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GUIDELINES FOR DEVELOPMENT OF A QUALITY ASSURANCE PROGRAM: VOLUME V - DETERMINATION OF SULFUR DIOXIDE EMISSIONS FROM STATIONARY SOURCES

U.S. Environmental Protection Agency
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GUIDELINES FOR DEVELOPMENT OF A QUALITY ASSURANCE PROGRAM: VOLUME V - DETERMINATION OF SULFUR DIOXIDE EMISSIONS FROM STATIONARY SOURCES

by

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SECTION I INTRODUCTION

This document presents guidelines for developing a quality assurance program for Method 6--Determination of Sulfur Dioxide Emissions from Stationary Sources. This method was initially published by the Environmental Protection Agency in the Federal Register, December 23, 1971, and a later version 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 operations manual sets forth recommended operating procedures to assure 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 intrateam basis and for collecting the information necessary to detect and/or identify trouble.

Section IV, Manual for Manager 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; a methodology for comparing action options for improving data quality and selecting the preferred action; and statistical properties of and procedures for carrying out a quality audit for an independent assessment of data quality.

The objectives of this quality assurance program for Method 6 are to:

1. Minimize systematic errors (biases) and control 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 contribute to the collection of poor quality data, and

4. Collect and supply information necessary to describe the quality of the data.

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.

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 sulfur dioxide emissions 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 error resulting from this component of variation is minimized by knowing the time characteristics of the source output and sampling proportionally. The sampling period should span at least one complete output cycle when possible. If the cycle is too long, either the sample collection should be made during a portion of the cycle average, or multiple samples should be collected and averaged.

Quality assurance guidelines for Method 6 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 will be contained in the final report under this contract.

SECTION II OPERATIONS MANUAL

2.0 GENERAL

This manual sets forth recommended procedures for determination of sulfur dioxide emissions from stationary sources according to Method 6. (Method 6 is reproduced from the Federal Register, and is included as appendix A of this document.) Quality control procedures and checks designed to give an indication or warning that invalid or poor quality data are being collected are written as part of the operating procedures and are to be performed by the operator on a routine basis. Results from certain strategic quality control checks will be used by the supervisor for the assessment of data quality.

The sequence of operations to be performed for each field test is given in figure 1. Each operation or step in the method is identified by a block. Quality checkpoints in the measurement process, for which appropriate quality control limits are assigned, are represented by blocks enclosed by heavy lines. Other quality checkpoints involve go/no-go checks and/or subjective judgments by the test team members with proper guidelines for decisionmaking 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 operator performs his various tasks. From equipment checks 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 are recommended to minimize operator error. Before using this document, the operator should study Method 6 as reproduced in appendix A in detail.

It is assumed that all apparatus satisfies the reference method specifications and that the manufacturer's recommendations will be followed when using a particular piece of equipment.

PRESAMPLING PREPARATION

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

2. CALIBRATE EQUIPMENT WHEN FIRST PURCHASED AND WHEN DAMAGED OR ERRATIC BEHAVIOR IS OBSERVED

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 POINT (SAMPLE POINT) 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.

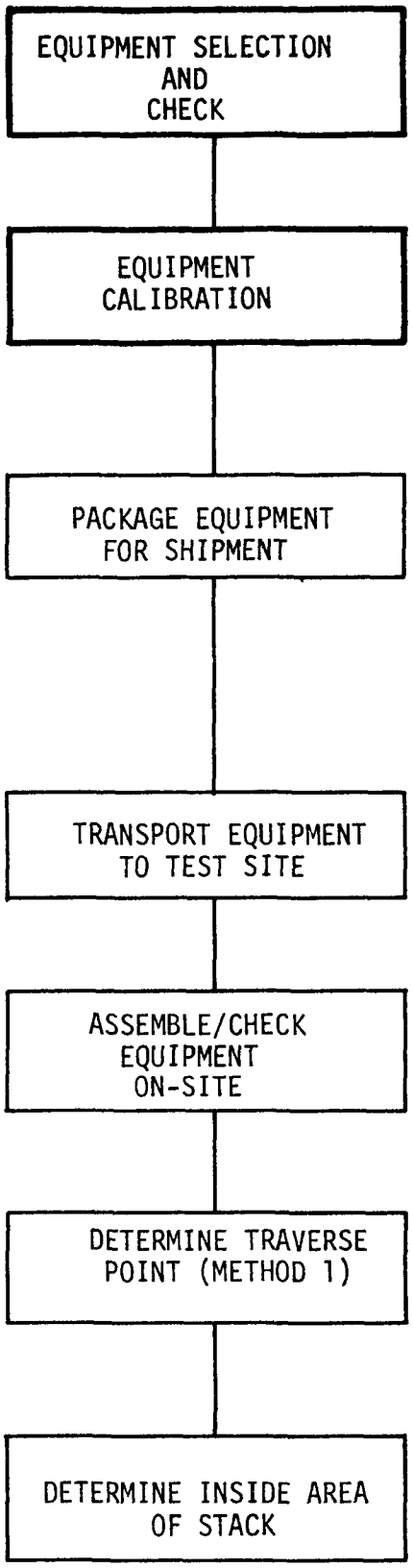


Figure 1. Operational flow chart of the measurement process.

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.

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. PREPARE ABSORBING REAGENTS AND PIPETTE 15 ml OF 80 PERCENT ISOPROPANOL (BUBBLER) AND 15 MI OF 3 PERCENT H_2O_2 (IMPINGERS).

13. SET UP SAMPLING TRAIN AND LEAK-CHECK SYSTEM.

14. PERFORM SAMPLE COLLECTION (PROPORTIONAL) ACCORDING TO THE PROCEDURE GIVEN IN SUBSECTION 2.3.3.

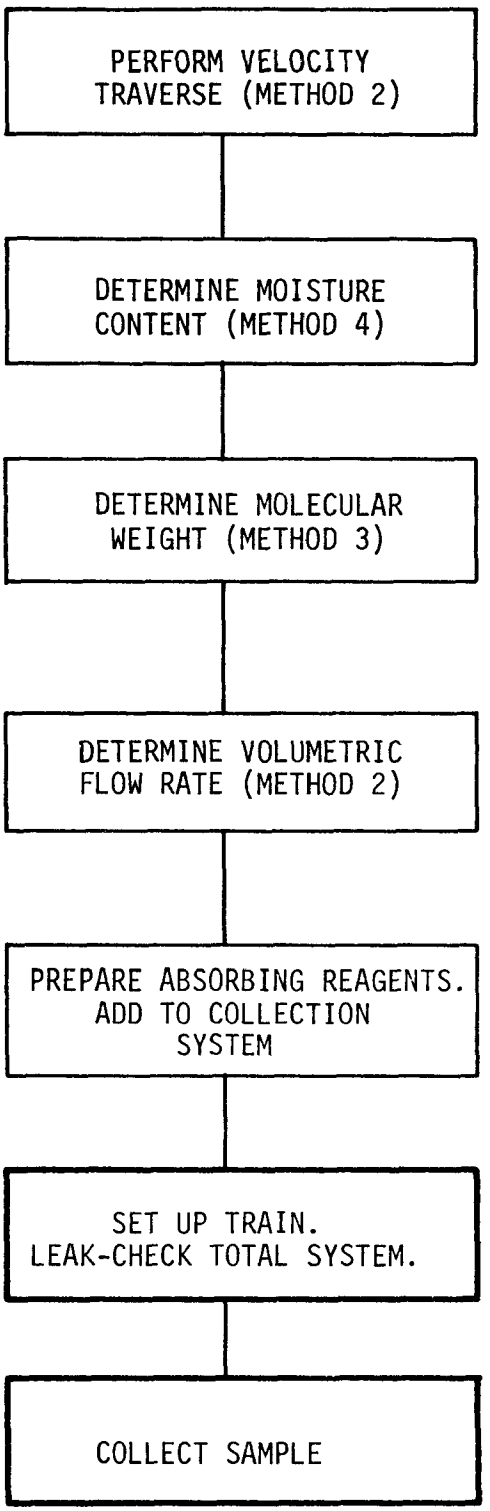


Figure 1. Operational flow chart of the measurement process (continued).

POSTSAMPLING OPERATIONS

15. PERFORM LEAK CHECK AT END OF TEST.

16. QUANTITATIVELY RECOVER IMPINGER SOLUTIONS.

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

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

19. PERFORM POST CALIBRATION AND ANALYSIS OF SAMPLES FOR SULFUR DIOXIDE.

20. PERFORM CALCULATIONS UTILIZING ALL FIELD AND CALIBRATION DATA.

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

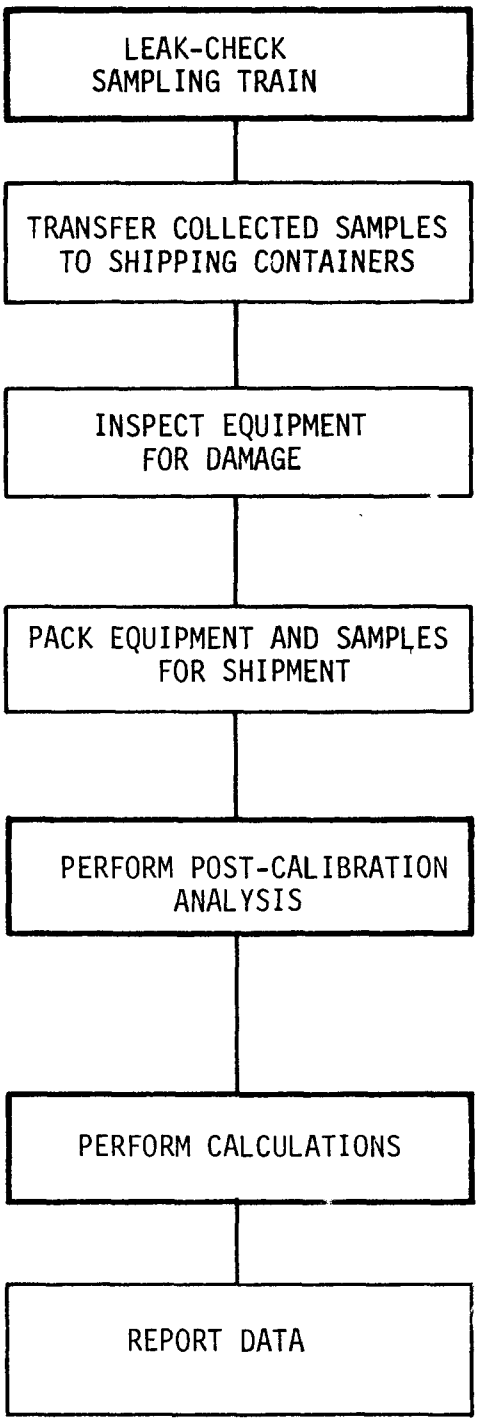


Figure 1. Operations flow chart of the measurement process (continued).

2.1 EQUIPMENT SELECTION

A schematic of an assembled sulfur dioxide sampling train with all components identified is shown in figure 6-1 of appendix A. Specifications, criteria, and/or design features as applicable are given in this section to aid in the selection of equipment to assure the collection of data of consistent quality. Procedures and, where applicable, limits for acceptance checks are given. The descriptive title, identification number, if applicable, and the results of the acceptance check are recorded in the receiving record file, dated, and signed by the individual performing the check. Also, if a calibration is required as part of the acceptance check, the data are recorded in the calibration log book.

2.1.1 Sampling Probe.

2.1.1.1 Design Characteristics. The sampling probe should be of borosilicate (Pyrex) glass of 5-6 mm inside diameter encased in a stainless steel sheath and equipped with a heating system capable of maintaining a gas temperature at $\geq$ 175° C (350° F) at the exit end of the probe during sampling (ref. 1). Stack gases at high temperatures should be cooled to less than 375° C (700° F). The sampling tip of the probe should have retaining ridges on both sides of the particulate filter to hold the filter in place. For stack gas temperatures in excess of 425° C (800° F), a probe fabricated from quartz can be used. The main objective is for the probe material to be nonreactive with the gas constituents; hence, not introducing a bias into the analytical method.

2.1.1.2 Acceptance Check. Upon receiving a new probe, it should be visually checked for specification; i.e., is it the length and composition ordered? The probe should be checked for cracks or breaks and leak-checked on a sampling train as described in subsection 2.2.2.2. Also, the probe heating system should be calibrated according to subsection 2.2.2.2. Any probe not satisfying the acceptance check should be repaired, if possible, or rejected.

2.1.2 Midget Bubbler/Impingers.

2.1.2.1 Design Characteristics. One midget bubbler (25 mℓ) per train is required, with glass wool packed in the top to prevent carryover of sulfuric acid mist. The porosity of the bubbler should be type A (145-175 microns).

Three midget impingers (25 mℓ) with orifices calibrated to deliver 2.5-3.0 lpm at 2.2 mmHg vacuum are required per sampling train. Connections between midget bubbler and impinger should be of inert materials (plastic or rubber tubing is not desirable because of absorption and desorption of gaseous species) (ref. 2).

2.1.2.2 Acceptance Check. Each bubbler/impinger is checked visually for damage, such as breaks or cracks; and manufacturing flaws, such as poorly shaped connections.

2.1.3 Vacuum Pump.

2.1.3.1 Design Characteristics. The vacuum pump should be capable of maintaining a flow rate of approximately 3 to 5 ℓ/min for pump inlet vacuums up to 500 mm of Hg with the pump outlet near standard pressure, i.e., 760 mm of Hg. The pump must be leak-free when running and pulling a vacuum (inlet plugged) of 380 mm of Hg. Two types of vacuum pumps are commonly used. They are a modified sliding fiber vane pump and a diaphragm pump. For safety reasons, the pump should be equipped with a three-wire electrical cord.

2.1.3.2 Acceptance Check. Install a vacuum gage or, preferably, a mercury manometer in the pump inlet line. Plug the inlet line and run the pump until the vacuum gage reads 380 mm of Hg. Vacuum, then clamp the pump outlet line and turn off the pump. The vacuum reading should not change noticeably in 5 minutes.

2.1.4 Dry Gas Meter.

2.1.4.1 Design Characteristics. The dry gas meter must be capable of measuring total volume with an accuracy of $\pm$ 2 percent. It should be rated at about 3 ℓ/minute.

2.1.4.2 Acceptance check. Check new dry gas meters visually for damage and perform a calibration according to subsection 2.2.2.7. Reject the dry gas meter if it is damaged, behaves erratically, or cannot be adjusted to agree to within ± 2 percent of the wet test meter over the flow rate range of interest.

2.1.5 Rotameter.

2.1.5.1 Design Characteristics. A rotameter or its equivalent (range of 0-5 ℓ/min) is used to monitor and control sample flow rate.

2.1.5.2 Acceptance Check. A calibration curve is to be supplied by the manufacturer. The rotameter is checked against the calibrated dry gas meter with which it is to be used. If the rotameter is not within ± 5 percent of the manufacturer's calibration curve, recalibrate and construct a new calibration curve (this procedure will also correct for local pressures that differ from standard pressure at which the manufacturer's calibration curve was developed).

2.1.6 Needle Valve.

2.1.6.1 Design Characteristics. A metering valve with convenient sized fittings is required in the sampling train to adjust the sample flow rate. It is recommended that the needle valve be placed on the vacuum side of the pump.

2.1.7 Drying Tube.

2.1.7.1 Design Characteristics. A drying tube packed with 6- to 16-mesh indicating-type silica gel, or equivalent, to dry the sample. A simple solution to this is utilizing polyethylene drying tubes and 3/8-in. i.d. tubing. Glass wool should be packed in each end of the tube to hold the silica gel and protect the sampling system. Plastic tubing can be utilized in connections past the collection system without the possibility of affecting the sample concentration. The drying tube should have a minimum capacity of 30-50 g of silica gel.

2.1.7.2 Acceptance Check. Visually check the drying tube for proper size and damage.

2.1.8 Thermometers.

2.1.8.1 Design Characteristics. Dial-type thermometers with ranges of -10° to 50° C are suitable for monitoring the inlet and outlet temperatures of the dry gas meter (only one is required if the average temperature is measured).

2.1.8.2 Acceptance Check. Dial-type thermometers are easily damaged. Each new thermometer is checked visually for damage, such as a dented or bent stem. Each thermometer should read within ± 3° C of the true value when checked in an ice water bath. Damaged thermometers that cannot be calibrated are rejected.

2.1.9 Barometer.

2.1.9.1 Design Characteristics. A barometer, usually an aneroid barometer, should be capable of measuring atmospheric pressure to within 2.5 mm of Hg (0.1 in. of Hg). An alternative is to obtain the uncorrected barometric pressure from a nearby weather station.

2.1.9.2 Acceptance Check. Check the field barometer against a mercury-in-glass barometer or equivalent. Adjust the field barometer to agree with the mercury barometer, if they differ by more than ± 5 mm of Hg (0.2 in. of Hg). Reject the barometer if it cannot be adjusted to agree with the reference barometer.

2.1.10 Stack Gas Velocity Measuring System.

See the Quality Assurance Document of this series for Method 2 - Determination of Stack Gas Velocity and Volumetric Flow Rate (type-S pitot tube) for a discussion of this system (ref. 5).

2.1.11 Stack Gas Temperature Measuring System.

This system is treated as a subsystem of the velocity measuring system and is discussed in the document referenced in subsection 2.1.10.

2.1.12 Stack Gas Pressure Measuring System.

This system is treated as a subsystem of the velocity measuring system and is discussed in the document referenced in subsection 2.1.10.

2.1.13 Sample Recovery Apparatus.

2.1.13.1 Design Characteristics. Sample recovery apparatus is described below.

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

2.1.13.1.2 Polyethylene storage bottles. One 125-mℓ polyethylene bottle is required for each collected sample, plus one polyethylene container to retain a blank for each absorbing solution used in testing.

2.1.13.2 Acceptance Check. Visually check wash bottles and/or storage bottles for damage.

2.1.14 Analysis Glassware.

2.1.14.1 Design Characteristics. Analysis glassware is described below.

2.1.14.1.1 Pipettes. Several volumetric pipettes (class A), including 5-, 10-, 20-, and 25-mℓ should be available for the analysis.

2.1.14.1.2 Volumetric flasks. Volumetric flasks (class A), are required and should include 50-, 100-, and 1000-mℓ sizes.

2.1.14.1.3 Burettes. A 5- or 10-mℓ microburette is required for samples of low concentrations and a 50-mℓ standard burette for all other titrations.

2.1.14.1.4 Erlenmeyer flasks. Several 125-mℓ Erlenmeyer flasks are required for titration of vessels.

2.1.14.2 Acceptance Check. Check all glassware for cracks, breaks, and manufacturing flaws.

2.2 PRESAMPLING PREPARATION

2.2.1 Preliminary Site Visit (Optional).

The primary objective of 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 set of sampling 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. Data from similar operations that have been tested should be noted for further consideration of the ifnal 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 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 in obtaining a valid test and to insure that all facilities meet minimum safety standards. If ports have to be installed, specify 75- or 100-mm (3- or 4-in.) 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-ampere 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 head

% H_2O = Moisture content

M_s = Gas constituent concentration.

The above parameters can be roughly determined using an inclined manometer with a 0- to 125-mm range, 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 technique (acid gases $\geq$ 10 ppm SO_3 will give high results) or by condensation (Method 4), and the gaseous constituents by hand-held indicator kits. Nomographs are useful in checking and/or estimating required preliminary data (ref. 4).

2.2.1.4 Method and Equipment for Transporting Apparatus to Test Site. The preliminary site visit (or correspondence) should include a logical plan between plant personnel and 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 can be 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 and 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 SO_2 train used by the EPA is given in appendix A of this document (fig. 6-1). Commercial models of this system are available. Each individual or fabricated train must be in compliance with the specifications in the reference method.

2.2.2.2 Probe (Filter). Clean the probe internally by brushing, first using tap water, then distilled, deionized water followed by acetone, and allow it to dry in the air. In extreme cases, the glass liner can be cleaned with stronger reagents. In either case, the objective is to leave the glass liner chemically inert. The probe's heating system should be checked to see that it is operating properly. The probe temperature can be profiled with a remote reading thermometer or by a thermocouple with readout device. The probe should be sealed on the filter side and checked for leaks at a vacuum of 380 mm of Hg (15 in. of Hg). The probe must be leak-free under these conditions. The glass liner should be sealed inside the metal sheath to prevent diluent air from entering the source (most stacks are under a negative pressure).

2.2.2.3 Midget Bubbler, Midget Impinger, and Glass Connections. All glassware should be cleaned with detergent and tap water, then distilled, deionized water. All glassware should be visually inspected for cracks or breakage and be repaired or discarded.

2.2.2.4 Drying Tubes. Drying tubes should be packed with silica gel and sealed at both ends.

2.2.2.5 Valve and Rotameter. The flow control valve and rotameter should be cleaned prior to each field trip or on any instance of erratic behavior. Follow the maintenance procedure as recommended by the manufacturer.

2.2.2.6 Pump. The vacuum pump should be serviced as recommended by the manufacturer every 3 months, or upon erratic operation.

2.2.2.7 Dry Gas Meter. The dry gas meter should be calibrated versus a calibrated wet test meter.

1. The wet test meter should be rated at about 3 ℓ/rev with a $\pm$ 1 percent accuracy. The wet test meter should be operated as directed by the manufacturer's instructions.
2. Connect the components as shown in figure 6-1 (appendix A). Charge the bubbler and two impingers with 15 mℓ of water each. Plug the inlet of the bubbler and leak check the system at 250 mm of Hg vacuum. Carefully release the vacuum and turn off the

pump. This leak test will check the total system (excluding probe) for leaks.

3. Connect the outlet of the wet test meter to the inlet of the midget bubbler. Run the pump for 15 minutes with the rotameter set at approximately 1.4 ℓ/min to allow the pump to warm up and to allow the interior surface of the wet test meter to be wetted.

4. Fill in the following data sheet (figure 2) and calculate γ = ratio of accuracy of wet test meter to dry gas meter:

$$\gamma = \frac{V_w (P_m + D_m)(t_d + 273)}{V_d P_m (t_w + 273)} . \qquad (1)$$

The pressure drop across the wet test meter, D_m, should be less than 25 mm of H_2O and can be ignored. Equation (1) then becomes

$$\gamma = \frac{V_w (t_d + 273)}{V_d (t_w + 273)} . \qquad (2)$$

Consider the dry test meter to be in calibration if γ is equal to 1.0 ± 0.02. This data can also be used to check the rotameter calibration curve ($\pm$ 5 percent) which is furnished by the manufacturer.

2.2.2.8 Pitot Tube. When used exclusively for proportional sampling, it is not necessary to calibrate the pitot tube. However, if the pitot tube is used to perform a velocity traverse, it must be calibrated. The pitot tube should be calibrated according to the procedures given in the quality assurance document of this series for Method 2 (ref. 5). During calibration, the pitot tube should be strapped to the sampling probe in the same configuration that it will be used in the field. Also, the sample flow rate commonly used in the field should be maintained during calibration.

2.2.3 Reagents and Equipment.

2.2.3.1 Sampling. The bubbler solution which consists of 80 percent

DATE _____ CALIBRATED BY _____

BAROMETER PRESSURE AT METERS, P_m = _____ mm of Hg DRY GAS METER NO. _____

WET TEST METER NO. _____

D_m PRESSURE DROP ON W.T.M. mm of Hg	ROTAMETER SETTING ℓ/min	GAS VOL. W.T.M. V_w (ℓ)	GAS VOL. D.T.M. V_d (ℓ)	W.T.M. t_w °C	D.T.M.				
					INLET t_{d_i} °C	OUTLET t_{d_o} °C	AVERAGE t_d °C	θ MIN	γ
	1								
	2								
	3								
	4								
	5								

Figure 2. Dry gas meter sample calibration data.

Symbols in figure 2 are:

D_m = Pressure drop on wet test meter, mm of Hg.

V_w = Gas volume passing through the wet test meter, ℓ.

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

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

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

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

t_d = Average temperature of the gas in the dry test meter, obtained by the average of t_{d_i} and t_{d_o}, °C.

θ = Time of calibration run, minutes.

γ = Ratio of volumetric measurement by wet test meter to dry test meter. Tolerance = $\pm$ 0.02.

isopropanol is prepared by mixing 80 mℓ of reagent-grade isopropanol with 20 mℓ of distilled, deionized water. The midget impinger absorbing reagent (hydrogen peroxide, 3 percent) is prepared by diluting 100 mℓ of 30 percent hydrogen peroxide to 1 ℓ with distilled, deionized water. All reagents are to be prepared fresh daily. All reagents must be ACS reagent grade. Solutions containing isopropanol should be kept in sealed containers to prevent evaporation.

2.2.3.2 Sample Recovery. Distilled, deionized water will be required on site for quantitative transfer of impinger solutions to storage containers. This water and reagent grade isopropanol will be used to clean the midget bubbler after testing and prior to taking of another sample.

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 13-mm (0.5-in.) 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 6 mm (0.25 in.) 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 guard rails 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 glasses and/or safety goggles.

d. Protective clothing including the following: appropriate suits, rain, heat, and cold, gloves (both asbestos and cloth) and steel-toed shoes.

e. Steel cable 5 mm (0.1875 in.) 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-ohmmeter (VOM)
5. Extension cords - light (No. 14 Avg) 2 x 25
6. 2 3-wire electrical adapters
7. 3-wire electrical triple taps
8. Fuses
9. Electrical wire

b. Tools

1. Tool boxes (one large, one small)
2. Screwdrivers
   one set flat blade
   one set philips
3. C-clamps--2 each; 150 mm (6 in.), 75 mm (3 in.)

c. Wrenches

1. Open end set--6 mm to 25 mm (0.25 to 1 in.)
2. Adjustables--150 mm (6 in.), 300 mm (12 in.)
3. One chain wrench
4. One 300 mm (12 in.) pipe wrench
5. One Allen wrench set

d. Miscellaneous

1. Silicone sealer
2. Silicone vacuum grease
3. Pump oil
4. Manometers (gage oil)
5. Anti-seize compound
6. Pipe fittings
7. Dry cell batteries
8. Flashlight
9. Valves
10. Thermometers (dial), 1 m (36 in.) and a remote reading thermometer
11. Vacuum gage
12. SS tubing - 6, 10, and 125 mm (0.25, 0.375, and 0.5 in.) 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. Data sheets or data notebook
2. Carbon paper
3. Slide rule or electronic calculator
4. Psychometric charts
5. Combustion nomographs (ref. 4)
6. Pencils, pens
7. Calibration data, γ, C_p, 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 under 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 Probe. Pack the probe in a case protected by polyethylene or other suitable packing material. The inlet and outlet should be sealed and protected from breakage. An ideal container is a wooden case or equivalent lined with foam material in which separate compartments are cut to hold individual devices. This case can also contain a pitot tube for velocity determinations. The case should have handles or eye hooks that can withstand hoisting and be rigid enough to prevent bending or twisting of the devices during shipping and handling.

2.2.4.2 Midget Bubblers, Impingers, Connectors and Assorted Glassware. All bubblers, impingers, and glassware should be packed in a rigid container and protected by polyethylene or other suitable packing material. Individual compartments for all glassware will help to organize and protect each individual piece.

2.2.4.3 Rotameter, Drying Tubes and Volumetric Glassware. A sturdy case lined with foam material can contain the rotameter, drying tubes, and assorted volumetric glassware.

2.2.4.4 Pump. The vacuum pump 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. It is advisable to always carry a spare pump in case of pump failure.

2.2.4.5 Wash Bottles and Storage Containers. Storage containers and miscellaneous glassware should be packed in a rigid foam-lined container. The storage requirement for polyethylene bottles is not as stringent as with glass bottles.

2.3 ON-SITE MEASUREMENTS

The on-site measurement activities include transporting the equipment to the test site, unpacking and assembling the equipment, confirming duct measurements and traverse points (if volumetric flow rate is to be determined), velocity traverse, determination of molecular weight and stack gas moisture content, sampling for 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 as decided during the preliminary site visit (or by prior correspondence) should be used to place the equipment on-site. Care should also be exercised to prevent damage to the test equipment or injury to test personnel during the moving phase. A "laboratory"-type area should be designated for preparation of the absorbing reagents, charging of the bubbler and impingers, and sample recovery.

2.3.2 Preliminary Measurements and Setup.

The reference method outlines the determination of the concentration of sulfur dioxide in the gas stream. The volumetric flow rate must be determined using Reference Methods 1, 2, 3, and 4 if the mass emission rate is to be determined (ref. 5).

Fill in the test identification required on the sample data sheet of figure 3, or on a similar form.

2.3.3 Sampling.

The on-site sampling includes preparation and/or addition of the absorbing reagents to the midget bubbler and impingers, setup of the sampling train, connection to the electrical service, preparation of the probe (leak check of entire sampling train and addition of particulate filter), insertion of the probe into stack, sealing the port, checking temperature of probe, sampling and recording of the data. A final leak check of the entire sampling train must always be performed.

2.3.3.1 Preparation and/or Addition of Absorbing Reagents to Collection System. If on-site preparation of absorbing reagent is necessary, follow directions as given in section 2.2.3.1 of this document. Pipette 15 mℓ of

3 percent hydrogen peroxide into each of the first two midget impingers. The final midget impinger is left dry. Glass wool must be placed at the top of the midget bubbler to serve as a filter to prevent sulfuric acid (H_2SO_4) mist carryover into the midget impingers; i.e., biasing the SO_2 results high.

2.3.3.2 Assembling Sampling Train. Assemble the sampling train as shown in figure 6-1 of appendix A and perform the following:

1. Leak check the sampling system by plugging the probe inlet and pulling 250 mm of Hg (10 in. of Hg) vacuum. Record the leak rate on the data sheet of figure 3.

   Caution: When releasing the vacuum after a leak test, release the vacuum slowly to prevent loss of reagent from the impinger, thus saturating the silica gel in the drying tube.

   A leakage rate not in excess of 1 percent of the sampling rate is acceptable. In practical circumstances, the system should be leak-free at this vacuum level. When the system is leak free (to pass test), turn on the probe heater.

   Note: A crossover system over the pump as used in the sampling train of EPA Method 8 is useful in leak testing. In the design of Method 8, the needle valve should be placed between the main valve and vacuum gauge. The rotameter should be positioned between the pump and the dry gas meter.
2. Place a loosely packed filter of glass or quartz wool in the end of the probe.
3. Attach the pitot lines of the type-S pitot tube to a differential pressure gauge.
4. Prior to taking of the sample, perform a preliminary velocity traverse of the stack to get a high, low and medium pressure of ΔP (mm of H_2O).
5. Take the square root of the high value $(\Delta P)^{1/2}$ and assign a rotameter setting of 3 ℓ/min to this value. If the stack gas velocity is constant or nearly so, set the rotameter to an approximate flow rate of 2 ℓ/min.
6. During the test the needle value is varied to provide a relative change in flow (rotameter setting) as a function of the stack gas velocity; i.e., as a function of $(\Delta P^{1/2}$, not of ΔP (velocity pressure head). From an initial velocity traverse, a table can be prepared ratioing the $(\Delta P)^{1/2}$ values to the scale of the rotameter;

thereby, the operator can readily set the flow rate during the sampling process. To reduce calibration in the field, a table of ΔP, $(\Delta P)^{1/2}$ and rotameter settings can be prepared prior to the field test for a ready reference.

2.3.3.3 Sampling (Proportional). Sampling must be proportional so that the resultant calculated concentration of SO_2 is an accurate representation of what actually exited the stack during the sampling period; that is, if the stack gas velocity is constant, the sample flow rate is kept constant, and if the stack gas velocity varies with time or position, the sample flow rate must be adjusted proportionally. For a discussion of proportional sampling, consult chapter 8 or reference 6.

1. Place crushed ice around the impingers. Add salt, if necessary, to keep the stack gas temperature down as it leaves the last impinger.
2. When the probe temperature is up to 175° C (350° F), insert the probe into the stack to the centroid of the cross section if the cross sectional area is less than 5.0 m^2, or at a point no closer to the walls than 1.0 m (3 ft) if the cross sectional area is 5.0 m^2 or more.
3. The minimum acceptable sampling time is 20 minutes and minimum sampling volume is 21.2 ℓ corrected to standard conditions. The total sample volume at meter conditions should be on the order of 28 ℓ (1 ft^3).
4. Perform a final leak check at a vacuum 25 to 50 mm of Hg greater than the highest vacuum recorded during the test period and record the leak rate on the data sheet of figure 3.
5. 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. An appropriate scrubber can be used to insure that the air is free from particulate sulfate and SO_2 (ref. 7). This purging process is to remove dissolved SO_2 from the midget bubbler into the midget impingers.
6. If SO_2 has been collected, the impinger absorbing solution should be acidic. Check the first impinger with pH indicating paper.

TEST IDENTIFICATION

Plant: Name _____ Location _____

Stack No. _____ Date _____

Team Supervisor _____

Operators _____

_____

EQUIPMENT IDENTIFICATION

Dry Gas Meter No. _____ Sample Bottle No. _____

Probe No. _____ Type Filter _____

Pitot Tube No. _____ C_p _____

PRELIMINARY MEASUREMENTS

Barometric Pressure, P_m, _____ mm of HG _____

Probe Temperature, T_p, _____ °C

Stack Area, A_s, _____ m^2

ΔP : Low _____, High _____ (mm of Hg) _____

DRY GAS METER DATA

Run No.	Volume Readings (ℓ) Initial	Final	Volume, Vm* (ℓ)
1			
2			
3			
4			
5			
6			

*Vm is the gas volume through the dry gas meter at the meter temperature and pressure.

LEAK TEST RESULTS

Run No.	Initial Leak Rate (ℓ/min)	Initial Vacuum (mm Hg)	Final Leak Rate (ℓ/min)	Final Vacuum (mm Hg)
1				
2				
3				
4				
5				
6				

SAMPLING DATA

Run No.	Sampling Time (m/h)	Meter Volume (ℓ)	Vacuum (mm Hg)	ΔP (mm H_2O)	Rotameter Setting	Temperature (°C)
1						
2						
3						
4						
5						
6						

Figure 3. On-site sampling data sheet.

If the absorbing reagent is not acidic and it is known that SO_2 is present in the stack gas, the sampling train and reagent should be checked and the run repeated.

The particulate filter should be changed at the end of each individual test. It has been suggested that particulate buildup on the probe filter may result in a loss of SO_2 due to reactions with the particulate matter (ref. 13).

2.3.4 Sample Recovery.

The reference method requires a transfer of the contents of the impingers and connection washings to a suitable storage container. This transfer should be done in a "laboratory-type area" to prevent contamination of the test sample.

2.3.4.1 Impinger Solution (H_2O_2). Disconnect the impingers after completion of the purge. Discard the contents of the midget bubbler into an appropriate container. Transfer the contents of the midget impingers into a labeled polyethylene sample bottle. Rinse the three midget impingers and the connecting tubes with distilled water and add these washings to the same sample bottle. The total rinse volume should be $\leq$ 10 mℓ.

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 (bubbler, impingers and connectors) are used in the next test, they should be rinsed with distilled water (impingers, connectors, and bubbler) and then with isopropanol (bubbler only). A new drying tube should be inserted into the sampling train. The following is recommended at the completion of the test:

1. Check all sample containers for proper labeling (time and date of test, location of test, number of test and any pertinent documentation).
2. All data recorded during the field test should be recorded in duplicate by carbon paper or by using 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 embarrassing mistake.

3. All sample containers and sampling 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 POSTSAMPLING 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. 5).

2.4.1.2 Dry Test Meter (Sampling Train). A postcheck (a postcheck for one test can serve as the presampling check for the next field test) should be made of the entire sampling train to check for proper operation of the probe, pump, dry gas meter, rotameter, valve(s), thermometer, and vacuum gage. Set up the sampling train. Leak-check the vacuum system at 250 mm of Hg vacuum. Determine γ as previously instructed in subsection 2.2.2.7. 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 procedures to improve 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. Calibrations 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-arsonophenyzlazo)-2-naphthal-3, 6-disulfonic acid, disodium salt]. Aliquots from the impinger solution are analyzed by titration with barium perchlorate to the pink-orange endpoint.

2.4.2.1 Reagent (Standardization and Analysis). The following reagents are required for the analysis of the SO_2 samples:

1. Water-deionized, distilled
2. Isopropanol
3. Thorin indicator - 1-(0-arsonophenylazo)-2-napthal-3, 6-disulfonic acid, disodium salt (or equivalent). Dissolve 0.20 g in 100 mℓ distilled water.

4. Barium perchlorate [$Ba(ClO_4)_2 \cdot 3H_2O$]. Dissolve 1.95 g 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). Standardized against 0.01 N NaOH which has previously been standardized against potassium acid phthalate [$C_6H_4(COOH)$ Cook primary standard].

2.4.2.2 Standardization of Sodium Hydroxide. Dry the potassium acid phthalate for 1 to 2 hours at 110° C and cool. Accurately weigh approximately 0.25 g in 250 mℓ of distilled, deionized water (preferably freshly boiled and cooled). Add two drops of phenolphthalein indicator and titrate with 0.1N sodium hydroxide (NaOH) to the first pink color that persists for 30 seconds. The base (NaOH, 0.1N) can be purchased commercially or prepared from reagent grade NaOH. Standard textbooks of analytical chemistry give instructions on preparation of NaOH solutions of any desired normality. The fresh 0.01N NaOH is prepared by pipetting 50 mℓ of the standardized solution into a 500-mℓ volumetric flask and diluting to the mark with distilled, deionized water. The final concentration of the base will be the standardized value divided by 10.

2.4.2.3 Standardization of Sulfuric Acid vs. 0.01N NaOH. The 0.01N sulfuric acid is standardized by pipetting 25 mℓ of the H_2SO_4 solution into a 250-mℓ Erlenmeyer flask that contains 25 mℓ of water. A blank should be prepared that contains 50 mℓ of distilled, deionized water. Add two drops of phenolphthalein indicator to the standard sample and to the blank and titrate with the above standardized 0.01N 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, with correction for the blanks.

2.4.2.4 Standardization of Barium Perchlorate (0.01N). Pipette 25 mℓ of sulfuric acid standard (0.01N) 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 0.01N barium perchlorate. Run a blank

acid, disodium salt (or equivalent). Dissolve 0.20 g in 100 mℓ distilled water.

4. Barium perchlorate [$Ba(ClO_4)_2 \cdot 3H_2O$]. Dissolve 1.95 g in 200 mℓ distilled water and dilute to 1 ℓ with isopropanol. Standardize with sulfuric acid (H_2SO).
5. Sulfuric standard (0.01 N). Standardized against 0.01 N NaOH which has previously been standardized against potassium acid phthalate [$C_6H_4(COOH)$ Cook primary standard].

2.4.2.2 Standardization of Sodium Hydroxide. Dry the potassium acid phthalate for 1 to 2 hours at 110° C and cool. Accurately weigh approximately 0.25 g in 250 mℓ of distilled, deionized water (preferably freshly boiled and cooled). Add two drops of phenolphthalein indicator and titrate with 0.1N sodium hydroxide (NaOH) to the first pink color that persists for 30 seconds. The base (NaOH, 0.1N) can be purchased commercially or prepared from reagent grade NaOH. Standard textbooks of analytical chemistry give instructions on preparation of NaOH solutions of any desired normality. The fresh 0.01N NaOH is prepared by pipetting 50 mℓ of the standardized solution into a 500-mℓ volumetric flask and diluting to the mark with distilled, deionized water. The final concentration of the base will be the standardized value divided by 10.

2.4.2.3 Standardization of Sulfuric Acid vs. 0.01N NaOH. The 0.01N sulfuric acid is standardized by pipetting 25 mℓ of the H_2SO_4 solution into a 250-mℓ Erlenmeyer flask that contains 25 mℓ of water. A blank should be prepared that contains 50 mℓ of distilled, deionized water. Add two drops of phenolphthalein indicator to the standard sample and to the blank and titrate with the above standardized 0.01N 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, with correction for the blanks.

2.4.2.4 Standardization of Barium Perchlorate (0.01N). Pipette 25 mℓ of sulfuric acid standard (0.01N) 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 0.01N barium perchlorate. Run a blank

which contains 25 mℓ of deionized, distilled water and 100 mℓ of isopropanol. Standardizations should be done in triplicate. 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 carry out titrations on aliquots at low, medium, and high concentrations. Pipette various aliquots of 0.01N H_2SO_4 and add four times this volume of 100 percent 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. 8). The normality of the $BaClO_4$ is calculated as:

$$N_{BaClO_4} = N_{H_2SO_4} \times \text{Volume}_{H_2SO_4} \Big/ \text{Volume}_{BaClO_4}$$

2.4.2.5 Sample Analysis. Transfer the contents of the sample bottle to a 50-mℓ volumetric flask (V_{soln}). Dilute to the mark with deionized, distilled water. Pipette a 10-mℓ aliquot (V_a) of this solution into a 125-mℓ Erlenmeyer flask and add 40 mℓ of isopropanol. Add two to four drops of thorin indicator and titrate to a pink endpoint (orange-pink) using standardized 0.01N barium perchlorate (the volume used in titration is recorded as V_t, mℓ). Run a blank with each series of samples from the absorbing solution used in the field (the volume of titrant used for blank is recorded as V_{tb}, mℓ).

As a check on the analysis, new aliquots should be taken from at least two of the six samples and analyzed. If either new analysis differs more than 10 percent from the original analysis, all samples should be reanalyzed until two or more analyses from each sample agree within 10 percent. The average of these values of V_t should be averaged and used in subsequent calculations.

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 each 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 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 (25° C and 760 mm of Hg) by

$$V_{m_{std}} = 0.3921 \left(\frac{^\circ K}{\text{mm of Hg}} \right) \frac{V_m P_m}{T_m} \qquad (2)$$

where $V_{m_{std}}$ = Volume of gas sample through the dry gas meter corrected to standard conditions, ℓ.

V_m = Volume of gas sample through the dry gas meter at meter conditions, ℓ.

T_m = Average dry gas meter temperature, ° K.

P_m = Barometric pressure at the dry gas meter, mm of Hg.

Compute $V_{m_{std}}$ to three significant digits and record the value on the sample analysis data sheet of figure 4.

2.4.3.2 Sample Concentration. Calculate the concentration of sulfur dioxide on a dry basis at standard conditions for a given sample by

$$C_{SO_2} = 32 \frac{g\ell^2}{(g\text{-eq})m^3\ m\ell} \frac{\left(N \left(V_t - V_{tb}\right)\right)\left(V_{soln}/V_a\right)}{V_{m_{std}}} \qquad (3)$$

where C_{SO_2} = Concentration of sulfur dioxide at standard conditions on a dry basis, g/m^3.

32 = Conversion factor, including the number of grams per gram equivalent of sulfur dioxide (32 g/g-eq), 1000 mℓ/ℓ, 1000 ℓ/m^3, g $\ell^2/(g\text{-eq})m^3/m\ell$.

N = Normality of barium perchlorate titrant, g-eq/ℓ.

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 sulfur dioxide, 50 mℓ.

V_a = Volume of sample aliquot titrated, mℓ.

Record the calculated concentration on the sample analysis data sheet of figure 5.

2.4.3.3 Emission Rate. To calculate the emission rate, first calculate the volumetric flow rate at standard conditions by

$$Q_s = 2.378 \times 10^5 \, (1 - B_{wo}) \, C_p \, (\sqrt{\Delta P})_{avg} \, A_s \left[\frac{P_s}{(T_s)_{avg} M_s} \right]^{1/2} \qquad (4)$$

where Q_s = Volumetric flow rate, dry basis, standard conditions, m^3/hr.

B_{wo} = Proportion by volume of water vapor in the stack gas (from Method 4), dimensionless.

C_p = Pitot tube calibration coefficient (Method 2), dimensionless.

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

A_s = Cross-sectional area of stack, m^2.

P_s = Absolute stack gas pressure, mm of Hg.

M_s = Molecular weight of stack gas (wet basis) (Methods 3 and 4) g/g-mole.

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

The emission rate (ER) is given by

$$ER = C_{SO_2} \times Q_s \qquad (5)$$

where ER = Emission rate, g/hr.

C_{SO_2} = SO_2 concentration, g/m^3.

Q_s = Volumetric flow rate, m^3/hr.

Record the values of Q_s and ER on the sample analysis data sheet of figure 4.

SAMPLE VOLUME

V_m = _____ ℓ, T_m = _____ °K, P_m = _____ mm of H_g

$$V_{m_{std}} = 0.3921 \frac{°K}{\text{mm of Hg}} \left(\frac{V_m P_m}{T_m} \right) = \underline{\quad\quad} \ \ell$$

SO_2 CONCENTRATION

N _____ (g-eq)/ℓ V_t _____ ml, V_{tb} _____ ml

V_{soln} _____ ml, V_a _____ ml,

$$C_{SO_2} = 32 \frac{N(V_t - V_{tb})(V_{soln} V_a)}{V_{m_{std}}} = \_\_\_\_\_ g/m^3 \text{ (see eq.(3), p. 32)}$$

VOLUMETRIC FLOW RATE

C_p _____ dimensionless, B_{wo} _____ dimensionless

P_{bar} _____ mm of Hg, $(\sqrt{\Delta P})_{avg}$ _____ or _____ $(\text{mm of } H_2O)^{1/2}$

A_s _____ m^2, P_s _____ mm of Hg, $(T_s)_{avg}$ _____ °K,

M_s _____ g/g-mole

$$Q_s = *.754 \times 10^5 (1 - B_{wo}) C_p (\sqrt{\Delta P})_{avg} A_s \left[\frac{P_s}{(T_s)_{avg} M_s} \right]^{1/2} = \_\_\_\_\_ m^3/hr$$

(see eq. (4), p. 31)

EMISSION RATE (ER)

$$ER = C_{SO_2} \times Q_s = \_\_\_\_\_ g/hr \text{ (see eq. (5), p. 32)}$$

Figure 4. Sample analysis data sheet.

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)

Sulfur dioxide concentration, $\bar{C}_{SO_2}$*, for a particular field test is the average of six replicates. Intrateam assessment of data quality as discussed herein provides for an estimate of the precision of the measurements. Precision in this case refers to replicability, i.e., the variability among replicates and is expressed as a coefficient of variation. This precision statement combines variability due to process changes and random measurement errors. This technique does not provide the information necessary for estimating measurement bias (see subsection 4.1.2 for a discussion of bias) which could occur, for example, 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

$$s\left\{C_{SO_2}\right\} = \left[\frac{\sum_{i=1}^{6}\left(C_{SO_2}(i) - \bar{C}_{SO_2}\right)^2}{5}\right]^{1/2} \qquad (6)$$

where $s\left\{C_{SO_2}\right\}$ = standard deviation for the 6 runs

$C_{SO_2}(i)$ = SO_2 concentration for the i^{th} run

$\bar{C}_{SO_2}$ = mean SO_2 concentration for the 6 runs

and 5 = number of runs minus 1, or the number of degrees of freedom.

*Throughout this document, C_{SO_2} is used to mean a single SO_2 determination and the notation $\bar{C}_{SO_2}$ is used to represent the result of a field test, and is the average of six replicates.

3.1.2 Reporting Data Quality.

It is recommended that the average measured sulfur dioxide concentration, $\bar{C}_{CO_2}$, be reported with 90 percent confidence limits. Assuming the $\bar{C}_{SO_2}$ is normally distributed (this is usually a valid assumption since sample means tend to be normally distributed even for nonnormal parent distributions) and using $s\{C_{SO_2}\}$ as calculated in 3.1.1 above to estimate the standard deviation, exact confidence limits can be calculated for the true C_{SO_2} value using the Student t-distribution with r - 1 = 5 degrees of freedom. This assumes no bias in the average values. The average measure value with 90 percent confidence limits is reported as

$$\bar{C}_{SO_2} \pm 2.02 \; s\{C_{SO_2}\} \qquad (7)$$

where $\bar{C}_{SO_2}$ = the average of 6 replicates, g/m^3

$s\{\bar{C}_{SO_2}\}$ = estimated standard deviation of C_{SO_2} 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 $\bar{C}_{SO_2}$ = 2 g/m^3 and 2 g/m^3 $s\{C_{SO_2}\}$ 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 sulfur dioxide concentration, $\bar{C}_{SO_2}$, would be assumed to be in the interval

$$1.84 \; g/m^3 \leq C_{SO_2(t)} \leq 2.16 \; g/m^3$$

The utility of the above statement follows from the fact that if this procedure for computing confidence limits is followed, the 90 percent of the time the true C_{SO_2} value will be contained within the given limits (assuming that $\bar{C}_{SO_2}$ 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:	$\pm 1^{o}$ C
(d)	Stack Temperature Measuring System:	$\pm 3^{o}$ 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 0.01N Barium Perchlorate:	$\leq$ 0.0005N of mean
(c)	Reference Gas:	$\leq$ 17 percent of reference value

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 preventive 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 sulfur dioxide concentration requires a sequence of operations and measurements that yields as an end result a number that serves to represent the average sulfur dioxide emission rate for that field test. There is no way of knowing the accuracy; i.e., the agreement between the measured and the 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 the sulfur dioxide emission rate of a stationary source was made to try to identify important components of system error. Also, results of a collaborative study of Method 6 (ref. 3) showed an average within-laboratory coefficient of variation of 4.0 percent and a between-laboratory coefficient of variation of 5.8 percent. These results were used as an estimate of overall system error, while the individual error components are estimated using professional judgment in a manner such that their combined variability is 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 sulfur dioxide emission rate is 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. 3) indicate that over 70 percent of the total variability in the method occurs during sample collection, leaving the analysis phase responsible for less than 30 percent.

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 rate 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. 5) 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 SO_2 concentration measurement and subsequently in the mass emissions rate measurement (see equations (3) and (5) of section II).

3.3.1.2 Sampling Train Leaks. Sampling train leaks result in measured sample volumes larger than the true sample volume. Leaks also introduce an error in the collected 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 Proportional Sampling. Proportional sampling implies that the sample gas velocity inside the sampling probe be maintained at a fixed fraction of the stack gas velocity throughout sample collection. Furthermore, collecting the sample at one point in the stack assumes a fixed spatial velocity profile in the stack; i.e., if the stack gas velocity increases by 10 percent at one point in the stack, it increases by 10 percent in all other points in the stack. Such an assumption is not always true. To more closely approximate true proportional sampling, it is suggested that proportional sampling at a point be carried out for each sample; i.e, a sample is collected at one point in the stack with the ratio of sampling and stack gas velocities maintained constant. Each of the 6 samples should be collected at a different cross-sectional point in the stack to average out errors from a variable stack gas velocity profile.

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 (subsec. 2.4.2.4) is directly reflected in the SO_2 concentration and mass emission rate (see equations (3) and (5) of section II).

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 operation 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 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 6, two control charts are recommended, as follows:

1. A range chart for the $BaClO_4$ normality determinations, and
2. A range chart for duplicate determinations of SO_2 samples.

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., 8½ x 11 inches or larger and to keep them posted on a wall for viewing by all concerned, rather than having 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. 5).

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 0.0100N is used and the control chart would be as shown in figure 5.

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 coefficient of variation (CV) for the Method 6 analytical phase is estimated as 1.6 percent (ref. 3). A control chart for the range, R, can be constructed as in figure 6. The range computed as the difference for duplicate analyses (to be made on two out of the six SO_2 samples taken per field test) is calculated as

$$\%\, d = \left[\frac{C_{SO_2(o)} - C_{SO_2(d)}}{.5 \left(C_{SO_2(o)} + C_{SO_2(d)} \right)} \right] \times 100 \qquad (8)$$

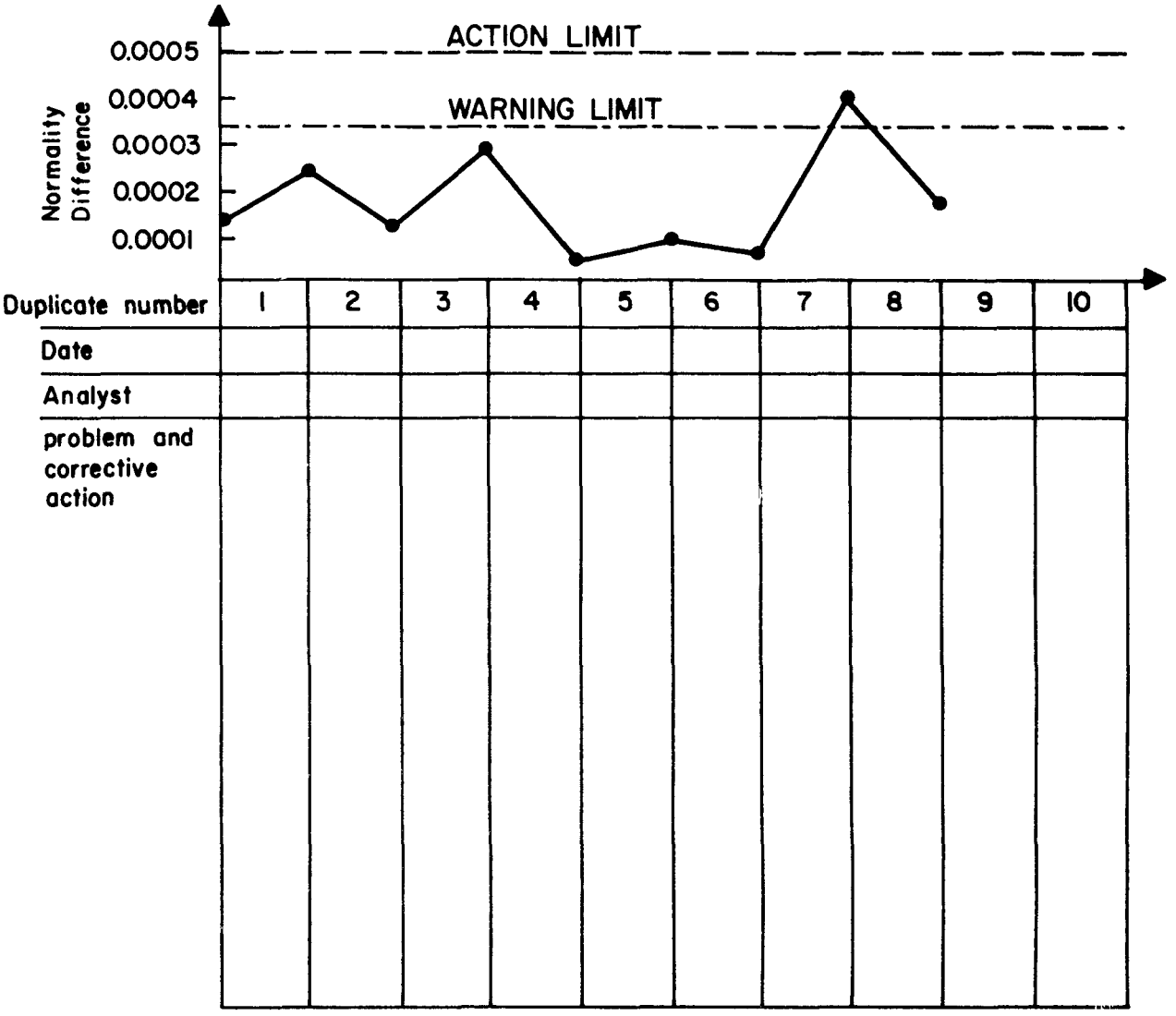
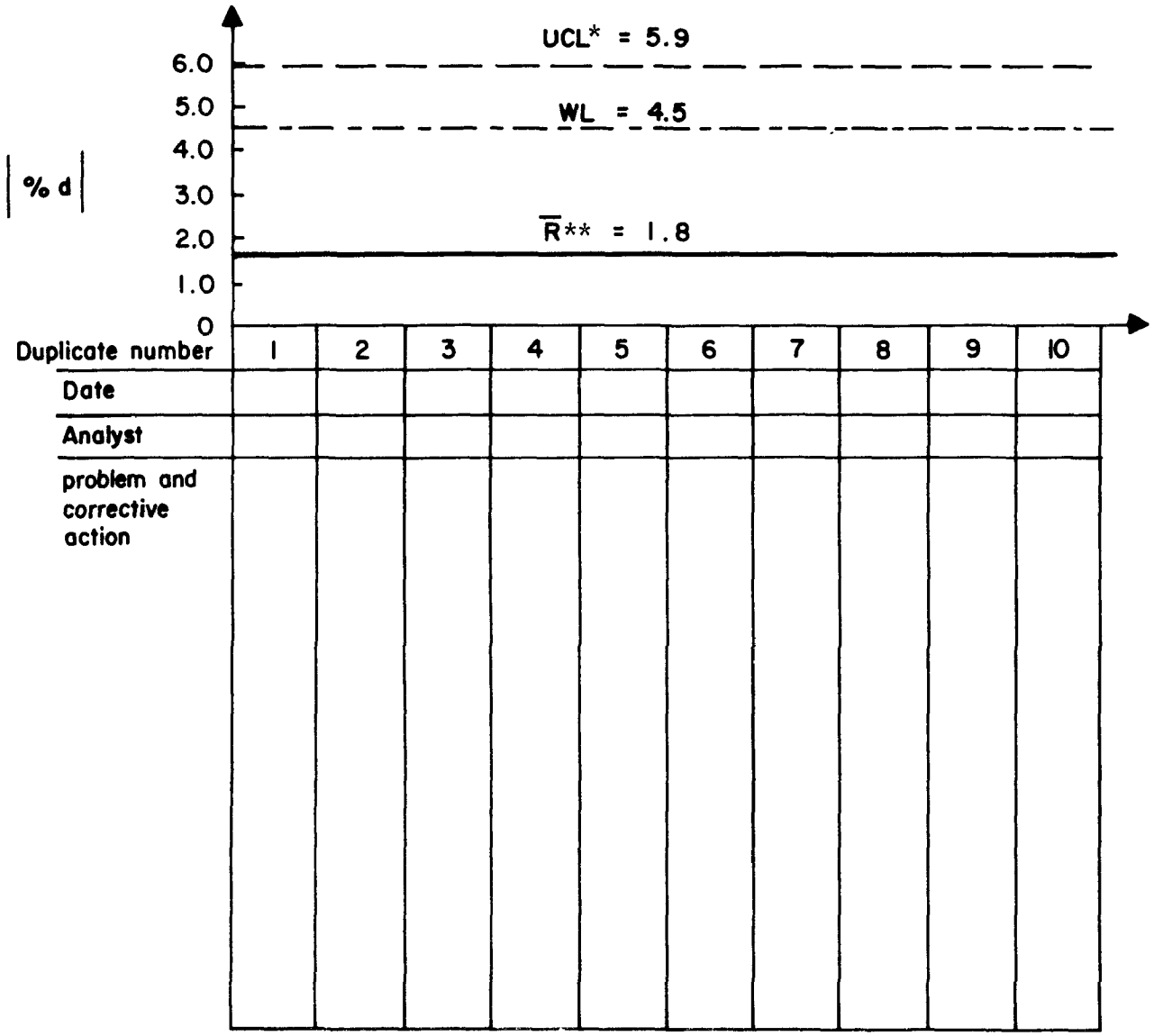


Figure 5. Sample control chart for standardized barium perchlorate solution.



* $UCL = D_4\overline{R} = 3.267 \times 1.8 = 5.9$

** $\overline{R} = d_2 \times CV = 1.128 \times 1.6 = 1.8$

Figure 6. Sample control chart for range of duplicate measurements.

where $C_{SO_2(o)}$ = original determination of SO_2 concentration

$C_{SO_2(d)}$ = duplicate determination of SO_2 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 upper control limit.
2. Two consecutive points fall between the warning limit and upper control limit.
3. Seven consecutive points fall above the $\bar{R}$ line.

When criterion 1 is exceeded, the six SO_2 samples for that field test should be reanalyzed, after the cause of the excess variability has been determined and corrected. Exceeding the second or third criteria will usually indicate poor technique and the need for additional supervision/training.

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 6 - Determination of 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 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 three-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 7 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.

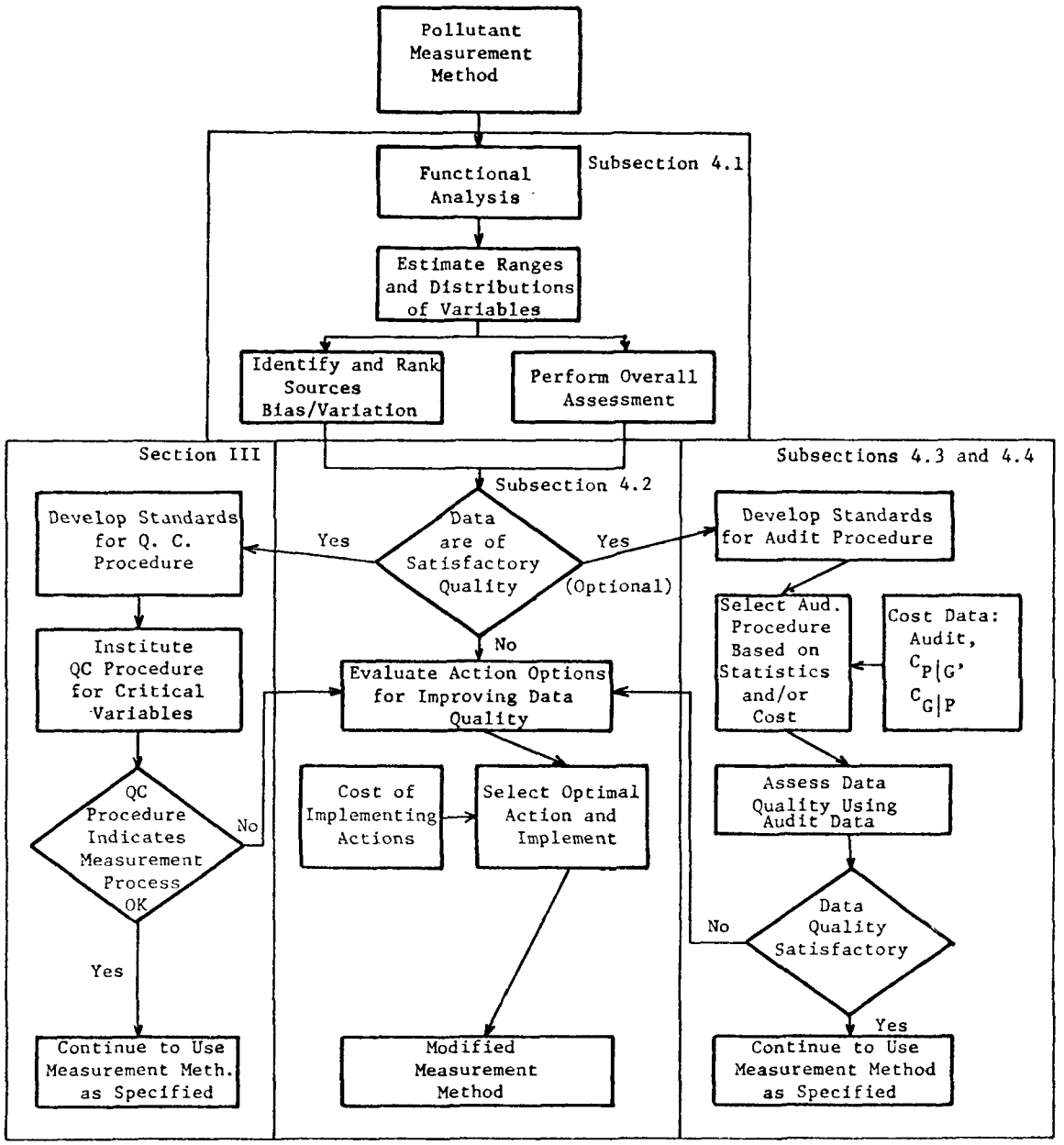


Figure 7. Summary of data quality assurance program.

4.1 FUNCTIONAL ANALYSIS OF THE TEST METHOD

Test Method 6--Determination of Sulfur Dioxide Emissions from Stationary Sources--is described in the Federal Register of December 31, 1971 and reproduced in appendix A of this document. This method is used to determine the concentration of sulfur dioxide in stack gas. Results from this method combined with the volumetric flow rate as measured by Method 2 yield a sulfur dioxide emission rate 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. 3) 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 sulfur dioxide concentration and the sulfur dioxide emission rate.

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_{SO_2} = A single determination of SO_2 concentration at standard conditions, on a dry basis, g/m^3.

$\bar{C}_{SO_2}$ = The average SO_2 concentration of six repetitions, g/m^3.

$CV\{C_{SO_2}\}$ = Within-laboratory coefficient of variation (same laboratory, personnel, equipment, and sample), percent.

$CV_b\{C_{SO_2}\}$ = Between-laboratory coefficient of variation (variation in simultaneous determinations of C_{SO_2} by different laboratories at the same true value of C_{SO_2}), percent.

$CV_L\{C_{SO_2}\}$ = Laboratory bias coefficient of variability in SO_2 determinations due to changes in personnel, equipment, and procedural details), percent.

$CV\{C_{SO_2}\}\sqrt{6}$ = Repeatability coefficient of variation for SO_2 determinations based on six replicates, percent.

$\sqrt{CV_L^2\{C_{SO_2}\} + CV^2\{C_{SO_2}\}/6}$ = 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 rate of sulfur dioxide is calculated from measured values by the relationship

$$ER = 280.1 \frac{N(V_t - V_{tb})(V_{soln}/V_a)T_m}{V_m P_m} (1 - B_{wo}) C_p (\sqrt{\Delta P})_{avg} A_s \left[\frac{P_s}{(T_s)_{avg} M_s}\right]^{1/2} \quad (8)$$

where ER = Sulfur dioxide emission rate, g/hr.

N = Normality of barium perchlorate titrate, g-eq/l.

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 sulfur dioxide, 100 mℓ.

V_a = Volume of sample aliquot titrated, mℓ.

T_m = Average dry gas meter temperature, °K.

V_m = Volume of gas sample through the dry gas meter at meter conditions, ℓ.

P_m = Barometric pressure at the dry gas meter, mm of Hg.

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 subsection.

Note: Measurements generally made only once per field test have a zero variability for within-laboratory determinations. This is indicated in table 2 for the last seven variables.

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 the above 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 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. (The variability of the analysis phase is only about one third of the variability due to sample collection (ref. 3).) However, the above term directly reflects the variability due to sample collection. Any difference in the mass of SO_2 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 volume of titrant that the sample would have required (had there been no error in sample collection) and the volume actually required in the analysis.

Differences in the true mass of 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 (ref. 9),

2. Less than 100 percent collection efficiency of the absorbing solution (ref. 3),
3. Loss of SO_2 due to reactions with particulate matter trapped by the particulate filter (ref. 13),
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 were determined by estimating the variances of all the other variables in table 2 then adding what was needed to make the total variability agree with the results of the collaborative test of the method (ref. 3).

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 bottle (see subsection 2.4.2.5) into a 100-mℓ volumetric flask and diluting to the mark. Errors due to the volumetric flask, incomplete transfer, and diluting to the mark 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 variation of 0.5 and 1.0 percent (for within-laboratory and between-laboratory, respectively) does 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 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. Inprecision 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 SO_2 concentration and volumetric flow rate. That is,

$$ER = C_{SO_2} \times Q_s \tag{9}$$

where the concentration, C_{SO_2}, in g/m^3 is given by

$$C_{SO_2} = 32 \frac{N(V_t - V_{tb})(V_{soln}/V_a)}{V_{m_{std}}} \tag{10}$$

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

$$V_{m_{std}} = 0.3921 \frac{V_m P_m}{T_m} \tag{11}$$

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

$$Q_s = 8.754 \times 10^5 (1 - B_{wo})\, C_p\, (\sqrt{\Delta P})_{avg}\, A_s \left[\frac{P_s}{(T_s)_{avg}\, M_s}\right]^{1/2} \tag{12}$$

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, the ER, in that order (tables 3, 4, 5, 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.

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	0.00	0.30
C_p	0.85 dimensionless	0.00	1.00
$(\sqrt{\Delta P})_{avg}$	7 (mm of $H_2O)^{\frac{1}{2}}$	0.00	1.70
A_s	0.7 m^2	0.00	1.00
P_s	760 mm of Hg	0.00	0.40
$(T_s)_{avg}$	294° K	0.00	1.00
M_s		0.00	0.71

We have defined that

$$CV_b^2\{C_{SO_2}\} = CV_L^2\{C_{SO_2}\} + CV^2\{C_{SO_2}\} \quad (13)$$

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 $CL_L\{C_{SO_2}\} = 4.1$ percent.

The reproducibility coefficient of variation then is taken as

$$CV(R) = CV_L^2\{C_{SO_2}\} + CV^2\{C_{SO_2}\}/6 \quad (14)$$

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

based on six (6) replicates.

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 $CV_b^2\{X\}$	x	Weighting Coefficient	=	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
$(\sqrt{\Delta})_{avg}$	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				$CV_b^2\{Q_s\} = 5.42$	
				$CV_b\{Q_s\} = 2.33\%$	

*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	5.44		1		5.4
ER				$CV^2\{ER\} = 25.3$	
				$CV\{ER\} = 5.0\%$	

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. 14) indicates that this problem is due to the presence of interfering cations (sodium and potassium). The introduction of a neutral pH* fine particulate filter in the sampling train will reduce the possibility of poor endpoints due to the presence of sodium and potassium-containing particulate matter.

4.1.2.2 Nitric oxide. Nitric oxide does not interfere with Method 6 results (ref. 13).

4.1.3 Bias Analysis.

The collaborative study of Method 6 (ref. 3) indicates that the method exhibited a "significant negative bias" at higher SO_2 concentrations, i.e., from 0.48 to 0.80 g SO_2/m^3. Another study (ref. 9) by the same organization also indicates a negative bias at high concentrations, although the investigators admit the possibility of sampling from a gas cylinder having a lower-than-indicated concentration of sulfur dioxide. The collaborative study (ref. 3) indicated that the negative bias was not due to the analytical phase of Method 6, which appeared to be unbiased. A very recent series of experiments conducted by Dr. Joseph Knoll at EPA (ref. 12) contradicts the results of previous studies and indicates no negative bias at very high SO_2 concentrations (up to 30,000 ppm). At such high concentrations it is important to limit the amount of gas sampled, to avoid exhausting the peroxide in the impinger tubes.

A good possibility for explaining low results, if one accepts the data indicating no analytical phase bias, is failure to carry out the purging procedure rigorously. A field evaluation of Method 6 (ref. 9) showed that up to 14 percent of the SO_2 may be retained in the bubblers if purging is not carried out. A negligible percentage of SO_2 remains in the bubblers if purging is done thoroughly (refs. 9, 13).

Subsection 4.1.1.1 indicates other possible reasons for incomplete sample collection, all of which would negatively bias the results. However,

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

there is no way to quantify the loss of sample due to these possibilities. In view of the very recent work (ref. 12) mentioned earlier, and assuming reasonable care in following the recommended collection and analysis procedure, results from Method 6 should be unbiased. 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 of $800/20 field tests)*

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

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

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

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.

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

A0: The collaborative study (ref. 3) estimates the precision of Method 6 as follows:

$CV = 4.00$ percent

$CV_b = 5.80$ percent

$CV_L = 4.19$ percent

The same study indicates the method has a negative bias at higher sulfur dioxide concentrations (from about 0.5 g/m^3 to 0.8 g/m^3). The magnitude is estimated at 5 to 10 percent at this concentration level. However, the work of Dr. Knoll at EPA indicates no significant bias, even at much higher concentrations, of the order of 10,000 to 30,000 ppm. Another evaluation of the method (ref. 9) reports "either a concentration bias in the method or an inaccuracy in the concentration of the 707 ppm (SO_2) cylinder."

The functional analysis (section 4.1) does not anticipate a bias in Method 6, and provided the procedures (both field and laboratory) stipulated in the method are rigorously adhered to, unbiased results should be obtained (ref. 12).

Table 7 shows estimated values for CV, CV_b, and CV_L for each alternate strategy, as well as estimated costs. Actual costs must be determined for each individual situation, and actual improvements in CV, CV_b, and CV_L can be determined only by implementation of the various options.

A1: A major problem associated with Method 6 is the poor visibility of the titration endpoint. Photometric endpoint detection would greatly reduce imprecision due to visual estimation of endpoint color and intensity. Unless the photometric technique became highly standardized, however, there would remain differences in technique among various laboratories, so that the improvement in CV_b is assumed not as great, and thus CV_L is virtually unchanged.

A2: From discussing this method with experienced field testers, it is felt that the method requires an operator that understands the system and its capability. Early detection of out-of-control conditions by the operator can substantially improve data quality.

Table 7. Assumed within-laboratory, between-laboratory, and laboratory bias for action options

		CV	CV_b	CV_L	ADDED COST PER 20 FIELD TESTS
A0	Reference*	CV_R	$(CV_b)_R$	$(CV_L)_R$	0
A1	Photometric End-Point Detection	$0.8\ CV_R$	$0.9(CV_b)_R$	$0.99(CV_L)_R$	$ 800
A2	Crew Training Workshop	$0.8\ CV_R$	$0.8(CV_b)_R$	$0.8(CV_L)_R$	$1000
A3	Calculations by Standard Computer Program	$1.0\ CV_R$	$0.89(CV_b)_R$	$0.8(CV_L)_R$	$ 200
A4	(A1 + A3)	$0.78\ CV_R$	$0.80(CV_b)_R$	$0.79(CV_L)_R$	$1000

*CV_R = 4.00, (CV_b) = 5.80, $(CV_L)_R$ = 4.19, taken directly from the collaborative test results.

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 one-week course once a year, or special OJT training, is estimated to cost approximately $1,000 per 20 field tests.

A3: This recommended option serves a twofold purpose:

1. It eliminates human error (in the field) in calculation of the SO_2 concentration. 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 round-off and all other aspects of the calculation steps.

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

Figure 8 shows the results in terms of cost and data quality. 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 9. It must be emphasized that figures 8 and 9 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 6 by a number of modifications of the method, and that there is a cost associated with each modification.

Figures 8 and 9 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.

Once determined for a given situation, graphs such as figures 8 and 9 can be used to select an "optimal" monitoring strategy; i.e., one which gives maximum increase in data quality for minimum cost.

In some instances a manager may need to know the total cost of attaining a prescribed reduction in variability. Figures 8 and 9 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 and 0.72, respectively.

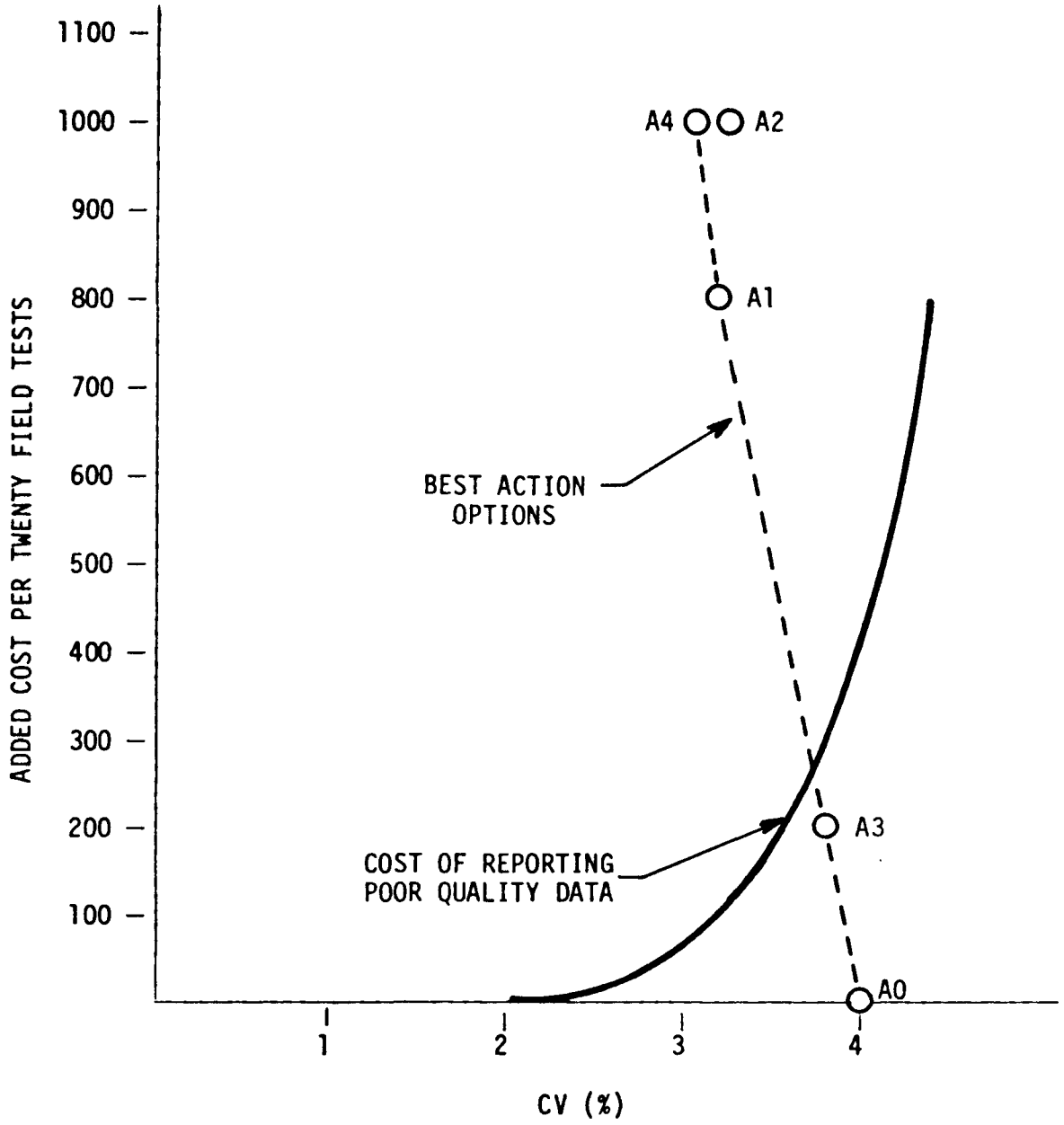

Figure 8. Added cost versus data quality (CV) for selected action options.

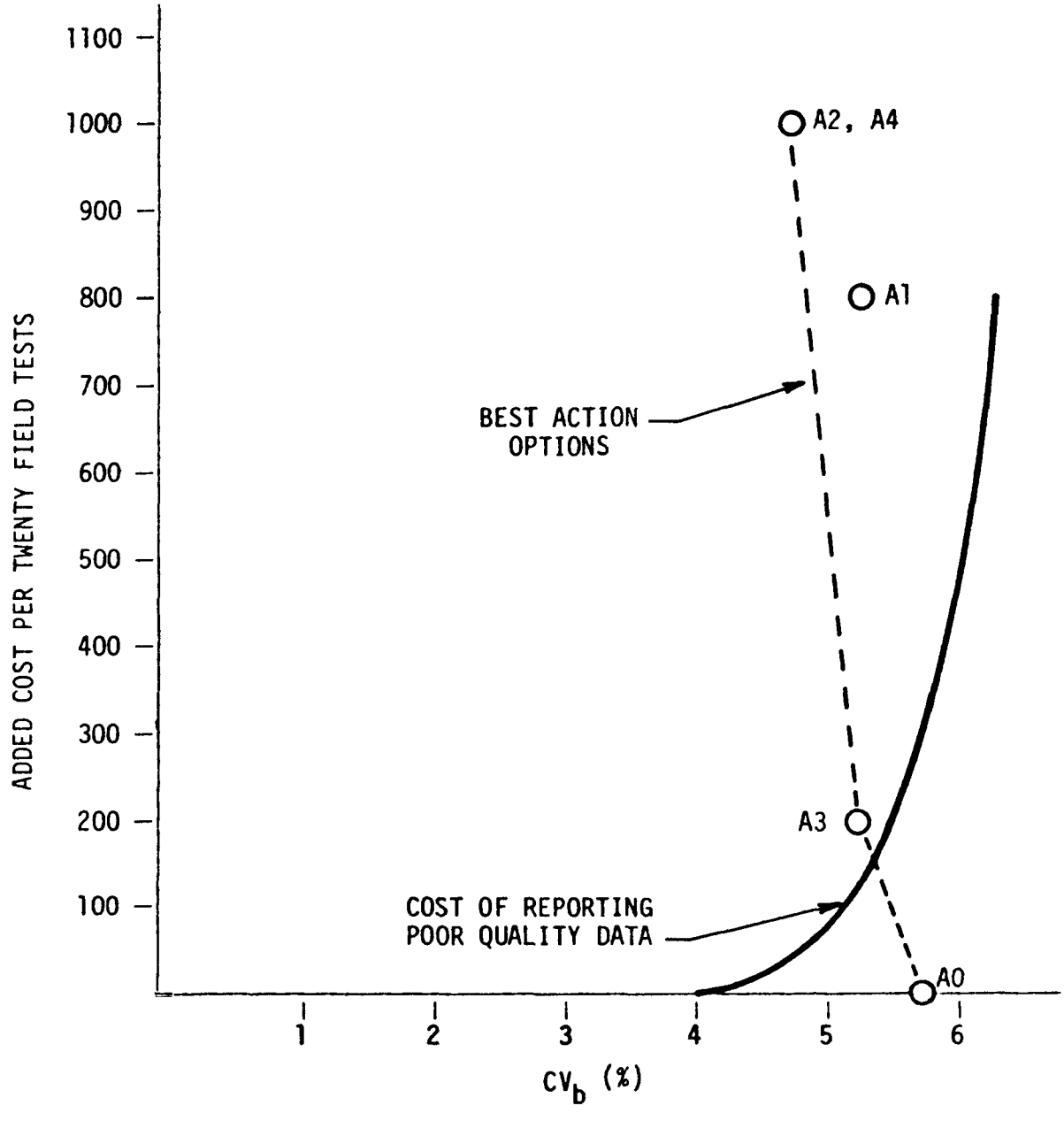

Figure 9. Added cost versus data quality (CV_b) for selection action options.

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 SO_2 in air and has the field team analyze the sample. The field team should not know the true SO_2 concentration. From these data, both bias and precision estimates can be made for the analysis phase of the measurement process.

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 procedures and techniques of the field team during on-site measurements.
2. Have field team measure sample from a reference cylinder with known SO_2 concentration.
3. Check/verify applicable records of equipment calibration checks and quality control charts in the field team's home laboratory.
4. Compare the audit value with the field team's test value.
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 On-Site 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;
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.

In addition to the above on-site observations, it is recommended that the auditor have the capability for preparation of reference samples of SO_2 in air for analysis by the field team. (See ref. 3 for details of SO_2-air sample preparation.)

4.3.3 Collecting Home Laboratory Information.

The auditor must also observe the analytical phase of Method 6. 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 6 can be audited with standard sulfate solutions, as discussed in reference 3.

4.3.3.1 Comparing Audit and Routine Values of SO_2. In field tests the audit and routine (field team) values are compared by

$$d_j = (SO_2)_j - (SO_2)_{aj} \qquad (15)$$

where

d_j = The difference in the audit and field test results for the j^{th} audit, mg/m^3

$(SO_2)_{aj}$ = Audit value of SO_2 concentration for j audit, mg/m^3

$(SO_2)_j$ = SO_2 concentration obtained by the field team, mg/m^3

Record the value of d_j 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 audit. However, unmeasurable errors can result from nonadherence to the prescribed operating procedures and/or from poor technique in executing the procedures. There 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 accuracy 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 SO_2 concentration were given in section 4.1. This section will indicate how the audit data collected in accordance with the procedure described in section 4.2 will be utilized to estimate the precision and accuracy of the measures of interest. Similar techniques can also be used by a specific firm or team to assess their own measurements. The differences between the field team results and the audited results for the respective measurements are

$$d_j = (SO_2)_j - (SO_2)_{aj} .$$

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

$$\bar{d} = \sum_{j=1}^{n} d_j/n, \qquad (16)$$

and

$$s_d = \left[\sum_{j=1}^{n} (d_j - \bar{d})^2/(n - 1) \right]^{1/2} \qquad (17)$$

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.,

$$t = \frac{\bar{d} - 0}{s_d/\sqrt{n}} . \qquad (18)$$

See ref. 15 for a discussion of the t-test.

If t is significantly large, say greater than the tabulated value of t with 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 much more accurate than the field measurements, then s_d is an estimate of $\sigma\{SO_2\}$, the population standard deviation for SO_2 concentration measurements. The standard deviation, s_d, can be utilized to check the reasonableness of the assumptions made in section 4.1 concerning $\sigma\{SO_2\}$*. For example, the estimated standard deviation, s_d, may be directly checked against the assumed value, $\sigma\{SO_2\}$, 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 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

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*Values for $\sigma\{SO_2\}$ and $\sigma_b\{SO_2\}$ are found by multiplying the values of CV or CV_b by the assumed value of the mean concentration of SO_2. This converts the percentages into concentrations.

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. 16-21. 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 value of SO_2 is designated as d_j, and the mean difference over n audits by $\bar{d}$ is

$$\bar{d} = 1/n \sum_{j=1}^{n} (SO_2)_j - (SO_2)_{aj} \qquad (20)$$

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. 19, a procedure for applying the variables sampling plan is described below. Figures 10 and 11 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. 19. 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,

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

   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 are 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

*12.0 mg/m^3 assumes for calculation purposes an SO_2 concentration mean of 100 mg/m^3, with CV = 4.00%, so that $3\sigma = 3 \times 4.00 = 12.0$ mg/m^3.

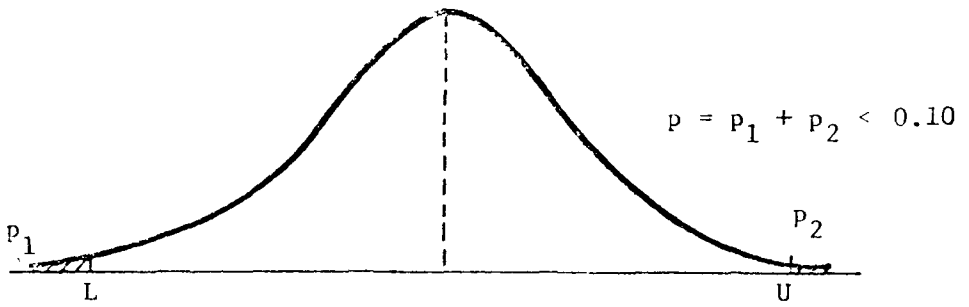

Figure 10. Example illustrating $p < 0.10$ and satisfactory data quality.

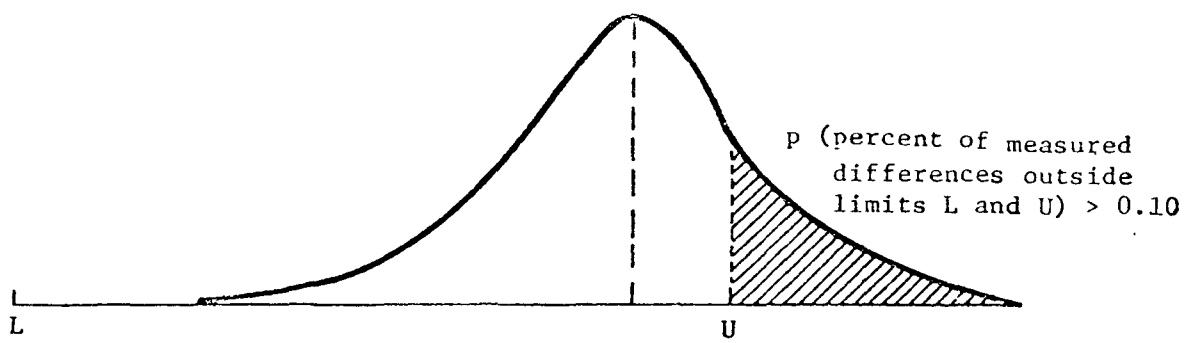

Figure 11. Example illustrating $p > 0.10$ and unsatisfactory data quality.

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
$\bar{d} = \frac{\Sigma d_j}{n}$		$\bar{d} = 5.6\ mg/m^3$	
$s_d^2 = \frac{\Sigma d_j^2 - \frac{(\Sigma d_j)^2}{n}}{(n-1)}$		$s_d^2 = 135$	
$s_d = \sqrt{s_d^2}$		$s_d = 11.6\ mg/m^3$	

field tests are performed. Data corrections should be made when possible, i.e., if a quantitative basis is determined for correction.

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 n = 7, and p = 0.10, the test criteria become

$$\bar{d} - k\, s_d = 5.6 - 2.334 \times 11.6 = -21.5 < L = -12\ mg/m^3$$

$$\bar{d} + k\, s_d = 5.6 + 2.334 \times 11.6 = 32.7 > U = +12\ mg/m^3$$

Table 9. Sample plan constants, k for P {not detecting a log 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

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 the designated limits L and U) with a risk of 0.10; that is, on the avarage, 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 12. 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

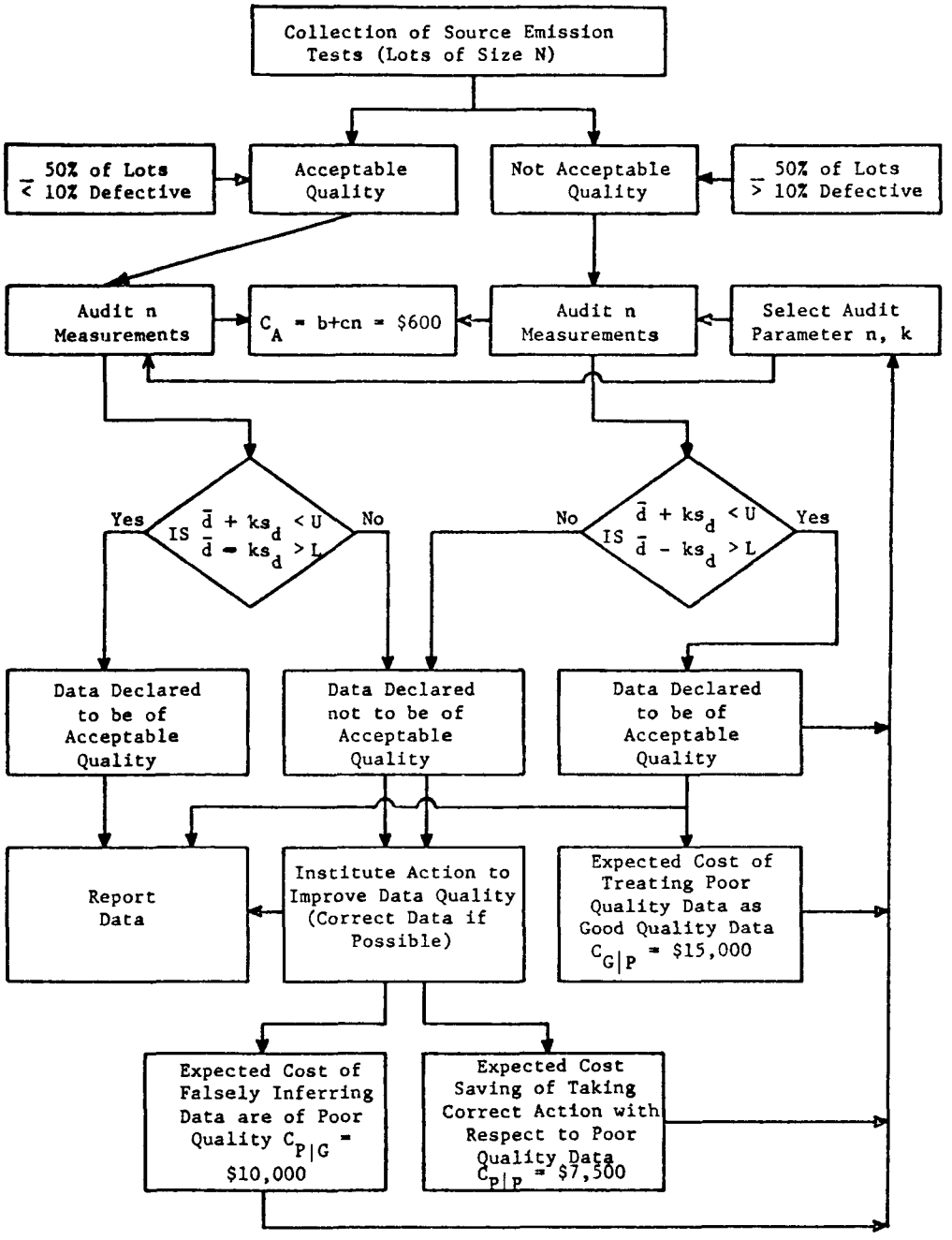

Figure 12. Flow chart of the audit level selection process.

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 section 4.1, 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 contain at most about 0.3 percent defective measurements (i.e., outside the limits defined by L and U). 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, given 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, given 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 13. 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

$$E(TC = -C_A - 0.5\ P_{P|G}\ C_{P|G} + 0.5\ P_{P|P}\ C_{P|P} - 0.5\ P_{G|P}\ C_{G|P} \qquad (22)$$

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

In order to complete the determination of n, it is necessary to calculate each of the conditonal probabilities, using the assumptions stated

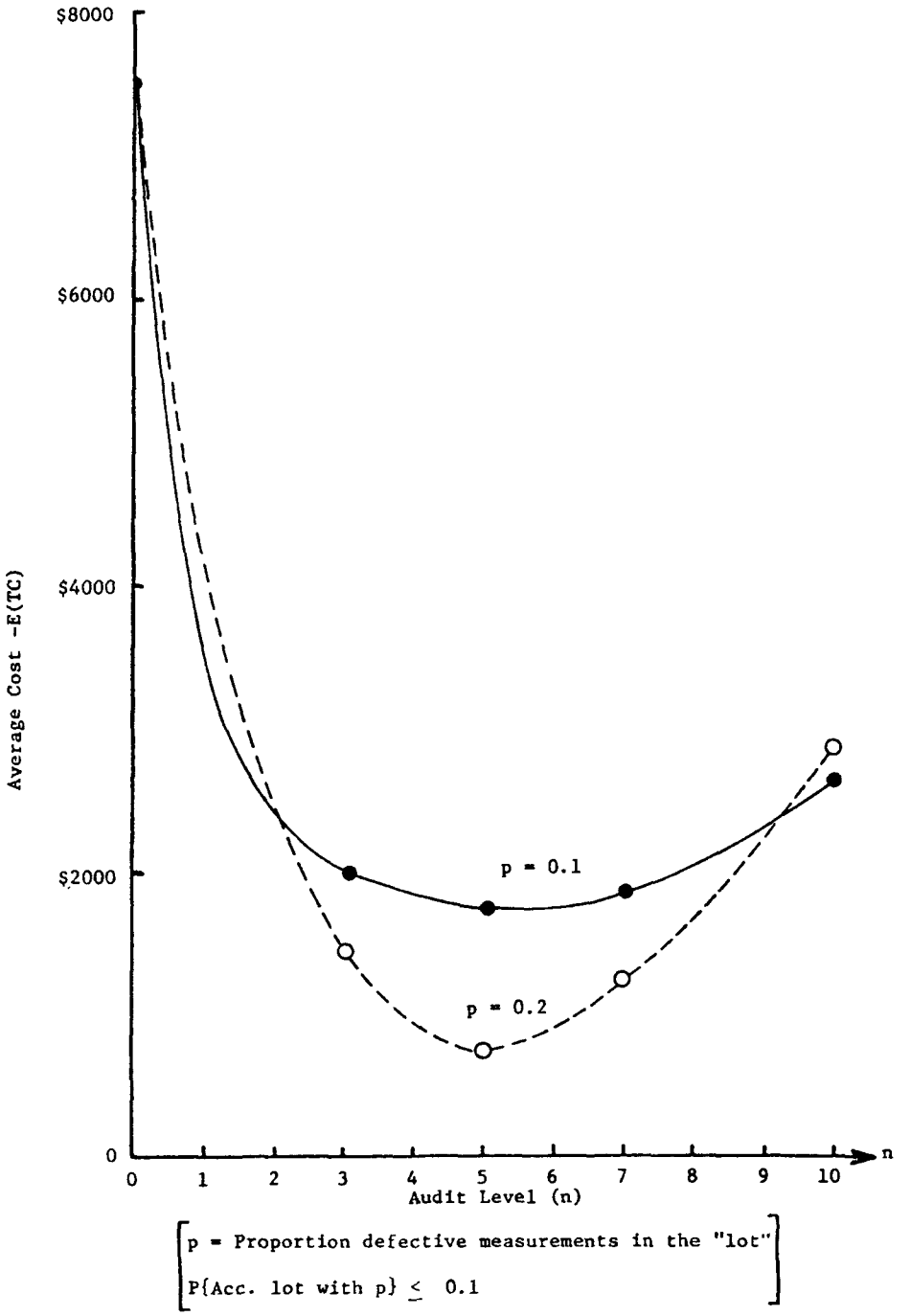

Figure 13. Average cost vs audit level (n).

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 than 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 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 equation (22) 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 14. 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 6--DETERMINATION OF SULFUR DIOXIDE EMISSIONS FROM STATIONARY SOURCES

1. Principle and Applicability

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

1.2 Applicability. This method is applicable for the determination of sulfur dioxide emissions from stationary sources only when specified by the test procedures for determining compliance with new source performance standards. The minimum detectable limit of the method has been determined to be 3.4 mg of SO_2/m^3 (2.1×10^7 lb/ft^3). No upper limit has been established.

2. Apparatus

2.1 Sampling. See figure 6-1.

2.1.1 Probe--Borosilicate glass, approximately 5 to 6 mm i.d., with a heating system to prevent water condensation and equipped with a filter (either in-stack or heated out-stack) to remove particulate matter including sulfuric acid mist.

2.1.2 Bubbler and impingers--One midget bubbler, with medium coarse glass frit and borosilicate or quartz glass wool packed in top (see figure 6-1) to prevent sulfuric acid mist carryover; and three midget impingers, each with 30-ml capacity, or equivalent. The bubbler and midget impingers shall be connected in series with leak free glass connectors. Silicone grease may be used, if necessary, to prevent leakage.

2.1.3 Glass wool--Borosilicate or quartz.

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

2.1.5 Drying tube--Tube packed with 6- to 16-mesh indicating-type silica gel, or equivalent, to dry the gas sample and to protect the meter and pump.

2.1.6 Valve--Needle valve, to regulate sample gas flow rate.

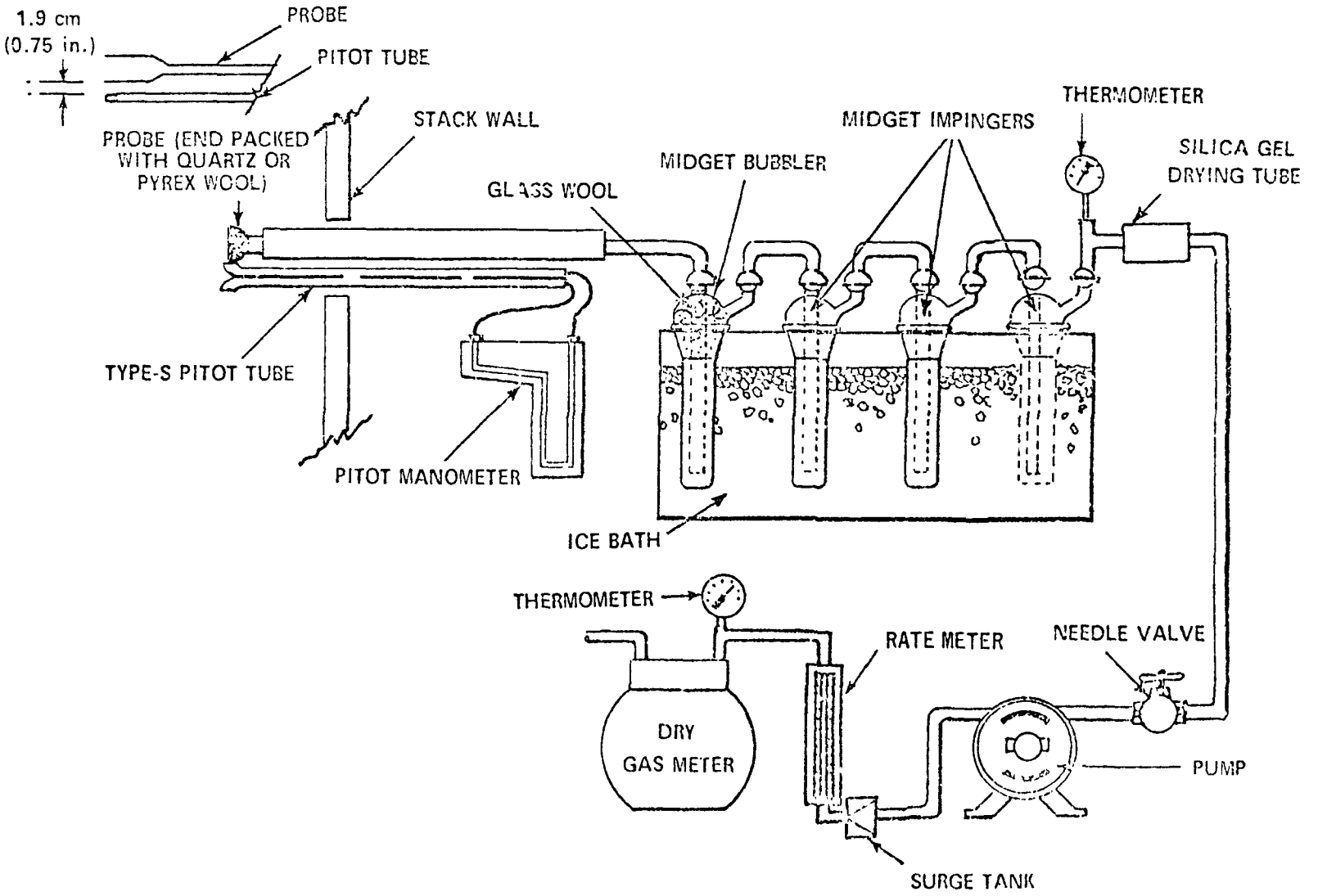

Figure 6-1. SO_2 sampling train.

2.1.7 Pump--Leak free, diaphragm pump, or equivalent, to pull gas through the train.

2.1.8 Volume meter--Dry gas meter, sufficiently accurate to measure the sample volume within 2 percent, calibrated over the range of flow rates and conditions actually used during sampling and equipped with a temperature gauge (dial thermometer, or equivalent).

2.1.9 Flow Meter--Potameter, or equivalent, to measure flow range from 0 to 2 l pm (0 to 5 cfh).

2.1.10 Pitot tube--Type S, or equivalent, attached to probe to allow constant monitoring of the stack gas velocity so that the sampling flow rate can be regulated proportional to the stack gas velocity. The tips of the probe and pitot tube shall be adjacent to each other and the free space between them shall be 1.9 cm (0.75 in.). 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.

The pitot tube shall be equipped with an inclined manometer, or equivalent device, capable of measuring velocity head to within 10 percent of the minimum measured value.

2.1.11 Temperature gauge--Dial thermometer, or equivalent, to measure temperature of gas leaving impinger train to within 1° C (2° F).

2.1.12 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 case 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.

2.2 Sample recovery.

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

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

2.3 Analysis.

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

2.3.2 Volumetric flasks--100-ml size (one per sample) and 1000 ml sizes.

2.3.3 Burettes--5-ml and 50-ml sizes.

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

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

2.3.6 Graduated cylinder--100-ml size.

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 Water-Deionized, distilled to conform to ASTM specification D1193-72, Type 3.

3.1.2 Isopropanol, 80%-Mix 80 ml of isopropanol with 20 ml of deionized, distilled water.

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

3.2 Sample recovery.

3.2.1 Water-Deionized, distilled, as in 3.1.1.

3.2.2 Isopropanol, 80%--Mix 80 ml of isopropanol with 20 ml of deionized, distilled water.

3.3 Analysis

3.3.1 Water--Deionized, distilled, as in 3.1.1.

3.3.2 Isopropanol, 100%.

3.3.3 Thorin indicator--1-(o-arsonophenylazo)-2-naphtol-3, 6-disulfonic acid, disodium salt, or equivalent. Dissolve 0.20 g in 100 ml of deionized, distilled water.

3.3.4 Barium perchlorate solution, 0.01 N--Dissolve 1.95 g of barium perchlorate trihydrate [$Ba(ClO_4)_2.3H_2O$] in 200 ml distilled water and dilute to 1 liter with isopropanol. $BaCl_2$ may also be used. Standardize as in section 5.2.

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 potassium acid phthalate (primary standard grade).

4. Procedure

4.1 Sampling.

4.1.1 Preparation of collection train. Measure 15 ml of 80% isopropanol into the midget bubbler and 15 ml of 3% hydrogen peroxide into each of the first two midget impingers. Leave the final midget impinger dry. Assemble the train as shown in figure 6-1. Adjust probe heater to operating temperature. Place crushed ice and water around the impingers. Leak check the sampling train just prior to use at the sampling site by plugging the probe inlet and pulling a vacuum (capacity of pump) with the flow regulator valve wide open. Observe the dry gas volume meter dial and time any apparent flow using a stop watch. A leakage rate not in excess of 1% of the sampling rate is acceptable. Close the flow regulator valve and carefully release the probe inlet plug and turn off the pump.

4.1.2 Sample collection. Record the initial dry gas meter reading and barometric pressure. To begin sampling, position the tip of the probe at the sampling point and start the pump. Adjust the sample flow to a rate of approximately 1 lpm as indicated by the rotameter. Sample at a rate that is proportional (within 20 percent of the average) to the stack gas velocity throughout the run. Take readings (dry gas meter, temperatures at dry gas meter and at impinger outlet, rate meter, and velocity head) at least every five minutes and when significant changes (20 percent variation in velocity head readings) in stack conditions necessitate additional adjustments in sample flow rate. Add more ice during the run to keep the temperature of the gases leaving the last impinger at 20° C (68° F) or less. At the conclusion of each run, turn off the pump and record the final readings. Conduct a leak check as before. If excessive leakage rate is found void the test 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 sampling rate. Note: Clean ambient air can be provided by passing air through a charcoal filter or through an extra midget impinger with 15 ml 3% H_2O_2.

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

4.3 Sample analysis. Note level of liquid in container and confirm whether or not any sample was lost during shipment by noting this on analytical data sheet. (Note: Protect the 0.01 N barium perchlorate solution from evaporation at all times.) Transfer the contents of the storage container to a 100-ml volumetric flask and dilute to exactly 100 ml with deionized, distilled water. Pipette a 20-ml aliquot of this solution into a 250-ml Erlenmeyer flask, add 80 ml of isopropanol, two to four drops of thorin indicator and titrate to a pink endpoint using 0.01 N barium perchlorate. Repeat and average the titration volumes. Run a blank with each series of samples. Replicate titrations shall agree within 1 percent.

5. Calibration

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

5.2 Standardize the barium perchlorate solution against 25 ml of standard sulfuric acid to which 100 ml of isopropanol has been added.

6. Calculations

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

6.1 Nomenclature.

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

N = Normality of barium perchlorate titrant, milliequivalents/ml.

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

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

T_m = Average dry gas meter absolute temperature, °K (°R).

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

V_a = Volume of sample aliquot titrated, ml.

V_m = Dry gas volume as measured by the dry gas meter, dcm (dcf).

$V_{m(std)}$ = Dry gas volume measured by the dry gas meter, corrected to standard conditions, dscm (dscf).

V_{soln} = Total volume of solution in which the sulfur dioxide sample is contained, 100 ml.

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

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

32.03 = Equivalent weight of sulfur dioxide.

6.2 Dry sample gas volume, corrected to standard conditions.

$$V_{m(std)} = V_m \left(\frac{T_{std}}{T_m}\right)\left(\frac{P_{bar}}{P_{std}}\right) = K \left(\frac{V_m P_{bar}}{T_m}\right) \qquad (6\text{-}1)$$

where:

$K = 0.3857\ ^{\circ}$ K/mmHg for metric units.

$= 17.65\ ^{\circ}$ R/in. Hg for English units.

6.3 Sulfur dioxide concentration.

$$C_{SO_2} = K \frac{(V_t - V_{tb})N \left(\frac{V_{soln}}{V_a}\right)}{V_{m(std)}} \qquad (6\text{-}2)$$

where:

$K = 32.03$ mg/meq. for metric units.

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

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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 $\sigma\{SO_2\} = 4.00\ mg/m^3$ (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).

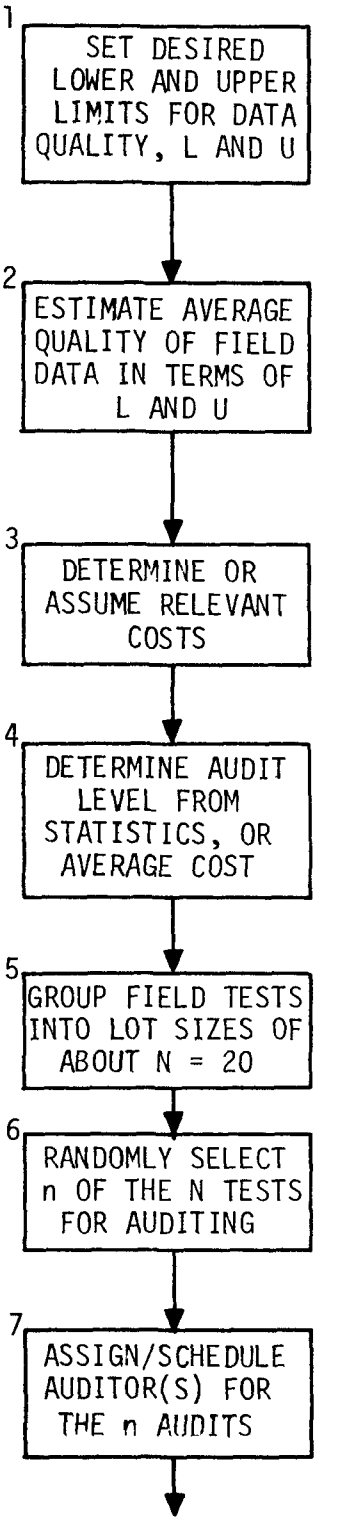
3. DETERMINE: (1) COST OF CONDUCTING AN AUDIT, (2) COST OF FALSELY INFERRING THAT GOOD DATA ARE BAD, (3) COST OF FALSELY INFERRING THAT BAD DATA ARE GOOD, AND (4) COST SAVINGS FOR CORRECTLY IDENTIFYING BAD DATA (subsec. 4.4.3).

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 = 5 (fig. 14).

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 CV = 4.00%.

AUDITOR

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

9. OBSERVE THE FIELD TEAM'S PERFORMANCE OF THE FIELD TEST (subsec. 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 (subsec. 4.3.4).

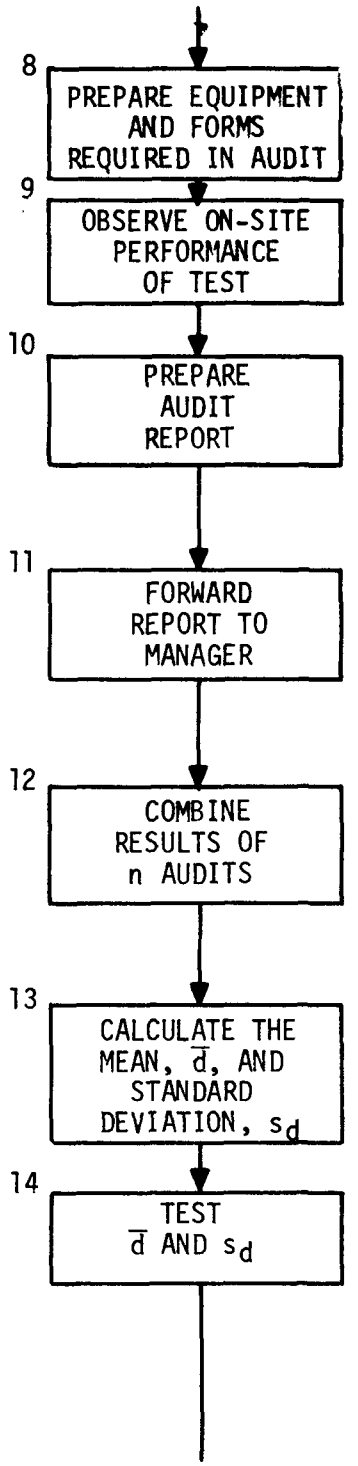
11. THE AUDITOR'S REPORT IS FORWARDED TO THE MANAGER.

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 4. RESULTS OF THIS SAMPLE CALCULATION SHOW $\bar{d} = 5.6$ AND $s_d = 11.6$ (table 8, subsec. 4.4.2).

14. USE A t-TEST TO CHECK $\bar{d}$ FOR SIGNIFICANCE, FOR THIS EXAMPLE $t = (5.6 \times \sqrt{7})/4.00 = 3.70$. THE TABULATED t-VALUE FOR 6 DEGREES OF FREEDOM AT THE 0.05 LEVEL IS 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 4.00 mg/m^3.



15. OBTAIN THE VALUE OF k FROM TABLE 6, FOR n = 7 AND p = 0.1. THIS VALUE IS 2.334, THEN $\bar{d} + k\ s_d = 32.7\ mg/m^3$ AND $\bar{d} - k\ s_d = -21.5\ mg/m^3$ (subsec. 4.4.2).

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

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

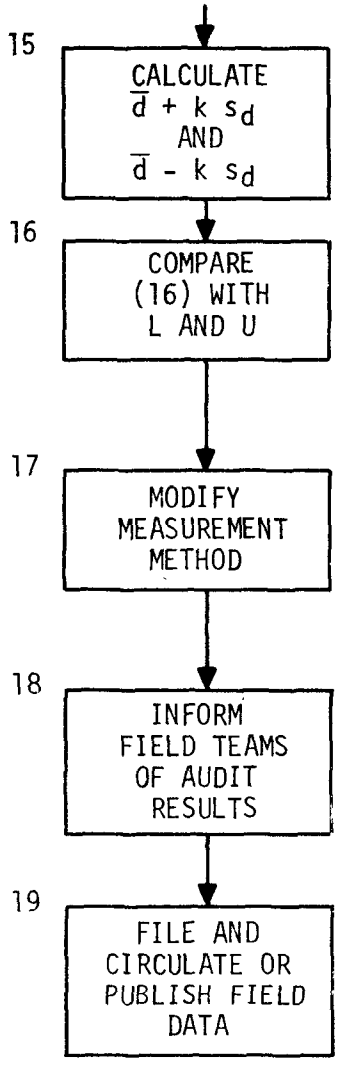
$$\bar{d} - k\ s_d = -21.5 < L = -12.0\ mg/m^3$$

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 (subsec. 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 ($100\ s_X/\bar{X}$) 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 of NO_2 arrived at by the field crew for the j^{th} audit.
$\bar{d}$	Mean difference between $(SO_2)_j$ and $(SO_2)_{aj}$ for n audits.
s_d	Computed standard deviation of differences between $(SO_2)_j$ and $(SO_2)_{aj}$.
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, $\bar{d}$, 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).

APPENDIX C 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.
SO_2	Sulfur dioxide reported by the field team for field test.
$(SO_2)_a$	Sulfur dioxide concentration used in an audit check.
$(SO_2)_m$	Measured value of a calibration gas.
$(SO_2)_t$	Assayed or known value of a calibration gas.

APPENDIX D GLOSSARY OF TERMS

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

Accuracy	A measure of the error of a process expressed as a comparison between the average of the measured values and the true or accepted value. It is a function of precision and bias.
Bias	The systematic or nonrandom component of measurement error.
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 controlled 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 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.

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16. ABSTRACT

Guidelines for the quality control of stack gas analysis for 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
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