eliminates human error (in the field) in calculation of the acid mist and SO_2 concentrations. There remains, of course, the possibility of errors due to computer malfunction, keypunch error and the like.

2. It largely eliminates the illegal practice of discarding "bad" runs and the reporting of only "acceptable" data by field personnel, since the raw field data is submitted.

Another comparable option could be the use of "canned" programs written for the various commercially available programmable calculators. These could be made available by EPA, thus allowing local calculation but standardizing the number of significant digits carried in each step, the treatment of roundoff and all other aspects of the calculation steps.

Since one reason for laboratory bias, P_L, could be improper calculation technique, A4 should in general reduce P_L. This is a systematic error (bias). In addition, a small percentage (about 3 percent) of random calculation errors contribute to P. If both P_L and P are reduced, then P_b should also be improved.

Figure 6 shows the results in terms of cost and data quality for acid mist.* Data quality for this purpose is given as CV, the within-laboratory coefficient of variation. The figure then illustrates options for the individual laboratory to consider. The manager of a number of teams would be more interested in how CV_b varies with cost, and this is given in figure 7. It must be emphasized that figures 6 and 7 are given for illustrative purposes only and should not in themselves be considered as basis for action by a laboratory or a group of laboratories. Both the reductions in CV and CV_b, as well as costs, are estimates based on professional judgment. In particular, the values of CV and CV_b are based solely on judgment and there is no experimental evidence to support these values. The figures illustrate that in principle it is possible to reduce the variability of Method 8 by a number of modifications of the method, and that there is a cost associated with each modification.

Figures 6 and 7 also show "cost of reporting bad data" curves, which assume that the cost increases as the data quality decreases. These function curves must be determined for each specific situation according to the monitoring objectives of the laboratory or group of laboratories.

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*Comparable charts for SO_2 could be constructed, but are not included, since the only difference in construction would be in the scale range of the abscissa.

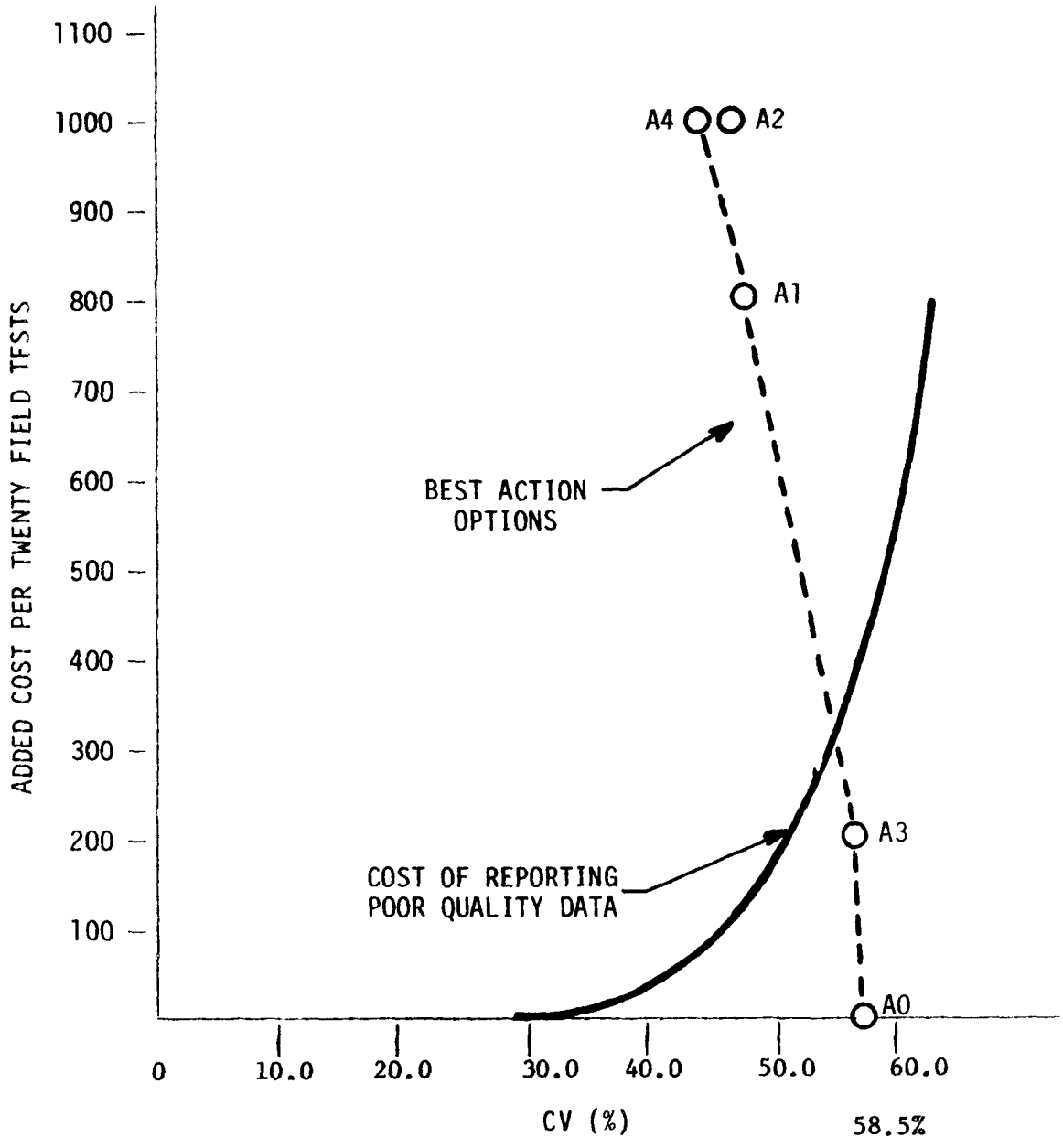

Figure 6. Added cost versus data quality (CV) for selected action options, for SO_3/H_2SO_4 data.

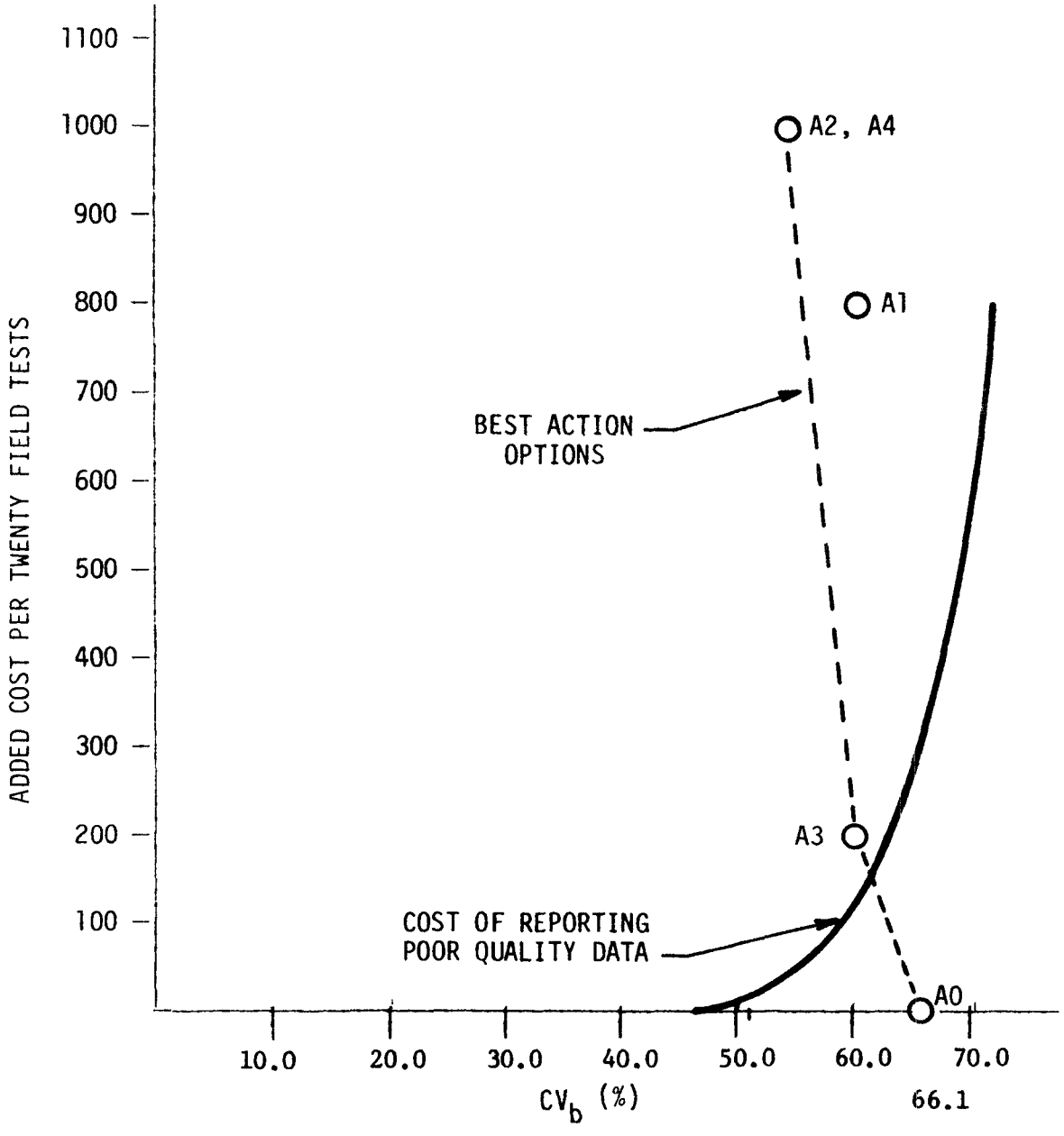

Figure 7. Added cost versus data quality (CV_b) for selection action options, for SO_3/H_2SO_4 data.

Once determined for a given situation, graphs such as figures 6 and 7 can be used to select an "optimal" monitoring strategy, i.e., one which gives maximum increase in data quality for minimum cost. Usually, the strategy point lying closest to the point of intersection of the two curves should be selected. In figures 6 and 7, this point is A3. Note that option A2 is not "best" since it lies to the right of the dashed line; i.e., A2 will not yield as large an improvement in data quality per dollar of cost as A4.

In some instances a manager may need to know the total cost of attaining a prescribed reduction in variability. Figures 6 and 7 can be used to find the method which most nearly meets the requirement. The cost of implementing the method, plus the cost of reporting bad quality data when that method is used, gives total cost.

It is, of course, possible to implement a combination of two or more action options, with costs being additive and precision values being multiplicative (assumed independent). For example, if one chooses to implement both A1 and A2, the total cost would be $1,800 and the values of CV and CV_b would be 0.64 P_R and 0.72 $(P_b)_R$, respectively.

4.3 PROCEDURES FOR PERFORMING A QUALITY AUDIT

"Quality audit" as used here implies a comprehensive system of planned and periodic audits to verify compliance with all aspects of the quality assurance program. Results from the quality audit provide an independent assessment of data quality. "Independent" in this case implies that the auditor prepares a reference sample of sulfate and has the field team analyze the sample. The field team should not know the true sulfate concentration. From these data, both bias and precision estimates can be made for the analysis phase of the measurement process only.

The auditor, i.e., the individual performing the audit, should have extensive background experience in source sampling, specifically with the characterization technique that he is auditing. He should be able to establish and maintain good rapport with field crews.

The functions of the auditor are summarized in the following list:

1. Observe, and where possible duplicate and verify procedures and techniques of the field team during sampling.
2. Check/verify applicable records of equipment calibration checks and quality control charts in the field team's home laboratory.
3. Compare the audit sulfate value with the field laboratory test value.
4. Randomly recheck, if possible, actual field analyses.
5. Inform the field team of the comparison results specifying any area(s) that need special attention or improvement.
6. File the records and forward the comparison results with appropriate comments to the manager.

4.3.1 Frequency of Audit.

The optimum frequency of audit is a function of certain costs and the desired level of confidence in the data quality assessment. A methodology for determining the optimum frequency, using relevant costs, is presented in the final report for this contract. Costs will vary among field teams and types of field tests. Therefore, the most cost-effective auditing level will have to be derived using relevant local cost data according to the procedure given in the final report on this contract.

4.3.2 Collecting Sampling Information.

While on site, the auditor should observe the field team's overall performance of the field test. Specific operations to observe should include, but not be limited to:

1. Setting up and leak testing the sampling train;
2. Preparation and pipetting of absorbing solutions into bubblers and impingers;
3. Sample collection, specifically the following techniques;
   a) achievement of isokinetic sampling rate, b) system purging, c) leak checks.
4. Sample recovery and preparation for shipment.

The above observations can be used in combination to make an overall evaluation of the team's proficiency in carrying out this portion of the field test.

4.3.3 Collecting Laboratory Information.

The auditor must also observe the analytical phase of Method 8. Here he should observe the following:

1. Sample aliquotting technique. This is particularly important, to verify that standard analytical technique is being followed.
2. Titration technique, particularly endpoint detection.
3. Calculation procedure.

The analysis phase of Method 8 can be audited with standard sulfate solutions, as discussed in reference 13.

4.3.3.1 Comparing Audit and Routine Values of Concentrations. In field tests, the audit and routine (field team) values are compared by

$$d_j = C_j - C_{aj}$$

where d_j = The difference in the audit and field test results for the jth audit, mg/m^3.

C_{aj} = Audit value of concentrations (acid mist and SO_2) for j audit, mg/m^3.

C_j = Concentrations obtained by the field team, mg/m^3.

Record the values of d_j for both species in the quality audit log book.

4.3.4 Overall Evaluation of Field Team Performance.

In a summary-type statement, the field team should be evaluated on its overall performance. Reporting the d_j value as previously computed is an adequate representation of the objective information collected for the analysis phase of the audit. However, unmeasurable errors can result from nonadherence to the prescribed operating procedures and/or from poor technique in executing the analytical procedures. These error sources have to be estimated subjectively by the auditor. Using the notes taken in the field, the team could be rated on a scale of 1 to 5 as follows:

5 - Excellent

4 - Above average

3 - Average

2 - Acceptable, but below average

1 - Unacceptable performance.

In conjunction with the numerical rating, the auditor should include justification for the rating. This could be in the form of a list of the team's strong and weak points.

4.4 Data Quality Assessment

Two aspects of data quality assessment are considered in this section. The first considers a means of estimating the precision and bias of the reported data, e.g., reporting the bias, if any, and the standard deviation associated with the measurements. The second consideration is that of testing the data quality against given standards, using sampling by variables. For example, lower and upper limits, L and U, may be selected to include a large percentage of the measurements. It is desired to control the percentage of measurements outside these limits to less than 10 percent. If the data quality is not consistent with the L and U limits, then action is taken to correct the possible deficiency before future field tests are performed and to correct the previous data when possible.

4.4.1 Estimating the Precision/Accuracy of the Reported Data.

Methods for estimating the precision (standard deviation) and accuracy (bias) of the acid mist and SO_2 concentrations were given in section 4.1. This section will indicate how the audit data collected in accordance with the procedure described in section 4.3 will be utilized to estimate the precision and accuracy of the measures of interest. Similar techniques can be also used by a specific firm or team to assess its own measurements. The differences between the field team results and the audited results for the respective measurements are

$$d_j = C_j - C_{aj}$$

Let the mean and standard deviation of the differences d_j, where j=1, ... n be denoted by $\bar{d}$, and s_d, respectively. Thus

$$\bar{d} = \sum_{j=1}^{n} d_j/n,$$

and

$$s_d = \left[\sum_{j=1}^{n} (d_j - \bar{d})^2/(n - 1) \right]^{1/2} .$$

Now $\bar{d}$ is an estimate of the bias in the measurements (i.e., relative to the audited value). Assuming the audited data to be unbiased, the existence of a bias in the field data can be checked by the appropriate t-test, i.e.,

$$t = \frac{\bar{d} - 0}{s_d/\sqrt{n}} \quad .$$

See ref. 20 for a discussion of the t-test.

If t is significantly large, say greater in absolute value than the tabulated value of t within n - 1 degrees of freedom, which is exceeded by chance only 5 percent of the time, then the bias is considered to be real, and some check should be made for a possible cause of the bias. If t is not significantly large, then the bias should be considered zero, and the accuracy of the data is acceptable.

The standard deviation s_d is a function of both the standard deviation of the field measurements and of the audit measurements. Assuming the audit values to be more accurate than the field measurements, then s_d values are an estimate of $\sigma\{SO_2\}$ and $\sigma\{H_2SO_4\}$, the population standard deviations for SO_2 and H_2SO_4 concentration measurements. The estimated standard deviations, s_d, may be directly checked against assumed values of $\sigma\{SO_2\}$ and $\sigma\{H_2SO_4\}$, by using the statistical test procedure

$$\frac{\chi^2}{f} = \frac{s_d^2}{\sigma^2_{\{SO_2\}}}^{*}$$

where χ^2/f is the value of a random variable having the chi-square distribution with f = n - 1 degrees of freedom. If χ^2/f is larger than the tabulated value exceeded only 5 percent of the time, then it would be concluded that the test procedure is yielding more variable results due to faulty equipment or operational procedure.

The measured values should be reported along with the estimated biases, standard deviations, the number of audits, n, and the total number of field tests, N, sampled ($n \leq N$). Estimates, i.e., s_d and $\bar{d}$ which are significantly

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*From this point the analysis is carried out for SO_2 only. An analysis for acid mist would be done in a similar fashion. It would be unduly repetitive to do both analyses in this document.

different from the assumed population parameters, should be identified on the data sheet.

The t-test and χ^2-test described above and in further detail in the final report on this contract, are used to check on the biases and standard deviations separately. In order to check on the overall data quality as measured by the percent of measurement deviations outside prescribed limits, it is necessary to use the approach described in subsection 4.4.2 below.

4.4.2 Sampling by Variables.

Because the lot size (i.e., the number of field tests performed by a team or laboratory during a particular time period, normally a calendar quarter) is small, N = 20, and because the sample size is, consequently, small (of the order of n = 3 to 8), it is important to consider a sampling by variables approach to assess the data quality with respect to prescribed limits. That is, it is desirable to make as much use of the data as possible. In the variables approach, the means and standard deviations of the sample of n audits are used in making a decision concerning the data quality.

Some background concerning the assumptions and the methodology is repeated below for convenience. However, one is referred to one of a number of publications having information on sampling by variables; e.g., see refs. 20-26. The discussion below will be given in regard to the specific problem in the variables approach, which has some unique features as compared with the usual variable sampling plans. In the following discussion, it is assumed that only SO_2 measurements are audited as directed in section 4.3. The difference between the team-measured and audited values of SO_2 is designated as d_j, and the mean difference over n audits by $\bar{d}$ is

$$\bar{d} = 1/n \sum_{j=1}^{n} (SO_2)_j - (SO_2)_{aj} .$$

Theoretically, (SO_2) and $(SO_2)_a$ should be measures of the same SO_2 concentration and their difference should have a mean zero on the average. In addition, this difference should have a standard deviation equal to that associated with the measurements of SO_2.

Assuming three standard deviation limits, the values $3\sigma = -12.0$ mg/m^3* and +12.0 mg/m^3 define the respective lower and upper limits, L and U, outside of which it is desired to control the proportion of differences, d_j. Following the method given in ref. 24, a procedure for applying the variables sampling plan is described below. Figures 9 and 10 illustrate examples of satisfactory and unsatisfactory data quality with respect to the prescribed limits L and U.

The variables sampling plan requires the following information: the sample mean difference, $\bar{d}$, the standard deviation of these differences, s_d, and a constant, k, which is determined by the value of p, the proportion of the differences outside the limits of L and U. For example, if it is desired to control at 0.10 the probability of not detecting lots with data qualities p equal to 0.10 (or 10 percent of the individual differences outside L and U), and if the sample size n = 7, then the value of k can be obtained from table 2 of ref. 24. The values of $\bar{d}$ and s_d are computed in the usual manner; see table 8 for formulas and a specific example. Given the above information, the test procedure is applied, and subsequent action is taken in accordance with the following criteria:

1. If <u>both</u> of the following conditions are satisfied,

$$\bar{d} - k\, s_d \geq L = -12 \text{ mg/m}^3$$

$$d + k\, s_d \leq U = +12 \text{ mg/m}^3$$

   the individual differences are considered to be consistent with the prescribed data quality limits, and no corrective action is required.

2. If one or both of these inequalities is violated, possible deficiencies exist in the measurement process as carried out for that particular lot (group) of field tests. These deficiencies should be identified and corrected before future field tests are performed. Data corrections should be made when possible, i.e., if a quantitative basis is determined for correction.

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*12.0 mg/m^3 assumes, for calculation purposes, an SO_2 concentration mean of 100 mg/m^3, with $\sigma = 4.0$ mg/m^3, so that $3\sigma = 12.0$ mg/m^3.

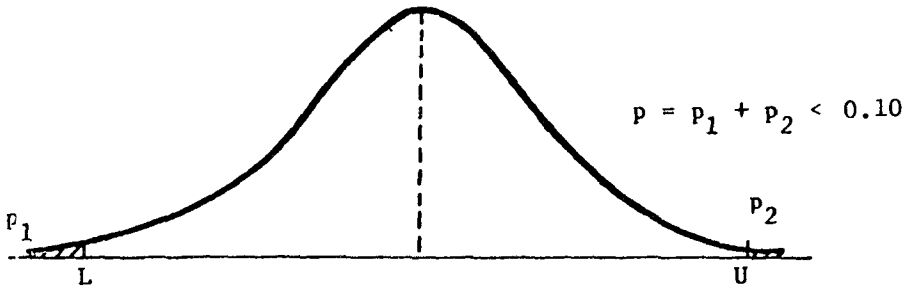


Figure 8. Example illustrating $p < 0.10$ and satisfactory data quality.

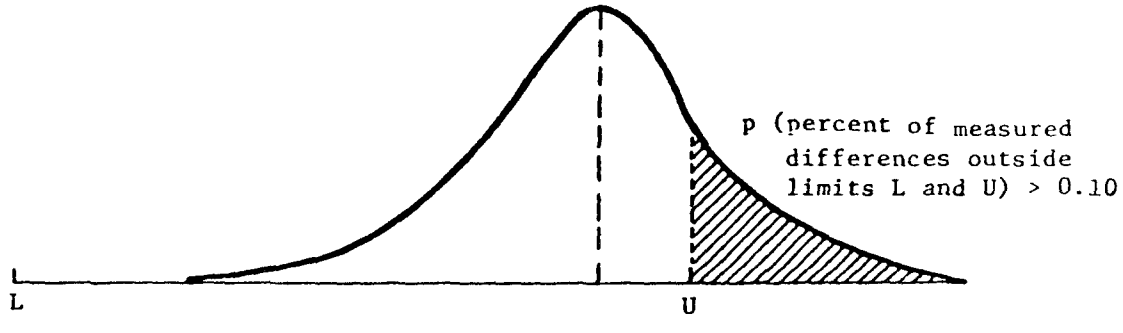


Figure 9. Example illustrating $p > 0.10$ and unsatisfactory data quality.

Table 8. Computation of mean difference, $\bar{d}$, and standard deviation of differences, s_d

General Formulas		Specific Example	
$d = (SO_2)_j - (SO_2)_{aj}$		Data mg/m^3	
d_1	d_1^2	-12.0	144
d_2	d_2^2	6.0	36
d_3	d_3^2	0.0	0
d_4	d_4^2	20.0	400
d_5	d_5^2	17.4	302.8
d_6	d_6^2	8.1	65.6
d_7	d_7^2	0.0	0
Σd_j	Σd_j^2	39.5	948
$\bar{d} = \frac{\Sigma d_j}{n}$		$\bar{d} = 5.6\ mg/m^3$	
$s_d^2 = \frac{\Sigma d_j^2 - \frac{(\Sigma d_j)^2}{n}}{(n-1)}$		$s_d^2 = 135$	
$s_d = \sqrt{s_d^2}$		$s_d = 11.6\ mg/m^3$	

Table 9 contains a few selected values of n, p, and k for convenient reference. Using the values of $\bar{d}$ and s_d in table 2, k = 2.334 for a sample size of n = 7, and p = 0.10, the test criteria become

$$\bar{d} - k\ s_d = 5.6 - 2.334 \times 11.6 = -21.5 < L = -12\ mg/m^3.$$
$$\bar{d} + k\ s_d = 5.6 + 2.334 \times 11.6 = 32.7 > U = +12\ mg/m^3.$$

Therefore, both conditions are violated and the lot of N = 20 measurements is not consistent with the prescribed quality limits. The plan is designed to aid in detecting lots with 10 percent or more defects (deviations falling outside

Table 9. Sample plan constants, k for P {not detecting a lot with proportion p outside limits L and U} $\leq$ 0.1

Sample Size n	p = 0.2	p = 0.1
3	3.039	4.258
5	1.976	2.742
7	1.721	2.334
10	1.595	2.112
12	1.550	2.045

the designated limits L and U) with a risk of 0.10; that is, on the average, 90 percent of the lots with 10 percent or more defects will be detected by this sampling plan.

4.4.3 Cost Versus Audit Level.

The determination of the audit level (sample size n) to be used in assessing the data quality, with reference to prescribed limits L and U, can be made either: (1) on a statistical basis, by defining acceptable risks for type I and type II errors, knowing or estimating the quality of the incoming data, and specifying the described level of confidence in the reported data; or (2) on a cost basis, as described herein. In this section, cost data associated with the audit procedure are estimated or assumed for the purpose of illustrating a method of approach and identifying which costs should be considered.

A model of the audit process, associated costs, and assumptions made in the determination of the audit level is provided in figure 10. It is assumed that a collection of source emissions tests for N stacks is to be made by a particular firm, and that n measurements ($n \leq N$) are to be audited at a cost, $C_A = b + cn$, where b is a constant independent of n and c is the cost per stack measurement audited. In order to make a specific determination of n, it is also necessary to make some assumptions about the quality of the source emissions data from several firms. For example, it is assumed in this analysis that 50 percent of the data lots are of good quality, i.e., one-half of the firms are adhering to good data quality assurance practice, and that 50 percent of the data lots are of poor quality. Based on the analysis in sections 4.1,

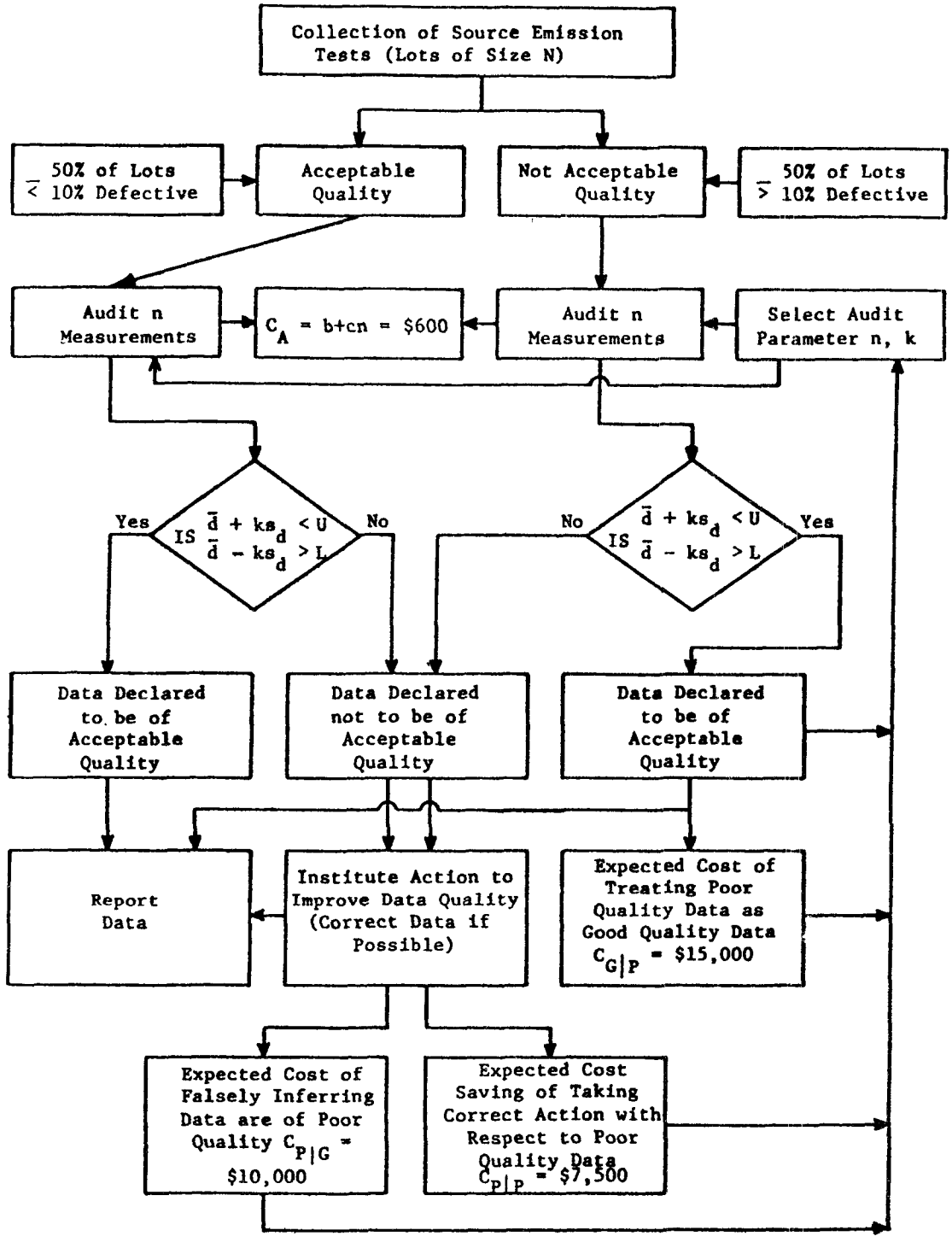


Figure 10. Flow chart of the audit level selection process.

good quality data is defined as that which is consistent with the estimated precision/bias using the reference method. Thus if the data quality limits L and U are taken to be the lower and upper 3σ limits, corresponding to limits used in a control chart, the quality of data provided by firmly adhering to the recommended quality assurance procedures should be such that at most about 0.3 percent defective measurements (i.e., outside the limits defined by L and U) are made. Herein, good quality data is defined as that containing at most 10 percent defective measurements. The definition of poor quality data is somewhat arbitrary; for this illustration it is taken as 25 percent outside L and U.

In this audit procedure, the data are declared to be of acceptable quality if both of the following inequalities are satisfied:

$$\bar{d} + ks_d < U$$

$$\bar{d} - ks_d > L$$

where $\bar{d}$ and s_d are the mean and standard deviation of the data quality characteristic (i.e., the difference of the field and audited measurements) being checked. The data are not of desired quality if one or both inequalities are violated, as described in section 4.3. The costs associated with these actions are assumed to be as follows:

C_A = Audit cost = b + cn. It is assumed that b is zero for this example, and c is taken as \$600/measurement.

$C_{P|G}$ = Cost of falsely inferring that the data are of poor quality, P, <u>given</u> that the data are of good quality, G. This cost is assumed to be one-half the cost of collecting emissions data for N = 20 stacks (i.e., 0.5 x \$1,000 x 20 = \$10,000). It would include the costs of searching for an assignable cause of the inferred data deficiency when none exists, of partial repetition of data collection, and of decisions resulting in the purchase of equipment to reduce emission levels of specific pollutants, etc.

$C_{G|P}$ = Cost of falsely stating that the data are of good quality, G, <u>given</u> that they are of poor quality, P. This cost is assumed to be \$15,000 (= 0.75 x \$1,000 x 20), and is associated with health effects, litigation, etc.

$C_{P|P}$ = Cost savings resulting from correct identification of poor quality data. This cost is taken to be \$7,500, i.e., equal to one-half of $C_{P|G}$ or equal to 0.375 x \$1,000 x 20, the total cost of data collection.

These costs are given in figure 11. The cost data are then used in conjunction with the a priori information concerning the data quality, to select an audit level n. Actually, the audit procedure requires the selection of the limits L and U, n, and k. L and U are determined on the basis of the analysis of section 4.1. The value of k is taken to be the value associated with n in table 9 of section 4.4.2, i.e., the value selected on a statistical basis to control the percentage of data outside the limits L and U. Thus, it is only necessary to vary n and determine the corresponding expected total cost E(TC) using the following cost model

$$E(TC) = -C_A - 0.5\ P_{P|G}\ C_{P|G} + 0.5\ P_{P|P}\ C_{P|P} - 0.5\ P_{G|P}\ C_{G|P}$$

where the costs are as previously defined. The probabilities are defined in a way similar to defining corresponding costs:

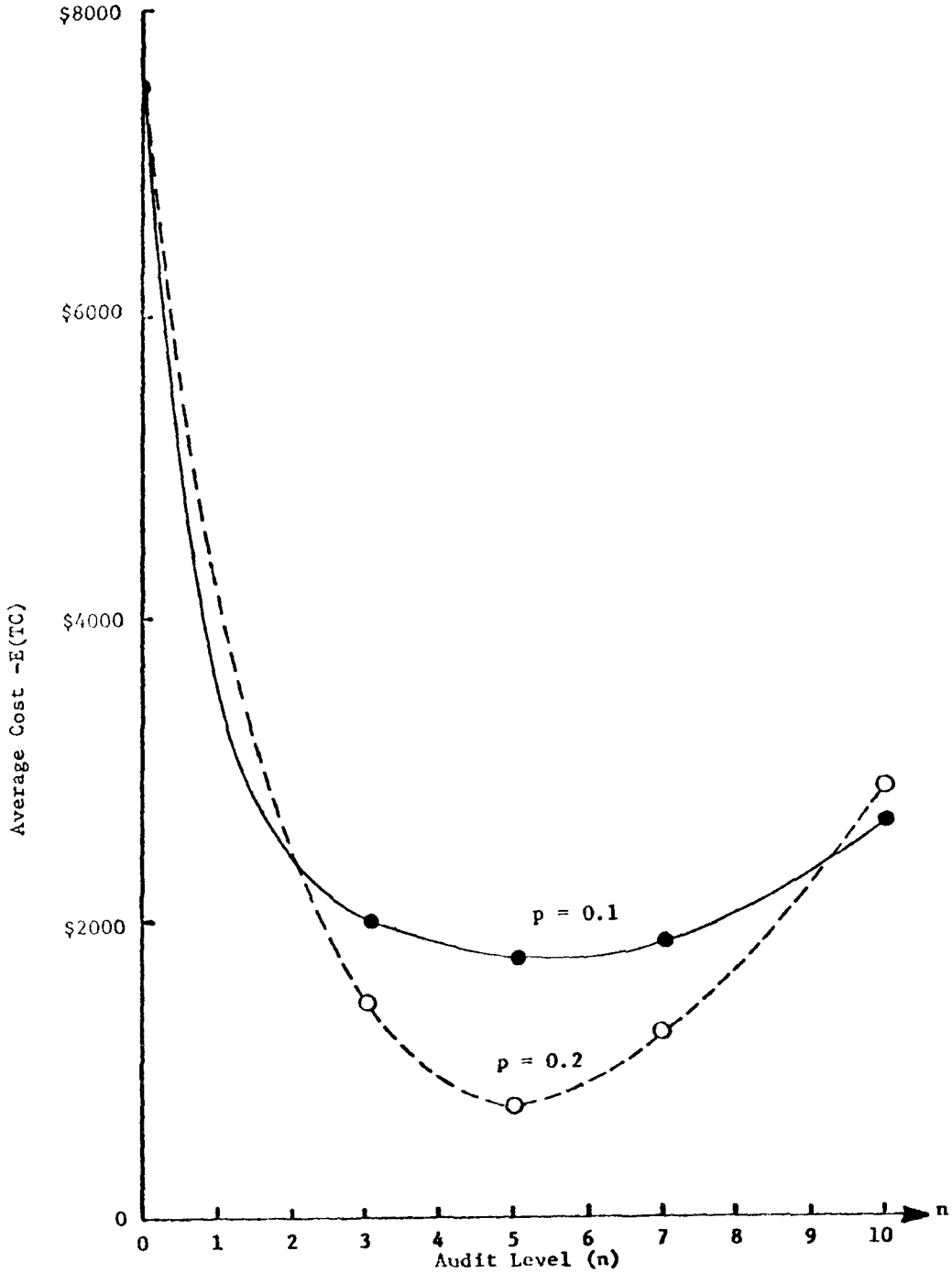
$P_{P|G}$ = Probability that a lot of good quality data is falsely inferred to be of poor quality, due to the random variations in the sample mean $\bar{d}$ and standard deviation, s_d, in small samples of size n.

$P_{P|P}$ = Probability that a lot of poor quality data is correctly identified as being of poor quality.

$P_{G|P}$ = Probability that a lot of poor quality data is incorrectly judged to be of good quality, due to sampling variations of $\bar{d}$ and s.

These three probabilities are conditional on the presumed lot quality and are preceded by a factor of 0.5 in the total cost model, to correspond to the assumed precentage of good (poor) quality data lots.

In order to complete the determination of n, it is necessary to calculate each of the conditional probabilities, using the assumptions stated for a series of values of n (and associated k, which is given in table 5). The computational procedure is given in the final report of this contract. These calculations were made for the cases n = 3, 5, 7, and 10 and for two degrees of control on the quality of the data that can be tolerated, i.e., p = 0.2 and p = 0.1, the portion outside the limits L and U for which it is desired to accept the data



[p = Proportion defective measurements in the "lot"
P{Acc. lot with p} $\leq$ 0.1]

Figure 11. Average cost versus audit level (n).

as good quality, with probability less than or equal to 0.10. These computed probabilities are then used in conjunction with the costs associated with each condition, applying the cost model equation above to obtain the average cost versus sample size n for the two cases $p = 0.1$ and 0.2. The curves obtained from these results are given in figure 11. It can be seen from these curves that the minimum cost is obtained by using $n \simeq 5$ independent of p. However, it must be recognized that the costs used in the example are for illustrative purposes and may vary from one region to another; thus, within the reasonable uncertainty of the estimated costs, it is suggested that $p = 0.2$ is more cost effective; this tends to permit data of poorer quality to be accepted.

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APPENDIX A 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 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) in the absence of other particulate matter and sulfur dioxide from stationary sources only when specified by the test procedures for determining compliance with the new source performance standards. Collaborative tests have shown that the minimum detectible limits of the method are 0.05 mg/m^3 (0.03×10^{-7} lb/ft^3) for sulfur trioxide and 1.2 mg/m^3 (0.74×10^{-7} lb/ft^3) for sulfur dioxide. No upper limits have been established.

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 heating of the filter holder is not required. Commercial models of this train are available. However, if one desires to build his own, complete construction details are described in APTD-0581; for changes from the APTD-0581 document and for allowable modifications to figure 8-1, see 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--Stainless steel (316) with sharp, tapered leading edge. The angle of taper shall be < 30° and the taper shall be on the outside to preserve a constant internal diameter. The probe nozzle shall be of the buttonhook or elbow design, unless otherwise specified by the administrator. The wall thickness of the nozzle shall be less than or equal to that of a 20-

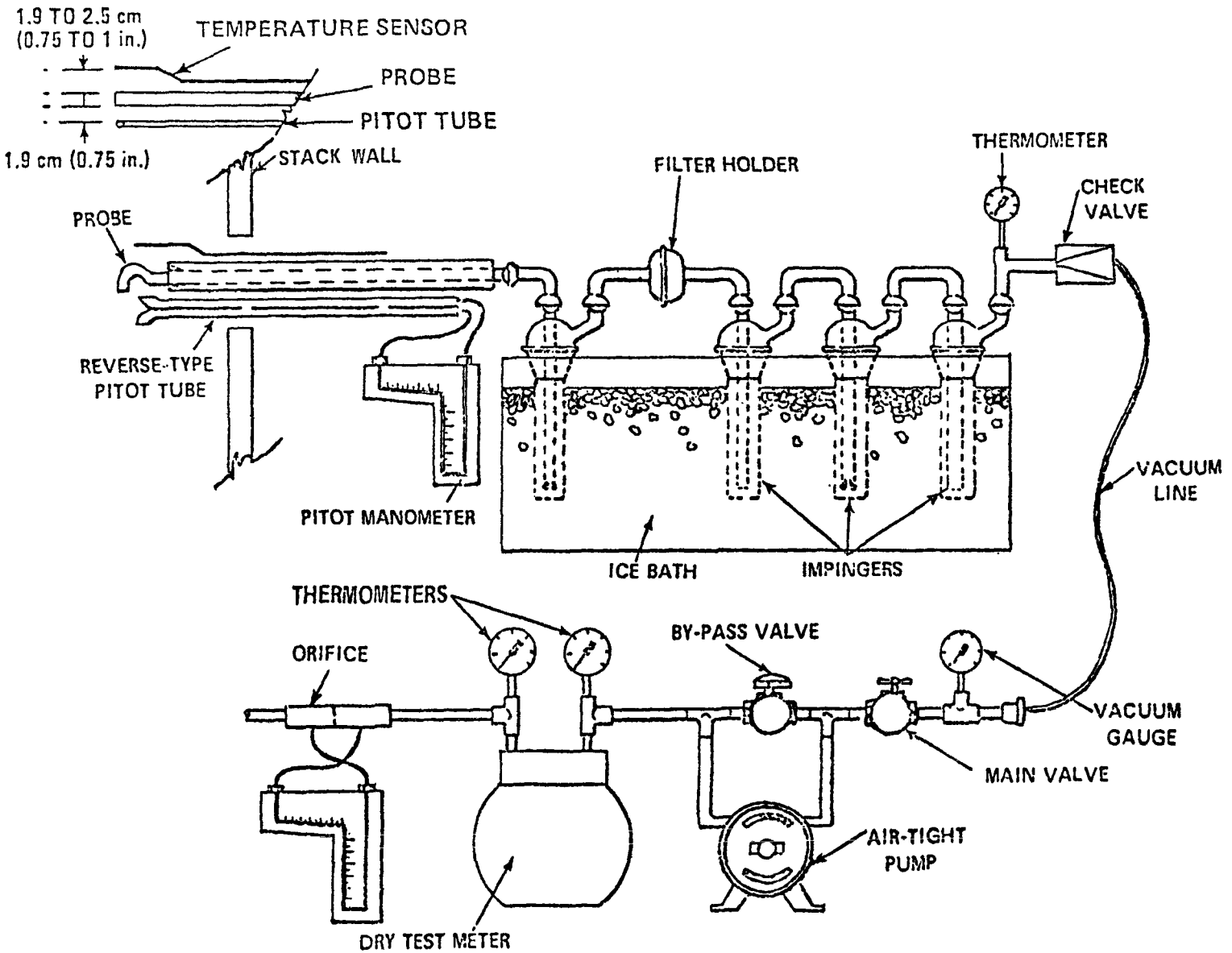


Figure 8-1. Sulfuric acid mist sampling train.

gauge tubing, i.e., 0.165 cm (0.065 in.) and the distance from the tip of the nozzle to the first bend or point of disturbance shall be at least two times the outside nozzle diameter. The nozzle shall be constructed from seamless stainless steel tubing. Other configurations and construction material may be used with approval from the Administrator.

A range of sizes suitable for isokinetic sampling should be available, e.g., 0.32 cm (1/8 in.) up to 1.27 cm (1/2 in. or larger if higher volume sampling trains are used) inside diameter (ID) nozzles in increments of 0.16 cm (1/16 in.). Each nozzle shall be calibrated according to the procedures outlined in the calibration section.

2.1.2 Probe liner--Porosilicate or quartz glass, with a heating system to prevent visible condensation during sampling.

2.1.3 Pitot tube--Type S, or other device approved by the administrator, attached to probe to allow constant monitoring of the stack gas velocity. The face openings of the pitot tube and the probe nozzle shall be adjacent and parallel to each other, not necessarily on the same plane, during sampling. The free space between the nozzle and pitot tube shall be at least 1.9 cm (0.75 in.). The free space shall be set based on a 1.3-cm (0.5-in.) ID nozzle. If the sampling train is designed for sampling at higher flow rates than that described in APTD-0581, thus necessitating the use of larger sized nozzles, the largest sized nozzle shall be used to set the free space.

The pitot tube must also meet the criteria specified in Method 2 and calibrated according to the procedure in the calibration section of that method.

2.1.4 Differential pressure gauge--Inclined manometer capable of measuring velocity head to within 10 percent of the minimum measured value. Below a differential pressure of 1.3 mm (0.05 in.) water gauge, micromanometers with sensitivities of 0.013 mm (0.0005 in.) should be used. However, micromanometers are not earily adaptable to field conditions and are not easy to use with pulsating flow. Thus, methods or other devices acceptable to the administrator may be used when conditions warrant.

2.1.5 Filger holder--Borosilicate glass with a glass frit filter support and a silicone rubber gasket. Other materials of construction may be used with approval from the administrator. The holder design shall provide a positive seal against leakage from the outside or around the filter.

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-mm (0.5-in.) ID glass tube, having an unconstricted 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--Vacuum gauge, leak-free pump, thermometers capable of measuring temperature to within 3° C (5.4° F), dry gas meter with 2 percent accuracy, and related equipment, or equivalent, as required to maintain an isokinetic sampling rate and to determine sample volume. When the metering system is used in conjunction with a pitot tube, the system shall enable checks of isokinetic rates.

2.1.8 Barometer--Mercury, aneroid, or other barometers capable of measuring atmospheric pressure to within 2.5 mmHg (0.1 in. Hg). In many cases, the barometric reading may be obtained from a nearby weather bureau station, in which the station value shall be requested and an adjustment for elevation differences shall be applied at a rate of minus 2.5 mmHg (0.1 in. Hg) per 30 m (100 ft) elevation increase.

2.1.9 Temperature gauge--Thermometer, or equivalent, to measure temperature of gas leaving impinger train to within 3° C (5° F).

2.2 Sample recovery.

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

2.2.2 Graduated cylinders--250 mℓ, 1 ℓ. (Volumetric flasks may also be used.)

2.2.3 Storage bottles--Leak-free polyethylene bottles, 1,000-mℓ size (two for each sampling run).

2.3 Analysis.

2.3.1 Pipette--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--300-g capacity, to measure to ± 0.5 g.

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

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 best available grade.

3.1 Sampling.

3.1.1 Filters--Glass fiber filters, without organic binder exhibiting at least 99.95 percent efficiency ($\leq$ 0.05 percent penetration) on 0.3 micron dioctyl phthalate smoke particles. The filter efficiency test shall be conducted in accordance with ASTM standard method D 2986-71. Test data from the supplier's quality control program is sufficient for this purpose.

3.1.2 Silica gel--Indicating type, 6-16 mesh. If previously used, dry at 175° C (350° F) for 2 hours. New silica gel may be used as received.

3.1.3 Water--Deionized, distilled, to conform to ASTM specifications D1193-72, type 3.

3.1.4 Isopropanol, 80%--Mix 800 mℓ of isopropanol with 200 mℓ of deionized distilled water. Note: Experience has shown that only ACS-grade isopropanol is satisfactory.

3.1.5 Hydrogen peroxide, 3%--Dilute 100 mℓ of 30 percent hydrogen peroxide to 1 ℓ with deionized, distilled water. Prepare fresh daily.

3.1.6 Crushed ice.

3.2 Sample recovery.

3.2.1 Water--Deionized, distilled, to conform to ASTM specifications D1193-72, type 3.

3.2.2 Isopropanol, 80%--Mix 800 mℓ of isopropanol with 200 mℓ of deionized distilled water. Note: Experience has shown that only ACS-grade isopropanol is satisfactory.

3.3 Analysis.

3.3.1 Water--Deionized, distilled, to conform to ASTM specifications D1193-72, type 3.

3.3.2 Isopropanol, 100%.

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 (0.01 N)--Dissolve 1.95 g of barium perchlorate trihydrate ($Ba(ClO_4)_2 \cdot 3H_2O$) in 200 mℓ deionized distilled water and dilute to 1 ℓ with isopropanol. Standardize with sulfuric acid as in section 5.2. This solution must be protected against evaporation at all times. ($BaCl_2$ may also be used.)

3.3.5 Sulfuric acid standard (0.01 N)--Purchase or standardize to ± 0.0002 N against 0.01 N NaOH which 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, except that the filter need not be weighed or identified. If the effluent gas is considered to be 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 use figure 8-1 instead of figure 5-1. Replace the second paragraph with: Place 100 mℓ of 80% isopropanol in the first impinger, 100 mℓ of 3% hydrogen peroxide in both the second and third impingers, and about 200 g of silica gel in the fourth impinger. Retain a portion of the reagents for use as blank solutions.

4.1.4 Leak-check procedure--Follow the procedure outlined in Method 5, section 4.1.4, except that the probe heater shall be adjusted to the minimum temperature required to prevent condensation.

4.1.5 Train operation--Follow the procedure outlined in Method 5, section 4.1.5, except record the data required on the example sheet shown in figure 8-2. During the sampling period, observe the line between the probe and the first impinger for signs of condensation. If it occurs, adjust the probe heater setting upward to the minimum temperature required to prevent condensation. After turning off the pump and recording the final readings at the conclusion of each run, remove the probe from the stack and disconnect it from the train. 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 average flow rate used for

sampling. Note: Clean ambient air can be provided by passing air through a charcoal filter.

4.2 Sample recovery.

4.2.1 Container No. 1--Transfer the contents of the first impinger to a 250-mℓ graduated cylinder. Rinse the probe, first impinger, and all connecting glassware before the filter with 80% isopropanol. Add the rinse solution to the cylinder. Dilute to 250 mℓ with 80% 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 container and identify the sample container.

4.2.2 Container No. 2--Transfer the solutions from the second and third impingers to a 1,000 mℓ graduated cylinder. Rinse all glassware between the filter and silica gel impinger with deionized, distilled water and add this rinse water to the cylinder. Dilute to a volume of 1,000 mℓ with deionized, distilled water. Transfer the solution to a storage container. Mark the level of liquid on container. Seal and identify the sample container.

4.3 Analysis.

Note level of liquid in containers 1 and 2 and confirm whether or not any sample was lost during shipment by noting this on analytical data sheet.

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 thorin indicator, and titrate to a pink endpoint using 0.01 N barium perchlorate. Repeat the titration with a second aliquot of sample and average the titration values. Replicate titrations should agree within 1 percent.

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 thorin indicator, and titrate to a pink endpoint using 0.01 N barium perchlorate. Repeat the titration with a second aliquot of sample and average the titration values. Replicate titrations should agree within 1 percent.

4.3.3 Blanks--Prepare blanks by adding 2 to 4 drops of thorin indicator to 100 mℓ of 80% isopropanol. Titrate the blanks in the same manner as the samples.

5. Calibration

5.1 Use methods and equipment as specified in Methods 2 and 5 and APTD-0576 to calibrate the orifice meter, pitot tube, dry gas meter, thermometers, and barometer.

5.2 Standardize the barium perchlorate solution with 25 mℓ of standard sulfuric acid, to which 100 mℓ of isopropanol have 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^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 barium perchlorate titrant, g equiv./liter

P_{bar} = Barometric pressure at the sampling site, mmHg (in. Hg)

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

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

T_m = Absolute average dry gas meter temperature (see figure 8-2), °K (°R)

T_s = Absolute average stack gas temperature (see figure 8-2), °K (°R)

T_{std} = Standard absolute temperature, 293° K (528° 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 (see figure 8-2), mℓ

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

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 _____

TRAVERSE POINT NUMBER	SAMPLING TIME (θ), min.	STATIC PRESSURE (P_S), mm Hg (in Hg)	STACK TEMPERATURE (T_S) °C (°F)	VELOCITY HEAD (ΔP_S),	PRESSURE DIFFERENTIAL ACROSS ORIFICE METER mm H_2O (in. H_2O)	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.

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_s = Stack gas velocity, calculated by Method 2, equation 2-7, 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 and 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.

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 mmHg or 68° F and 29.92 in. Hg) by using equation 8-1.

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

Equation 8-1

where:

K = 0.3855 °K/mmHg for metric units

= 17.65 °R/in. Hg for English units.

6.4 Volume of water vapor and moisture content. Use equations 5-2 and 5-3 of Method 5. If the effluent gas is considered to be dry, these calculations need not be carried out.

6.5 Sulfuric acid (including SO_3) concentration.

$$C_{H_2SO_4} = \frac{N (V_t - V_{tb}) \frac{V_{soln}}{V_a}}{V_{m(std)}}$$

Equation 8-2

where:

$K = 0.04904$ g/equivalent for metric units

$= 1.08 \times 10^{-4} \quad \frac{(lb)(\ell)}{(g)(m\ell)}$ for English units.

6.6 Sulfur dioxide concentration.

$$C_{SO_2} = K \frac{N\,(V_t - V_{tb})\,\frac{V_{soln}}{V_a}}{V_{m(std)}} \qquad \text{Equation 8-3}$$

where:

$K = 0.03203$ g/equivalent for metric units

$= 7.05 \times 10^{-5} \quad \frac{(lb)(\ell)}{(g)(m\ell)}$ for English units.

6.7 Isokinetic variation.

6.7.1 Calculations from raw data.

$$I = \frac{100\ T_s\ [K\ V_{lc} + (V_m/T_m)\ (P_{bar} + \Delta H/13.6)]}{60\ \Theta\ v_s\ P_s\ A_n}$$

Equation 8-4

where:

$K = 0.00346$ mmHg-m^3/ml-°K for metric units

$= 0.00267$ in. Hg-ft^3/mℓ-°R for English units

6.7.2 Calculations from intermediate values.

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

$$= K\ \frac{T_s\ V_{m(std)}}{P_s\ v_s\ A_n\ \Theta\ (1-B_{ws})} \qquad \text{Equation 8-5}$$

where:

$K = 4.323$ for metric units

$= 0.0944$ for English units.

6.8 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 option to accept the results. Use reference 7.4 of Method 5 to make judgments. Otherwise, reject the results and repeat the test.

7. References

7.1 Atmospheric Emissions from Sulfuric Acid Manufacturing Processer, U.S. DHEW, PHS, Division of Air Pollution, Public Health Service Publication No. 999-AP-13, Cincinnati, Ohio, 1965.

7.2 Corbett, D. F., "The Determination of SO_2 and SO_3 in Flue Gases," Journal of the Institute of Fuel, 24; 237-243, 1961.

7.3 Martin, Robert M., "Construction Details of Isokinetic Source Sampling Equipment," Environmental Protection Agency, Air Pollution Control Office Publication No. APTD-0581.

7.4 Patton, W. F., and Brink, Jr., J. A., New Equipment and Techniques for Sampling Chemical Process Gases, J. Air Pollution Control Assoc. 13, 162 (1963).

7.5 Rom, J. J., "Maintenance, Calibration, and Operation of Isokinetic Source-Sampling Equipment," Office of Air Programs, Environmental Protection Agency, Research Triangle Park, N.C., March 1972. APTD-0576.

7.6 Hamil, H. F., and Camann, D. E., Collaborative Study of Method for the Determination of Sulfur Dioxide Emissions from Stationary Sources. Prepared for Methods Standardization Branch, Quality Assurance and Environmental Monitoring Laboratory, National Environmental Research Center, Environmental Protection Agency, Research Triangle Park, N.C., 27709.

7.7 Annual Book of ASTM Standards. Part 23; Water, Atmospheric Analysis. pp. 203-205. American Society for Testing Materials, Philadelphia, Penn. (1972

APPENDIX B ILLUSTRATED AUDIT PROCEDURES AND CALCULATIONS

A flow chart of the operations involved in an auditing program, from first setting desired limits on the data quality to filing the results, is given in the following pages. Assumed numbers are used and a sample calculation of an audit is performed in the flow chart. Each operation has references to the section in the text of the report where it is discussed.

MANAGER

1. LIMITS FOR DATA QUALITY CAN BE SET BY WHAT IS DESIRED OR FROM THE NATURAL VARIABILITY OF THE METHOD WHEN USED BY TRAINED AND COMPETENT PERSONNEL. FOR THIS EXAMPLE, IT IS ASSUMED THAT $\sigma\{SO_2\} = 4.0$ mg/m^3 (subsec. 4.1)*, AND USING $\pm 3\,\sigma\{SO_2\}$, THE LIMITS ARE L = 12.0 mg/m^3 AND U = +12.0 mg/m^3.

2. FROM PRIOR KNOWLEDGE OF DATA QUALITY, ESTIMATE THE PERCENTAGE OF FIELD MEASUREMENTS FALLING OUTSIDE THE ABOVE LIMITS. IF NO INFORMATION IS AVAILABLE, MAKE AN EDUCATED GUESS. IT IS ASSUMED IN THIS EXAMPLE THAT 50 PERCENT OF THE FIELD DATA ARE OUTSIDE THE LIMITS L AND U (subsec. 4.4.3).

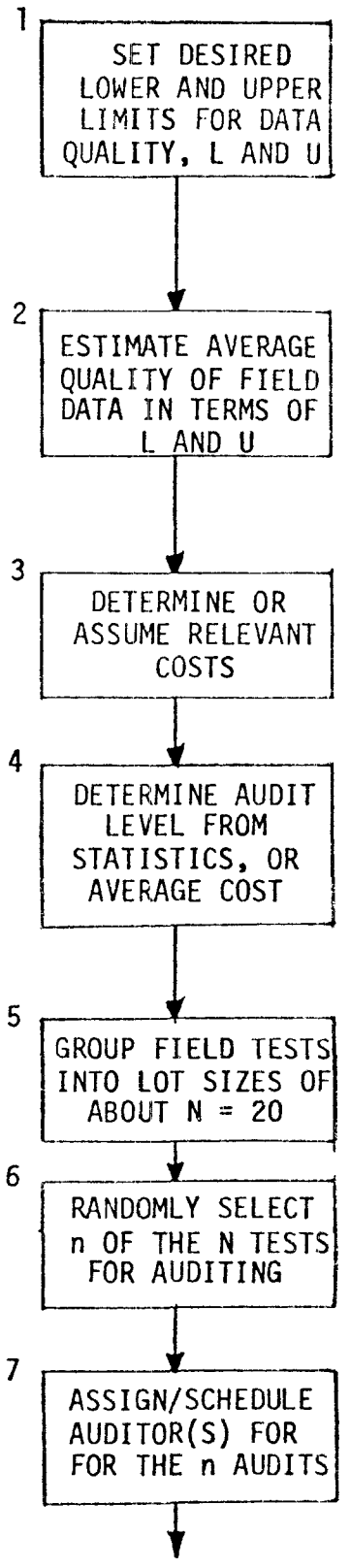
3. DETERMINE: (1) COST OF CONDUCTING AN AUDIT, (2) COST OF FALSELY INFERRING THAT GOOD DATA ARE BAD, (3) COST OF FALSELY INFERRING THAT BAD DATA ARE GOOD, AND (4) COST SAVINGS FOR CORRECTLY IDENTIFYING BAD DATA (subsec. 4.4.3).

4. DETERMINE THE AUDIT LEVEL EITHER BY (1) MINIMIZING AVERAGE COST USING EQUATION (22) OF SUBSECTION 4.4.3, OR (2) ASSURING A DESIRED LEVEL OF CONFIDENCE IN THE REPORTED DATA THROUGH STATISTICS. FOR THIS EXAMPLE, THE AUDIT LEVEL IS TAKEN AS n = 7.

5. BY TEAMS, TYPES OF SOURCES, OR GEOGRAPHY, GROUP FIELD TESTS INTO LOTS (GROUPS) OF ABOUT 20 THAT WILL BE PERFORMED IN A PERIOD OF ONE CALENDAR QUARTER.

6. SELECT n OF THE N TESTS FOR AUDITING. COMPLETE RANDOMIZATION MAY NOT BE POSSIBLE DUE TO AUDITOR'S SCHEDULE. THE PRIMARY POINT IS THAT THE FIELD TEAM SHOULD NOT KNOW IN ADVANCE THAT THEIR TEST IS TO BE AUDITED.

7. ASSIGN OR SCHEDULE AN AUDITOR FOR EACH FIELD TEST.



*Based on a 100 mg/m^3 sample mean and $\sigma = 4.0$ mg/m^3.

AUDITOR

8. THE AUDITOR OBTAINS APPROPRIATE CALIBRATED EQUIPMENT AND SUPPLIES FOR THE AUDIT (subsection 4.3).

9. OBSERVE THE FIELD TEAM'S PERFORMANCE OF THE FIELD TEST (subsection 4.3.2 AND 4.3.3) AND NOTE ANY UNUSUAL CONDITIONS THAT OCCURRED DURING THE TEST.

10. THE AUDITOR'S REPORT SHOULD INCLUDE (1) DATA SHEET FILLED OUT BY THE FIELD TEAM, (2) AUDITOR'S COMMENTS, (3) AUDIT DATA SHEET WITH CALCULATIONS, AND (4) A SUMMARY OF THE TEAM'S PERFORMANCE WITH A NUMERICAL RATING (subsection 4.3.4).

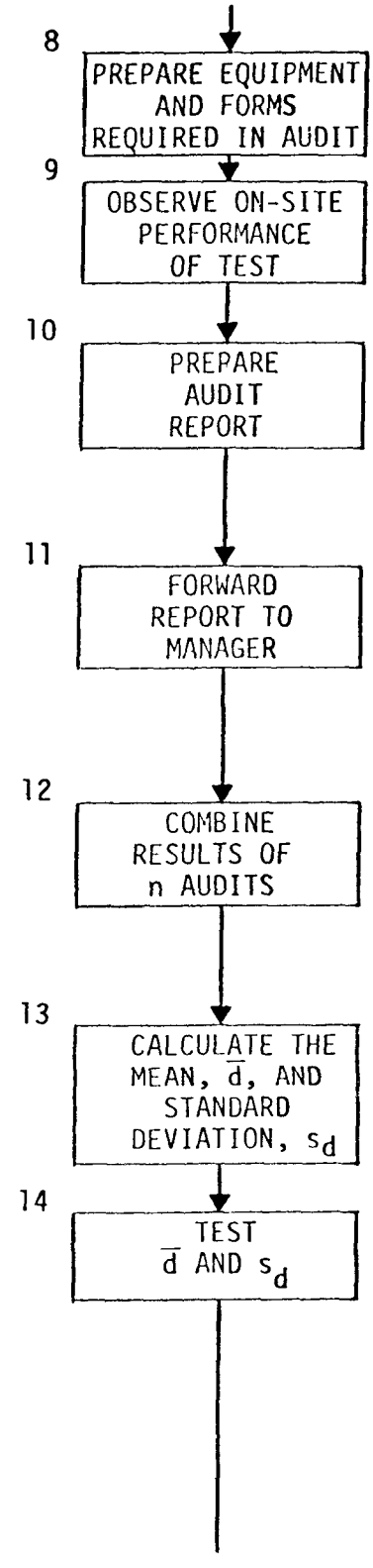
11. THE AUDITOR'S REPORT IS FORWARDED TO THE MANAGER.

MANAGER

12. COLLECT THE AUDITOR'S REPORTS FROM THE n AUDITS OF THE LOT OF N STACKS. IN THIS CASE n = 7 AND ASSUMED VALUES FOR THE AUDITS ARE $d_1 = -12$, $d_2 = 6$, $d_3 = 0$, $d_4 = 20$, $d_5 = 17.4$, $d_6 = 8.1$, and $d_7 = 0$ (table 8).

13. CALCULATE $\bar{d}$ AND s_d ACCORDING TO THE SAMPLE IN TABLE 8. RESULTS OF THIS SAMPLE CALCULATION SHOW $\bar{d} = 5.6$ and $s_d = 11.6$ (table 8, subsection 4.4.2).

14. USE A t-TEST TO CHECK $\bar{d}$ FOR SIGNIFICANCE, FOR THIS EXAMPLE $t = (5.6 \times \sqrt{7})/4.0 = 3.70$. THE TABULATED t-VALUE FOR 6 DEGREES OF FREEDOM AT THE 0.05 LEVEL OS 1.943; HENCE, $\bar{d}$ IS SIGNIFICANTLY DIFFERENT FROM 0 AT THIS LEVEL. ALSO, s_d IS CHECKED AGAINST THE ASSUMED VALUE OF 4.00 mg/m^3 BY A CHI-SQUARE TEST.
$\chi^2/f = s_d^2/\sigma^2\{\bar{d}\} = (11.6)^2/(4.00)^2 = 8.4$, THE TABULATED VALUE OF $\chi^2/6$ AT THE 95 PERCENT LEVEL IS 1.64; HENCE, s_d IS SIGNIFICANTLY DIFFERENT FROM 4.0 mg/m^3.



15. OBTAIN THE VALUE OF k FROM TABLE 9, FOR $n = 7$ AND $p = 0.1$. THIS VALUE IS 2.334, THEN $\bar{d} + k\ s_d = 32.7\ mg/m^3$ AND $\bar{d} - k\ s_d = -21.5\ mg/m^3$ (subsection 4.4.2).

16. COMPARE THE ABOVE CALCULATIONS WITH LIMITS L AND U (subsec. 4.4.2). FOR THIS EXAMPLE

$$\bar{d} + k\ s_d = 32.7 > U = 12.0\ mg/m^3$$

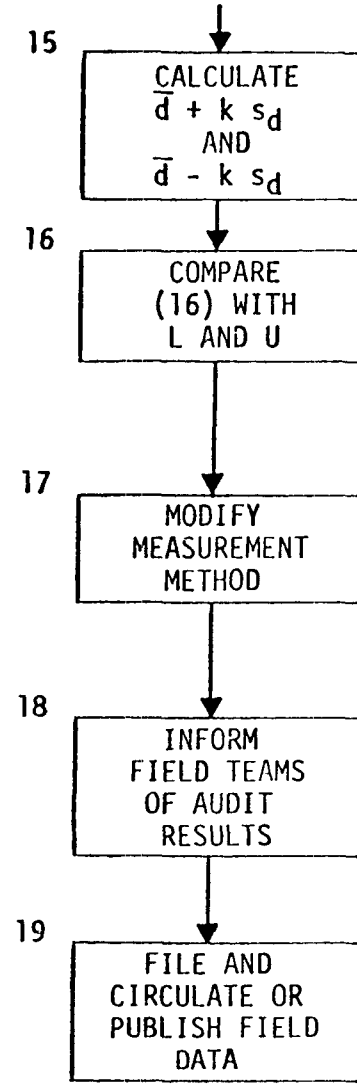
$$\bar{d} - k\ s_d = -21.5 < L = -12.0\ mg/m^3$$

BOTH CONDITIONS ARE VIOLATED.

17. STUDY THE AUDIT AND FIELD DATA FOR SPECIFIC AREAS OF VARIABILITY, SELECT THE MOST COST-EFFECTIVE ACTION OPTION (S) THAT WILL RESULT IN GOOD QUALITY DATA (subsection 4.2). NOTIFY THE FIELD TEAMS TO IMPLEMENT THE SELECTED ACTION OPTION(S).

18. A COPY OF THE AUDITOR'S REPORT SHOULD BE SENT TO THE RESPECTIVE FIELD TEAM. ALSO, THE DATA ASSESSMENT RESULTS, i.e., CALCULATED VALUES OF $\bar{d}$, s_d, AND COMPARISON WITH THE LIMITS L AND U SHOULD BE FORWARDED TO EACH TEAM INVOLVED IN THE N FIELD TESTS.

19. THE FIELD DATA WITH AUDIT RESULTS ATTACHED ARE FILED. THE AUDIT DATA SHOULD REMAIN WITH THE FIELD DATA FOR ANY FUTURE USES.



APPENDIX C GLOSSARY OF SYMBOLS

This is glossary of symbols as used in this document. Symbols used and defined in the reference method (appendix A) are not repeated here.

SYMBOL	DEFINITION
N	Lot size, i.e., the number of field tests to be treated as a group.
n	Sample size for the quality audit (section IV).
$CV\{X\}$	Assumed or known coefficient of variation ($100\ \sigma_X/\mu_X$).
$\hat{CV}\{X\}$	Computed coefficient of variation ($100\ s_X/\overline{X}$) from a finite sample of measurements.
$\sigma\{X\}$	Assumed standard deviation of the parameter X (population standard deviation).
$\hat{\tau}\{X\}$	Computed bias of the parameter X for a finite sample (sample bias).
d_j	The difference in the audit value and the value arrived at by the field crew for the jth audit.
$\overline{d}$	Mean difference between C_j and C_{aj} for n audits.
s_d	Computed standard deviation of differences between C_j and C_{aj}.
p	Percent of measurements outside specified limits L and U.
k	Constant used in sampling by variables (section IV).
$P\{Y\}$	Probability of event Y occurring.
$t_{(n-1)}$	Statistic used to determine if the sample bias, $\overline{d}$, is significantly different from zero (t-test).
$\chi^2/(n-1)$	Statistic used to determine if the sample variance, s^2, is significantly different from the assumed variance, σ^2, of the parent distribution (chi-square test).

GLOSSARY OF SYMBOLS (CONTINUED)

SYMBOL	DEFINITION
L	Lower quality limit used in sampling by variables.
U	Upper quality limit used in sampling by variables.
CL	Center line of a quality control chart.
LCL	Lower control limit of a quality control chart.
UCL	Upper control limit of a quality control chart.
C	Concentration reported by the field team for field test.
C_a	Concentration used in an audit check.
C_m	Measured value of a calibration sample.
C_t	Assayed or known value of a calibration sample.

APPENDIX D GLOSSARY OF TERMS

The following glossary lists and defines the statistical terms used in this document.

Accuracy	The degree of agreement of a measurement (or an average of measurements of the same thing), X, with an accepted reference or true value, T, usually expressed as the difference between the two values, X - T.
Bias	The systematic or nonrandom component of measurement error. A measure of lack of agreement. If the measured value is compared with an assumed true value, bias is a measure of lack of accuracy.
Lot	A specified number of objects to be treated as a group, e.g., the number of field tests to be conducted by an organization during a specified period of time (usually a calendar quarter).
Measurement method	A set of procedures for making a measurement.
Measurement process	The process of making a measurement, including method, personnel, equipment, and environmental conditions.
Population	The totality of the set of items, units, or measurements, real or conceptual, that is under consideration.
Precision	The degree of variation among successive, independent measurements (e.g., on a homogeneous material) under known conditions, and usually expressed as a standard deviation or as a coefficient of variation.
Quality audit	A management tool for independently assessing data quality.
Quality control check	Checks made by the field and/or laboratory crew on certain items of equipment and procedures to assure data of good quality.
Sample	Objects drawn, usually at random, from the lot for checking or auditing purposes.

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

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16. ABSTRACT

Guidelines for the quality control of stack gas analysis for sulfuric acid mist and sulfur dioxide emissions by the Federal reference method are presented. These include:

1. Good operating practices;
2. Directions on how to assess performance and to qualify data;
3. Directions on how to identify trouble and to improve data quality;
4. Directions to permit design of auditing activities.

The document is not a research report. It is designed for use by operating personnel.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Quality Assurance		13H
Quality Control		14D
Air Pollution		13B
Gas Sampling		14B
Stack Gases		21B

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