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GUIDELINES FOR DEVELOPMENT OF A QUALITY ASSURANCE PROGRAM: VOLUME VI - DETERMINATION OF NITROGEN OXIDE EMISSIONS FROM STATIONARY SOURCES

Office of Research and Development
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GUIDELINES FOR DEVELOPMENT OF A QUALITY ASSURANCE PROGRAM: VOLUME VI - DETERMINATION OF NITROGEN OXIDE EMISSIONS FROM STATIONARY SOURCES

by

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ABSTRACT

Guidelines for the quality control of stack gas analysis for nitrogen oxides, except nitrous oxide, emissions by the Federal reference method are presented. These include:

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

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

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

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SECTION I INTRODUCTION

This document presents guidelines for developing a quality assurance program for Method 7, Determination of Nitrogen Oxide, Except Nitrous Oxide, 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 manual sets forth recommended operating procedures to insure the collection of data of high quality, and instructions for performing quality control checks designed to give an indication or warning that invalid data or data of poor quality are being collected, allowing for corrective action to be taken before future measurements are made. A Plan Activity Matrix is included.

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

Section IV, Manual for 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, and statistical properties of and procedures for carrying out auditing procedures for an independent assessment of data quality.

The objectives of this quality assurance program for Method 7 are to:

1. Minimize systematic errors (biases) and maintain precision within acceptable limits in the measurement process,
2. Provide routine indications for operating purposes of satisfactory performance of personnel and/or equipment,
3. Provide for prompt detection and correction of conditions that 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 for all the methods in the final report of this contract. All other components are treated in this document.

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

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

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

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

Quality assurance guidelines for Method 7 as presented here are designed to insure the collection of data of acceptable quality by prevention, detection, and quantification of equipment and personnel variations in both the field and the laboratory through:

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

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

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

SECTION II OPERATIONS MANUAL

2.0 GENERAL

This manual sets forth recommended procedures for determination of nitrogen oxide emissions from stationary sources according to Method 7. (Method 7 is reproduced and 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. In addition, the performance of special quality control procedures and/or checks as prescribed by the supervisor for assurance of data quality may be required of the operator on special occasions.

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 7 as reproduced in appendix A in detail. In addition, the quality assurance documents of this series for Methods 2, 3, and 4 should be read and followed.

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.

EQUIPMENT SELECTION

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

EQUIPMENT CHECK AND CALIBRATION

2. CALIBRATE EQUIPMENT WHEN FIRST PURCHASED AND WHEN DAMAGED OR ERRATIC BEHAVIOR IS OBSERVED. (Subsection 2.3)

PRESAMPLING PREPARATION

3. OBTAIN PROCESS DATA, SELECT/PREPARE SAMPLING SITE, DETERMINE LOGISTICS FOR PLACING EQUIPMENT ON-SITE, AND DETERMINE STACK CONDITIONS T_s, V_s, B_w, and M_d. (Subsection 2.4.1)

4. CHECK OUT SAMPLE TRAIN AND RELATED COMPONENTS. (Subsection 2.4.2)

5. PACKAGE EQUIPMENT IN A MANNER TO PREVENT BREAKAGE OR DAMAGE DURING HANDLING AND SHIPMENT. SHIP EQUIPMENT BY THE BEST MEANS AVAILABLE. (Subsection 2.4.4)

ON-SITE NO_x MEASUREMENT

6. MOVEMENT OF EQUIPMENT TO SAMPLING SITE AND SAMPLE RECOVERY AREA. (Subsection 2.5.1)

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

8. DETERMINE THE TRAVERSE POINT (SAMPLE POINT) ACCORDING TO METHOD ONE.

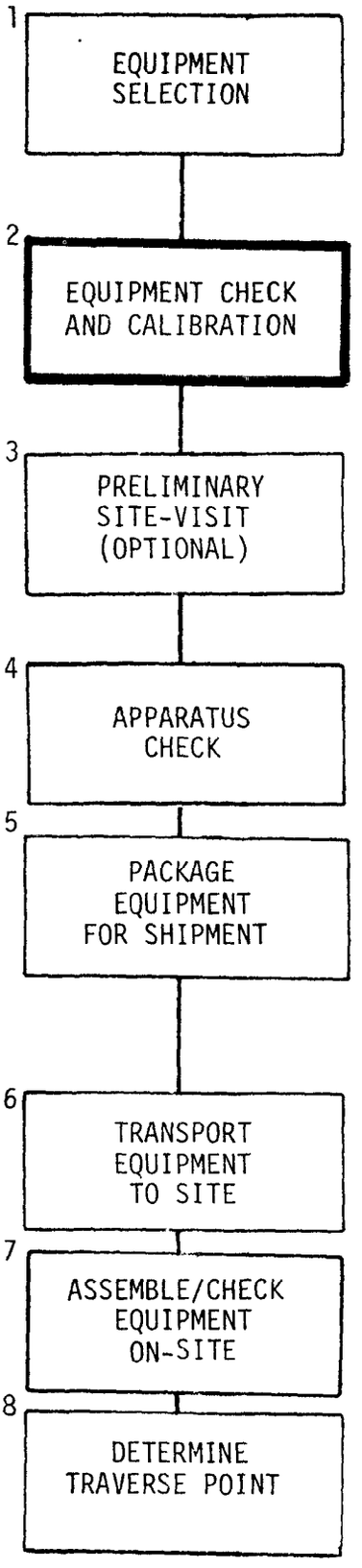

Figure 1. Operational flow chart of the measurement process.

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

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

11. DETERMINE THE MOISTURE CONTENT OF THE STACK GAS USING THE QUALITY ASSURANCE DOCUMENT FOR METHOD 4.

12. DETERMINE THE MOLECULAR WEIGHT OF THE STACK GAS (WET BASIS) USING THE QUALITY ASSURANCE DOCUMENT FOR METHOD 3 AND THE RESULTS OF STEP 11 ABOVE.

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

14. PREPARE ABSORBING REAGENT AND/OR ACCURATELY PIPETTE 25 ml OF REAGENT INTO THE COLLECTION FLASK(S).

15. EVACUATE FLASK(S), MEASURE AND RECORD FINAL FLASK PRESSURE AND AMBIENT TEMPERATURE.

16. PERFORM SAMPLE COLLECTION ACCORDING TO THE PROCEDURE GIVEN IN SUBSECTION (Subsection 2.5.3.3)

17. MEASURE AND RECORD THE INTERNAL PRESSURE (ABSOLUTE) OF THE COLLECTION FLASK(S).

18. MAKE SOLUTION ALKALINE BY ADDING 1 N NAOH.

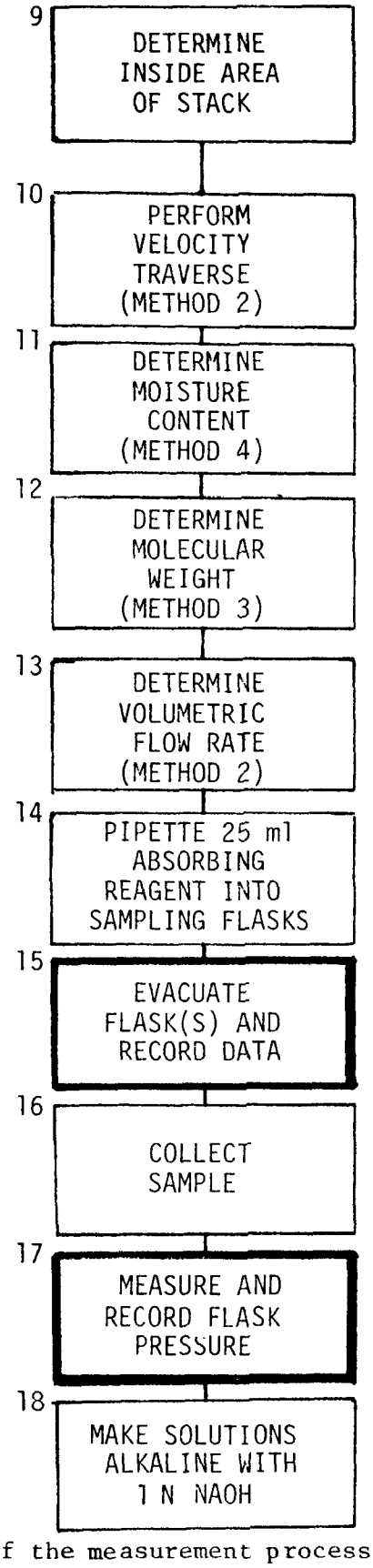

Figure 1. Operational flow chart of the measurement process (continued).

19. DISASSEMBLE AND INSPECT EQUIPMENT FOR DAMAGE SUSTAINED BUT NOT DETECTED DURING SAMPLING.

20. PACKAGE EQUIPMENT AND SAMPLES FOR RETURN TRIP TO BASE LABORATORY.

POSTSAMPLING OPERATIONS

21. ANALYZE SAMPLES FOR OXIDES OF NITROGEN BY THE PHENOL-DISULFURIC ACID PROCEDURE (Subsection 2.6.1)

22. PERFORM CALCULATIONS UTILIZING ALL FIELD AND CALIBRATION DATA (Subsection 2.6.2)

23. FORWARD THE DATA FOR FURTHER INTERNAL REVIEW OR TO THE USER.

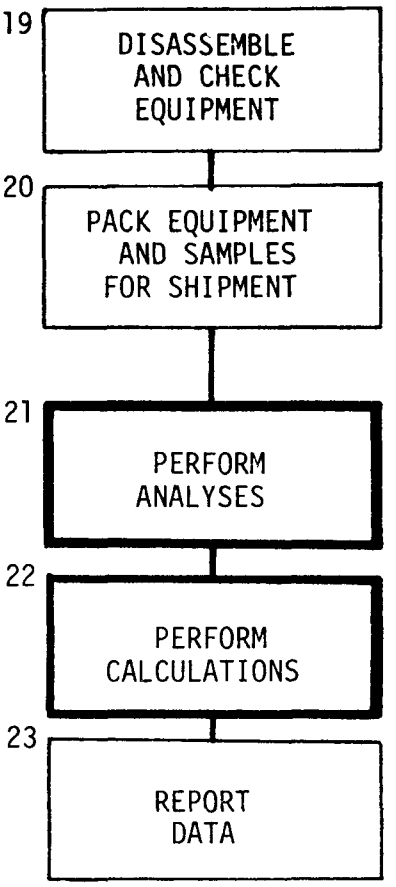

Figure 1. Operational flow chart of the measurement process.

2.1 PLAN ACTIVITY MATRIX

This section consists of a Plan Activity Matrix which summarizes the entire measurement procedure and includes acceptance criteria for procurement of materials, preparation of reagents, calibration of equipment and maintenance.

PLAN ACTIVITY MATRIX

Characteristic	Acceptance Limits	Frequency of Check or Measurement	Method of Measurement	Action Required if outside Limits	Record of Checks
Section 2.1.1 Absorbing Reagent Preparation See Section 2.3.5.2 for detailed information.					
(1) Sulfuric Acid (concentrated)	2.8 mℓ per liter	On makeup of solution	Graduated pipette	Make up new solution	Lab Data Log Book
(2) Hydrogen Peroxide, 3%	6 mℓ per liter	On makeup of solution	Graduated pipette	Make up new solution	Lab Data Log Book
Section 2.1.2 Sample Recovery Reagent Preparation See Section 2.3.5.2 for detailed information.					
Sodium Hydroxide	40 g per liter	On makeup of solution	Triple-beam balance, Class A volumetric flask	Make up fresh solution	Lab Data Log Book
Water	Deionized, distilled to ASTM specifications D11 93-82, Type 3	-----	-----	Prepare fresh for each analysis period	Lab Data Log Book

Apparatus Assembly

Sampling train should be assembled as shown in appendix A, figure 7-1 and a leak check performed.

Leak Checks:

(1) Careful, visual/physical inspection of all connections.

(2) Operational check as by Section.

PLAN ACTIVITY MATRIX

Characteristic	Acceptance Limits	Frequency of Check or Measurement	Method of Measurement	Action Required if outside Limits	Record of Checks
Section 2.1.3 Sample Collection See Section 2.5.3 for detailed information.					
Operational Check	(1) Vacuum of 75 mm Hg (3 inches Hg) or less absolute pressure	Before sample collection	Hg-filled U-tube manometer	Check system for leaks, then check vacuum pump	Sample record sheet
	(2) Leakage rate no greater than 10 mm Hg (0.4 inches Hg) per minute	Before sample collection.	Hg-filled U-tube manometer	Check all joints and valves for source of leakage	Sample record sheet
Sampling Time Period	30 seconds or less	Each collection	Watch with second-hand	Check for plugging of probe and void sample	Sample record sheet
Sample Recovery	(1) Flask pressure and temperature recorded.	Each collection, after 16-hour absorption period	Manometer, centigrade thermometer		
	(2) pH of absorbing solution between 9-12	Each collection, after transfer to polyethylene bottle	pH paper	Add more sodium hydroxide solution	Sample record sheet

PLAN ACTIVITY MATRIX

Characteristic	Acceptance Limits	Frequency of Check or Measurement	Method of Measurement	Action Required if outside Limits	Record of Checks
Section 2.1.4 Analytical Reagent Preparation See Section 2.3.5.3 for detailed information.					
Standard Potassium Nitrate Solution	2.198 ± 0.001 g per liter	On makeup of solution	Analytical balance, Class A volumetric flask	Make up fresh solution	Lab Data Log Book
Phenoldisulfonic Acid Solution	(1) 25 g white phenol in 150 mℓ concentrated sulfuric acid	On makeup of solution	Triple-beam balance, Class A graduated cylinder	Make up fresh solution	Lab Data Log Book
	(2) 75 mℓ fuming sulfuric acid	On makeup of solution	Class A graduated cylinder	Make up fresh solution	Lab Data Log Book
Section 2.1.5 Sample Analysis See Section 2.6 for detailed information.					
Verify documentation	(1) Complete information	Each sample	Visual check	Void sample	Lab Data Log Book
	(2) Confirm whether or not sample volume is same as when shipped	Each sample	Visual check	Void sample	Lab Data Log Book

PLAN ACTIVITY MATRIX

Characteristic	Acceptance Limits	Frequency of Check or Measurement	Method of Measurement	Action Required if outside Limits	Record of Checks
Section 2.1.5 Sample Analysis (continued) See Section 2.6.1 for detailed information.					
Colorimetric Analysis	(1) Blank	Each set of determinations	Spectrophotometer at λ 410 nm	Replicate blank, control sample and calibration curve until within limits	Lab Data Log Book
	(2) Control	Each set of determinations	Spectrophotometer at λ 410 nm		Lab Data Log Book
Section 2.1.6 Data Reduction, Validation and Reporting See Section 2.6.2 for detailed information.					
Sample Volume Calculation	All data available	Each sample	Data examination	Void sample	Lab Data Log Book
Sample Mass Calculation	All data available	Each sample	Data examination	Void sample	Lab Data Log Book
Sample Concentration	All data available	Each sample	Data examination	Void sample	Lab Data Log Book
Document and Report Results	All data available	Each sample	Data examination	Void sample	Lab Data Log Book

PLAN ACTIVITY MATRIX

Characteristic	Acceptance Limits	Frequency of Check or Measurement	Method of Measurement	Action Required if outside Limits	Record of Checks
Section 2.1.7 Calibration See Sections indicated for detailed information.					
Sample Flask Volume (2.3.3)	± 10 mℓ	On receipt of flask	Graduated cylinder	Recalibrate	Calibration Log Book
Spectrophotometer Calibration Curve for NO_3 (2.6.2.1)	Slope = 0.135 ± 0.05 absorbance units/ µg/mℓ intercept = 0.00 ± 0.02 absorbance units/ µg/mℓ	(1) When a new batch of reagents is made (2) When a control sample cannot be measured within 12% of its known value	Standard nitrate solutions	Make new solutions, check spectrophotometer λ, scale and absorbance scale	Calibration Log Book
Barometer (2.2.2.6)	± 1 mm Hg	Every calendar quarter	Compare with certified Hg barometer	Adjust to agreement with certified barometer	Calibration Log Book
Temperature Gage (2.3.4)	± 1° Centigrade	Every calendar quarter	Compare with Hg-in-glass thermometer	Adjust to agreement with Hg thermometer	Calibration Log Book
Section 2.1.8 Regular and Preventative Maintenance					
Sampling Pump Maintenance	----	As per manufacturer's instructions	----	Remove from service	Maintenance Log Book

PLAN ACTIVITY MATRIX

Characteristic	Acceptance Limits	Frequency of Check or Measurement	Method of Measurement	Action Required if outside Limits	Record of Checks
Section 2.1.9 Procurement of Apparatus and Reagents See Section 2.2 for detailed information.					
Probe *	O/Borosilicate glass tubing, 11 mm ID	Upon receipt	Visual check	Return	Procurement Log Book
Probe Filter	O/glass wool	"	"	"	"
Probe Sheath	O/2.54 cm ID stainless steel tube, 183 cm length	"	"	"	"
Probe Heater	O/heating tape or wire	"	"	"	"
Collection Flask	O/Two-liter borosilicate round-bottom, short neck w/24/40 standard taper opening	"	"	"	"
Flask Encasement	O/Urethane foam incasement or similar material	"	"	"	"

*See ref. 12, p. 163, fig. 6.3 for probe detail.

PLAN ACTIVITY MATRIX

Characteristic	Acceptance Limits	Frequency of Check or Measurement	Method of Measurement	Action Required if outside Limits	Record of Checks
Section 2.1.9	Procurement of Apparatus and Reagents (continued) See Section 2.2 for detailed information.				
Flask Valve(s)	O/Borosilicate glass T-bore stopcock w/ 24/40 standard taper male joint (joint connection to be made by glassblower)	Upon receipt	Visual check	Return	Procurement Log Book
Temperature Gage	O/Dial-type, capable of measuring from -5 to +50° Centigrade w/in 1° Centigrade	Upon receipt	Visual check	Return	Procurement Log Book
Vacuum Line Tubing	O/Borosilicate glass tubing, minimum wall thickness 1 mm	Upon receipt	Visual check	Return	Procurement Log Book
Pressure Gage	O/U-Tube manometer, open end, 1 meter w/1 mm divisions	Upon receipt	Visual check	Return	Procurement Log Book
Vacuum Pump	O/Pump capable of pulling vacuum of 75 mm Hg or better	Upon receipt	Attach to suitable pressure gage	Return	Procurement Log Book

PLAN ACTIVITY MATRIX

Characteristic	Acceptance Limits	Frequency of Check or Measurement	Method of Measurement	Action Required if outside Limits	Record of Checks
Section 2.1.9 Procurement of Apparatus and Reagents (continued) See Section 2.2 for detailed information.					
Squeeze Bulb	O/Rubber, one-way	Upon receipt	Visual check	Return	Procurement Log Book
Stopcock Grease	O/High vacuum, high temperature chloro-fluorocarbon grease	Upon receipt	Visual check	Return	Procurement Log Book
Volumetric Pipettes	O/1, 2, 3, 4, 10, 25 mℓ (Class A)	Upon receipt	Visual check	Return	Procurement Log Book
Barometer (or consult local weather station)	O/Capable of reading atmospheric pressure to ± 2 mm	Upon receipt	Visual check	Return	Procurement Log Book
Graduated Cylinders	O/50, 100 mℓ (Class A)	Upon receipt	Visual check	Return	Procurement Log Book
Sample Storage Containers	O/Polyethylene, 50 mℓ, or greater capacity, screw cap	Upon receipt	Visual check	Return	Procurement Log Book
Wash Bottle	O/Polyethylene or glass	Upon receipt	Visual check	Return	Procurement Log Book

PLAN ACTIVITY MATRIX

Characteristic	Acceptance Limits	Frequency of Check or Measurement	Method of Measurement	Action Required if outside Limits	Record of Checks
Section 2.1.9 Procurement of Apparatus and Reagents (continued) See Section 2.2 for detailed information.					
pH Paper	O/Sensitive in range pH 7-14	Upon receipt	Check against known basic solutions	Return	Procurement Log Book
Steam Bath	O/Commercial brand or in-house	Upon receipt	Visual check	Return	Procurement Log Book
Evaporating Dishes	O/175-250 mℓ w/lip (such as Coors #45006)	Upon receipt	Visual check	Return	Procurement Log Book
Dropping Pipettes	O/Medicine dropper	Upon receipt	Visual check	Return	Procurement Log Book
Volumetric Flasks	O/50, 100, 1000 mℓ (Class A)	Upon receipt	Visual check	Return	Procurement Log Book
Graduated Pipette	O/10 mℓ w/0.1 mℓ divisions (Class A)	Upon receipt	Visual check	Return	Procurement Log Book
Analytical Balance	O/Capable of weighing to 0.1 mg	One each calendar quarter	Set of NBS weights	Adjust by manufacturer's instructions, or return	Procurement Log Book
Triple Beam Balance	O/Capable of weighing to 0.01 g	One each calendar quarter	Set of known weights	Adjust by manufacturer's instructions, or return	Procurement Log Book

PLAN ACTIVITY MATRIX

Characteristic	Acceptance Limits	Frequency of Check or Measurement	Method of Measurement	Action Required if outside Limits	Record of Checks
Section 2.1.9 Procurement of Apparatus and Reagents (continued) See Section 2.2 for detailed information.					
Spectrophotometer	O/capable of measuring absorbance at 410 nm (such as Bauch & Lomb Spectronic 70)	Before each set of measurements	Set of neutral density filters for absorance, dydimium glass for wavelength	Adjust, recalibrate	Procurement Log Book
Sulfuric Acid	O/Concentrated, ACS Reagent Grade	Upon receipt	Visual check	Return	Procurement Log Book
Hydrogen Peroxide	30% aqueous solution, ACS Reagent Grade	Upon receipt	Visual check	Return	Procurement Log Book
Sodium Hydroxide	ACS Reagent Grade pellets	Upon receipt	Visual check	Return	Procurement Log Book
Sulfuric Acid	Fuming, 15-18% free sulfur trioxide	Upon receipt	Visual check	Return	Procurement Log Book
Phenol	White solid, best grade available	Upon receipt	Visual check	Return	Procurement Log Book
Potassium Nitrate	ACS Reagent Grade	Upon receipt	Visual check	Return	Procurement Log Book

2.2 EQUIPMENT SELECTION

In addition to the Plan Activity Matrix (section 2.1), a listing of the required apparatus for a sampling train (configured as shown in figure 7-1 of appendix A) and the reagents, along with certain miscellaneous equipment and tools to aid in source testing, is given in subsection 2.3. Additional specifications, criteria, and/or design features as applicable are given here to aid in the selection of equipment to insure the collection of data of consistent quality. All new items of equipment are inspected visually for identification and damage before acceptance. Also, if applicable, new equipment is calibrated according to section 2.3 as part of the acceptance check. The descriptive title, identifcation number, if applicable, and the results of the acceptance check are recorded in the procurement log book, dated, and signed by the individual performing the check. Calibration data generated in the acceptance check is recorded in the calibration log book.

2.2.1 Sampling

2.2.1.1 Sampling Probe. A glass probe (borosilicate glass) with provisions for heating, with a filter (either in stack or heated out of stack) to remove particulate matter. The glass liner should be protected with an outer sheath of stainless steel. The sampling tip of the probe should have retainers fabricated of glass to hold the particulate filter in place. Heating is not required if the probe remains dry during the purging period. It is recommended that an all-purpose probe have provisions for heating. High temperature probes can be fabricated from quartz. A knowledge of the stack gas composition and temperature is necessary in order to select a probe of proper composition. Special probes must be approved by the EPA.

2.2.1.2 Collection Flask(s). Two liter borosilicate round bottom flasks with a short neck and 24/40 standard taper opening. The collection flask should be protected against implosion or breakage by (1) tape, or by using a (2) commercial unit encased in foam, or (3) a fabricated closed cell foam system.

2.2.1.3 Flask Valve(s). A T-bore stopcock is connected to a 24/40 standard taper joint. Bores should be numbered and not switched to prevent leakage problems. The T-bore should be marked to avoid turning the stopcock in the wrong direction when sampling.

2.2.1.4 Temperature Gauge. Dial-type thermometer, or equivalent, capable of measuring in 1° C (2° F) intervals from -5 to 50° C (25 to 125° F).

2.2.1.5 Vacuum Line. Sufficient tubing which is capable of withstanding a vacuum of 75 mm (3 inches) Hg absolute pressure. This tubing must be equipped with a "T" connection and a three-way valve (T-bore stopcock) or its equivalent. When possible, glass ball-joint connections should be replaced by plastic components to minimize leakage problems.

Note: Plastic components must not contact the sample gas before entering the flask.

2.2.1.6 Pressure Gauge. A U-tube manometer, 1 meter with 1 mm divisions, or equivalent.

2.2.1.7 Pump. One vacuum pump capable of producing a vacuum of $\geq$75 mmHg (3 inches Hg) absolute pressure in the sample flask.

2.2.1.8 Squeeze Bulb. A one-way bulb (rubber) to purge the sampling system.

2.2.1.9 Stopcock Grease. An inert, high vacuum, high temperature chlorofluorocarbon grease should be used.

2.2.1.10 Volumetric Pipette. A 25 mℓ volumetric pipette for addition of reagent to the collection flask.

2.2.1.11 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.

(b) A 1/2" 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 (1/4") for securing equipment and tarpaulin.

(d) One 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 for both heat and cold, gloves (both asbestos and cloth) and steel-toes shoes.

(e) Steel cable (3/16") with thimbles, cable clips and turn buckles. These are required for installing a safety line or securing equipment to the stack structure.

(3) Tools and Spare Parts

(a) Electrical and Power Equipment

(1) Circular saw

(2) Variable voltage transformer

(3) Variable speed electrical drill and bits

(4) Ammeter-voltmeter-ohmeter (VOM)

(5) Extension cords - light (#14 Avg) 2 x 25

(6) 2 3-wire electrical adapters

(7) 3-wire electrical triple taps

(8) Thermocouple extension wire

(9) Thermocouple plugs

(10) Fuses

(11) Electrical wire

(b) Tools

(1) Tool boxes (1 large, 1 small)

(2) Screwdrivers

1 set flat blade

1 set philips

(3) C-clamps (2) 6", 3"

(c) Wrenches

(1) Open end set 1/4" to 1"

(2) Adjustables (12", 6")

(3) 1 chain wrench

(4) 1 12" pipe wrench

(5) 1 Allen wrench set

(d) Miscellaneous

(1) Silicone sealer

(2) Silicone vacuum grease

(3) Pump oil

(4) Manometers (gauge oil)

(5) Anti-seize compound

(6) Pipe fittings

(7) Dry cell batteries

(8) Flashlight

(9) Valves

(10) Thermometers (Dial (6"-36")
and a remote reading thermometer

(11) Vacuum gauge

(12) SS tubing (1/4", 3/8", 1/2") short lengths

(13) Heavy-duty wire (telephone type)

(14) Adjustable packing gland

(4) Data Recording

(a) Data sheets or data notebook

(b) Carbon paper

(c) Slide rule or electronic calculator

(d) Psychometric charts

(e) Combustion nomographs (Ref. 15)

(f) Pencils, pens

2.2.2 Sample Recovery

2.2.2.1 Volumetric Pipette or Dropper. A 25 mℓ volumetric pipette or dropper for neutralization. The pipette (25 mℓ) can also be used to add 25 mℓ of reagent to the flask before sampling (2.2.1.10).

2.2.2.2 Storage Containers. An adequate number of leak-free glass or polyethylene bottles for recovery of samples. The containers should be packed in a cushioned container (box or foot locker) for shipment.

2.2.2.3 Wash Bottle. A glass or polyethylene wash bottle for rinsing (transferral) of sample solution to storage containers.

2.2.2.4 Glass Stirring Rod. A stirring rod (glass or polyethylene) is required to check the pH of the absorbing reagent.

2.2.2.5 pH Indicating Paper. pH paper with the range of 7-14 is required to test the alkalinity of the absorbing reagent.

2.2.2.6 Barometer. A calibrated barometer (shock mounted) for measuring the barometric pressure. An alternate is to obtain the uncorrected barometric pressure from a nearby weather station and correct for altitude.

2.2.3 Analysis

2.2.3.1 Steam Bath. A steam bath is required to evaporate the absorbing solution. A hot plate is not acceptable for this analysis, as it may cause sample loss by spattering.

2.2.3.2 Beakers or Casseroles. A reactor vessel is required for the evaporation step. Beakers of borosilicate glass or porcelain evaporating dishes are acceptable. Beakers (glass) must be discarded or used for other purposes when the bottoms become etched.

2.2.3.3 Polyethylene Policemen. One stirring rod (polyethylene policemen) is required for each sample and standard. A glass stirring rod is not recommended.

2.2.3.4 Volumetric Glassware. Several volumetric pipettes are required (1, 2, and 10 mℓ). One transfer pipette (10 mℓ with 0.1 mℓ divisions) and one 100 mℓ volumetric flask for each sample. Two 1,000 mℓ volumetric flasks are required for the blank and standard nitrate. Additional volumetric flasks (50 mℓ) are required for aliquots (for analysis) and dilution of samples that fall outside the calibration range (absorbance > 400 μg standard).

2.2.3.5 Spectrophotometer. A spectrophotometer which is capable of measuring the absorption at 410 nm (or the peak maximum). A set of neutral density filters and a filter for wavelength calibration should be available (ref. 17).

2.2.3.6 Buret. A 50 mℓ buret or its equivalent for addition of ammonium hydroxide to the reaction vessel.

2.2.3.7 Graduated Cylinder. A 50 mℓ graduated cylinder with 1.0 mℓ divisions for additions of distilled water.

2.2.3.8 Analytical Balance. One analytical balance that weighs to 0.1 mg. A set of calibration weights to check the accuracy of the balance (± 0.3 mg).

2.3 EQUIPMENT CHECK AND CALIBRATION

2.3.1 Sampling Train

The design specifications of the NO_x train used by the EPA is given in Appendix A of this document (figure 7-1). Commercial models of this system are available. Each individual commercial or fabricated train must be in compliance with the specifications in the reference method.

2.3.2 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 object is to leave the glass liner chemically inert to oxides of nitrogen. If the probe is equipped with a heating system, check to see if it is operating properly. The probe should be sealed on the filter side and checked for leaks at a pressure of < 380 mm (15 inches) of mercury 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.

2.3.3 Collection Flask, Flask Valve and Evacuation System

The collection flask and valve (in contact with sample gas) should be cleaned with a strong detergent and hot water, rinsed with tap water, and distilled, deionized water. Periodically, the glassware can be cleaned with a grease remover such as decahydronapthalene ($C_{10}H_{18}$) followed by acetone and then by the procedure above. An alternate procedure is to use dichromate cleaning solution. Assemble the clean flasks and valves and fill with water (room temperature) to the stopcock. Measure the volume to ± 10 mℓ by transferring the water to a graduate. Do three volume determinations and use the mean value. Number and record the volume mean value

on the flask or foam encasement and in the laboratory log book. This volume measurement is required only on the initial calibration provided the flask valves are not switched. Lubrication of stopcocks and joints should be with a chemically inert lubricant. An inert hydrogen-free chlorofluorocarbon lubricant can be used. The evacuation system as depicted in appendix A is assembled and a vacuum of 3 inches of mercury absolute pressure is produced in each flask. The vacuum should be held for at least one minute without appreciable fluctuation [$\leq$ 10 mm (0.4 in.) Hg]; if this is not obtained, check for leaks.

2.3.4 Temperature Gauge

All thermometers should be checked versus a mercury bulb thermometer at room temperature. Accuracy of $\pm$ 1° C (2° F) is sufficient.

2.3.5 Reagents

2.3.5.1 Sampling. The absorbing reagent is prepared by adding 2.8 mℓ of concentrated sulfuric acid (H_2SO_4) to 1 liter of distilled, deionized water. Mix well and add 6 mℓ of 3 percent hydrogen peroxide (H_2O_2). Prepare a fresh absorbing solution weekly and do not expose to extreme heat or direct sunlight. All reagent must be ACS grade or equivalent. If the reagent must be shipped to the field site, it is advisable that the absorbing reagent is prepared fresh on-site. All reagents must be reagent grade.

Note: If the concentration of peroxide solution (H_2O_2, 3 percent) is in question, analyze with 0.1 N permanganate in acid solution.

2.3.5.2 Sample Recovery. A sodium hydroxide solution (1N) is prepared by dissolving 40 g NaOH in distilled water and diluting to 1 liter. This solution can be transferred to a polyethylene 1,000 ml (32-oz.) jar for shipment. Distilled, deionized water and pH paper are required to test basicity and for transferral of samples.

2.3.5.3 Analysis. All reagents must be ACS reagent grade. The following reagents are needed for analysis and standardization:

(1) Fuming sulfuric acid - 15 to 18% (by weight) free sulfur trioxide (SO_3)

(2) Phenol - White solid reagent grade

(3) Sulfuric Acid - concentrated reagent

(4) Standard solution - dissolve 2.1980 g dried potassium nitrate (KNO_3) in distilled water and dilute to 1 liter in a volumetric flask. For the working standard solution, pipette 10 mℓ of the resulting solution into a 100 mℓ volumetric flask and dilute to the mark.

Note: One mℓ of the working standard solution is equivalent to 100 μg nitrogen dioxide.

(5) Water - deionized, distilled.

(6) Phenoldisulfuric acid solution - dissolve 25 g of pure white phenol (no discoloration) in 150 mℓ concentrated sulfuric acid on a steam bath. Cool, add 75 mℓ fuming sulfuric acid, and heat at 100° C (212° F) (on a steam bath) for two hours. Store in a dark, stoppered bottle.

2.4 PRESAMPLING PREPARATION

2.4.1 Preliminary Site Visit (Optional)

The main purpose of a preliminary site visit is to gather information to design and implement an efficient source test. Prior preparation will result in the prevention of unwarranted loss of time, expenses, and injury to test and/or plant personnel. A test plan conceived from a thorough set of parameters will result in more precise and accurate results. This preliminary investigation (on-site) is optional and not a requirement. An experienced test group can, in some cases, obtain sufficient information on the source through communications with the plant engineer. The information should include pictures (or diagrams) of the facilities. In most cases, there is no substitute for an on-site presurvey.

2.4.1.1 Process(Background Data on Process and Controls). It is recommended that the tester, 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 reviewed if they are available.

The role of certain combustion effluents as interfering substances have not been ascertained; therefore, any background data on stack gas species should be noted for further consideration of the final analytical results (refs. 4.12).

2.4.1.2 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 available as to the time of the sequence and the duration of the cycle. This individual or individuals will supervise installation of ports, sampling platform, and electrical power. If the above installations are already in existence, they must be examined for their suitability in obtaining a valid test and that all facilities meet minimum safety standards. If ports have to be installed, specify 4-inch ports with plugs. Port locations should be based upon Method 1 of the Federal Register (ref. 14). Port locations must be based upon existing technical knowledge and sound judgment. An electrical service should be available at the sampling area with 115-volt and 20-amp service.

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

1. $T_{s_{avg}}$ = average stack gas temperature.
2. P_s = the static pressure (positive or negative).
3. ΔP_{avg} = the average velocity heads.
4. B_{wo} = approximate moisture content.
5. M_c = molecular weight calculated from approximate gas constituent concentrations

The above parameters can be roughly determined using an inclined manometer (0-5 inches), a Type-S pitot tube, manual thermometer or thermocouple attach d to the pitot tube with potentiometric readout device. The moisture content (approximate) can be determined with wet bulb-dry bulb and the gaseous constituents by hand-held indicator kits. Nomographs are useful in checking and estimating your preliminary data required (ref. 15).

2.4.1.4 Methods and Equipment for Transporting Apparatus to Test Site. Ropes, block and tackle, and other hoisting equipment should belong in the repertoire of any stack sampler. The initial site visit should include a preconceived plan between plant personnel and tester on how the equipment can best be transported to the sampling site. Electric forklifts, when available, should be utilized if needed. In addition to the above, it is recommended, when permissible, that pictures be taken of the hoisting area and sampling area, so that any further discussions (either by letter or telephone) will be clarified.

2.4.2 Apparatus Check

Previously used equipment should be visually checked for damage and/or excessive wear before each field test. Items should be repaired or replaced as applicable if judged to be unsuitable for use by the visual inspection.

Table 1 is designed to serve as a sample checklist for the three phases of a field test. It is meant to serve as an aid to the individuals concerned with procuring and checking the required equipment, and as a means for readily determining the equipment status at any point in time. The completed form should be dated, signed by the field crew supervisor, and filed in the operational log book upon completion of a field test. This includes initiating the replacement of worn or damaged items of equipment. Procedures for performing the checks are given in the appropriate subsections of this operation manual, a check is placed in the proper row and column of table 1 as the check/operation is completed. Each team will have to construct its own checklist according to the type of sampling train and equipment it uses.

2.4.3 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 packing of equipment with regard to (1) accessibility in the field, (2) ease 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.

2.4.3.1 Probe. Pack the probe in a case protected by polyethylene or other suitable packing material. An ideal container is a wooden case or equivalent lined with foam material in which separate compartments are cut to hold the individual devices. This case can also contain a pitot tube for velocity determinations. The case should have handles that can withstand hoisting and be rigid enough to prevent bending or twisting of the devices during shipping and handling.

2.4.3.2 Collection Flask and Valve. The collection flasks and valves should be packed securely in a suitable shipping container. An ideal shipping container is a case or foot locker of approximately the following dimensions: 30" x 15" x 15". This container when lined with foam will accomodate eight collection flasks with the appropriate mated flask valves.

2.4.3.3 Evacuation System, Temperature Gauges, Vacuum Lines and Reagents. A sturdy case lined with foam material can contain the evacuation manifold, squeeze bulb, manometer, and reagent for sampling and recovery.

2. .3.4 Evacuation 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.

2.4.3.5 Glass Storage Containers. All glass storage containers must be packed with cushion material at the top and bottom of the case with some form of dividers to separate the components.

2.5 ON-SITE MEASUREMENTS

The on-site measurement activities include transporting the equipment to the test site, unpacking and assembling the equipment, confirming duct measurements and traverse points (if volumetric flow rate is to be determined), velocity traverse, molecular weight determination of the stack gas, moisture content, sampling for oxides of nitrogen, and data recording.

2.5.1 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 should be used to place the equipment on-site. Care should always be exercised against damage to the test equipment or injury to test personnel during the moving phase. A "laboratory" type area should be designated for preparation of absorbing reagent and charging of the flasks. Utilization of plant personnel or equipment (winches and forklifts) in movement of the sampling gear is highly recommended.

2.5.2 Preliminary Measurements and Set Up

The reference method outlines the determination of the concentration of oxides of nitrogen in the gas stream. The volumetric flow rate must be determined utilizing Reference Methods 1, 2, 3, and 4 if the mass emission rate is to be determined (ref. 14). Consult the Quality Assurance Document for Method 2 for a more thorough discussion of the determination of the volumetric flow rate (ref. 16).

2.5.3 Sampling

The on-site sampling includes preparation and/or addition of the absorbing reagent to collection flasks, setup of the evacuation system, connection of the electric service, preparation of probe (leak check and addition of particulate filter), insertion of probe into the stack, sealing the port, evacuation of flasks, sampling and recording of the data, and a final leak-check.

2.5.3.1 Preparation and/or Addition of Absorbing Reagent to Collection Flasks. If preparation of absorbing reagent is necessary on-site, follow directions as given in section 2.3.5.1 of the document. Pipette 25 mℓ of absorbing reagent into sample flask. Place a properly lubricated flask valve into the collection flask with the valve turned in the purge position. Lubrication of joints is intended to prevent leaks and should not seal the bore of the stopcock or contaminate the sample.

2.5.3.2 Assembling Sampling Train. Assemble the sampling train as shown in figure 7-1 of the reference method (contained as appendix A of this document) and perform the following:

(1) Visually check probe for liner separation, (racks, etc.)
(2) Place a loosely packed filter of glass or quartz wool in the end of the probe.

(11) Turn the flask valve to the "purge" position at the conclusion of collection.

(12) Shake the flask for five minutes.

The particulate filter should be changed at the end of each sampling run. This is to help to prevent plugging of the probe.

2.5.4 Sample Recovery

The reference method requires a sample absorption period of $\geq$ 16 hours. If the laboratory is close by, the samples may be left in the flasks for return to the laboratory. Otherwise the appropriate data must be taken in the field, solutions made alkaline and transferred to glass storage containers.

2.5.4.1 Flask Pressure, Temperature and Barometric Pressure. After the absorption period is completed ($\geq$ 16 hours), record the barometric pressure and the room temperature on a data sheet and a field laboratory notebook.

(1) Shake the flask and contents for 2 minutes.

(2) Connect one leg of the sample flask valve to the open-end manometer.

(3) Turn the stopcock to open the flask to the manometer.

(4) Record the flask pressure by reading the difference between the mercury levels in the manometer.

(5) Transfer the flask contents to a container for shipment or to a 250 ml beaker or porcelain evaporating dish for analysis. (Transferral to a beaker or evaporating dish is only done in the laboratory.)

(6) Rinse the flask with several portions of distilled water.

Note: A quantitative transfer is required. No less than 2 rinses are acceptable. The total rinse should be $\leq$ 10 mℓ. The total rinse should be the same for all flasks.

(7) A blank should be prepared by pipetting 25 ml of absorbing solution into a clean sample bottle and adding the same volume of distilled water as used in rinsing the flask in (6) above.

(3) Insert the probe into the stack to the sampling point and seal the opening around the probe.

2.5.3.3 Evacuation, Purge, and Sample. A sample is taken by the following:

(1) Turn the pump and flask valves to the "evacuate" positions. The flask should be evacuated to 76 mm (3 inches) of mercury absolute pressure or until the apparent boiling point is reached (bubbling of absorbing solution).

(2) Turn the pump valve to the "vent" position and turn off the pump. Check the manometer for fluctuations. The manometer should stay stable ($\leq$ 10 mm (0.4 inches) Hg) for at least a minute. If the mercury level changes, check and eliminate the problem.

(3) Record the initial volume of the flask, temperature, and barometric pressure on a data sheet or in a field laboratory notebook.

(4) Turn the flask valve to the "purge" position.

(5) Turn the pump valve to the "purge" position.

(6) Purge the probe and the vacuum line using the one-way squeeze bulb.

(7) If condensation occurs in the probe or the flask valve, the probe must be heated until (upon purging) the condensation disappears.

(8) Turn the pump valve to the "vent" position.

(9) Turn the flask valve to the "sample" position and allow sample to enter the flask $\geq$ 15 seconds. The object here is to get a good sample.* This will usually require approximately 15 seconds. A longer period of time indicates that the probe is plugged. A generally accepted period of sampling is less than 30 seconds.

(10) Record final flask pressure.

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*A "good" sample includes sufficient oxygen for the conversion of all NO to NO_2. Without excess molecular oxygen present in the flask, some NO will remain and the datum obtained for NO_x concentration will be biased low. If it is suspected that there is not enough oxygen, then terminate sampling before flask pressure has reached stack pressure (with minimum 50 mm to g differential) and open to the atmosphere. This is not normal procedure and should not be done unless the situation so requires.

(8) Prior to shipping or analysis, add sodium hydroxide (NaOH, 1 N) dropwise (about 25 to 35 drops) into both the sample and the blank until alkaline to pH paper.

Note: Test for alkalinity by touching the top of a glass rod into the sample blank and then applying this to a moistened strip of pH paper. The solution is considered alkaline when a pH range of 9-12 is attained.

Caution: Do not do this in the presence of ammonia fumes. This will give a false test for alkalinity.

2.5.5 Sample Logistics (Data) and Packing of Equipment

The above procedures are followed until the required number of tests are completed. The following is recommended at the completion of testing:

(1) Check all sample containers, or collection flasks for proper labeling. (Time and date of test, location of testing, number of test, and any other pertinent documentation.) Mark the height of the liquid level in the sample container to determine whether or not leakage occurred during transport.

(2) All data recorded during field testing should be recorded in duplicate by carbon paper or by utilizing data sheets (figure 2) 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, flasks and equipment should be properly packed for shipment to the base laboratory. All shipping containers should be properly labeled to prevent loss of samples or equipment.

PLANT _____	DATE _____
SAMPLE COLLECTED BY _____	RUN NO. _____
PROBE TEMPERATURE SETTING _____	REAGENT (ABSORBING) PREPARATION DATA _____
COLLECTION DATA _____	CLOCK TIME _____
FLASK NO. _____	VOLUME OF FLASK AND VALVE, mℓ _____
BAROMETER PRESSURE, mm Hg _____	V_a, VOLUME OF ABSORBING SOLUTION, mℓ _____
P_c, INITIAL ABSOLUTE PRESSURE, mm Hg _____	P_f, FINAL ABSOLUTE PRESSURE, mm Hg _____
T_i, INITIAL TEMPERATURE OF FLASK, [°C +273] _____	T_f, FINAL TEMPERATURE OF FLASK [°C +273](ABSOLUTE) _____

Figure 2. NO_x field data sheet.

2.6 POST-SAMPLING OPERATIONS (LABORATORY)

2.6.1 Analysis (Base Laboratory)

The requirements for a precise and accurate analysis are an experienced analyst and familiarity with the analytical method. Calibration is of the utmost importance and neglect in this area cannot be accepted. Extrapolation of standardization curves at very low and high concentrations is not justified. Blanks must be used to correct for reagent and sample conditions.

2.6.1.1 Calibration of Spectrophotometer (Wavelength and Linearity). Calibration of the wavelength scale should be checked periodically, at least once each calendar quarter. The absorption spectrum of a didymium glass has been found useful for this purpose. For checking the transmittance scale, a set of neutral density filters is satisfactory. The reference method calls for samples and standards absorbance to be determined at 410 nm. The spectra produced by scanning samples and standards in a calibrated dual-beam instrument or in a single beam instrument (ref. 17) produce a maximum absorbance at ≈405 nm. It is recommended that standardization curves and samples be done at a constant wavelength of 405 ± 5 nm. Calibration is a critical part of the analytical technique and should be done with great care.

2.6.1.2 Recommended Procedures in Operating a Spectrophotometer. The correct manipulation of sample cells is critical. The following points should be adhered to:

(1) Cuvettes are not always matched; therefore, one should designate the "blank" and sample cells. Do not interchange the cells during an analysis.

(2) Do not touch the bottom of the cuvette with your fingers.

(3) Rinse the cuvette at least twice with the solution you are about to measure.

(4) Remove lint, liquid, etc., with a lens tissue or its equivalent.

(5) Careless technique is unacceptable.

2.6.1.3 Standardization and Analysis of Samples. Add 0.0 to 4.0 mℓ of working standard solution (1 mℓ = 100 μg NO_2) to a series of beakers. To each beaker add 25 mℓ of absorbing reagent and add sodium hydroxide (1N) dropwise until alkaline. Check for alkalinity by touching a glass rod to the solution and then to pH paper (pH range 9-12). A series of solutions, for example, would be 0, 1, 2, 3, and 4 mℓ. Analyze the standards and sample as follows:

(1) If the sample has been shipped in a container, transfer the contents to a 50 mℓ volumetric flask, using several small portions of distilled water.

Note: Before transfer of sample, check the level in the container to confirm whether or not any sample was lost during shipment. If loss is detected, it should be recorded on the analytical data sheet, and the sample discarded.

Dilute to the mark with distilled, deionized water. Transfer a 25 mℓ aliquot to a porcelain evaporating dish or a 250-mℓ beaker.

(2) Standards and samples must be alkaline before evaporation.

(3) Evaporate the solution (standards, blanks, and sample solutions) to dryness on a steam bath and then cool.

Note: Do not evaporate these solutions on a hot plate. Do not evaporate to bone dryness.

(4) Add 2 mℓ phenoldisulfonic acid reagent to the dried residue and titurate thoroughly with a stirring rod.

(5) Add 1 mℓ distilled water and four drops of concentrated sulfuric acid. Heat the solution in a steam bath for three minutes with occasional stirring.

(6) Cool, add 20 mℓ distilled water, mix well by stirring.

(7) Add concentrated ammonium hydroxide dropwise (a 50 mℓ burette is helpful) with constant stirring until alkaline to pH paper. Check for alkalinity by touching a glass rod to the solution and then to a piece of pH paper. (pH = 9-12).

(8) Transfer the solution to a 100-mℓ volumetric flask and wash the beaker three times with 5-mℓ portions of distilled water. Dilute to the mark and mix thoroughly.

(9) If the sample contains solids, transfer a portion of the solution to a clean, dry centrifuge tube and centrifuge or filter a portion of the solution.

(10) Measure the absorbance of each sample at 410 nm (or the previously determined analytical wavelength--≈ 405 nm) using the blank solution as a zero.

(11) Dilute the sample and the blank with a suitable amount of distilled water (to double, triple, etc. the original volume) if absorbance fall outside the range of the calibration curve.

Note: The calibration curve should be verified at a low, medium and high concentration with each sample run.

(12) Record all pertinent data on the laboratory data sheet (figure 3).

2.6.2 Calculations

Calculation errors due to procedure 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 every third calculation, preferably by a team member other than the one that performed the original calculations. If a difference greater than five percent 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.

2.6.2.1 Calibration Curve, Spectrophotomer Calibration. Each working standard (0.0 mℓ, 1.0 mℓ, 2.0 mℓ, 3.0 mℓ and 4.0 mℓ) should be analyzed as directed in subsection 2.5.1.3. Plot a calibration curve of absorbance versus µg NO_2 per sample from the data obtained. Check visually for linearity.

RUN NO. _____

DATE COLLECTED _____ DATE ANALYZED _____

LIQUID LEVEL CHECK _____ K_C, CALIBRATION FACTOR _____

A, ABSORBANCE OF SAMPLE _____ A´, BLANK ABSORBANCE _____

F, DILUTION FACTOR _____ V_{sc} (CORRECTED SAMPLE VOLUME, mℓ) _____

m = μg OF NO_x AS NO_2 _____ Q_s, VOLUMETRIC FLOW RATE _____

C (EMISSION, mg/scm) _____ SAMPLES ANALYZED BY _____

$$V_{sc} = \frac{T_{std}(V_f - V_a)}{P_{std}} \left(\frac{P_f}{T_f} - \frac{P_i}{T_i}\right) = K(V_f - 25) \left(\frac{P_f}{T_f} - \frac{P_i}{T_i}\right) \quad \text{(Equation 7-2)}$$

$$m = 2 K_c AF \quad \text{(Equation 7-3)}$$

$$C = K \left(\frac{m}{V_{sc}}\right) \quad \text{(Equation 7-4)}$$

Figure 3. NO_x laboratory data sheet

All samples must be mixed thoroughly and the absorbance measured using the blank solution as a zero reference. An alternate approach is to measure the sample absorbance (A_1) and correct for the blank absorbance (A').

Determine the spectrophotometer calibration factor using equation 7-1.

$$K_c = 100 \frac{A_1 + 2A_2 + 3A_3 + 4A_4}{A_1^2 + A_2^2 + A_3^2 + A_4^2}$$

where

K_c = Calibration factor.
A_1 = Absorbance of the 100 µg NO_2 standard (1 mℓ = 100 µg NO_2).
A_2 = Absorbance of the 200 µg NO_2 standard.
A_3 = Absorbance of the 300 µg NO_2 standard.
A_4 = Absorbance of the 400 µg NO_2 standard.

2.6.2.2 Sample Volume. Calculate the sample volume at standard conditions on a dry basis [760 mmHg (29.92 in Hg), 293° K (528° R)] by using the following equation.

$$V_{sc} = \frac{T_{std}\left(V_f - V_a\right)}{P_{std}}\left(\frac{P_f}{T_f} - \frac{P_i}{T_i}\right) = K\left(V_f - 25\right)\left(\frac{P_f}{T_f} - \frac{P_i}{T_i}\right) \text{ (Equation 7-2)}$$

where

$K = 0.3855 \frac{°K}{mmHg}$ for metric units
$= 17.65 \frac{°R}{in.\ Hg}$ for English units.
V_{sc} = Sample volume at standard conditions (dry basis), mℓ.
T_{std} = Absolute temperature at standard conditions, 293°K (528°R).
P_{std} = Pressure at standard conditions, 760 mm (29.92 in. Hg).
V_f = Volume of flask and valve, mℓ.
V_a = Volume of absorbing solution, 25 mℓ.
P_f = Final absolute pressure of flask, mm Hg (in. Hg).
P_i = Initial absolute pressure of flask, mm Hg (in. Hg).
T_f = Final absolute temperature of flask, °K (°R).
T_i = Initial absolute temperature of flask, °K (°R).

Temperatures are converted to degrees Kelvin (Rankin) [(273 + °C) or (460 + °F)] and all pressures are recorded to the nearest mm (tenths of an inch) of mercury. The absolute pressure in a flask is the barometric pressure minus the difference in the two legs of the U-tube manometer.

2.6.2.3 Total μg NO_2 per Sample. Calculate the total μg NO_2 per sample by

$$m = 2\ K_c\ AF \qquad \text{(Equation 7-3)}$$

where

K_c = Calibration factor (spectrophotometer)

A = Sample absorbance (corrected for blank)

F = Dilution factor (i.e., 25/5, 25/10, etc., required only if sample dilution was needed to reduce the absorbance into the range of calibration; otherwise F = 1.)

2 = 50/25 the aliquot factor. (If other than a 25 mℓ aliquot was used for analysis, the corresponding factor must be substituted.)

2.6.2.4 Sample Concentration and Emission Rate. Calculate the sample concentration on a dry basis at standard conditions by equation 7-4.

$$C = K \frac{m}{V_{sc}} \qquad \text{(Equation 7-4)}$$

where

C = Concentration of NO_x as NO_2, dry basis, corrected to standard conditions, mg/dscm (lb/dscf).

$K = 10^3 \frac{(ml)(mg)}{(m^3)(\mu g)}$ for metric units

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

m = Mass of NO_x as NO_2 in sample, μg (2.5.2.3)

V_{sc} = Sample volume at standard conditions (dry basis), mℓ (2.6.2.2).

The emission rate is determined by either of the following equations:

$$ER = \frac{mg}{min} = Q_s \times C \qquad \text{(Metric units)}$$

where

Q_s = Volumetric rate of the effluent in scm/min at standard conditions on a dry basis.

C = NO_x concentration in mg/scm.

or

$$ER\left(\frac{lb}{hr}\right) = Q_s \times C \qquad \text{(English units)}$$

where

Q_s = volumetric flow rate of the effluent in ft^3/hr at standard conditions on a dry basis as determined by the Quality Control document for reference Method 2 (ref. 16).

C = NO_x concentration in lb/scf.

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 that 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, to 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 list.

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.
   b) Examine the team's log books periodically for completeness and adherence to operating procedures.
   c) Approve data sheets, data from 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. Isolation, evaluation, and monitoring of major components of system error.
3. Collection and analysis of information necessary for controlling data quality.

3.1 ASSESSMENT OF DATA QUALITY (INTRATEAM)

Intrateam or within-team assessment of data quality as discussed herein provides for an estimate of the precision of the measurements made by a particular field team. Precision in this case refers to replicability: i.e., the variability among replicates, and is expressed as a standard deviation. This technique does not provide the information necessary for estimating measurement bias (see subsection 4.1.3 for a discussion of bias) which might occur, for example, from failure to collect a representative sample, sampling train leaks, or inadvertent exposure of the sample to ambient air. However, if the operating procedures given in the Operations Manual (section II) are followed, the bias should be small in most cases. The performance of an independent quality audit that would make possible an interteam assessment of data quality is suggested and discussed in subsection 4.2 of the Manual for Managers of Groups of Field Teams.

The primary measurement of interest here is the concentration of nitrogen oxides (except nitrous oxide) in the sample. The data from which this concentration is derived are:

1. An absorbance reading which is converted to an equivalent mass of nitrogen dioxide by means of a calibration of the spectrophotometer with standard nitrate solutions.
2. A sample volume, corrected to standard temperature and pressure.

3.1.1 Absorbance Determination

Collaborative studies of Method 7 (refs. 1,3) showed that, for the analytical part of this method, the laboratory-to-laboratory variation was largely due to daily within-laboratory measurement variations rather than significant biases from laboratory to laboratory. This within-laboratory variation is due largely to the failure to check and recalibrate spectrophotometers on a daily basis. A second factor involved larger errors when sample concentrations were low, i.e., below 2 μg/mℓ. Optimal analytical conditions for minimizing replicate variability would then involve daily (or even more frequent) calibration checks and the use of only the upper portion of the working curve (from about 2 to 4 μg/mℓ concentration) for sample analysis. Section 3.2 will include a control chart for monitoring spectrophotometer response by means of control (known) nitrate samples.

3.1.2 Sample Volume Determination

The sample volume is a function of the flask volume, absorbing solution volume, initial and firal pressure readings, and initial and final temperature readings. Calibration of the flask and valve volume is a relatively large source of error, and it is therefore recommended that the volume be obtained as the mean of three determinations. Provided that reasonable care is exercised in making the temperature and pressure readings, these measurements will not introduce a significant error into the volume determinations.

The largest potential source of variability in volume determination is calculation error. Use of a general Method 7 computer program would eliminate this problem and has been strongly recommended (refs. 1,3). Field teams should be cautioned that calculation errors are prevalent in this method, and advised to double-check each calculation before reporting the data. It would also be advisable to keep a visible record posted of the number of calculation errors found (by audit or otherwise), by date and name of person. This would provide a negative incentive to exercise care in carrying out the data processing steps.

3.1.3 Interference of Hydrogen Chloride

The field team should be alert to the possible presence of hydrogen chloride in the stack gas. Certain types of coal, in particular, contain chlorides and release HCl on burning (ref. 12). This is a negative interferent, and the results will be biased, in an approximately linear fashion, with HCl concentration (ref. 4). It would be possible to make an approximate correction for this effect if the HCl concentration were known, but this is not likely. However, it should be anticipated in a qualitative way that the results are highly questionable if HCl is a component of the stack gas.

3.2 MONITORING DATA QUALITY

In general, if the procedures outlined in the operations manual are followed, the major sources of variability will be in control. It is felt, however, that as a means of verification of data quality, as well as a technique for monitoring personnel and equipment variability, quality control charts are highly desirable. These provide a basis for action with regard to the measurement process: namely, whether the process is satisfactory and should be left alone, or whether the process is out of control and action should be taken to find and eliminate the causes of excess variability.

For Method 7 it is appropriate to have a chart to monitor variability and accuracy of the analytical phase. The chart should plot the results of reference (audit) samples dispersed randomly throughout an analysis period. Specifically, the difference, d_j, between the true value, $C_{NO_2}(T)$, and the measured value, $C_{NO_2}(M)$, is divided by the true value and the resulting number multiplied by 100 to convert to a percent, i.e.,

$$d_j = \frac{C_{NO_2}(T) - C_{NO_2}(M)}{C_{NO_2}(T)} \times 100$$

This value, d_j, is then plotted versus audit date. An upper warning limit and upper control limit, as well as the corresponding lower limits, are provided to serve as indicators of data quality. These limits are normally established by experience; i.e., over a period of time the precision of the technique can be established and a reasonable value for the standard deviation of d_j can be assigned. Warning limits are then taken as $+2\sigma$ and -2σ, and control (or action) limits as $+3\sigma$ and -3σ.

Collaborative tests for Method 7 (refs. 1,3) showed that, because of dubious spectrophotometer recalibration practices, most of the reproducibility variation occurs in the analytical phase. It should be possible to reduce this analytical variation by more stringent calibration practices. Judging from a typical calibration curve such as is given in a collaborative study (ref. 1) and reproduced in this document as figure 4, if one restricts sample concentrations to those giving absorbances from about 0.3 to 0.5 the calibration error should be minimized. This can be done in some cases by dilution, but in other cases it will be impossible due to the sample itself being of low concentration. For purposes of illustration, a σ of 4% is assumed in this document. The warning and control limits are then 8% and 12%, respectively. A quality control chart is shown in figure 5. The audit values are plotted sequentially as they are obtained and connected to the previously plotted point with a straight line. Corrective action, such as review of operating technique and/or calibration check, should be taken any time one of the following criteria is exceeded:

1. One point falls outside either the upper or lower control (3σ) limit.
2. Two consecutive points fall between the warning and control limits.
3. Three consecutive points fall outside the σ range (here assumed to be $\pm$4%).

Quality control charts also serve to point up method bias in an obvious visual way; i.e., if a large number of points fall on the same side of the center line representing the "true" reference value, an attempt should be made to identify a possible cause or causes.

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 assure the collection of data of good quality. These checks are written as part of the routine operating procedures in section II. In order to

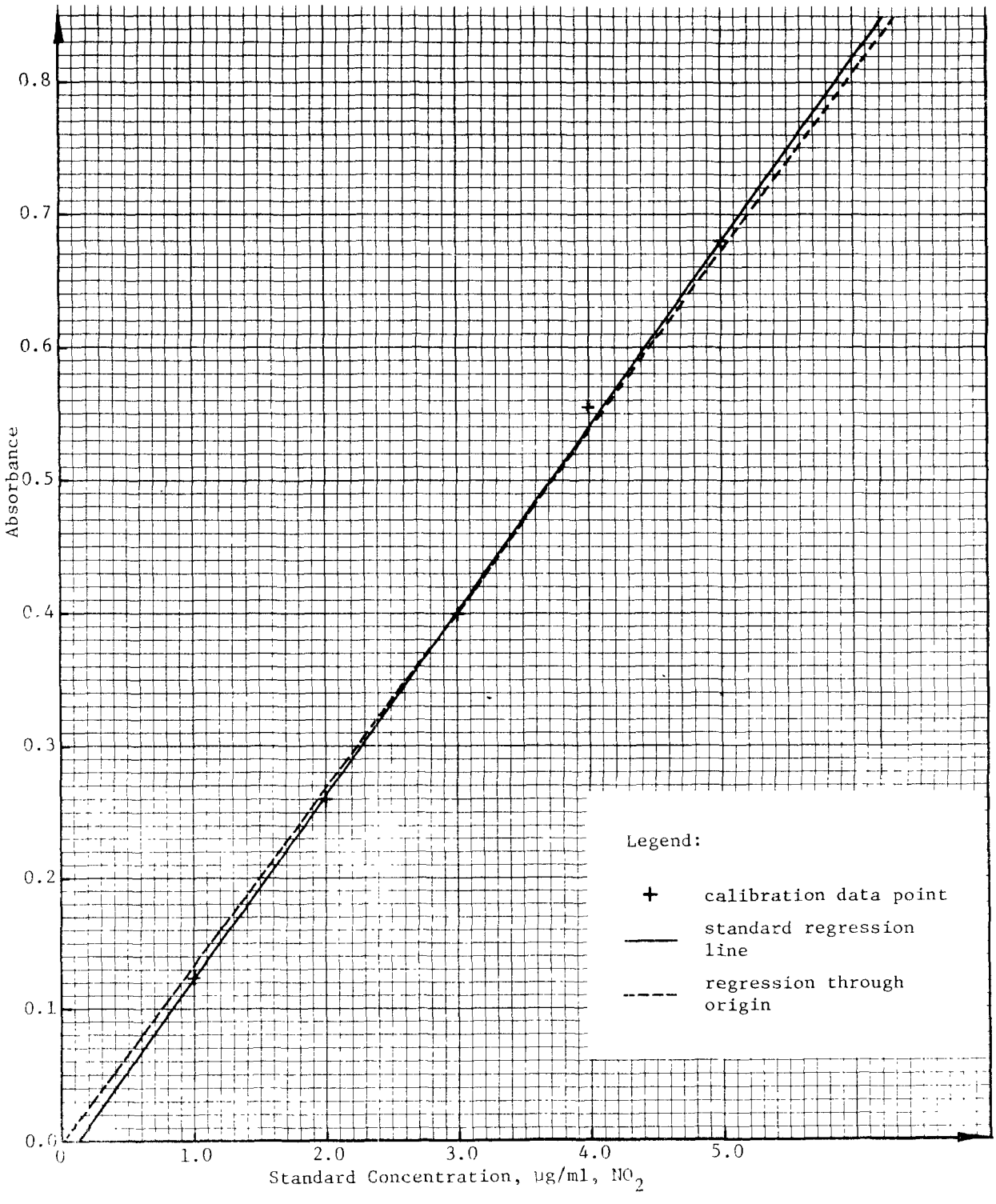

Figure 4. Typical calibration curve for determination of NO_x concentration from absorbance.

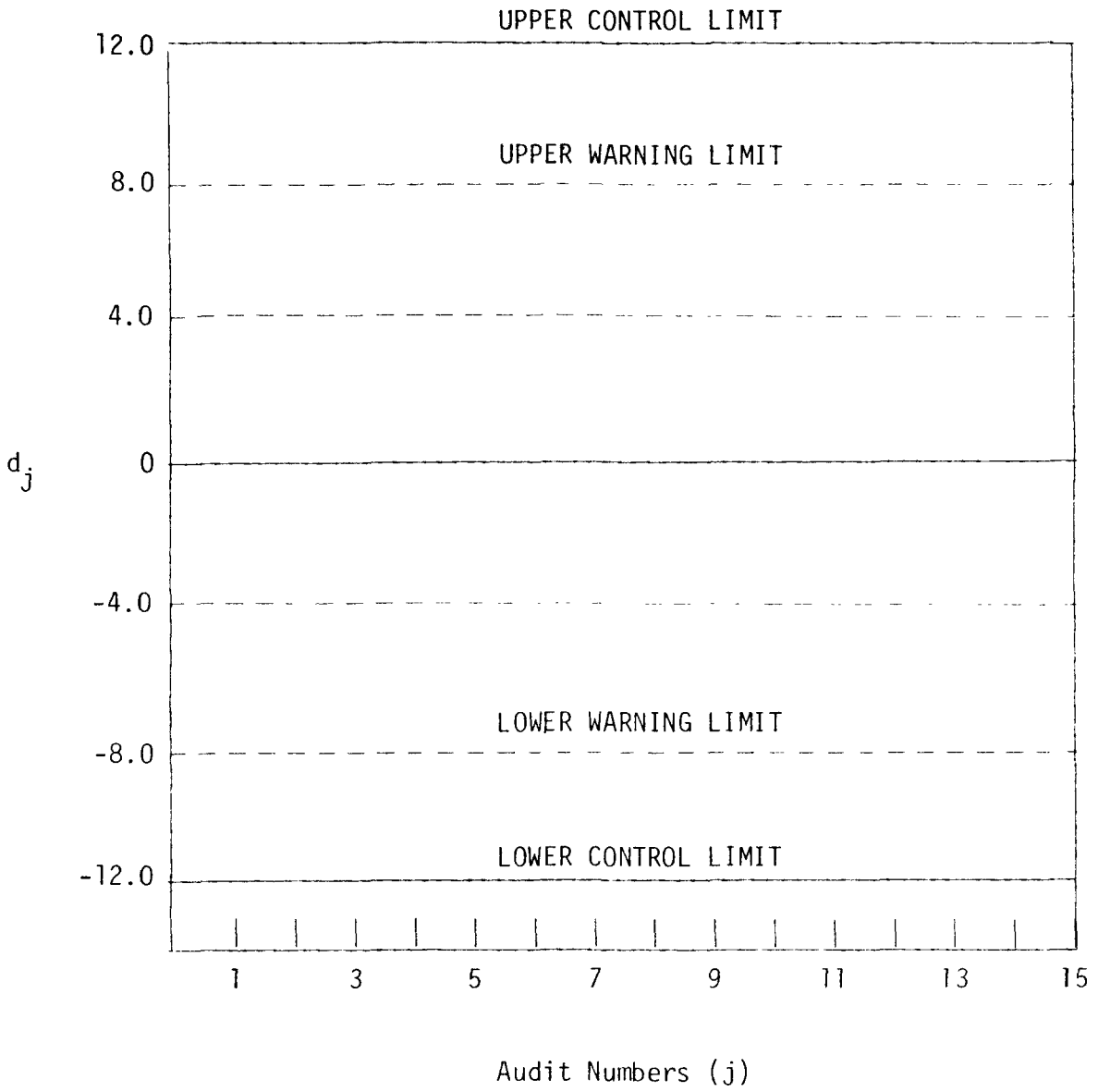

Figure 5. Quality control chart for d_j.

effectively apply preventative-type maintenance procedures to the measurement process, the supervisor must know the important variables in the process, know how to monitor the critical variables, and know how to interpret the data obtained from monitoring operations. These subjects are discussed in the following subsections.

3.3.1 Identification of Important Variables

Determination of stack gas composition requires a sequence of operations and measurements that yields, as an end result, a number that represents the average concentration of a component gas 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 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.

Several variables can affect the expected precision and accuracy of measurements made by Method 7. Certain of these are related to analysis uncertainties and others to the collection procedure. Major sources of error are:

1. Spectrophotometer-Related Errors. Because these errors are the single largest cause of both inaccuracy and imprecision in Method D, it is very important to carry out calibrations (of both the wavelength scale and transmittance scale) at least once each calendar quarter. However, it is essential that the calibration be checked every time an analysis is done. The check is accomplished by carefully preparing standard nitrate solutions at low, medium, and high absorbance levels. Because of the advisability of restricting analyses to the 0.3 to 0.5 absorbance range, a good set of calibration check standards would have nitrate concentrations of 2.0, 3.0, and 4.0 μg/mℓ. Whenever there is a discrepancy of greater than the 3σ value for the analytical procedure, a checking-rechecking process involving the use of another set of standard solutions and recalibration of the spectrophotometer must be carried out until the cause of the discrepancy is determined and corrected.

A second check on spectrophotometer performance is how closely the calibration curve regresses to zero absorbance at zero nitrate concentration. It has been suggested (ref. 1) that the curve be forced through the origin, either graphically or by linear regression.

2. Data Processing Errors. Calculation errors are prevalent in Method 7. The collaborative studies recommend that a computer program be written to carry out all calculations, and that all data processing be carried out by the EPA.

So long as calculations are done in the field, it is necessary to emphasize to all personnel involved that great care must be taken to avoid careless errors. It is imperative that each person understand the calculation, so that when a miscalculation produces a clearly erroneous result the person involved will be able to recognize that an error has occurred.

The magnitude of data processing errors can be estimated from the auditing program, which involves periodic calculation checks and the correction of errors turned up by these checks. On a day-to-day basis, however, it is important that field personnel be impressed with the importance of rechecking all calculations before submission to the team supervisor.

3. Method Errors. Because Method 7 is very tedious, especially in the time involved and techniques of the analytical phase, there are numerous opportunities for sample loss and/or contamination. It is difficult to systematically monitor technique errors in pipetting, aliquotting, and the like. Such errors can hopefully be minimized through careful instruction and supervision of field and laboratory personnel. Again, it is important that the personnel involved have an understanding of the method in order to be able to detect obvious mistakes and either make a correction or void the sample. Auditing of the analytical technique by reference samples will uncover serious systematic technique errors.

4. Interference of Hydrogen Chloride. At least one study (ref. 4) has shown that Method 7 results are affected by the presence of HCl, either as the dry gas or in the form of hydrochloric acid. If HCl is a possible component of the stack gas being sampled, it is important to obtain at least a rough estimate of its concentration. Hydrogen chloride acts as a negative

interferent, and the magnitude of the effect is dependent on HCl concentration. Figure 6 is taken from an SWRI study (ref. 4) which shows that at high concentrations the effect is quite large. Driscoll (ref. 12) suggests the removal of chloride by an excess of silver sulfate and filtration, prior to the evaportation step. Another study (ref. 13) indicates that chloride is effectively precipitated as lead chlorofluoride. Method 7 makes no provision for elimination of chloride or any of several other interferents and it is not acceptable to modify the reference method. It is desirable to be aware of possible interferents, however, in order to anticipate the collection of bad data in their presence.

3.3.2 How to Monitor Important Variables

Spectrophotometer readings and data processing errors are monitored routinely by calibration checks and calculation checks. "Method" errors are not separately monitored other than by observation of personnel actually carrying out the operations of sampling and analysis. The presence and approximate concentration of HCl can be anticipated if the nature of the combusting material is known. Table 1 summaries the variables and how they can be monitored.

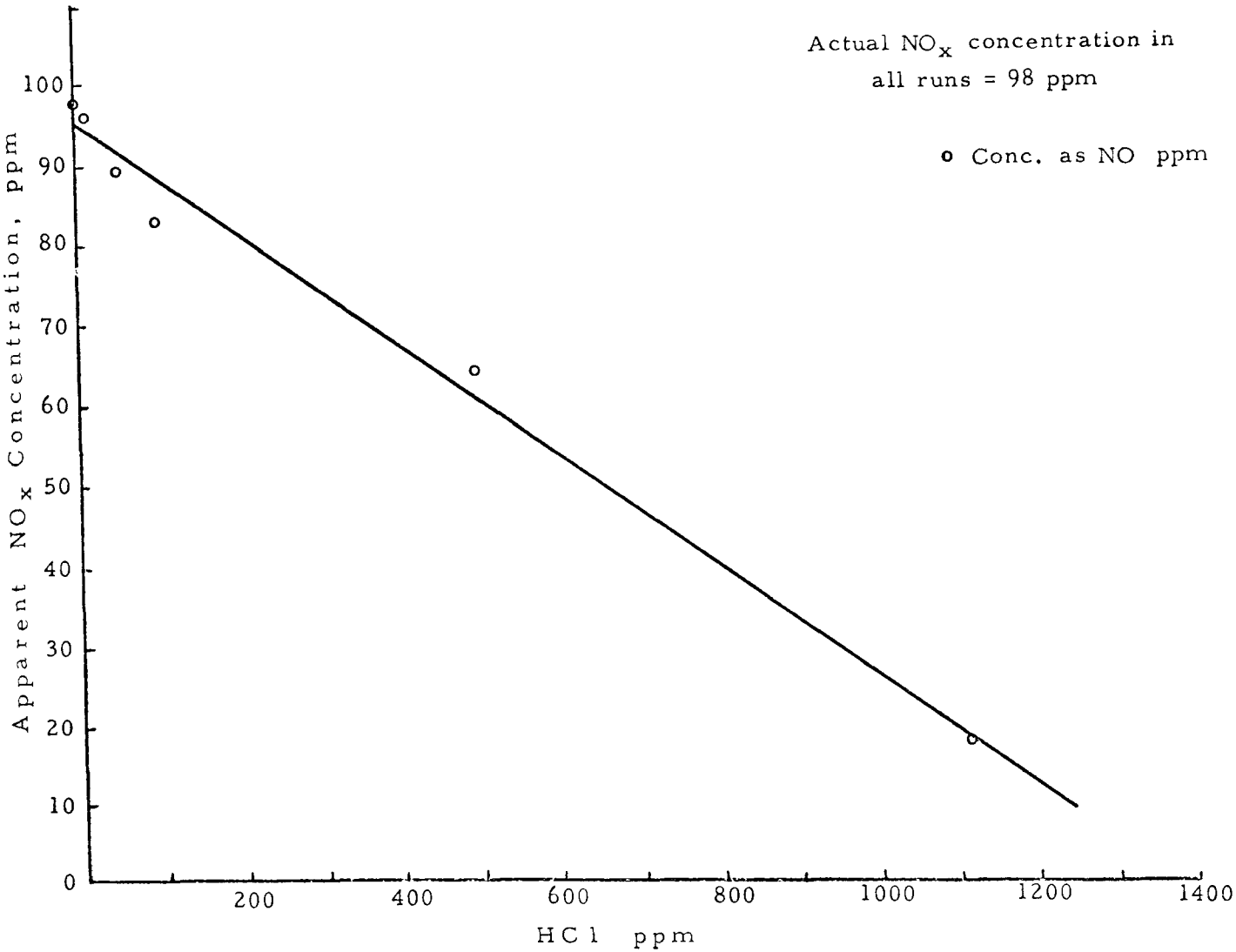

Figure 6. Interference of HCl with the determination of NO_x - EPA Method 7.

Table 1. Methods of monitoring variables

VARIABLE	METHOD OF MONITORING
1. a. Spectrophotometer Wavelength Scale	Check against a didymium glass spectrum.
b. Spectrophotometer Absorbance Scale	Check against a set of neutral density filters.
2. c. Spectrophotometer Calibration Curve	Check against standard nitrate solutions of low, medium, and high concentration. Also check by measurement of reference samples.
3. Data Processing Errors	Recalculation before submission, as well as auditing checks.
Method Errors	Periodic observation of personnel actually doing sampling and analysis.
4. HCl Interference	Knowledge of gases, and approximate concentrations being emitted at stack.

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 7--Determination of Nitrogen Oxide Emissions from Stationary Sources, are given in this part of the field document. This information is written for the manager of several teams that measure 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 for 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 objectives of identifying the most important factors that 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 pitot tubes into the stack and collecting two samples simultaneously) is not considered practical due to the constrained environmental and space conditions under which the data are being collected. Hence, a combination of an on-site system audit, including visual observation of adherence to operating procedures and a quantitative performance quality audit check, is recommended as a dual means of independently checking on the source emissions data.

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

The data quality audit procedure is an independent check of data collection and analysis techniques with respect to the important variables. It provides a means of assessing data collected by several teams and/or firms with the potential of identifying biases/excessive variation in the data collection procedures. A quality audit should not only provide an

independent quality check, but also identify the weak points in the measurement process. Thus, the auditor, an individual chosen for his background knowledge of the measurement process, will be able to guide field teams in using improved techniques. In addition, the auditor is in a position to identify procedures employed by some field teams which are improvements over the currently 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; it is particularly adaptable to the small lot size and consequently to 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 4.4.3 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 costs 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.

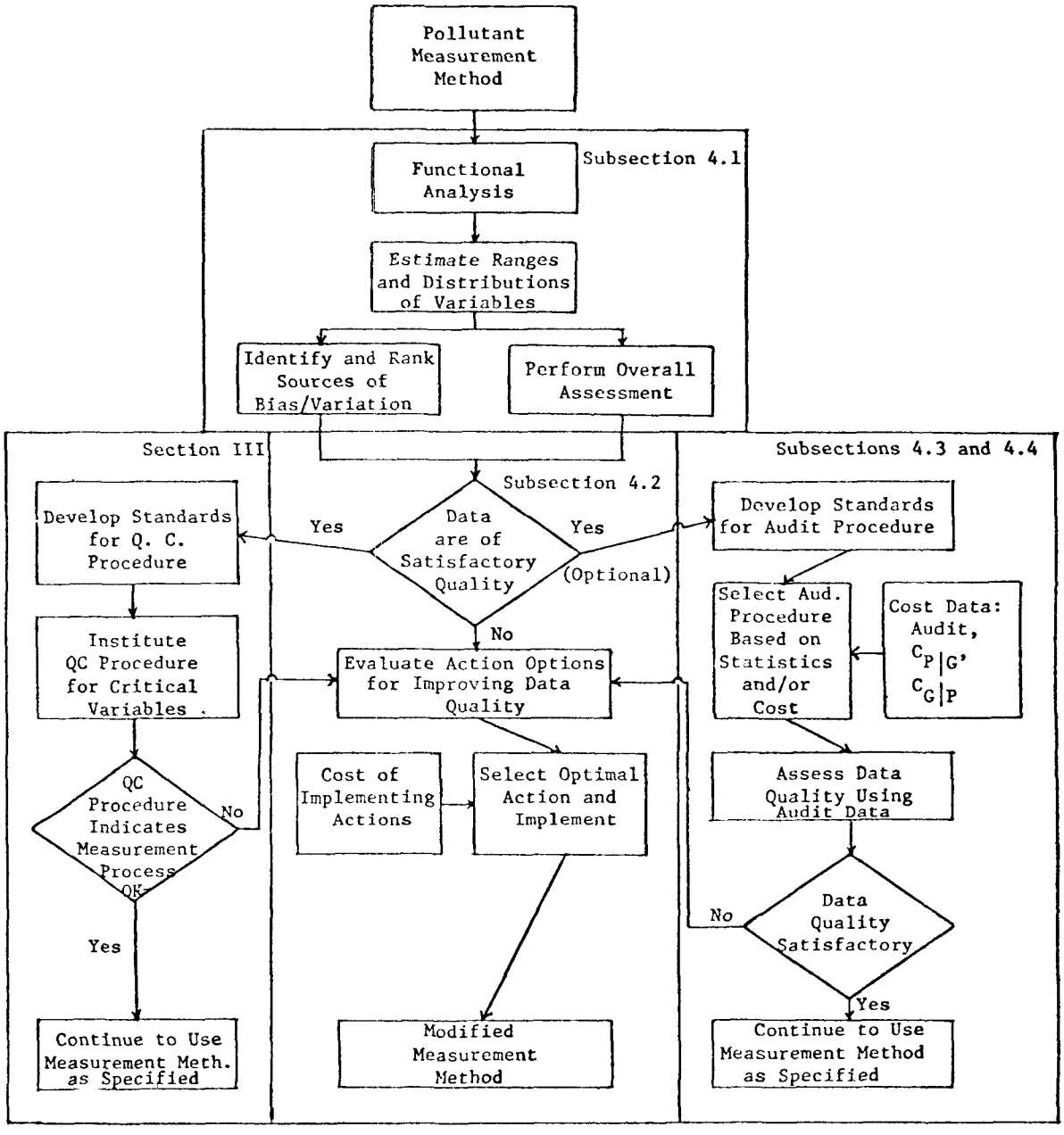

Figure 7. Summary of data quality assurance program.

4.1 FUNCTIONAL ANALYSIS OF THE TEST METHOD

Test Method 7--Determination of Nitrogen Oxide Emissions from Stationary Sources--is described in the Federal Register of December 23, 1971, and a later version is reproduced as appendix A of this document. This method is used to determine the concentration of nitrogen oxides (except nitrous oxide) in the stack gas. In conjunction with the volumetric flow rate as measured by Method 2, a nitrogen oxides emission rate may be determined 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. Use is made of the results from collaborative tests of the method (refs. 1,2,3) for overall variability and for the division of variability due to the sample collection and analysis phases of the process.

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

C_{NO_x} = NO_x concentration (as NO_2) dry basis, corrected to standard conditions, mg/scm.

$\bar{C}_{NO_x}$ = The average NO_x concentration (as NO_2) of three repetitions, where each repetition is the average of four measurements.

$CV\{X\}$ = Within-laboratory coefficient of variation, percent.

$CV_b\{X\}$ = Between-laboratory coefficient of variation, percent.

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

$CV\{C_{NO_x}\}/\sqrt{12}$ = Repeatability coefficient of variation for NO_x determinations based on twelve replicates, percent.

$\sqrt{CV_L^2\{C_{NO_x}\} + CV^2\{C_{NO_x}\}/12}$ = Reproducibility coefficient of variation for a test result based on twelve replicates, percent.

4.1.1 Variable Evaluation and Error Range Estimates

The emission rate (mg/hr) of nitrogen oxides (as NO_2) is calculated from measured values by the relationship

$$ER = C_{NO_x} \cdot Q_s$$

where Q_s = volumetric flow rate, scm/hr and C_{NO_x} has already been defined (4.1).

Both the nitrogen oxides concentration (as NO_2) and the volumetric flow rate depend upon a number of variables. They are further broken down in the following discussion:

$$C_{NO_2} = Km/V_{sc}$$

where $K = 10^3 \frac{(m\ell)(mg)}{(m^3)(\mu g)}$

m = Total μg NO_2 per sample

V_{sc} = Sample volume at standard conditions (dry basis), $m\ell$.

In turn,

$$m = 2 K_c AF$$

where 2 = 50/25 = Aliquot factor

K_c = Spectrophotometer calibration factor

F = Dilution factor (1, unless sample dilution was required to bring the absorbance into the calibrated range).

$$K_c = 100 \frac{A_1 + 2A_2 + 3A_3 + 4A_4}{A_1^2 + A_2^2 + A_3^2 + A_4^2}$$

where A_1 = Absorbance of the 100 μg NO_2 standard

A_2 = Absorbance of the 200 μg NO_2 standard

A_3 = Absorbance of the 300 μg NO_2 standard

A_4 = Absorbance of the 400 μg NO_2 standard

The volume, V_{sc}, of the sample is calculated as

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

where $T_{std} = 293^\circ$ K.

$P_{std} = 760$ mmHg.

V_f = Volume of flask and valve, mℓ.

V_a = Volume of absorbing solution, 25 mℓ.

P_f = Final absolute pressure in flask, mmHg.

P_i = Initial absolute pressure in flask, mmHg.

T_f = Final temperature of flask, $^\circ$K.

T_i = Initial temperature of flask, $^\circ$K.

Finally, the volumetric flow rate, Q_s, is a function of a number of variables, as given below:

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

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

C_p = Pitot tube calibration coefficient, dimensionless.

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

A_s = Stack cross-sectional area, m^2.

P_s = Absolute stack pressure, mmHg

$(T_s)_{avg}$ = Average stack temperature, $^\circ$K.

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

A systematic analysis of the variance of ER for NO_x must include estimates of the variances of each parameter mentioned above. A variance analysis for Q_s has been done and appears in the Quality Assurance Guidelines document for Method 6, Determination of Sulfur Dioxide Emissions from Stationary Sources. The value of $CV_b\{Q_s\}$ is given as 2.33%.

The $CV\{C_{NO_x}\}$ must be determined in order to obtain an estimate of $CV\{ER\}$, since

$$CV^2\{ER\} = CV^2\{C_{NO_x}\} + CV^2\{Q_s\}.$$

C_{NO_x} depends on both the total mass of NO_x (as NO_2) and the volume of the collected sample; i.e., on m and V_{sc}. These must be examined for sources of variability.

A spectrophotometer calibration check must be made before each analysis. A collaborative study (ref. 1) of Method 7 indicates that by far the most significant source of reproducibility variation (93%) is attributable to negligence in recalibration procedures. At low nitrate concentration (1.25 μg NO_2/m), the analytical procedure was responsible for 100% of the reproducibility variation. It is therefore highly desirable to avoid solution concentrations that give readings on the extreme lower end of the absorbance scale. At a concentration of 3.75 μg NO_2/mℓ, analytical and field procedures accounted for about equal parts of the total reproducibility variation. As a general statement, the calibration curves used in the collaborative test were found to be so imprecise that concentration readings were from 5% to 8% in error. This translates directly to an equivalent error in the mass calculation. The C_{NO_x} then may vary 5-8% unless a recalibration of the spectrophotometer is carried out before each analysis. In addition, there is an uncertainty in the value of V_{sc}, which depends on measurements of temperature, pressure, and volume. Table 2 lists reasonable reading errors in these variables.

Table 2. Estimates of reading errors in determination of V_{sc}

Variable	Measurement Method	Error	Mean Values	% Error
1. Temperature	Dial thermometer	± 1° K	300° K	0.33
2. Pressure	U-Tube manometer	± 1 mm	700 mm	0.14
3. Volume	Graduated cylinder	± 10 mℓ	2,000 mℓ	0.50

Propagating these errors through the equation for determination of V_{sc}, the maximum error in V_{sc} should be about 0.8%. It is apparent that the error in a determination of C_{NO_x} depends largely on the accuracy of the spectrophotometer calibration and sample readings.

An estimate of the reproducibility is given as 7.48%, as shown in table 3.

Table 3. Estimate for reproducibility of ER

Variable	Assumed $CV^2\{X\}$*
$\bar{C}_{NO_x}$	$CV_L^2\{\bar{C}_{NO_x}\} = 46.92$
	$CV^2/12 = 3.57$
	$CV^2\{Q_s\} = 5.43$
ER	$(R)^2 = 55.92$
	$R = 7.48$

4.1.2 Interferences

Hydrogen chloride has been shown to be a negative interferent (ref. 4). The effect appears to be linear with HCl concentration and is drastic at high concentrations. With a test gas of approximately 100 ppm NO_x and 1120 ppm HCl, results were 78% low. At HCl concentrations below 100 ppm the effect becomes minor (less than 10%).

4.1.3 Bias

The method shows no appreciable bias in either direction, so long as the absorbing solution concentration remains sufficiently high, i.e., within the normal working range of the calibration curve (ref. 2).

*$CV^2\{X\}$ values are taken from a collaborative study (ref. 2), and are consistent with spectrophotometer-associated errors of about 6%, and other method errors of 3-4%. The study gives CV = 6.56, CV_b = 9.49 and CV_L = 6.85.

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, five 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: Take aliquots of sample so as to have several replicate results from each sample (cost of $400*/20 field tests)

A2: Take integrated rather than grab sample, and irradiate during sample collection to shorten absorption/oxidation step (cost of $200/20 field tests)

A3: Thermostat spectrophotometer, standard solutions and samples to minimize absorbance variances due to temperature fluctuations (cost of $250/20 field tests)

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

A4: Do all calculations by a standard computer program, thus eliminating personnel errors in calculation of results (cost of $200/20 field tests)

A5: Conduct one-week workshop for all personnel involved in the method, to minimize technique errors (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.

A1: The reference method allows the taking of only one aliquot, so that only one absorbance reading is obtained per sample. It would reduce the danger of sample voiding due to laboratory handling error if three aliquots were taken. Also, a mean of three absorbances would be more precise than a single value. The major effect of A1 then would be to reduce the within-laboratory relative standard deviation, CV. This in turn will reduce the between-laboratory deviation, CV_b, since the values for NO_x concentration from different laboratories will be grouped more tightly about the "true" value. Without any experimental data, it is impossible to verify the above assumptions, and certainly the estimation of numerical values for CV, CV_b, and CV_L is subject to a great deal of uncertainty. The estimated values as given in table 4 for A0 through A5 serve to illustrate the methodology of cost-benefit analysis. The actual costs must be determined in each individual situation, and the actual changes in CV, CV_b, and CV_L could be determined as the various options are implemented. Figure 8 plots added cost versus data quality for the various options, and includes a function curve for the assumed cost of reporting poor quality data.

A2: An integrated sample normally gives a more reliable indication of mean stack gas composition than a series of grab samples, since sharp fluctuations in composition are smoothed out over time. A series of grab samples may yield a mean value for the concentration of NO_x which is widely different from the true concentration, if the timing of the grab samples is such that the mean does not reflect the true mean averaged over time. The major effect of

Table 4. 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	Three Aliquots Per Sample	$0.58\ CV_R^*$	$0.8(CV_b)_R^{**}$	$0.96(CV_L)_R$	$ 400
A2	Integrated Sampling	$0.7\ CV_R$	$0.7(CV_b)_R$	$0.70(CV_L)_R$	$ 200
A3	Temperature Control During Analysis	$0.8\ CV_R$	$0.9(CV_b)_R$	$0.98(CV_L)_R$	$ 250
A4	Calculations by Standard Computer Program	$1.0\ CV_R$	$0.90(CV_b)_R$	$0.8(CV_L)_R$	$ 200
A5	Personnel Workshop	$0.8\ CV_R$	$0.8(CV_b)_R$	$0.73(CV_L)_R$	$1,000

* $CV_R/\sqrt{3}$

** Values stated to one place are estimations based on engineering judgment.

A2 then should be to reduce the between-laboratory coefficient of variation, CV_b, since the values become more tightly clustered about the "true" value and it is assumed that this reduction in CV_b is reflected in CV and CV_L, both becoming smaller.

A3: Thermostating the spectrophotometer cells and solutions reduces the small fluctuations in absorbance values due to temperature changes, and thus reduces CV by making a closer correspondence between the calibration conditions and sample analysis conditions. This relatively small improvement in CV is assumed to carry over to both CV_b and CV_L, since it amounts to fixing a parameter; namely, the temperature, which in AO is allowed to fluctuate with ambient laboratory temperature. In order to justify the assumption of a carry-over improvement in CV_b, it must be required that laboratory thermometer calibrations be against an NBS set of calibrated thermometers. Otherwise, different laboratories will be reading absorbances at different temperatures due to inaccurate calibration.

A4: This recommended option serves a twofold purpose:

1. It eliminates human error (in the field) in calculation of the NO_x concentration. There remains, of course, the possibility of errors due to computer malfunction, key punch 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 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%)

of random calculation errors contribute to CV. If both CV_L and CV are reduced, then CV_b should also be improved.

A5: 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. It is assumed here that crew training could affect all sources or variability, and therefore an improvement in all three measures of variability is shown.

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 7 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 both cases illustrated here, choosing strategy A2 would be optimal.

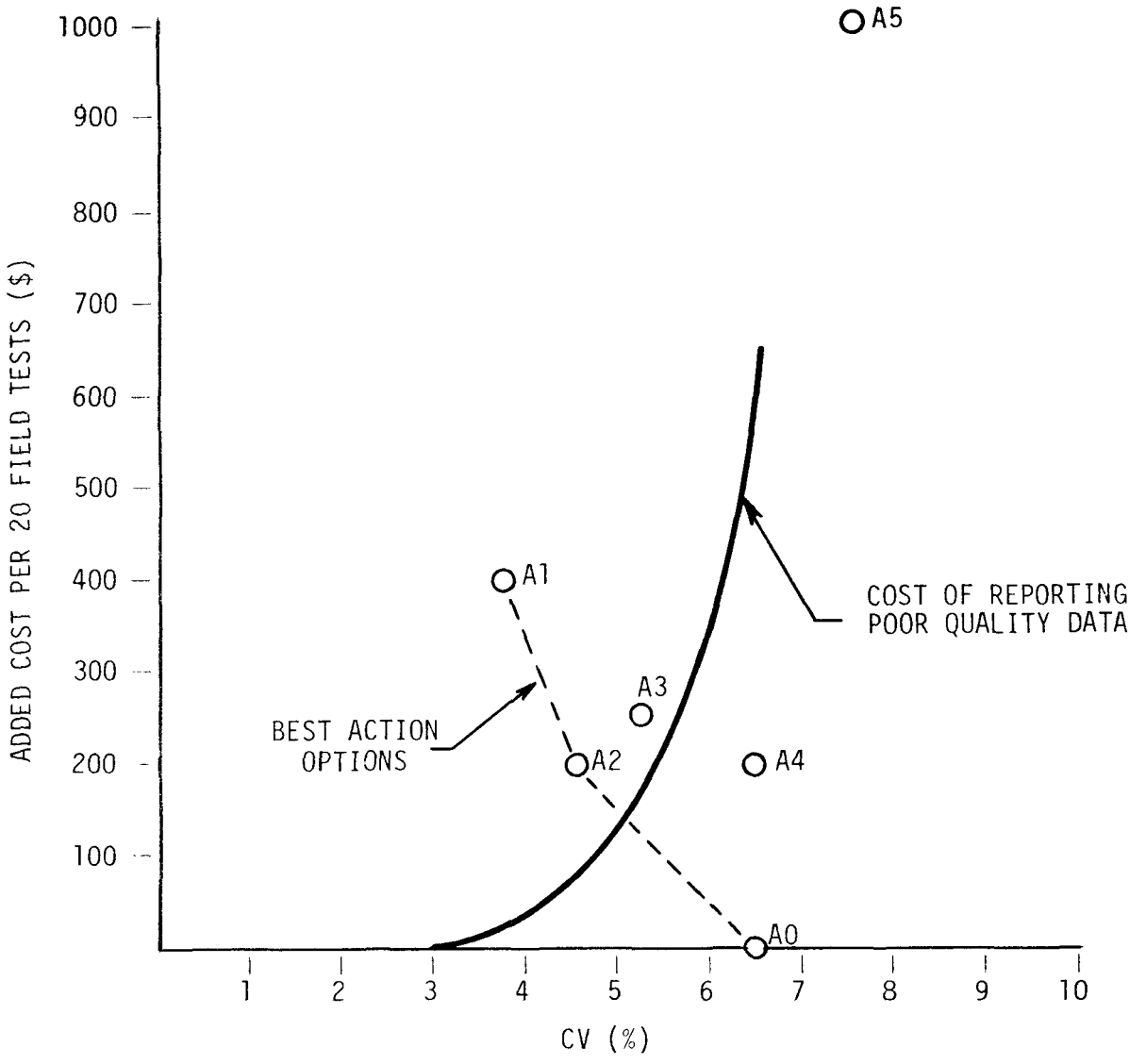

Figure 8. Added cost versus data quality (CV) for selected action options.

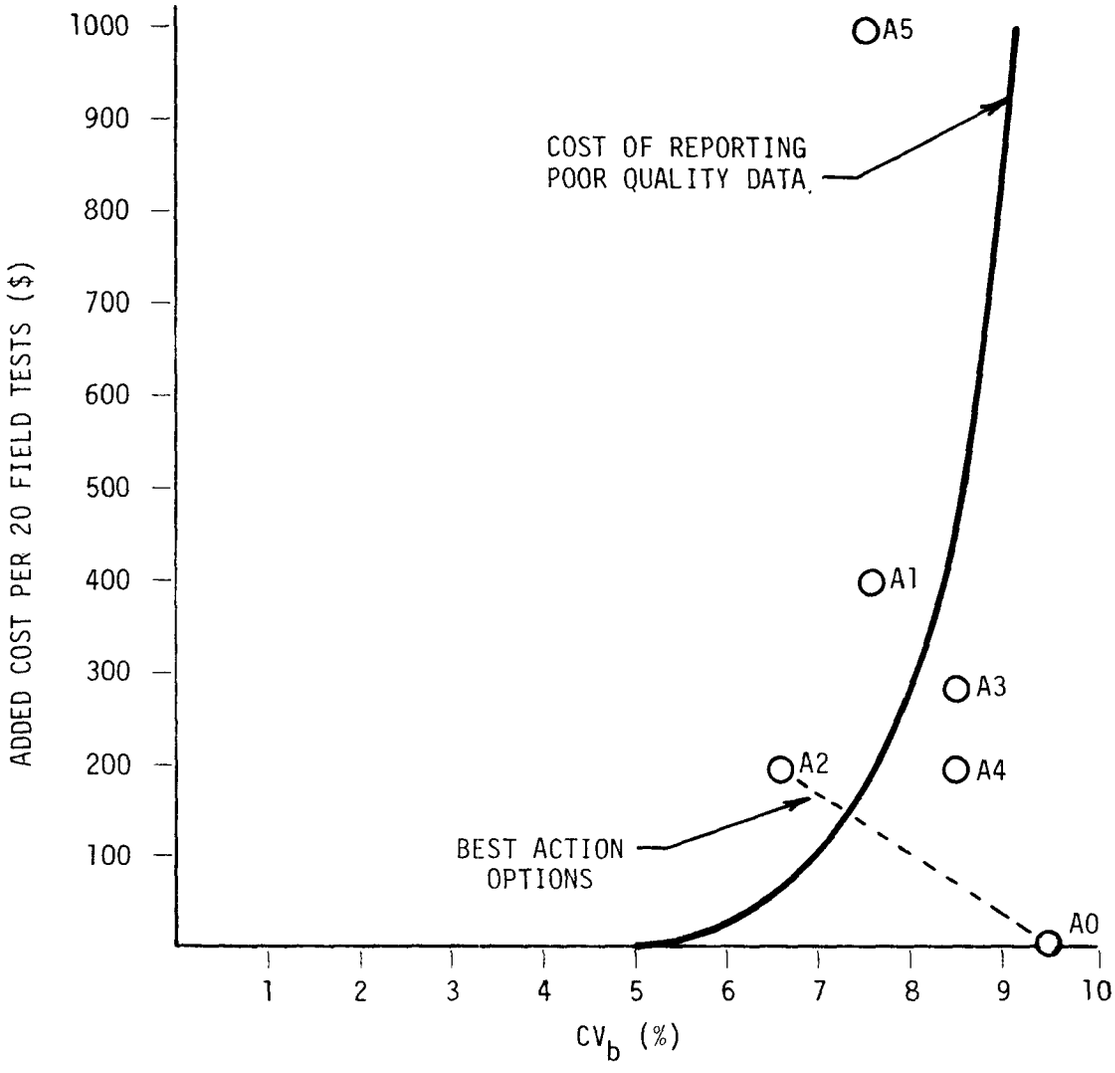

Figure 9. Added cost versus data quality (CV_b) for selected action options.

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 A1 and A3 were both implemented, the total cost would be \$650 (\$400 + \$250) and the values of CV and CV_b would be as given below.

	CV	CV_b
A0	6.56 ($=CV_R$)	9.49 ($=(CV_b)_R$)
A1	0.58 (CV_R)	0.8 $(CV_b)_R$
A3	0.8 (CV_R)	0.9 $(CV_b)_R$
(A1 + A3)	(0.58) (0.8) (CV_R)	(0.8) (0.9) $(CV_b)_R$
	= 0.46 (CV_R)	= (.72) $(CV_b)_R$
	= 3.04	= 6.83

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 NO in air and has the field team analyze the sample. The field team should not know the true NO 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 NO 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 solution into sampling flask;
3. Sample collection;
4. Sample absorption, 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.

Reference gas samples can be prepared by air dilution of cylinder NO in N_2. For details, see pages 2-5 of reference 3. These reference samples should then be analyzed by the field team.

4.3.3 Collecting Home Laboratory Information

The auditor must also observe the analytical phase of Method 7. Here he should observe the following:

1. Sample aliquotting technique. This is particularly important, to verify that standard analytical technique is being followed.
2. Evaporation and chemical treatment of sample, including filtration and washing steps.
3. Spectrophotometric technique, including -
   a. Preparation of standard nitrate samples;
   b. Technique of making absorbance measurements, including measurement of blanks;
   c. Preparation of calibration curve, including technique used for drawing of curve (visual, linear regression);
   d. Wavelength and absorbance calibrations using didymium glass and filters.
4. Calculation procedure.

The analysis phase of Method 7 can be audited with standard nitrate solutions, as discussed on pages 33-36 of reference 3.

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

$$d_j = (NO_2)_j - (NO_2)_{a_j}$$

where

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

$(NO_2)_{a_j}$ = Audit value of NO_2 concentration, mg/m^3

$(NO_2)_j$ = NO_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. These error sources have to be estimated subjectively by the auditor. Using the notes taken in the field, the team could be rated on a scale of 1 to 5 as follows:

5 - Excellent
4 - Above average
3 - Average
2 - Acceptable, but below average
1 - Unacceptable performance.

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

4.4 DATA QUALITY ASSESSMENT

Two aspects of data quality assessment are considered in this section. The first considers a means of estimating the precision and 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 NO_x 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 in order 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

$$d_j = (NO_2)_j - (NO_2)_{aj}.$$

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

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

and

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

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

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

See ref. 5 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 $\sigma\{NO_2\}$, the population standard deviation for NO_2 measurements The standard deviation, s_d, can be utilized to check the reasonableness of the assumptions made in section 4.1 concerning $\sigma\{NO_2\}$*. For example, the estimated standard deviation, s_d, may be directly checked against the assumed value, $\sigma\{NO_2\}$, by using the statistical test procedure

$$\frac{\chi^2}{f} = \frac{s_d^2}{\sigma^2_{\{NO_2\}}} ,$$

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.

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*Values for $\sigma\{NO_2\}$ and $\sigma_b\{NO_2\}$ are found by multiplying the values of CV or CV_b by the assumed value of the mean concentration of NO_2. This converts the percentages into concentrations.

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 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. 6-11. 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 NO_2 measurements are audited as directed in section 4.3. The difference between the team-measured and audited value of NO_2 is designated as d_j, and the mean difference over n audits by $\bar{d}$ is

$$\bar{d} = 1/n \sum_{j=1}^{n} (NO_2)_j - (NO_2)_{aj}$$

Theoretically, (NO_2) and $(NO_2)_a$ should be measures of the same NO_2 concentration and their difference should have a mean of zero on the average. In addition, this difference should have a standard deviation approximately equal to that associated with the measurements of NO_2.

Assuming three standard deviation limits, the values $3\sigma = -19.7$ mg/m^3 * and + 19.7 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. 9, 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 II of ref. 9. The values of $\bar{d}$ and s_d are computed in the usual manner; see table 5 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:

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* 19.7 mg/m^3 assumes for calculation purposes an NO_2 concentration mean of 100 mg/m^3, with CV = 6.56%, so that $3\sigma = 3 \times 6.56 = 19.7$ mg/m^3

Table 5. Computation of mean difference, $\bar{d}$, and standard deviation of differences, s_d

General Formulas		Specific Example	
$d = (NO_2)_j - (NO_2)_{aj}$		Data mg/m^3	
d_1	d_1^2	-17.0	289
d_2	d_2^2	8.5	72
d_3	d_3^2	0.0	0
d_4	d_4^2	33.9	1149
d_5	d_5^2	25.4	645
d_6	d_6^2	12.7	161
d_7	d_7^2	0.0	0
Σd_j	Σd_j^2	+63.5	2316
$\bar{d} = \frac{\Sigma d_j}{n}$		$\bar{d} = +9.1\ mg/m^3$	
$s_d^2 = \frac{\Sigma d_j^2 - \frac{(\Sigma d_j)^2}{n}}{(n-1)}$		$s_d^2 = 331$	
$s_d = \sqrt{s_d^2}$		$s_d = 18.2\ mg/m^3$	

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

$$\bar{d} - k\, s_d \geq L = -19.7\ mg/m^3$$

$$d + k\, s_d \leq U = +19.7\ mg/m^3$$

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

2. If one or both of these inequalities is violated, possible deficiencies exist in the measurement process as carried out for that

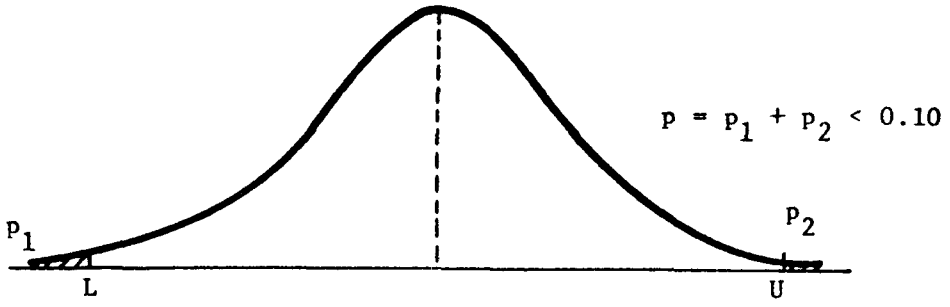

Figure 10. Example illustrating $p < 0.10$ and satisfactory data quality.

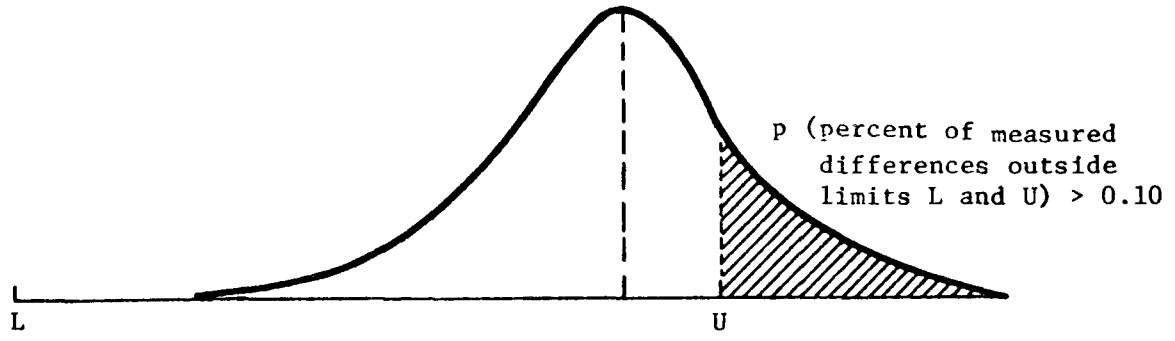

Figure 11. Example illustrating $p > 0.10$ and unsatisfactory data quality.

particular lot (group) of field tests. These deficiencies should be identified and corrected before future field tests are performed. Data corrections should be made when possible, i.e., if a quantitative basis is determined for correction.

Table 6 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

$$\bar{d} - k\, s_d = 9.1 - 2.334 \times 18.2 = -33.4 < L = -19.7 \text{ mg/m}^3$$

$$\bar{d} + k\, s_d = 9.1 + 2.334 \times 18.2 = 51.6 > U = +19.7 \text{ mg/m}^3$$

Table 6. Sample plan constants, k for P {not detecting a lot with proportion p outside limits L and U} $\leq$ 0.1

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

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 average, 90 percent of the lots with 10 percent or more defects will be detected by this sampling plan.

4.4.3 Cost Versus Audit Level

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

A model of the audit process, associated costs, and assumptions made in the determination of the audit level is provided in figure 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

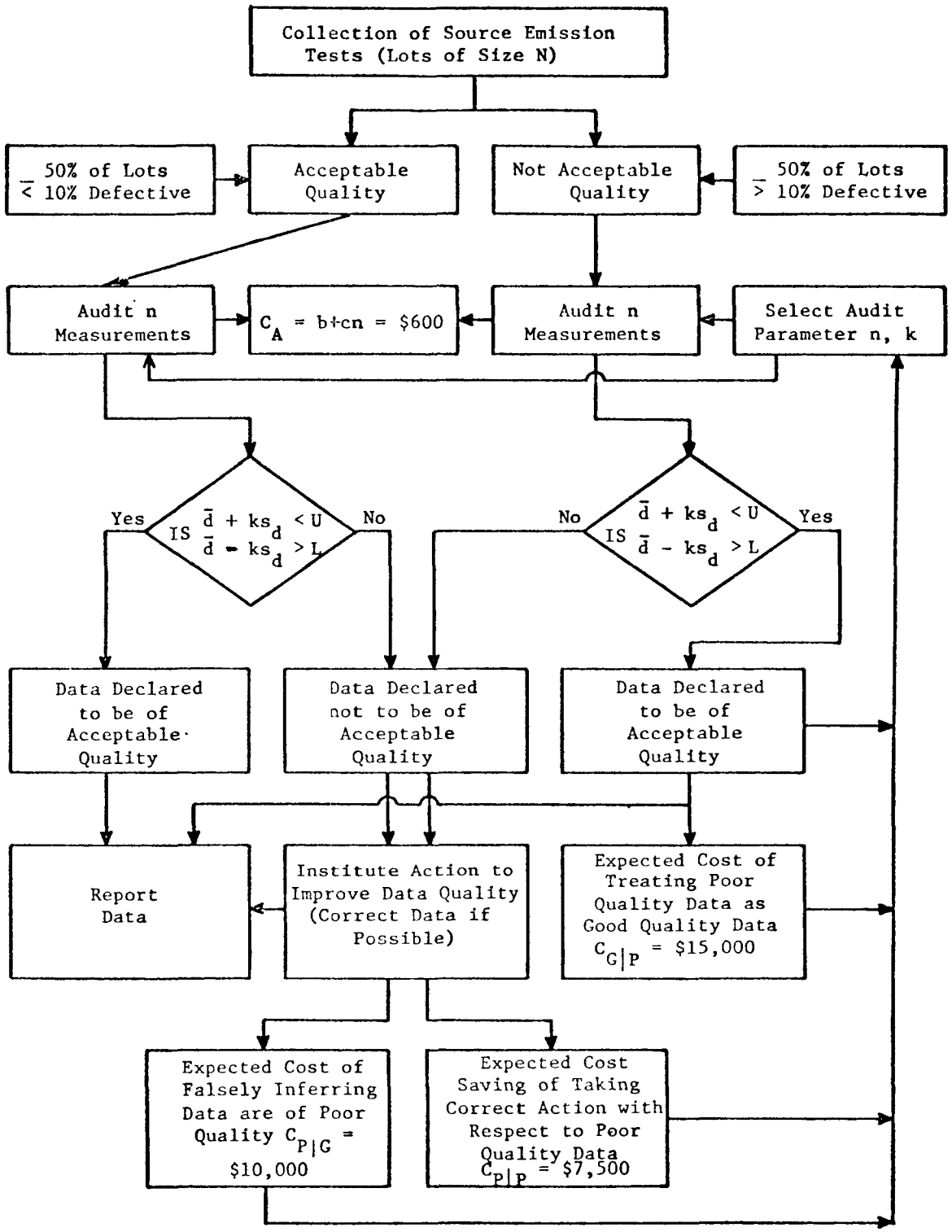

Figure 12 . Flow chart of the audit level selection process.

quality of the source emissions data from several firms. For example, it is assumed in this analysis that 50 percent of the data lots are of good quality, i.e., one-half of the firms are adhering to good data quality assurance practice, and that 50 percent of the data lots are of poor quality. Based on the analysis in 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 \$1000 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 12 . 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 6 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 conditional on the presumed lot quality and are preceded by a factor of 0.5 in the total cost model, to correspond to the assumed percentage of good (poor) quality data lots.

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

for a series of values of n (and associated k, which is given in table 5). The computational procedure is given in the Final Report of this contract. These calculations were made for the cases n = 3, 5, 7, and 10 and for two degrees of control on the quality of the data that can be tolerated, i.e., p = 0.2 and p = 0.1, the portion outside the limits L and U for which it is desired to accept the data 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 13. It can be seen from these curves that the minimum cost is obtained by using n ≃ 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.

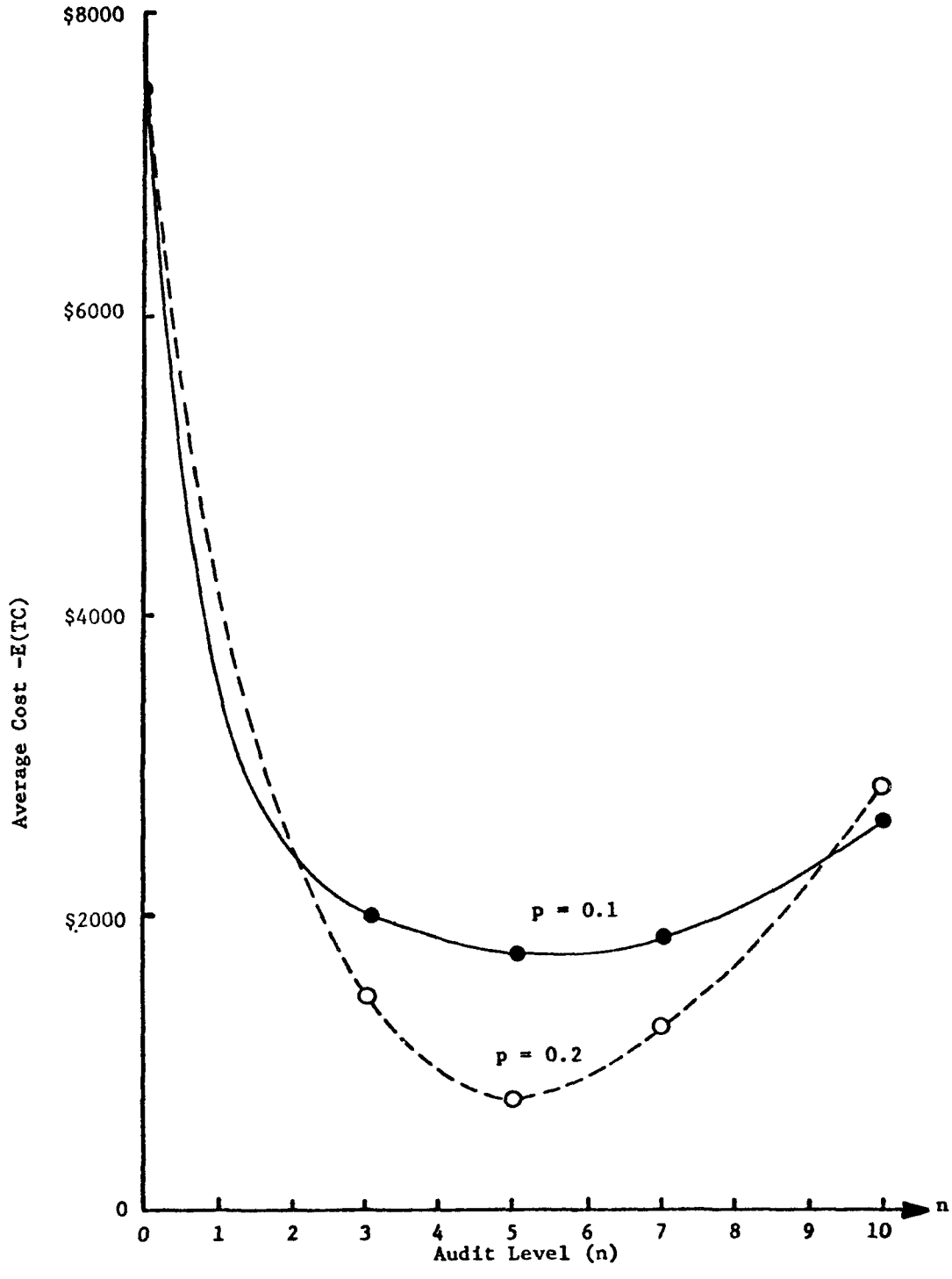

Figure 13. Average Cost vs Audit Level (n).

SECTION V REFERENCES

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3. H. F. Hamil and R.E. Thomas. "Collaborative Study of Method for the Determination of Nitrogen Oxide from Stationary Sources (Nitric Acid Plants)." Final Report, EPA Contract No. 68-02-0626, Southwest Research Institute, San Antonio, Texas 78284.
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APPENDIX A METHOD 7 - DETERMINATION OF NITROGEN OXIDE EMISSIONS FROM STATIONARY SOURCES

1. Principle and Applicability

1.1 Principle. A grab sample is collected in an evacuated flask containing a dilute sulfuric acid-hydrogen peroxide absorbing solution, and the nitrogen oxides, except nitrous oxide, are measured colorimetrically using the phenoldisulfonic acid (PDS) procedure.

1.2 Applicability. This method is applicable to the measurement of nitrogen oxides emitted from stationary sources only when specified by the test procedures for determining compliance with new source performance standards. The range of the method has been determined to be 2 to 400 milligrams NO_x as NO_2 per dry standard cubic meter without having to dilute the sample.

2. Apparatus

2.1 Sampling (See Figure 7-1).

2.1.1 Probe--Borosilicate glass tubing sufficiently heated to prevent water condensation and equipped with a filter (either in-stack or heated out of stack) to remove particulate matter. Heating is unnecessary if the probe remains dry during the purging period.

2.1.2 Collection flask--Two-liter borosilicate, round bottom with short neck and 24/40 standard taper opening, protected against implosion or breakage.

2.1.3 Flask valve--T-bore stopcock connected to a 24/40 standard taper joint.

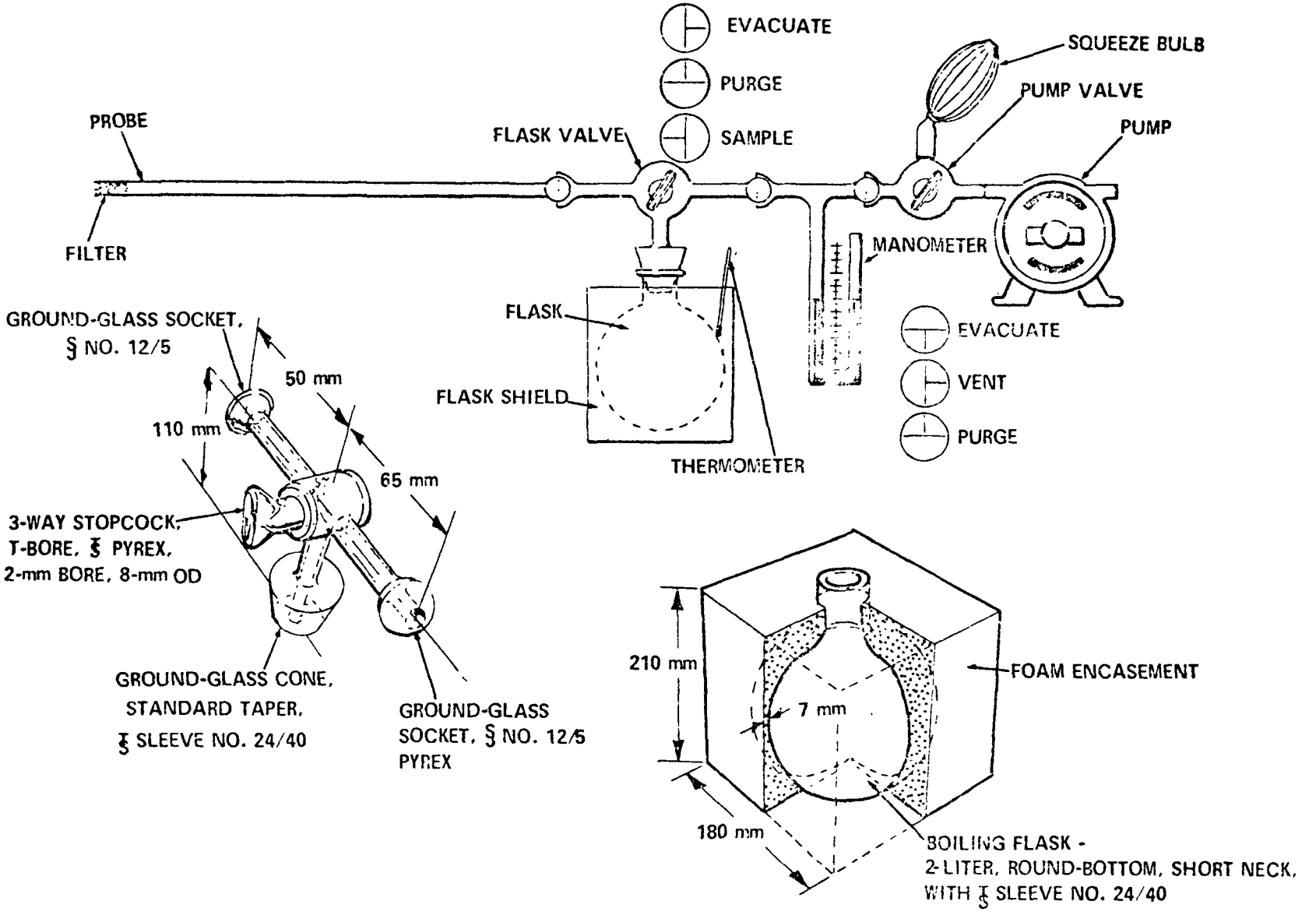

Figure 7-1. Sampling train, flask valve, and flask.

2.1.4 Temperature gauge--Dial-type thermometer, or equivalent, capable of measuring 1°C (2°F) intervals from -5 to 50°C (25 to 125°F).

2.1.5 Vacuum line--Tubing capable of withstanding a vacuum of 75 mm Hg (3 in. Hg) absolute pressure, with "T" connection and T-bore stopcock.

2.1.6 Pressure gauge--U-tube manometer, 1-meter, with 1-mm (36-in., with 0.1-in.) divisions, or equivalent.

2.1.7 Pump--Capable of evacuating the collection flask to a pressure equal to or less than 75 mm Hg (3 in. Hg) absolute.

2.1.8 Squeeze bulb--One-way

2.1.9 Volumetric pipette--25-ml.

2.1.10 Stopcock and ground joint grease--A high vacuum, high temperature chlorofluorocarbon grease is required. Halocarbon[1] 25-5S has been found to be effective.

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

2.2 Sample recovery.

2.2.1 Volumetric pipette--One 25-ml for each sample.

2.2.2 Graduated cylinder--50-ml with 1-ml divisions.

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

2.2.3 Storage containers--Leak-free polyethylene bottles.

2.2.4 Wash bottle--Polyethylene or glass.

2.2.5 Glass stirring rod.

2.2.6 pH indicating test paper--To cover the pH range of 7-14.

2.3 Analysis.

2.3.1 Volumetric pipettes--Two 1-ml, two 2-ml, one 3-ml, one 4-ml and two 10-ml. and one 25-ml for each sample and standard.

2.3.2 Porcelain evaporating dishes. 175 to 250-ml capacity with lip for pouring, one for each sample and each standard. The Coors[1] #45006 (shallow-form, 195 ml) has been found to be satisfactory.

2.3.3 Steam bath. (A hot plate is not acceptable.)

2.3.4 Dropping pipette or dropper--Three required.

2.3.5 Polyethylene policeman--One for each sample and each standard.

2.3.6 Graduated cylinder--100-ml with 1-ml divisions.

2.3.7 Volumetric flasks--50-ml (one for each sample), 100-ml (one for each sample, each standard and one for the working standard KNO_3 solution), and one 1000-ml.

2.3.8 Spectrophotometer--To measure absorbance at 410 nm.

2.3.9 Graduated pipette--10-ml, with 0.1-ml divisions.

2.3.10 pH Indicating test paper--To cover the pH range of 7-14.

2.3.11 Analytical balance--To measure to 0.1 mg.

3. Reagents

Unless otherwise indicated, it is intended that all reagents conform to the specifications established by the Committee on

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

Analytical Reagents of the American Chemical Society, where such specifications are available; otherwise, use best available grade.

3.1 Sampling.

3.1.1 Absorbing solution--Cautiously add 2.8 ml concentrated H_2SO_4 to 1 liter of deionized, distilled water. Mix well and add 6 ml of 3 percent hydrogen peroxide, freshly prepared from 30 percent hydrogen perioxide solution. The solution should be used within one week of its preparation. Do not expose to extreme heat or direct sunlight.

3.2 Sample recovery.

3.2.1 Sodium hydroxide (1 N)--Dissolve 40 g NaOH in deionized, distilled water and dilute to 1 liter.

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

3.3 Analysis.

3.3.1 Fuming sulfuric acid--15 to 18 percent by weight free sulfur trioxide. Handle with caution.

3.3.2 Phenol--White solid.

3.3.3 Sulfuric acid--Concentrated, 95% minimum assay. Handle with caution.

3.3.4 Potassium nitrate--Dried at 105-110^{o} C for a minimum of two hours just prior to preparation of standard solution.

3.3.5 Standard solution--Dissolve exactly 2.1980 g of dried potassium nitrate (KNO_3) in deionized, distilled water and dilute to 1 liter with deionized, distilled water in a 1000-ml volumetric

flask. For the working standard solution, dilute 10 ml of the standard solution to 100 ml with deionized distilled water. One ml of the working standard solution is equivalent to 100 µg nitrogen dioxide (NO_2).

3.3.6 Water--Deionized, distilled as in section 3.2.2.

3.3.7 Phenoldisulfonic acid solution--Dissolve 25 g of pure white phenol in 150 ml concentrated sulfuric acid on a steam bath. Cool, add 75 ml fuming sulfuric acid, and heat at 100°C (212°F) for 2 hours. Store in a dark, stoppered bottle.

4. Procedure

4.1 Sampling.

4.1.1 Pipette 25 ml of absorbing solution into a sample flask, retaining a sufficient quantity for use in preparing the calibration standards. Insert the flask valve stopper into the flask with the valve in the "purge" position. Assemble the sampling train as shown in figure 7-1 and place the probe at the sampling point. Make sure that all fittings are tight and leak free, and that all ground glass joints have been properly greased with a high vacuum, high temperature chlorofluorocarbon-based stopcock grease. Turn the flask valve and the pump valve to their "evacuate" positions. Evacuate the flask to 75 mm Hg (3 in. Hg) absolute pressure, or less. Evacuation to a lower pressure (approaching the vapor pressure of water at the existing temperature) is even more desirable. Turn the pump valve to its "vent" position and turn off the pump. Check for leakage by observing the

manometer for any pressure fluctuation. (Any variation greater than 10 mm Hg (0.4 in. Hg) over a period of 1 minute is not acceptable, and the flask is not to be used until the leakage problem is corrected. Pressure in the flask is not to exceed 75 mm Hg (3 in. Hg) absolute at the time sampling is commenced.) Record the volume of the flask and valve (V_f), the flask temperature (T_i), and the barometric pressure. Turn the flask valve counterclockwise to its "purge" position and do the same with the pump valve. Purge the probe and the vacuum tube using the squeeze bulb. If condensation occurs in the probe and the flask valve area, heat the probe and purge until the condensation disappears. Then turn the pump valve to its "vent" position. Turn the flask valve clockwise to its "evacuate" position and record the difference in the mercury levels in the manometer. The absolute internal pressure in the flask (P_i) is equal to the barometric pressure less the manometer reading. Immediately turn the flask valve to the "sample" position and permit the gas to enter the flask until pressures in the flask and sample line (i.e., duct, stack) are virtually equal. This will usually require about 15 seconds. A longer period indicates a "plug" in the probe which must be corrected before sampling is continued. After collecting the sample, turn the flask valve to its "purge" position and disconnect the flask from the sampling train. Shake the flask for at least 5 minutes.

4.1.2 If the gas being sampled contains insufficient oxygen for the conversion of NO to NO_2, e.g. an applicable subpart of the standard

may require taking a sample of a calibration gas mixture of NO in N_2, then oxygen shall be introduced into the flask to permit this conversion. Oxygen may be injected into the flask after sampling or the sampling may be terminated with a minimum of two inches of mercury vacuum remaining in the flask. This final pressure is recorded and then the flask is vented to the atmosphere until the flask pressure is almost equal to atmospheric pressure.

4.2 Sample recovery.

4.2.1 Let the flask set for a minimum of 16 hours and then shake the contents for 2 minutes. Connect the flask to a mercury filled U-tube manometer, open the valve from the flask to the manometer, and record the flask temperature (T_f), the barometric pressure and the difference between the mercury levels in the manometer. The absolute internal pressure in the flask (P_f) is the barometric pressure less the manometer reading. Transfer the contents of the flask to a leak-free polyethylene bottle. Rinse the flask twice with 5-ml portions of deionized, distilled water and add the rinse water to the bottle. Adjust the pH to 9 - 12 by adding sodium hydroxide (1 N) dropwise (about 25 to 35 drops). Check the pH by dipping a stirring rod into the solution and then touching it to the pH test paper. Remove as little material as possible during this step. Mark the height of the liquid level to determine whether or not leakage occurred during transport. Label container to clearly identify its contents. Seal the container for shipping.

4.3 Analysis.

4.3.1 Note level of liquid in container and confirm whether or not any sample was lost during shipment by noting this on analytical data sheet. Transfer the contents of the shipping container to a 50-ml volumetric flask, rinse the container twice with 5-ml portions of deionized, distilled water, add the rinse water to the flask and dilute to the mark with deionized, distilled water. Mix thoroughly and pipette a 25-ml aliquot into the porcelain evaporating dish. Evaporate the solution to dryness on a steam bath and allow to cool. (Use only a steam bath--a hot plate is not acceptable.) Add 2 ml phenoldisulfonic acid solution to the dried residue and triturate thoroughly with a polyethylene policeman. Make sure the solution contacts all the residue. Add 1 ml deionized, distilled water and four drops of concentrated sulfuric acid. Heat the solution on a steam bath for 3 minutes with occasional stirring. Cool, add 20 ml deionized, distilled water, mix well by stirring and add concentrated ammonium hydroxide dropwise with constant stirring until pH is 10 (as determined by pH paper). If the sample contains solids, filter through Whatman No. 41 filter paper into a 100-ml volumetric flask; rinse the evaporating dish with three 5-ml portions of deionized, distilled water and add these to the filter. Wash the filter with at least three 15-ml portions of deionized, distilled water. Add the filter washings to the contents of the volumetric flask and dilute to the mark with deionized, distilled water. If

solids are absent, transfer the solution directly to the 100-ml volumetric flask and dilute to the mark with deionized, distilled water. Mix thoroughly and measure the absorbance at 410 nm using the blank solution as a zero reference. Dilute the sample and the blank with a suitable amount of deionized, distilled water if absorbance exceeds A_4, the absorbance of the 400 µg NO_2 standard (See section 5.3).

5. Calibration

5.1 Flask volume. Assemble the flask and flask valve and fill with water to the stopcock. Measure the volume of water to ± 10 ml. Number and record the volume on the flask.

5.2 Spectrophotometer calibration. Add 0.0 ml, 1.0 ml, 2.0 ml, 3.0 ml and 4.0 ml of the KNO_3 working standard solution (1 ml = 100 µg NO_2) to a series of five porcelain evaporating dishes. To each, add 25 ml of absorbing solution, 10 ml deionized, distilled water and sodium hydroxide (1 N) dropwise until the pH is 9 - 12 (about 25 to 35 drops each). Beginning with the evaporation step, follow the analysis procedure of Section 4.3 to collect the data necessary to calculate the calibration factor (Section 5.3). This calibration procedure must be repeated on each day that samples are analyzed.

5.3 Determination of spectrophotometer calibration factor K_c.

$$K_c = 100 \frac{A_1 + 2A_2 + 3A_3 + 4A_4}{A_1^2 + A_2^2 + A_3^2 + A_4^2} \qquad \text{Equation 7-1.}$$

where:

K_c = Calibration factor.

A_1 = Absorbance of the 100 µg NO_2 standard.

A_2 = Absorbance of the 200 µg NO_2 standard.

A_3 = Absorbance of the 300 µg NO_2 standard.

A_4 = Absorbance of the 400 µg NO_2 standard.

5.4 Barometer. Calibrate against a mercury barometer.

5.5 Temperature gauge. Calibrate dial thermometers against mercury-in-glass thermometers.

6. Calculations

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

6.1 Nomenclature.

A = Absorbance of sample

C = Concentration of NO_x as NO_2, dry basis, corrected to standard conditions, mg/dscm (lb/dscf).

F = Dilution factor (i.e., 25/5, 25/10, etc, required only if sample dilution was needed to reduce the absorbance into the range of calibration).

K_c= Spectrophotometer calibration factor.

m = Mass of NO_x as NO_2 in gas sample, µg.

P_f = Final absolute pressure of flask, mm Hg (in. Hg).

P_i = Initial absolute pressure of flask, mm Hg (in. Hg).

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

T_f = Final absolute temperature of flask, ^oK (^oR).

T_i = Initial absolute temperature of flask, ^oK (^oR).

T_{std} = Standard absolute temperature, 293^oK (528^oR).

V_{sc} = Sample volume at standard conditions (dry basis), ml.

V_f = Volume of flask and valve, ml.

V_a = Volume of absorbing solution, 25 ml.

2 = 50/25. the aliquot factor. (If other than a 25-ml aliquot was used for analysis, the corresponding factor must be substituted.)

6.2 Sample volume, dry basis, corrected to standard conditions.

$$V_{sc} = \frac{T_{std}}{P_{std}} (V_f - V_a)\left[\frac{P_f}{T_f} - \frac{P_i}{T_i}\right] = K(V_f - 25\ ml)\left[\frac{P_f}{T_f} - \frac{P_i}{T_i}\right]$$

Equation 7-2

Where:

$K = 0.3855 \frac{^oK}{mm\ Hg}$ for metric units

$= 17.65 \frac{^oR}{in.\ Hg}$ for English units

6.3 Total µg NO_2 per sample.

$$m = 2K_c AF$$ Equation 7-3

Note: If other than a 25-ml aliquot is used for analyses, the factor 2 must be substituted by a corresponding factor.

6.3 Sample concentration, dry basis, corrected to standard conditions.

$$C = K \frac{m}{V_{sc}} \qquad \text{Equation 7-4}$$

where:

$K = 10^3 \frac{(ml)\ (mg)}{(m^3)\ (\mu g)}$ for metric units

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

7. References

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7.3 Jacob, M.B., The Chemical Analysis of Air Pollutants, New York, N. Y., Interscience Publishers, Inc., 1960, vol. 10, p. 351-356.

7.4 Beatty, R. L., Berger, L. B. and Schrenk, H. H., Determination of Oxides of Nitrogen by the Phenoldisulfonic Acid Method, R. I. 3687, Bureau of Mines, U. S. Dept. Interior, February (1943).

7.5 Hamil, H. F., and Camann, D. E., Collaborative Study of Method for the Determination of Nitrogen Oxide Emissions from Stationary Sources (Fossil Fuel-Fired Steam Generators), Southwest Research Institute report for Environmental Protection Agency, October 5, 1973.

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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 $\sigma\{NO_2\} = 6.56$ mg/m^3 (subsec. 4.1)*, AND USING $\pm 3\ \sigma\ \{NO_2\}$, THE LIMITS ARE L = -19.7 mg/m^3 AND U = 19.7 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).

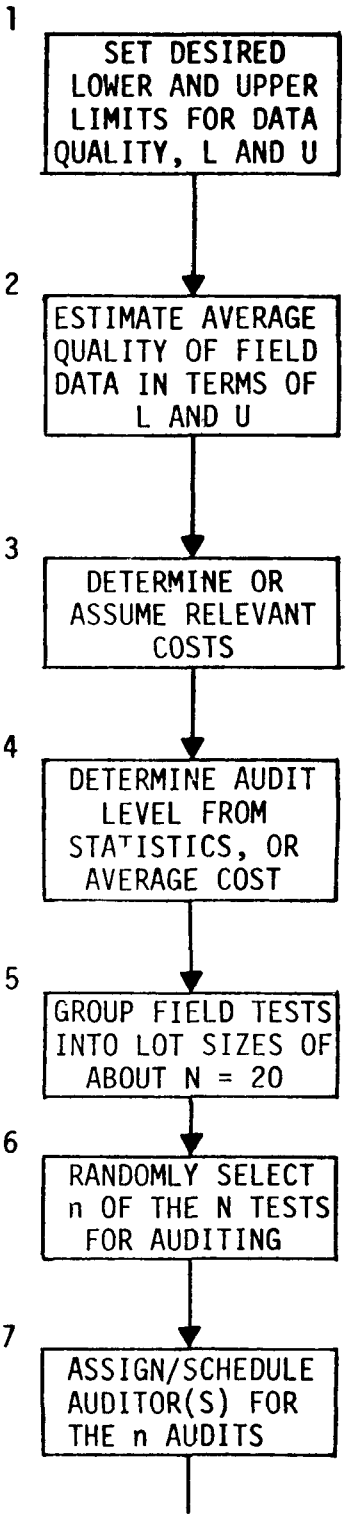
3. DETERMINE: (1) COST OF CONDUCTING AN AUDIT, (2) COST OF FALSELY INFERRING THAT GOOD DATA ARE BAD, (3) COST OF FALSELY INFERRING THAT BAD DATA ARE GOOD, AND (4) COST SAVINGS FOR CORRECTLY IDENTIFYING BAD DATA (subsec. 4.4.3).

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. 13).

5. BY TEAMS, TYPES OF SOURCES, OR GEOGRAPHY, GROUP FIELD TESTS INTO LOTS (GROUPS) OF ABOUT 20, TO 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 = 6.56%.

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).

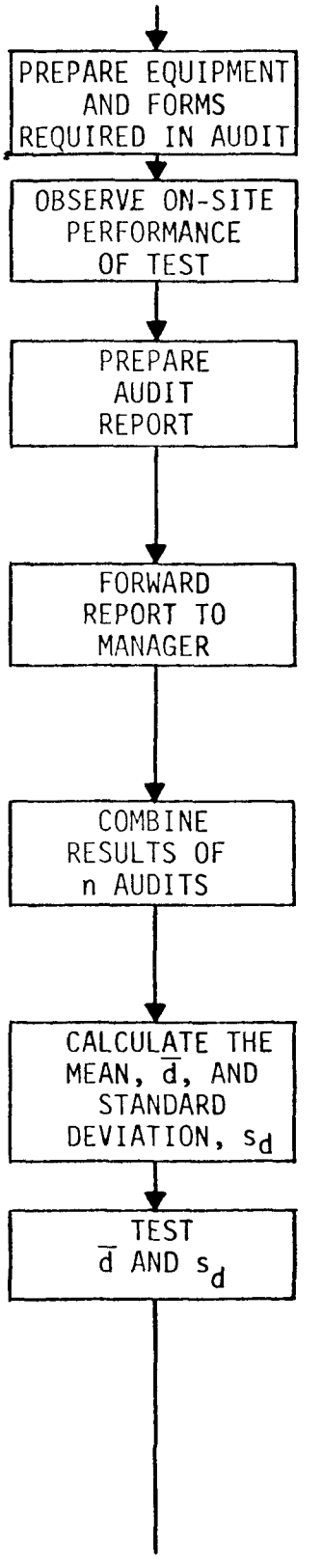
11. THE AUDITOR'S REPORT IS FORWARDED TO THE MANAGER.

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 $d_1 = -17$, $d_2 = 8.5$, $d_3 = 0$, $d_4 = 33.9$, $d_5 = 25.4$, $d_6 = 12.7$, and $d_7 = 0$ (table 5).

13. CALCULATE $\bar{d}$ AND s_d ACCORDING TO THE SAMPLE IN TABLE 4. RESULTS OF THIS SAMPLE CALCULATION SHOW $\bar{d} = 9.1$ AND $s_d = 18.2$ (table 5, subsec. 4.4.2).

14. USE A t-TEST TO CHECK $\bar{d}$ FOR SIGNIFICANCE, FOR THIS EXAMPLE $t = (9.1 \times \sqrt{7})/6.56 = 3.67$. 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 6.56 mg/m^3 BY A CHI-SQUARE TEST. $\chi^2/f = s_d^2/\sigma^2\{\bar{d}\} = (18.2)^2/(6.56)^2 = 7.7$, THE TABULATED VALUE OF $\chi^2/6$ AT THE 95 PERCENT LEVEL IS 1.64; HENCE, s_d IS SIGNIFICANTLY DIFFERENT FROM 6.56 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 $\bar{d} + k\, s_d = 51.6$ mg/m^3 AND $\bar{d} - k\, s_d = -33.4$ mg/m^3 (subsec. 4.4.2).

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

$$\bar{d} + k\, s_d = 51.6 > U = 19.7 \text{ mg/m}^3$$

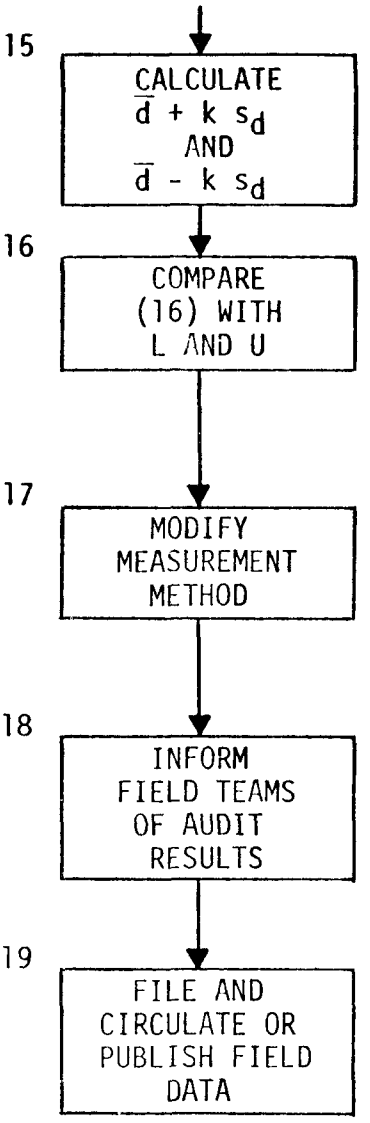
$$\bar{d} - k\, s_d = -33.4 < L = -19.7 \text{ mg/m}^3$$

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 $(NO_2)_j$ and $(NO_2)_{aj}$ for n audits.
s_d	Computed standard deviation of differences between $(NO_2)_j$ and $(NO_2)_{aj}$.
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).

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.
NO_2	Nitrogen dioxide reported by the field team for field test.
$(NO_2)_a$	Nitrogen dioxide concentration used in an audit check.
$(NO_2)_m$	Measured value of a calibration gas.
$(NO_2)_t$	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 nitrogen oxides, except nitrous oxide, emissions by the Federal reference methods 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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Quality control		14D
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