Section 3.6

METHOD 7--DETERMINATION OF NITROGEN OXIDE EMISSIONS FROM STATIONARY SOURCES

OUTLINE

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SUMMARY

A gas sample is extracted from the sampling point in the stack. The sample is collected in an evacuated 2-ℓ round bottom borosilicate flask containing 25 ml of dilute sulfuric acid-hydrogen peroxide absorbing solution. The nitrogen oxides, except nitrous oxide, are measured colorimetrically using the phenoldisulfonic acid (PDS) method for analysis.

If the gas being sampled contains insufficient oxygen for the conversion of NO to NO_2, then oxygen should be introduced into the flask to permit this conversion. Oxygen may be introduced into the flask by one of three methods: (1) Before evacuating the sampling flask, flush with pure cylinder oxygen, and then evacuate flask to 75 mm (3.0 in.) Hg absolute pressure or less; or (2) inject oxygen into the flask after sampling; or (3) terminate sampling with a minimum of 50 mm (2.0 in.) Hg vacuum remaining in the flask, record this final pressure, and then open the flask to the atmosphere until the flask pressure is almost equal to atmospheric pressure. The chemical reactions that occur during sampling absorption are:

NO sample: $NO + H_2O_2 \rightarrow NO_2 + H_2O \rightarrow 2NO_2 + H_2O_2 \rightarrow 2HNO_3$.

NO_2 sample: $2NO_2 + H_2O_2 \rightarrow 2HNO_3$.

NO sample: $(2NO)$ gaseous $+ O_2 \rightarrow 2NO_2 + H_2O_2 \rightarrow 2HNO_3$.

Method 7 is applicable to the measurement of nitrogen oxides emitted from stationary sources. The range of the method has been determined to be 2 to 400 mg NO_x, expressed as NO_2 per dry standard cubic meter without having to dilute the sample.

The precision of the method (as measured by repeatability and reproducibility of the measurements) in the collaborative

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studies varies from 6.6% to 15% (repeatability) and from 9.5% to 19% (reproducibility). See Appendixes A and K, Volume I of this Handbook[1] for definition and discussion of these measures of data quality.

The method description given herein draws heavily on the corresponding guideline document,[2] the collaborative test reports,[3,4,5] and the Reference Method from the 40 CFR 60, July 1, 1978. Section 3.6.10 contains a complete copy of the Reference Method. Blank data forms are provided in Section 3.6.12 for the convenience of the Handbook user.

METHOD HIGHLIGHTS

Section 3.6 provides the procedures for collecting and analyzing a grab sample of oxides of nitrogen (NO_x). The results are expressed as concentrations of nitrogen dioxide (NO_2). The applicable regulation should be consulted to determine any additional requirements (i.e., velocity traverse or O_2 grab sample). Method 7 requires less experience and manpower to collect the sample than most of the other reference methods. However, based on the wide variations in the collaborative results of analyses on aqueous ammonia nitrate audit samples, it is imperative that the analyst be familiar with the analytical techniques described in the Reference Method in Section 3.6.10. A larger number of samples (normally 12) is also required to be taken because the method collects a grab sample not an integrated sample over an extended time.

The four blank data forms at the end of this section may be removed from the Handbook and used in the pretest, test, and posttest operations. Each form has a subtitle (e.g., Method 7, Figure 3.1) for helping the user find a similiar filled-in form in the method description (Section 3.6.3). On the blank and filled-in forms, the items/parameters that can cause the most significant errors are starred.

1. Procurement of Equipment

Section 3.6.1 (Procurement of Apparatus and Supplies) gives the specifications, criteria, and design features of the equipment and material required to perform Method 7 tests with the evacuated flask sampling train. This section is designed to guide the tester in the procurement and initial check of equipment and supplies. The activity matrix (Table 1.1) at the end of Section 3.6.1 can be used as a quick reference and is a summary of the corresponding written description.

2. Pretest Preparations

Section 3.6.2 (Calibration of Apparatus) provides a step-by-step description of the calibration procedures along with the

required accuracy for each component. The optimum wavelength should be determined every 6 mo, and the calibration factor should be determined each time the spectrophotometer is used to analyze NO_x samples. The volume of each collection flask must be determined with stopcock in place. This volume measurement is required only on the initial calibration, provided the stopcock is not changed. The calibration section may be removed along with the corresponding sections from the other methods and made into a separate quality assurance reference manual for use by calibration personnel.

Section 3.6.3 (Presampling Operations) provides the tester with a guide for equipment and supplies preparation for the field test. The calibration data should be summarized on a pretest checklist (Figure 3.1, Section 3.6.3) or similar form. A pretest preparation form (Figure 3.2, Section 3.6.3) can be used as an equipment checkout and packing list. The flasks may be charged with the absorbing reagent in the base laboratory. The method of packing and the use of the described packing containers should help protect the equipment, but neither is required by the Reference Method.

3. On-Site Measurements

Section 3.6.4 (On-Site Measurements) contains step-by-step procedures for the sample collection and for the sample recovery. The on-site checklist (Figure 4.3, Section 3.6.4) provides the tester with a quick method of checking the requirements. When high negative stack pressures are present, extra care should be taken to purge the leak-tested sample system and to be sure the flask is $\leq$75 mm (3 in.) Hg absolute pressure prior to testing. Also the 16-h sample residence time in the flask must be observed.

4. Posttest Operations

Section 3.6.5 (Postsampling Operations) gives the posttest equipment procedures and a step-by-step analytical procedure for determination of NO_x, expressed as NO_2. Posttest calibration is not required on any of the sampling equipment. The posttest

operation forms (Figure 5.3, Section 3.6.5) provide some key parameters to be checked by the tester and laboratory personnel. The step-by-step analytical procedure description can be removed and made into a separate quality assurance analytical reference manual for the laboratory personnel. Analysis of a control sample is required prior to the analysis of the field samples. This analysis of an independently prepared known standard will provide the laboratory with quality control checks on the accuracy and precision of the analytical techniques. Strict adherence to the Reference Method analytical procedures must be observed; for example in the evaporation of the sample, the substitution of a hot plate for the steam bath is not acceptable.

Section 3.6.6 (Calculations) provides the tester with the required equations, nomenclature, and significant digits. It is suggested that a calculator be used if available to reduce the chance of calculation error.

Section 3.6.7 (Maintenance) provides the tester with a guide for a maintenance program. This program is not required, but should reduce equipment malfunctions.

5. Auditing Procedure

Section 3.6.8 (Auditing Procedure) provides a description of necessary activities for conducting performance and system audits. The performance audit of the analytical phase can be conducted using an aqueous ammonium nitrate solution. Performance audits for the analytical phase and the data processing are described in Section 3.6.8. A checklist for a systems audit is also included in this section.

Section 3.6.9 (Recommended Standards for Establishing Traceability) provides the primary standards to which the data should be traceable. The analysis of NO_x is traceable to primary standard grade ammonium nitrate.

6. Reference Material

Section 3.6.10 (Reference Method) is a copy of the Reference Method, on which the quality assurance method description was based.

Section 3.6.11 (References) is a listing of the references that were used in this method description.

PRETEST SAMPLING CHECKS
(Method 7, Figure 3.1)

Date _____ Calibrated by _____

Flask Volume

Flask volumes measured with valves? ___yes ___no

Volume measured within ±10 ml of actual volume? ____yes ____no

Temperature Gauge

Was a pretest temperature correction used? ___yes ___no

If yes, temperature correction _____ (within ±1°C (2°F) of reference values for calibration and within ±2°C (4°F) of reference values for calibration check)

Vacuum Gauge

Was gauge calibrated against a U-tube mercury manometer (If it was a mechanical gauge)? ___yes ___no _____not applicable?

Barometer

Was the pretest field barometer reading within ±2.5 mm (0.1 in.) Hg of the mercury-in-glass barometer? ___yes ___no

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* Most significant items/parameters to be checked.

PRETEST PREPARATIONS

(Method 7, Figure 3.2)

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

* Most significant items/parameters to be checked.

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ON-SITE MEASUREMENTS
(Method 7, Figure 4.3)

Sampling

Volume of 25 ml of absorbing solution placed in flask? _____

Flask valve stopper in purge position? _____

Sampling train properly assembled? _____

Leak free?* _____ Stopcock grease used? _____

Type? _____

Flask evacuated to 75 mm (3 in.) Hg pressure? _____

Leakage from manometer observation?* _____

(e.g., maximum change in manometer of ≤10 mm (0.4 in.) Hg/min) _____

Initial pressure of flask recorded?* _____

Initial temperature of flask recorded? _____

Probe purged before sampling? _____

Sample collected properly?* _____

Flask shaken for 5 min after collection and disassembly from train?* _____

Oxygen introduced to flask? _____ Method used? _____

Samples properly labeled and sealed and stored for shipment?

_____

Sample Recovery

Samples allowed to remain in flasks for minimum of 16 h?*

_____

Final flask temperature and pressure recorded?* _____

Sample transferred to leak-free polyethylene bottle? _____

Flask rinsed twice with 5-ml portions of distilled water and rinse added to bottle containing sample? _____

pH adjusted to between 9 and 12?* _____

_____

* Most significant items/parameters to be checked.

POSTTEST OPERATIONS
(Method 7, Figure 5.3)

Reagents

Phenoldisulfonic acid stored in dark stoppered bottle? _____

Sulfuric acid, concentrated, 95% minimum assay reagent grade? _____

Ammonium hydroxide, concentrated reagent grade? _____

Sample Preparation

Has liquid level noticeably changed?* _____

Original volume _____ Corrected volume _____

Analysis

Spectrophotometer calibrated?* _____

Setting for maximum absorbance of standard _____ nm

Control sample prepared?* _____

Any solids in sample removed through Whatman No. 41 filter paper? _____

Absorbance measured at optimum wavelength used for the standards, using the blank solution as a zero reference? _____

All analytical data recorded on checklist and laboratory form?

_____

_____

* Most significant items/parameters to be checked.

1.0 PROCUREMENT OF APPARATUS AND SUPPLIES

The activity matrix for apparatus is given in Table 1.1 at the end of this section. The required apparatus for a Method 7 sampling train is shown in Figure 1.1. Additional specifications, criteria, and/or design features as applicable are given here to aid in the selection of equipment to ensure the collection of good quality data. All new items of equipment are to be inspected visually for identification and damage before acceptance. Also, if applicable, new equipment is to be calibrated according to Section 3.6.2, as part of the acceptance check.

During the procurement of equipment and supplies, it is suggested that a procurement log be used to record the descriptive title of the equipment, identification number (if applicable), and the results of acceptance checks. An example of a procurement log is shown in Figure 1.2. A blank copy of this form is given in Section 3.6.12 for the Handbook user. Calibration data generated in the acceptance check are to be recorded in the calibration log book. Alternative grab sampling systems or equipment capable of measuring sample volume to within ±2% and collecting a sufficient sample volume to allow analytical repeatability to within ±5% is acceptable, subject to approval. The following equipment is specified in the Reference Method.

1.1 Sampling

1.1.1 Sampling Probe - The sampling probe should be made of glass (borosilicate) encased in a stainless steel sheath and equipped with a heating system capable of preventing water condensation and with a filter (either in-stack or heated out of stack) to remove particulate matter. A plug of glass wool in the sample probe is satisfactory for the in-stack filter. Stainless

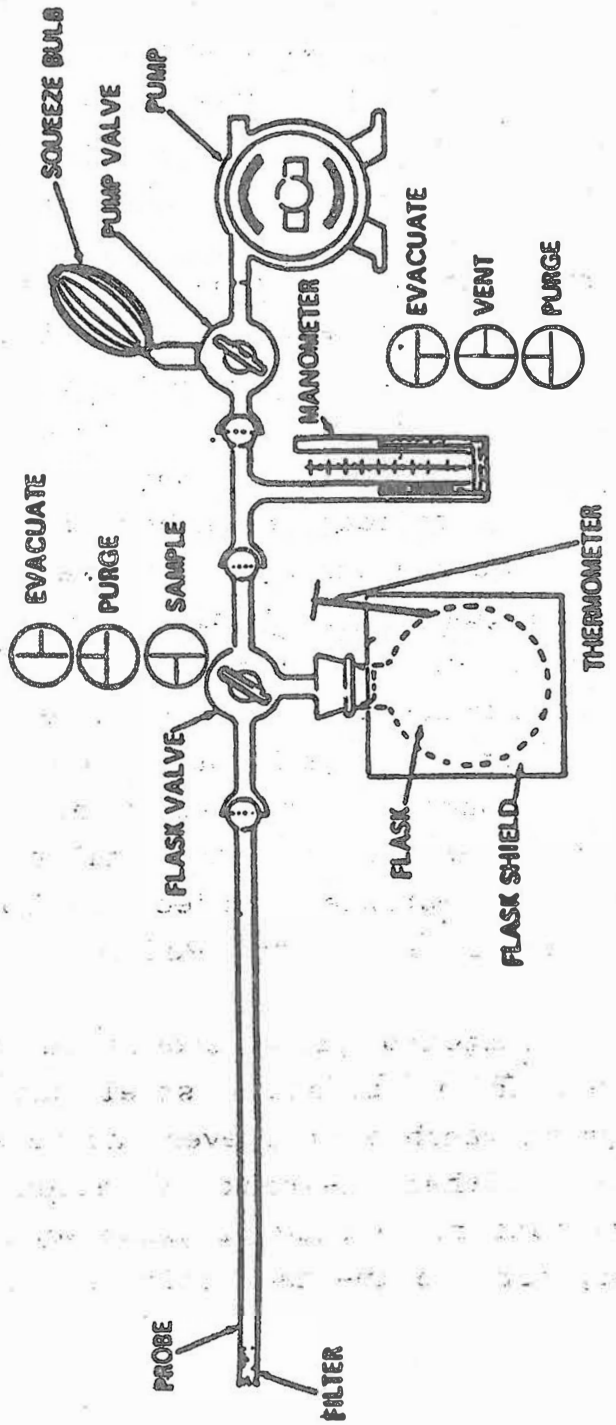

Figure 1.1. Evacuated flask sampling train.

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Item description	Qty.	Purchase order number	Vendor	Date Ord.	Date Rec.	Cost	Disposition	Comments
Spectrophotometer	1	1035	Bausch & Lomb	2/11/77	2/14/77	$ 2500	OK	

Figure 1.2. Example of a procurement log.

steel or Teflon[R] tubing may also be used for the probe liner. Heating is not required if the probe remains dry during the purging period, but it is recommended that the probe have provision for heating. The in-stack end of the probe should have an expanded diameter for about the first 4 cm to be used for the glass-wool filter. A probe of approximately 1.2 m (4 ft) total length is usually sufficient for sampling. However, the probe tip can be no closer than 1 m (3.28 ft) from the inner wall of stacks >2 m in diameter. When stack gas temperatures exceed 480°C (900°F), a probe fabricated from quartz (Vycor) should be used along with quartz wool for filter material. The main criterion in selecting a probe material is that it be nonreactive with the gas constituents and therefore not introduce a bias into the analysis.

A new probe should be checked visually for specifications (i.e., the length and composition ordered). It should be checked for cracks, breaks, and leaks on a sampling train. The probe heating system should be checked as follows:

1. Connect the probe (without filter) to the inlet of the pump.

2. Electrically connect and turn on the probe heater for 2 or 3 min. If functioning properly, it will become warm to the touch.

3. Start the pump and adjust for a flow rate of about 1.0 ℓ/min.

4. Check the probe. It should remain warm to the touch. The heater must be capable of maintaining the exit air temperature at a minimum of 100°C (212°F) under the above conditions. If it cannot, the probe should be replaced. Any probe not satisfying the acceptance check should be repaired if possible, or returned to the supplier.

1.1.2 Collection Flask - A 2-ℓ borosilicate round bottom flask, with a short neck and 24/40 standard taper opening is required.

[R]Trade name.

The collection flask should be protected from implosion or breakage by using (1) tape, (2) a commercial unit encased in foam, or (3) a fabricated closed-cell foam enclosure. Once the flask has been connected to the flask valve, both should be marked as a set and neither should be used at random with other flasks as this will cause volume fluctuations with the sample.

1.1.3 Flask Valve - A T-bore stopcock is connected to a 24/40 standard taper joint. Bores should be numbered but not switched to prevent leakage problems. The T-bore should be marked to avoid turning the stopcock in the wrong direction when sampling. The flask valve should be marked to identify its matched flask.

1.1.4 Temperature Gauge - A temperature gauge should consist of a dial-type thermometer, or equivalent, capable of measuring 1°C (2°F) intervals from -5° to 50°C (25° to 125°F). Dial-type thermometers are easily damaged, so each new thermometer must be checked visually for damage, such as a dented or bent stem. Each thermometer should read within ±1°C (2°F) of the true value when checked in an ice water bath and at room temperature against a mercury-in-glass thermometer that conforms to ASTM E-1 No. 63C or 63F. Damaged thermometers that cannot be calibrated must be replaced.

1.1.5 Vacuum Line - The vacuum line should be of a nonreactive, thick wall type and should be leak checked at 75 mm (3 in.) Hg of absolute pressure while connected to the sampling train. The tubing should be flexible and approximately 1 to 1.6 m (3 to 5 ft) in total length. If the tubing is found to leak, it should be rejected.

1.1.6 Vacuum Gauge - A U-tube manometer should be about 1 m (36 in.) in length with 1-mm (0.1 in.) divisions, or the equivalent, capable of measuring pressure to within ±2.5 mm (0.1 in.) Hg. If a U-tube manometer is used, no calibration is required. Upon receipt, the user should verify by reading the instructions that the manometer was designed to use mercury. If the manometer is acceptable, it must then be leak checked. When a mechanical vacuum gauge is used, it must be calibrated upon receipt by the

procedures described in Section 3.6.2. If it fails to calibrate, it should be replaced.

The vacuum gauge should be leak checked as follows: (1) connect vacuum line to the manometer at the end that connects to the sampling train, as shown in Figure 1.1 (2) pull a vacuum of 75 mm (3 in.) Hg or less, (3) shut off the valve between the manometer and the pump, (4) shut off the pump, (5) observe the vacuum registered on the manometer for any deviation over a 1-min period. If there is no deviation, the vacuum gauge is acceptable; if there is a deviation, the gauge is unacceptable and should be corrected or replaced.

1.1.7 Vacuum Pump - The vacuum pump should be capable of producing a vacuum of 75 mm (3 in.) Hg or less. The pump must be leak free when running and when pulling a vacuum (inlet plugged) of 75 mm (3 in.) Hg. Two types of vacuum pumps are commonly used--a modified sliding fiber vane pump or a diaphragm pump. For safety reasons, the pump should be equipped with a three-wire electrical cord. To check the pump for leaks, install a vacuum gauge in the pump inlet line. Plug the inlet line and run the pump until the vacuum gauge reads 75 mm (3 in.) Hg of vacuum. The vacuum reading should remain stable for 30 seconds.

1.1.8 Squeeze Bulb - A one-way, hard rubber bulb with about a 50-ml capacity is needed to purge the sampling system.

1.1.9 Volumetric Pipette - A 25-ml volumetric glass pipette (Class A) is needed for addition of reagent to the collection flask.

1.1.10 Stopcock Grease - An inert, high-vacuum, high-temperature chlorofluorocarbon grease should be used. Halocarbon 25 - 55 has been found to be effective.

1.1.11 Barometer - Mercury, aneroid, or other barometers capable of measuring atmospheric pressure to within 2.5 mm (0.1 in.) Hg are required. In many cases, the barometric reading may be obtained from a nearby National Weather Service Station, in which

case the station value (which is the absolute barometric pressure) should be requested and an adjustment for elevation differences between the weather station and the sampling point should be applied at a rate of -2.5 mm Hg/30 m (0.1 in. Hg/100 ft) of elevation increase, or vice versa for elevation decrease. Upon receipt, check the barometer against a mercury-in-glass barometer. Replace it if it cannot be calibrated to read correctly.

1.2 Sample Recovery

1.2.1 Graduated Cylinder - A 50-ml glass or polyethylene graduated cylinder with 1-ml divisions is required.

1.2.2 Storage Bottles - A minimum of 12 leak-free polyethylene bottles for recovery of samples are needed. The bottles should be packed in a cushioned, locked container (box or footlocker) for shipment. The leak-free seal can be initially checked by putting water in each, sealing, and then shaking the container upside down.

1.2.3 Wash Bottle - Glass or polyethylene wash bottles are needed for rinsing (transferral) of the sample solution to storage bottles.

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

1.2.5 pH Indicating Paper - pH paper with the range of 7 - 14 is required to test the alkalinity of the samples.

1.3 Analysis

1.3.1 Pipettes - Several volumetric pipettes are required (two 1 ml, two 2 ml, one 3 ml, one 4 ml, two 10 ml, and one 25 ml); one transfer pipette (10 ml with 0.1-ml divisions) is required.

1.3.2 Volumetric Flasks - One 100-ml volumetric flask, is needed for each sample and each standard. Two 1000-ml volumetric flasks are required for the blank and the standard nitrate. Additional volumetric flasks (50 ml) are required for aliquots for analysis and for dilution of samples that fall outside the calibration range (absorbance >400-µg standard).

1.3.3 Evaporating Dishes - Several 175- to 250-ml capacity porcelain dishes with lip for pouring are needed, one for each sample and one for each standard. The Coors No. 45006 (shallow, 195 ml) has been found to be satisfactory. Alternatively, polymethyl-pentene beakers (Nalge No. 1203, 150 ml) or glass beakers (150 ml) may be used. When glass beakers are used, etching of the beakers may cause solid matter to be present in the analytical step; the solids should be removed by filtration. For this reason, glass beakers should be used only if necessary.

1.3.4 Steam Bath - A steam bath is required to evaporate the absorbing solution. Low-temperature ovens or thermostatically controlled hot plates kept below 70°C (160°F) are acceptable alternatives.

1.3.5 Polyethylene Policeman - One stirring rod (polyethylene policeman) is required for each sample and standard. A glass stirring rod is not recommended.

1.3.6 Graduated Cylinder - A 100-ml graduated glass cylinder (Class A) with 1-ml divisions is required for additions of distilled water.

1.3.7 Spectrophotometer - A spectrophotometer capable of measuring the absorption at 410 nm (or the maximum peak), a set of neutral density filters, and a filter for wavelength calibration are required.

1.3.8 pH Paper - The paper should cover the pH range of 7 - 14 with intervals of 1-pH unit.

1.3.9 Analytical Balance - One analytical balance that weighs to 0.1 mg and a set of Class-S calibration weights to check the accuracy of the balance ($\pm$0.3 mg) upon receipt are needed. The balance should be serviced by or returned to the manufacturer if agreement cannot be met.

1.3.10 Dropping Pipette or Dropper - A dropping pipette, or a dropper, or its equivalent for addition of ammonium hydroxide to the evaporation dish is needed.

1.4 Reagents

Unless otherwise indicated, it is intended that all reagents conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society (ACS), where such specifications are available; otherwise, use the best available grade.

1.4.1 Sampling - To prepare the absorbing solution, cautiously add 2.8 ml of concentrated H_2SO_4 to 1 ℓ of deionized distilled water and mix well. Add 6 ml of 3% hydrogen peroxide, freshly prepared from 30% hydrogen peroxide (ACS reagent grade) solution. The absorbing solution must be used within 1 week of its preparation and if possible within 24 h. Store in a dark-colored bottle. Do not expose to extreme heat or direct sunlight. Note: The 30% hydrogen should be stored in the refrigerator.

1.4.2 Sample Recovery - Two reagents are required for sample recovery.

Sodium hydroxide (1N) - Dissolve 40 g of NaOH ACS reagent grade in deionized distilled water and dilute to 1 ℓ.

Water - Use deionized distilled to conform to ASTM specification D1193-74, Type 3. At the option of the analyst, the $KMnO_4$ test for oxidizable organic matter may be omitted whenever high concentrations of organic matter are not expected to be present.

1.4.3 Analysis - For the analysis, the following reagents are required.

Fuming sulfuric acid - Use 15% to 18% by weight of free sulfur trioxide, ACS reagent grade. Note: Handle with caution.

Phenol - Use white solid, ACS reagent grade.

Sulfuric acid - Use concentrated, 95% minimum assay, ACS reagent grade. Note: Handle with caution.

Potassium nitrate - Dry at 105° to 110°C (220° to 230°F) for a minimum of 2 h just prior to preparation of standard solution, ACS reagent grade.

Standard KNO_3 solution - Dissolve exactly 2.198 g of dried potassium nitrate (KNO_3) in deionized distilled water and dilute

to 1 ℓ with deionized distilled water. One ml of the working standard solution is equivalent to 100 μg of nitrogen dioxide (NO_2).

Water - Deionized distilled as in Subsection 1.4.2.

Phenoldisulfonic acid solution - Dissolve 25 g of pure white phenol in 150 ml of concentrated sulfuric acid on a steam bath. Cool; add 75 ml of fuming sulfuric acid; and heat at 100°C (212°F) for 2 h. Store in a dark, stoppered bottle. Alternatively, this solution may be purchased prepared, if it meets the American Public Health Association specification for nitrate-nitrogen in water.

Ammonium hydroxide - Use concentrated, ACS reagent grade.

Table 1.1. ACTIVITY MATRIX FOR PROCUREMENT OF APPARATUS AND SUPPLIES

Apparatus/ reagents	Acceptance limits	Frequency and method of measurement	Action if requirements are not met
Probe	Borosilicate glass tubing, stainless steel or Teflon capable of removing particulate and preventing moisture condensation	Upon receipt, visually check for cracks or flaws and heating capability	Return to supplier and note in procurement log
Collection flask	Two-liter borosilcate glass round bottom, short neck w/24/40 standard taper opening	Upon receipt visually check and leak check	As above
Flask valve	Borosilicate glass T-bore stopcock w/24/40 standard taper male joint (joint connection to be made by glassblower)	Visually check upon receipt	As above
Temperature gauge	Dial-type, capable of measuring from -5° to +50°C within 1°C	Visually check upon receipt, and compare against Hg-in-glass thermometer	As above
Vacuum line tubing	Capable of withstanding 75 mm absolute pressure	Upon receipt visually check and leak check	As above
Vacuum gauge	U-tube manometer, open end, 1 m with 1-mm divisions	Visually check upon receipt	As above
Vacuum pump	Pump capable of pulling vacuum of 75 mm Hg or less	Upon receipt check with suitable pressure gauge	As above
Squeeze bulb	Rubber, one-way	Visually check upon receipt	As above
Volumetric pipettes	1-, 2-, 3-, 4-, 10-, 25-ml glass (Class A)	As above	As above

(continued)

Table 1.1 (continued)

Apparatus/ reagents	Acceptance limits	Frequency and method of measurement	Action if requirements are not met
Stopcock grease	High vacuum, high temperature chlorofluorocarbon grease	As above	As above
Barometer (or consult local weather station	Capable of reading atmospheric pressure to ±2.5 mm Hg	Visually check; calibrate against mercury-in-glass barometer	As above
Storage bottle	Polyethylene, 100-ml, or greater capacity, screw cap	Visually check upon receipt	Return to supplier and note in procurement log
Wash bottle	Polyethylene or glass	Visually check label upon receipt	As above
Glass stirring rod	As above	As above	As above
pH paper	Sensitive in pH range 7-14	As above	Return to supplier
Volumetric flasks	50-, 100-, 1000-ml glass (Class A)	As above	As above
Evaporating dishes	Porcelain evaporating dishes or polymethylpentene beakers	As above	Discard when the bottoms become etched
Steam bath	Evaporate the sample solution at a low controlled temperature	As above	Return to supplier
Polyethylene policeman	Polyethylene stirring rod	As above	As above
Graduated cylinders	50, 100 ml (Class A) with 1-ml divisions	As above	As above

(continued)

Table 1.1 (continued)

Apparatus/ reagents	Acceptance limits	Frequency and method of measurement	Action if requirements are not met
Spectrophotometer	Capable of measuring absorbance at 410 nm (such as Bausch & Lomb Spectronic 70)	Upon receipt, either check wavelength with filters or ensure optimum wavelength is between 400 and 415 nm	Adjust, recalibrate as per manufacturer's instructions, and note in procurement log
Dropping pipette or dropper	Able to add reagents dropwise	Visually check upon receipt	Return to supplier
Sulfuric acid	Concentrated, ACS reagent grade	Visually check upon receipt; check specifications	As above
Hydrogen peroxide	30% aqueous solution, ACS reagent grade	As above	As above
Sodium hydroxide	ACS reagent grade pellets	Visually check upon receipt; check specifications	Return to supplier
Sulfuric acid	Fuming, 15-18% free sulfur trioxide	As above	As above
Phenol	White solid, ACS reagent grade	As above	As above
Potassium nitrate	ACS reagent grade	As above	As above

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2.0 CALIBRATION OF APPARATUS

Calibration of the apparatus is one of the most important functions in maintaining data quality. The detailed calibration procedures included in this section are designed for the equipment specified by Method 7 and described in the previous section. Table 2.1 at the end of this section summarizes the quality assurance functions for calibration. All calibrations should be recorded on standardized record forms and retained in a calibration log book.

2.1 Collection Flask

Assemble the clean flasks and valves and fill with water (room temperature) to the stopcock. Measure the volume to ±10 ml by transferring the water to a 500-ml glass (Class A) graduated cylinder. Do duplicate volume determinations, and use the mean value. Number and record the volume mean value on the flask or foam encasement and in the laboratory log book. This volume measurement is required only on the initial calibration if the flask valves are not switched.

2.2 Spectrophotometer

2.2.1 Determination of Optimum Wavelength - Calibrate the wavelength scale of the spectrophotometer every 6 mo. The calibration may be accomplished by using an energy source with an intense line emission such as a mercury lamp, or by using a series of glass filters spanning the measuring range of the spectrophotometer. Calibration materials are available commercially and from the National Bureau of Standards. Specific details on the uses of such materials should be supplied by the vendor.

In general, when using glass filters, each filter is inserted into the light path and the wavelength dial is rotated until the instrument response is greatest. Then the reading on the dial is noted and can be compared with the true value. When using an alternate light source, the instrument lamp is replaced

by the alternate lamp. The wavelength dial is rotated, and the dial reading is noted at each peak for comparison with the true value. The wavelength scale of the spectrophotometer must read correctly within ±5 nm of the true wavelength at all calibration points; otherwise, the spectrophotometer should be repaired and recalibrated. Once the wavelength scale of the spectrophotometer is properly calibrated, use 410 nm as the optimum wavelength for the measurement of the absorbance of the standards and samples.

Alternatively, a scanning procedure may be employed to determine the optimum wavelength. If the instrument is a double-beam spectrophotometer, scan the spectrum between 400 and 415 nm using a 200 µg NO_2 standard solution in the sample cell and a blank solution in the reference cell. If a peak does not occur, the spectrophotometer is probably malfunctioning and should be repaired. If a peak is obtained within the 400- to 415-nm range, the wavelength at which this peak occurs should be the optimum wavelength for the measurement of absorbance of both the standards and the samples. For a single-beam spectrophotometer, follow the scanning procedure described, but scan the blank and the standard solutions separately. The optimum wavelength should be the one at which the maximum difference in absorbance between the standard and the blank occurs. The data obtained for this alternative optimum wavelength determination should be recorded on the data form as shown in Figure 2.1.

2.2.2 Determination of Calibration Factor - K_c - The calibration factor (K_c) must be determined in the verification of the analytical technique and solution preparation prior to sample analysis with the control sample. After the analytical technique and solutions have been verified as to their accuracy and precision, a new calibration factor should be determined simultaneously with the field sample analysis. Since a detailed discussion of this procedure is included in the sample analysis Section 3.6.5, it is omitted here.

2.3 Barometer

The field barometer should be adjusted initially and before each test series to agree within 2.5 mm (0.1 in.) Hg of the

Spectrophotometer number PEI-2 Date 2/10/77

Calibrated by B. Plummer Reviewed by T. Seaver

Spectrophotometer setting, nm	Absorbance of standard OD[a]	Absorbance of blank OD[b]	Actual absorbance of OD[c]
399	.955	.185	.770
400	.934	.157	.777
401	.920	.136	.784
402	.905	.116	.789
403	.895	.097	.798
404	.891	.086	.805
405	.888	.080	.808
406	.884	.074	.810
407	.879	.066	.813
408	.877	.056	.821
409	.873	.057	.816
410	.844	.043	.801
411	.830	.036	.794
412	.823	.031	.892
413	.811	.028	.783
414	.806	.015	.791
415	.785	.009	.776
416	.777	.000	.777

[a] Absorbance of the 200 µg NO_2 standard in a single beam spectrophotometer.

[b] Absorbance of the blank in a single-beam spectrophotometer.

[c] For a single-beam spectrophotometer--absorbance of the standard minus absorbance of the blank. For a double beam spectrophotometer--absorbance of the 200 µg NO_2 standard with the blank in the reference cell.

Spectrophotometer setting for maximum actual absorbance of standard 408 nm.

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

Figure 2.1. Optimun wavelength determination data form.

mercury-in-glass barometer or with the pressure value reported from a nearby National Weather Service Station and corrected for elevation. The correction for elevation difference between the station and sampling point should be applied at a rate of -2.5 mm Hg/30 m (-0.1 in Hg/100 ft) elevation increase, or vice versa for elevation decrease.

2.4 Thermometer

The thermometers used to measure the temperature of the sample flask should be initially compared with a mercury-in-glass thermometer that meets ASTM E-1 No. 63C or 63F specifications as follows:

1. Place both the mercury-in-glass and the dial-type or an equivalent thermometer in an ice bath. Compare readings after the bath stabilizes.

2. Allow both thermometers to come to room temperature. Compare readings after both stabilize.

3. The dial-type or equivalent thermometer is acceptable if values agree within 1°C (2°F) at both room and ice bath temperatures. If the difference is greater than ±1°C (2°F), the thermometer should be either adjusted and recalibrated until the above criteria are met, or replaced.

4. Prior to each field trip the temperatures should then be compared at room temperature with the thermometer in the equipment. If the value is not within ±2°C (4°F) of the mercury-in-glass thermometer value, the meter thermometer should be replaced or recalibrated.

2.5 Vacuum Gauge

When a mercury U-tube manometer is used, no calibration is required. The U-tube manometer should be checked initially to ensure that it is leak free.

When a mechanical gauge is used, it must be calibrated against a mercury U-tube manometer before the field test unless otherwise specified by the administrator. The mechanical gauge should be calibrated in the following manner:

1. Connect the mechanical gauge and the U-tube manometer in parallel with the vacuum pump. This can be accomplished with a T-connection. One line should be placed on the vacuum side of the pump, and the other two lines should be placed on the vacuum side of the gauge and manometer.

2. Turn the pump on, and pull a vacuum of about 25 to 50 mm (1 to 2 in.) Hg. Shut off main pump valve and then shut off pump.

3. Observe the U-tube manometer to be sure that the system is leak free. Any variation >10 mm (0.4 in.) Hg over a 1-min period is not acceptable. The manometer and gauge readings must agree within ±2.5 mm (0.1 in.) Hg, or the gauge should be repaired or replaced.

4. Turn the pump on, and pull the maximum vacuum for which the pump is capable (must be within 75 mm (3 in.) Hg of absolute pressure). Shut off the main valve, and then the pump.

5. Be sure that the system is leak free and again compare readings.

6. The gauge must agree within 2.5 mm (0.1 in.) Hg at both vacuums, or the gauge is not acceptable.

2.6 Analytical Balance

The analytical balance should always be zeroed and calibrated against a standard Class-S weight(s) just before the potassium nitrate (KNO_3) is weighed for the formulation of the working standard. This calibration should be done in the following manner:

1. Zero the balance.

2. Place a 5-g and then a 10-g standard weight on the balance.

3. Be sure the balance readings of the standardized weights agree within ±2 mg of the standard weights.

4. Enter the data on the calibration form, Figure 2.2.

5. The weight of the weighing boat and the potassium nitrate should be <10 g; if not, heavier standard weights should be used to calibrate the balance.

Balance name PERFECTO Number B114F6

Classification of standard weights "S"

Date	0.5000 g	1.0000 g	10.000 g	50.0000 g	100.0000 g	Analyst
6/17/78	0.5004	0.9998	10.0002	50.0006	100.0004	BLJ

Figure 2.2. Analytical balance calibration form.

Table 2.1. ACTIVITY MATRIX FOR CALIBRATION OF EQUIPMENT

Apparatus	Acceptance limits	Frequency and method of measurement	Action if requirements are not met
Collection flask	Measure volume within ±10 ml	On receipt, measure with graduated cylinder	Recalibrate
Spectrophotometer	1. *Calibrate wavelength scale	1. Upon receipt and every 6 mo, use glass filters or light source	1. Return to manufacturer for repair
	2. *Determine optimum wavelength within 399 to 416 nm	2. Upon receipt and every 6 mo scan between 400 and 415 nm with 200 mg NO_2 standard solution	2. As above
Barometer	Reading agrees within ±2.5 mm (0.1 in.) Hg of mercury-in-glass barometer	Upon receipt and before each field test	Repair or return
Thermometer	Reading agrees within ±1°C (2°F) of mercury-in-glass thermometer	As above	As above
Vacuum gauge (mechanical only)	Reading agrees within ±2.5 mm (0.1 in.) Hg of mercury U-tube manometer	As above	As above
Analytical balance	Weight within ±2 mg of standard weights (Class S)	Use standard weight before preparation of working solution	Repair or return to manufacturer

* The tester may opt to perform either step 1 or 2, both are not required.

3.0 PRESAMPLING OPERATIONS

The quality assurance functions for presampling operations are summarized in Table 3.1 at the end of this section. See Section 3.0.1, Planning the Test Program, of this Handbook for details on preliminary site visits.

3.1 Apparatus Check and Calibration

Previously used equipment should be visually checked for damage and/or excessive wear before each field test. Items should be repaired or replaced (as applicable) if judged to be unsuitable for use. A pretest checklist (Figure 3.1) summarizes equipment calibration. The pretest operations form (Figure 3.2) can be used as an equipment check and packing list. The completed form should be dated, signed by the field crew supervisor, and filed in the operational log book. The replacement of worn or damaged items of equipment should be initiated. Procedures for performing the checks are given herein; a check is placed in the proper row and column as the check/operation is completed. Each team will have to construct its own checklist according to the type of sampling train and equipment it uses.

3.1.1 Probe (Filter) - Clean the probe internally by brushing first using tap water, then with distilled deionized water, next with acetone, and finally allow it to dry in the air. In extreme cases, the glass liner can be cleaned with stronger reagents. Note: Do not use nitric acid to clean the probe unless a thorough cleaning is performed to remove all the nitrates. In either case, the object is to leave the glass liner chemically inert to oxides of nitrogen. If the probe is equipped with a heating system, check to see whether it is operating properly. The probe should be sealed on the filter side and checked for leaks at an absolute pressure of <380 mm (15 in.) Hg. The probe must be leak free under these conditions. This leak check may be performed following the leak check of the sample flask and using the same

Date 2/15/77 Calibrated by B. Plummer

Flask Volume

Flask volumes measured with valves? ✓ yes ___ no

Volume measured within ±10 ml? ___ yes ___ no

Temperature Gauge

Was a pretest temperature correction used? ___ yes ✓ no

If yes, temperature correction ___ (within ±1°C (2°F) of reference values for calibration and within ±2°C (4°F) of reference values for calibration check).

Vacuum Gauge

Was gauge calibrated against a U-tube mercury manometer (If it was a mechanical gauge)? ___ yes ___ no ✓ not applicable?

Barometer

Was the pretest field barometer reading within ±2.5 mm (0.1 in.) Hg of the mercury-in-glass barometer? ✓ yes ___ no

* Most significant items/parameters to be checked.

Figure 3.1. Pretest sampling checks.

Apparatus check	Acceptable		Quantity required	Ready		Loaded and packed	
	Yes	No		Yes	No	Yes	No
Probe			3	✓		✓	
Glass liner clean	✓						
Heated properly	✓						
Leak checked	✓						
Collection Flask			14	✓		✓	
Clean	✓						
Leak checked	✓						
Temperature gauge	✓						
Evacuation System				✓		✓	
Leak-free pumps	✓		2				
Manifold and tubing	✓		3	✓		✓	
U-tube manometer	✓		2	✓		✓	
Barometer	✓		1	✓		✓	
Reagents							
Distilled water	✓		1 liter	✓		✓	
Absorbing solution*	✓		1 liter	✓		✓	
Sodium hydroxide, 1 N	✓		1 liter	✓		✓	
pH paper	✓		1 pkg.	✓		✓	
Sample Recovery				✓		✓	
Dropper or burette	✓		2				
Sample bottles	✓		14	✓		✓	
Pipette, 25 ml	✓		2	✓		✓	

* Most significant items/parameters to be checked.

Figure 3.2. Pretest preparations.

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setup as described below in Subsection 3.1.2. The glass liner should be sealed inside the metal sheath to prevent ambient air from entering the duct.

3.1.2 Collection Flask, Flask Valve, and Evacuation System - The collection flask and valve in contact with sample gas should be cleaned with a strong detergent and hot water, and rinsed with tap water and deionized distilled water. Periodically, the glassware can be cleaned with a grease remover such as decahydronapthalene ($C_{10}H_{18}$), followed with acetone, and then with the cleaning agents named above. An alternate procedure is to use dichromate cleaning solution. Do not use solutions containing nitrogen. Vapor degreaser can be used to remove the stale vacuum grease.

Stopcocks and joints should be lubricated with a chemically inert lubricant. An inert hydrogen-free chlorofluorocarbon lubricant can be used.

The evacuation system (Figure 1.1) is assembled, and a minimum vacuum of 75 mm (3 in.) Hg absolute pressure is produced in each flask with the flask valve in the "evacuation" position. The vacuum should be held for at least 1 min with the pump valve in the "vent" position without appreciable fluctuation ($\leq$10 mm (0.4 in.) Hg); if this is not possible, check for leaks.

If the leak check of the probe is to be performed using the same setup, the probe tip should be plugged with a rubber stopper. Immediately after the sample flask has been determined to be leak free, turn the flask valve to the "purge" position. The vacuum will initially drop. After the vacuum stabilizes there should not be any appreciable fluctuation--that is $\leq$10 mm (0.4 in.) Hg over a 1-min period. If stabilization is not obtained, check for leaks and correct.

3.2 Reagents

Unless otherwise indicated, it is intended that all reagents conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society (ACS), where

such specifications are available; otherwise, use the best available grade.

Chloride is an interference in the phenoldisulfonic acid method because even rather low concentrations of chloride result in nitrate losses. It is important that the chloride content be reduced to a minimum, preferably below 10 mg/ℓ.

3.2.1 Sampling - The absorbing reagent is prepared by adding 2.8 ml of concentrated sulfuric acid (H_2SO_4) to 1 ℓ of deionized distilled water. Mix well, and add 6 ml of 3% hydrogen peroxide (H_2O_2). Prepare a fresh absorbing solution weekly, store in a dark-colored pyrex container, and do not expose to extreme heat or direct sunlight. If the reagent must be shipped to the field site, it is advisable that the absorbing reagent be prepared fresh on site.

3.2.2 Sample Recovery - A sodium hydroxide solution (NaOH) is prepared by dissolving 40 g NaOH in distilled water and diluting to 1 ℓ. This solution can be transferred to a polyethylene 1000-ml (32-oz) jar for shipment. Deionized distilled water and pH paper are required to test for basicity and for transferral of samples.

3.2.3 Analysis - The following reagents are needed for analysis and standardization:

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

Phenol - White solid ACS reagent grade.

Sulfuric acid - Concentrated reagent, 95% minimum assay, ACS reagent grade.

Standard solution - Dissolve 2.198 g of dried potassium nitrate (KNO_3) ACS reagent grade in distilled water, and dilute to 1 ℓ in a volumetric flask. For the working standard solution, pipette 10 ml of the resulting solution into a 100-ml volumetric flask and dilute to the mark. Note: One ml of the working standard solution is equivalent to 100 µg of nitrogen dioxide.

Water - Deionized distilled.

Phenoldisulfonic acid solution - Dissolve 25 g of pure white phenol (no discoloration) in 150 ml of concentrated sulfuric acid on a steam bath. Cool. Add 75 ml of fuming sulfuric acid, and heat at 100°C (212°F) on a steam bath for 2 h. Store in a dark stoppered bottle. This acid may also be purchased if it meets the American Public Health Association specification for nitrate-nitrogen in water.

3.3 Packing Equipment for Shipment

Equipment should be packed in rigid containers to protect it against rough handling during shipping and field operations (not mandatory).

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

3.3.2 Collection Flask and Valve - The collection flasks and valves should be packed securely in a suitable shipping container. An ideal container is a case or footlocker of approximately the following dimensions: 30 in. × 15 in. × 15 in. This container, when lined with foam, will accommodate eight collection flasks with the appropriate mated flask valves.

3.3.3 Evacuation System, Temperature Gauges, Vacuum Lines, and Reagents - A sturdy case lined with foam material can contain the evacuation manifold, squeeze bulb, manometer, and reagents for sample recovery. Special care should be taken with mercury U-tube manometers to avoid any spillages.

3.3.4 Evacuation Pump - The vacuum pump should be packed in a shipping container unless its housing is sufficient for travel. Additional pump oil and oiler jar should be packed with the pump if oil is required for its operation.

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

Table 3.1. ACTIVITY MATRIX FOR PRESAMPLING PREPARATION

Characteristic	Acceptance limits	Frequency and method of measurement	Action if requirements are not met
Apparatus Check			
Probe	1. Clean; glass liner inert to oxides of nitrogen	1. Before each test	Must be replaced
	2. Heating properly if equipped with heating system	2. As above	
	3. Leak free	3. Pressure <380 mm (15 in.) Hg	
Collection flask	Clean; volume within ±10 ml	Before each test, clean with strong detergent and hot water and rinse with tap and deionized distilled water; periodically clean with grease remover	Repeat cleansing of flask and/or measure volume
Evacuation system	Vacuum of 75 mm (3 in.) Hg absolute pressure in each flask; leakage rate <10 mm (0.4 in.) Hg/min	Before each test, check for leaks using Hg-filled U-tube manometer	Correct leaks
Absorbing Reagents			
Sulfuric acid, concentrated	2.8 ml/ℓ	Prepare fresh absorbing solution weekly; use graduated pipette	Make up new solution
Hydrogen peroxide, 3%	6 ml/ℓ	As above	As above

(continued)

Table 3.1. (continued)

Characteristic	Acceptance limits	Frequency and method of measurement	Action if requirements are not met
Sample Recovery Reagents			
Sodium hydroxide	40 g ACS reagent grade NaOH in a 1-ℓ volumetric flask (Class A)	On makeup of solution, use triple-beam balance and Class A volumetric flask	As above
Water	Deionized distilled to ASTM specifications D11 93-82, Type 3		Prepare fresh for each analysis period
Analytical Reagent			
Potassium nitrate	2.198 ±0.001 g KNO_3 ACS reagent grade into a 1-ℓ volumetric flask (Class A)	On makeup of solution, use analytical balance	Purchase new solution
Phenoldisulfonic acid solution	25 g white phenol ACS reagent grade in 150-ml concentrated cylinder (Class A)	On makeup of solution, use triple-beam balance and graduated cylinder	Make up new solution.
	75 ml fuming sulfuric acid	On makeup of solution, graduated cylinder (Class A)	As above

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4.0 ON-SITE MEASUREMENTS

The on-site measurement activities include transporting the equipment to the test site, unpacking and assembling the equipment, confirming duct measurements and traverse points (if volumetric flow rate is to be determined), velocity traverse, molecular weight determination of the stack gas, moisture content, sampling for oxides of nitrogen, and data recording. Table 4.1 at the end of this section summarizes the quality assurance activities relative to on-site measurements.

4.1 Transport of Equipment to the Sampling Site

The most efficient means of transporting or moving the equipment from ground level to the sampling site (as decided during the preliminary site visit) should be used to place the equipment on site. Care should always be exercised against damage to the test equipment or injury to test personnel during the moving phase. A "laboratory" type area should be designated for preparation of absorbing reagent and charging of the flasks. An acceptable alternative is to charge the flasks in the home laboratory. Utilization of plant personnel or equipment (winches and forklifts) in movement of the sampling gear is highly recommended.

4.2 Preliminary Measurements and Setup

The Reference Method outlines the determination of the concentration of oxides of nitrogen in the gas stream. The volumetric flow rate must be determined utilizing Method 2, Section 3.1, and Method 4, Section 3.3 of this Handbook so that mass emission rate may be determined.

4.3 Sampling

The on-site sampling includes preparation and/or addition of the absorbing reagent to collection flasks (if not performed at home laboratory), setup of the evacuation system, connection

of the electric service, preparation of the probe (leak check and addition of particulate filter), insertion of probe into the stack, purging of the probe, sealing of the port, evacuation of flasks, sampling and recording of the data, and a final leak check. In addition, EPA Reference Methods 1, 2, 3, and/or 4 may have to be performed simultaneously with Method 7. This will be specified by the applicable regulation, and the applicable reference method should be followed.

4.3.1 Preparation and/or Addition of Absorbing Reagent to Collection Flasks - If preparation of absorbing reagent is necessary on site, follow directions given in Section 3.6.3. Pipette exactly 25 ml of absorbing reagent into the sample flask. Place a properly lubricated flask valve into the collection flask with the valve turned in the "purge" position. Lubrication of joints is intended to prevent leaks and should not seal the bore of the stopcock or contaminate the sample.

4.3.2 Assembling Sampling Train - Assemble the sampling train as shown in Figure 1.1 and perform the following:

1. Visually check probe for liner separation (cracks, etc.).

2. Place a loosely packed filter of glass or quartz wool in the inlet end of the probe to trap any particulates.

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

4.3.3 Evacuation, Purge, and Sampling - A sample is taken as follows:

1. Turn the pump and flask valves to the "evacuate" positions and evacuate to a minimum of 75 mm (3 in.) Hg absolute pressure or until the apparent boiling point is reached (bubbling of absorbing solution).

2. Turn the pump valve to the "vent" position, turn off the pump and check the manometer for fluctuations. The manometer should stay stable (maximum deviation $\leq$10 mm (0.4 in.) Hg) for at least 1 minute. If the mercury level changes, check for leaks

and eliminate the problem. Pressure in the flask should be ≤75 mm (3 in.) Hg absolute when sampling is commenced.

3. Record the volume of the flask and valve (V_F), the flask temperature (t_i), and the barometric pressure (P_{bar}) on a data form (see Figure 4.1A or 4.1B) or in a field laboratory notebook.

4. Turn the flask valve counterclockwise to the "purge" position.

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

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

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

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

9. Turn the flask valve clockwise to its "evacuate" position, and record the difference in the mercury levels in the manometer. The absolute internal pressure in the flask (P_i) is equal to the barometric pressure less the manometer reading (Leg A and Leg B).

10. Immediately turn the flask valve to the sample position, and permit the gas to enter the flask until pressures in the flask and sample line (i.e., duct, stack) are equal. This will usually require about 15 s; a longer period indicates a "plug" in the probe, which must be corrected before sampling is continued.

11. After collecting the sample, turn the flask valve to its "purge" position.

12. Disconnect the flask and valve from the sampling train and shake the flask for at least 5 min.

4.3.4 Chemical Reactions of Sample Collection - If the gas being sampled contains insufficient oxygen for the conversion of NO to 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 should be introduced into the flask to permit this

Plant Acme Power Plant City Acme, Ohio

Sample location ESP Outlet Boiler #2 Date 2/31/77

Operator _____ Barometric pressure (P_{bar}) 29.84 in. Hg

Sample number	Sample point location	Sample time 24-hr	Probe temperature, °F	Flask and valve number	Volume of flask and valve (V_F), ml	Initial pressure in. Hg			Initial temperature	
						Leg A_i	Leg B_i	P_i [a]	°F (t_i)	°R (T_i) [b]
AP-1	B-11	0733	210	Pf-13	2013	13.6	13.7	2.54	73	533
AP-2	B-10	0745	210	Pf-10	2010	13.7	13.8	2.34	73	533
AP-3	C-10	0801	210	Pf-8	2008	13.7	13.7	2.44	74	534

[a] $P_i = P_{bar} - (A_i + B_i)$.

[b] $T_i = t_i + 460°F$.

Figure 4.1A. Nitrogen oxide field data form (English units).

Plant Acme Power Plant City Acme, Ohio

Sample location ESP Outlet Boiler #1 Date 2/29/77

Operator P. Rose Barometric pressure (P_{bar}) 706.2 mm Hg

Sample number	Sample point location	Sample time 24-hr	Probe temperature, °C	Flask and valve number	Volume of flask and valve (V_F), ml	Initial pressure mm Hg			Initial temperature	
						Leg A_i	Leg B_i	P_i [a]	°C (t_i)	°K (T_i) [b]
AP-1	B-11	0733	100	Pf-13	2013	372	371	17.2	22.2	295.2
AP-2	B-10	0745	100	Pf-10	2010	373	370.5	16.7	21.2	294.2
AP-3	C-10	0801	100	Pf-8	2008	372.5	370	17.7	23.5	296.5

[a] $P_i = P_{bar} - (A_i + B_i)$.

[b] $T_i = t_i + 273°C$.

Figure 4.1B. Nitrogen oxide field data form (metric units).

conversion. Oxygen may be introduced into the flask by one of three methods: (1) Before evacuating the sampling flask, flush with pure cylinder oxygen, and then evacuate flask to 75 mm (3.0 in.) Hg absolute pressure or less; or (2) inject oxygen into the flask after sampling; or (3) terminate sampling with a minimum of 50 mm (2.0 in.) Hg vacuum remaining in the flask, record this final pressure, and then vent the flask to the atmosphere until the flask pressure is almost equal to atmospheric pressure.

Chemical reactions which occur during sampling adsorbtion are:

NO sample: $NO + H_2O_2 \rightarrow NO_2 + H_2O \rightarrow 2NO_2 + H_2O_2 \rightarrow 2HNO_3$.

NO_2 sample: $2NO_2 + H_2O_2 \rightarrow 2HNO_3$.

NO sample: $(2NO)$ gaseous $+ O_2 \rightarrow 2NO_2 + H_2O_2 \rightarrow 2HNO_3$.

4.4 Sample Recovery

The Reference Method requires a minimum sample absorption period of 16 h in the flask. If the laboratory is close by, the sample may be left in the flasks for return to the laboratory. Otherwise, the appropriate data may be taken in the field, solutions made alkaline and transferred to leak-free polyethylene bottles after the required absorption period.

4.4.1 Flask Pressure, Temperature, and Barometric Pressure - After the absorption period is completed ($\geq$16 h), record the barometric pressure and the room temperature (final temperature (t_f) on the integrity data forms (Figures 4.2A or 4.2B.)

1. Shake the flask and contents for 2 min.
2. Connect the flask to a mercury-filled U-tube manometer.
3. Open the valve from the flask to the manometer and record the flask temperature (t_f), the barometric pressure, and the difference between the mercury levels in the manometer (Leg A and Leg B). The absolute internal pressure in the flask (P_f) is the barometric pressure less the manometer reading.
4. Transfer the contents of the flask to a leak-free polyethylene bottle.

Plant Acme Power Plant Date 2/3/77

Sample recovery personnel S. Morgan Barometric pressure, (P_{bar}) 29.84 in. Hg

Person with direct responsibility for recovered samples P. Rose

Sample number	Final pressure, in. Hg			Final temperature,		Sample recovery time, 24-h	pH adjusted 9 to 12	Liquid level marked	Samples stored in locked container
	Leg A_f	Leg B_f	P_f [a]	^oF (t_f)	^oR (T_f) [b]				
AP-1	1.6	0.6	27.64	73	533	1322	✓	✓	✓
AP-2	1.2	0.8	27.84	72	532	1340	✓	✓	✓
AP-3	2.0	1.0	25.84	73	533	1415	✓	✓	✓

$P_f = P_{bar} - (A_f + B_f)$. $T_f = t_f + 460^oF$.

Lab person with direct responsibility for recovered samples G. Foster

Date recovered samples received 3/2/77 Analyst S. Morgan

All samples identifiable? yes All liquids at marked level? yes

Remarks

Signature of lab sample trustee George Foster

Figure 4.2A. NO_x sample recovery and integrity data form (English units).

Plant Acme Power Plant Date 2/3/77

Sample recovery personnel J. Morgan Barometric pressure, (P_{bar}) 758 mm Hg

Person with direct responsibility for recovered samples P. Rose

Sample number	Final pressure, mm Hg			Final temperature,		Sample recovery time, 24-h	pH adjusted 9 to 12	Liquid level marked	Samples stored in locked container
	Leg A_f	Leg B_f	P_f	°C (t_f)	K (T_f)				
AP-1	40.6	15.2	702	22.7	295.7	1322	✓	✓	✓
AP-2	30.5	20.3	707	22.2	295.2	1330	✓	✓	✓
AP-3	50.8	25.4	682	22.7	295.7	1341	✓	✓	✓

$P_f = P_{bar} - (A_f + B_f)$. $T_f = t_f + 273°C$.

Lab person with direct responsibility for recovered samples G. Foster

Date recovered samples received 3/2/77 Analyst J. Morgan

All samples identifiable? yes All liquids at marked level? yes

Remarks

Signature of lab sample trustee George Foster

Figure 4.2B. NO_x sample recovery and integrity data form (metric units).

5. Rinse the flask three times with 5-ml portions of deionized distilled water, and add the rinse water to the bottle.

6. Adjust the pH to between 9 and 12 by adding sodium hydroxide (1N) dropwise (about 25 to 35 drops). Check the pH by dipping a stirring rod into the solution and then touching the rod to the pH test paper. Remove as little material as possible during this step. The pH adjustment is mandatory. The NaOH changes the sample, which is in the form of HNO_3, to $NaNO_3$. If the pH is not adjusted, the HNO_3 will be liberated during the evaporation phase of analysis.

4.5 Sample Logistics (Data) and Packing of Equipment

The above procedures are followed until the required number of runs are completed. Log all data on the form shown in Figure 4.2 A or 4.2.B

1. Check all sample containers for proper labeling (time, date, location, number of test, and any pertinent documentation). Be sure that a blank has been taken.

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

3. Examine all sample containers and sampling equipment for damage, and pack them properly for shipment to the base laboratory. All shipping containers should be properly labeled to prevent loss of samples or equipment.

4. The sampling procedures can be reviewed after testing or during the testing using an on site measurement checklist (Figure 4.3).

Sampling

Volume of 25 ml of absorbing solution placed in flask? ✓

Flask valve stopper in purge position? ✓

Sampling train properly assembled? ✓

Leak free?* ✓ Stopcock grease used? ✓

Type? C-7340

Flask evacuated to 75 mm (3 in.) Hg pressure? ✓

Leakage from manometer observation?* 0.1/min

(e.g., maximum change in manometer of ≤10 mm (0.4 in.) Hg/min)

Initial pressure of flask recorded?* ✓

Initial temperature of flask recorded? ✓

Probe purged before sampling? ✓

Sample collected properly?* ✓

Flask shaken for 5 min after collection and disassembly from train?* ✓

Oxygen introduced to flask? N/A Method used?

Samples properly labeled and sealed and stored for shipment? flasks labeled

Sample Recovery

Samples allowed to remain in flasks for minimum of 16 h?* ✓

Final flask temperature and pressure recorded?* ✓

Sample transferred to leak-free polyethylene bottle? ✓

Flask rinsed twice with 5-ml portions of distilled water and rinse added to bottle containing sample? ✓

pH adjusted to between 9 and 12?* ✓

* Most significant items/parameters to be checked.

Figure 4.3. On-site measurements.

Table 4.1. ACTIVITY MATRIX FOR ON-SITE MEASUREMENTS

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

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5.0 POSTSAMPLING OPERATIONS

Table 5.1 at the end of this section summarizes the quality assurance activities for sample analysis. If the laboratory receives the samples in the sample flask, laboratory personnel will have to complete the sample recovery procedures previously explained in Section 3.6.4.

5.1 Procedures For Operating a Spectrophotometer

The correct manipulations of blanks and sample cells are critical. Careless technique is unacceptable. The following points are recommended and should be adhered to.

1. Designate the cuvettes as either a blank or a sample cell. Do not interchange the cells during an analysis because they are not always matched.
2. Do not touch the bottom of the cuvette with your fingers.
3. Rinse the cuvette at least twice with the solution you are about to measure.
4. Remove lint, liquid, and so forth with a lens tissue or its equivalent.

5.2 Base Laboratory (Analysis)

5.2.1 Check of Field Sample Integrity - If the field samples have been shipped in sample containers, be sure that all samples are identifiable and that the liquid level of each is at its mark. If a sample is not identifiable or if a loss of liquid is detected, note it on the data form, as shown in Figures 4.2A and 4.2B. When a noticeable amount of leakage has occurred, use an alternative method, subject to the approval of the administrator, to correct the final value; approval should have been requested prior to testing. An alternative method is as follows:

1. Mark the new level of the sample.

2. Transfer the sample to a 50-ml volumetric flask, along with two 5-ml deionized distilled water rinsings of the container.

3. Add water to the sample storage container to the initial sample mark, and measure the initial sample volume (V_{soln_i}) in ml.

4. Add water to the sample storage container to the mark of the transferred sample, and measure the final volume (V_{soln_f}) in ml.

5. If (V_{soln_f}) $< V_{soln_i}$, correct the sample volume (V_{soln}) by using Equation 5-1.

$$V_{soln'} = V_{soln}\left[\frac{V_{soln_i}}{V_{soln_f}}\right]. \qquad \text{Equation 5-1}$$

where

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

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

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

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

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

5.2.2 Control Samples and Working Standards Preparation - The accuracy and precision of the analytical technique can be determined with control samples. For analysts that are unfamiliar with these procedures it is recommended that acceptable accuracy and precision be demonstrated with the working solution prior to the analysis of the field samples. This procedure may help the testing company to detect analytical errors prior to

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sample analysis and thus prevent having to invalidate the field samples and to require a complete retest of the source.

The control samples and the standard KNO_3 solution should be prepared using the following procedure.

1. Dry the potassium nitrate (KNO_3) ACS reagent grade at 105° to 110°C for a minimum of 2 h prior to the preparation of the control sample and the standard solution.

2. Place a 2 g Class-S weight on the balance. The balance must agree within ±2 mg of the Class-S standard weight.

3. Cool and store KNO_3 in desiccator. Weigh and then dissolve 2.198 ±0.002 g of dried KNO_3 in about 800 ml of deionized distilled water in a 1-ℓ volumetric flask (Class A).

4. Dilute to the mark with deionized distilled water, and label and date the solution.

5. Dilute 10.0 ml of the standard solution to the mark in a 100-ml volumetric flask with deionized distilled water, and label as "control sample" for analysis.

6. Weigh and then dissolve 2.198 ±0.002 g of dried KNO_3 in about 800 ml of deionized distilled water in a 1-ℓ volumetric flask (Class A).

7. Dilute to the mark with distilled deionized water, and label and date as the standard KNO_3 solution.

8. Dilute 10.0 ml of the standard KNO_3 solution to the mark in a 100-ml volumetric flask with deionized distilled water, and label as "working standard KNO_3 solution" for analysis.

9. Pipette 0.0, 2.0, 4.0, 6.0, and 8.0 ml of the working standard KNO_3 solution into five 50-ml volumetric flasks.

10. Pipette 2.0, 4.0, and 6.0 ml of the control sample into another set of 50-ml volumetric flasks.

11. Add 25 ml of absorbing solution, 10 ml of deionized distilled water, and then sodium hydroxide (1N) dropwise to each of the eight flasks until the pH is between 9 and 12 (about 25 to 35 drops each). Check for alkalinity by touching a glass rod first to the solution and then to pH paper. Note: The pH check is mandatory.

12. Dilute to the mark with deionized distilled water, and mix thoroughly.

5.2.3 Analysis of Control Samples, Standard Solutions, and Field Samples - The analysis of the samples has a time-dependent color change. To provide an estimate of the accuracy and precision of the analysis, the control sample is analyzed at the same time as the field sample. The standard solutions, field samples, and control samples should be analyzed in the following manner.

1. Pipette a 25-ml aliquot of each solution into a separate porcelain evaporating dish.

2. Evaporate the solutions (standards, field samples, and control samples) to dryness on a steam bath and then cool. Note: Do not evaporate on a hot plate or in an oven unless it is thermostatically controlled below 70°C (160°F). Remove samples from steam bath just before complete dryness is reached (the bottom of the dish should be covered with a smooth film), so that the last droplet evaporates as the dishes cool.

3. Add 2.0 ml of phenoldisulfonic acid reagent to each dried residue and either mix thoroughly with a polyethylene policeman or let the solution stand for 5 min.

4. Add 1.0 ml of deionized distilled water and four drops of concentrated sulfuric acid, and then heat the solution on a steam bath for 3 min with occasional stirring.

5. Cool. Add 20 ml of deionized distilled water, and mix well by stirring.

6. Add concentrated ammonium hydroxide dropwise (a 50-ml burette is suggested) with constant stirring until the pH is 10, as determined either by pH paper or by the first yellow color that does not fade.

7. Transfer directly to a 100-ml volumetric flask if the sample does not contain solids. Rinse the evaporating dish with at least three 5-ml portions of deionized distilled water, and then add the washings to the contents of the flask.

8. Remove any solids from the sample by filtering the sample through a Whatman No. 41 filter paper into a 100-ml volumetric flask; rinse each evaporating dish with three 5-ml portions of deionized distilled water; filter these three rinses. Wash the filter with at least three 15-ml portions of deionized distilled water, and then add the filter washings to the contents of the volumetric flask.

9. Dilute to the 100-ml mark with deionized distilled water and mix the contents of the flask thoroughly.

10. Measure the absorbance of the standard solutions at the optimum wavelength, using the blank solution as a zero reference. Note: The flasks should not sit in warm or light areas for very long before analysis because precipitates may form.

11. Record the standard solutions and control sample data on Figure 5.1 or similar form.

12. Read the absorbance of the field samples from Run 1 and then one of the control samples; Run 2 and another control sample; and Run 3 and the last control sample.

13. If the absorbance reading of any field sample is greater than the absorbance reading of the standard sample A_4 (the absorbance of the 400 µg NO_2 standard), then dilute the sample and the blank with equal volumes of deionized distilled water using pipettes to get ratios of 25/5, 25/10, and so forth.

14. Record all field sample analysis data as shown in Figure 5.2, and calculate the mass (m) of NO_x for each sample as µg of NO_2.

15. Perform the calculations and the accuracy checks of the three control samples as shown in Figure 5.1. It is recommended that the agreement for each control sample be within ±15%. The standard solution and control sample analytical form should be included in the emission test report as a documentation of the analytical accuracy. This accuracy limit of ±15% for intralaboratory control samples is recommended based on the control limit of ±20% for interlaboratory audit results discussed in Section 3.6.8.

Plant ACME POWER PLANT Date 3-3-77

Analyst J. Morgan Optimum wavelength 408 nm

Blank used as reference? YES

Sample number	Sample, µg	Working solution	Control sample	Measured, absorbance, OD	Calculated absorbance,[a] OD	Absorbance comparison error,[b] %
A1	100	x		0.192	-	-
A2	200	x		0.380	-	-
A3	300	x		0.560	-	-
A4	400	x		0.770	-	-
S1	100		x	0.190	0.191	-0.5
S2	200		x	0.381	0.381	0.0
S3	300		x	0.570	0.571	-0.2
						Avg[c] 0.2

[a] OD = (µg)/K_c; i.e., S1 calculated absorbance = 100/K_c.

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

[b] Absorbance comparison errors:

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

[c] Average of absolute values.

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

Plant ACME POWER PLANT Run number(s) AP-1 THROUGH AP-12

Date samples received 3/2/77 Date analyzed 3/3/77

Aliquot factor 2 Samples analyzed by J. MORGAN

Blank absorbance USED AS REFERENCE Date reviewed by T. SEAVER

Calibration factor (K_c) 528 Date of review 3/5/77

Sample number	Sample absorbance, A	Dilution factor, F	Total mass of NO_x as NO_2 in sample, m
AP-1	0.743	1.0	784
AP-2	0.631	1.0	666
AP-3	0.450	2.0	950

m = 2 K_c AF, Note: If other than a 25 ml aliquot is used for analysis, the factor 2 must be replaced by a corresponding factor.

Figure 5.2 NO_x laboratory data form.

16. When the above criteria cannot be met, it is recommended that the analytical techniques be checked and then the field sample and control sample analysis be repeated using a 20.0-ml aliquot of the remaining field samples.

17. The main parameters of the analytical procedures may be checked during or after the analysis, using a posttest operations form (Figure 5.3).

Reagents

Phenoldisulfonic acid stored in dark stoppered bottle? ✓

Sulfuric acid, concentrated, 95% minimum assay reagent grade? ✓

Ammonium hydroxide, concentrated reagent grade? ✓

Sample Preparation

Has liquid level noticeably changed?* No

Original volume _____ Corrected volume _____

Analysis

Spectrophotometer calibrated?* ✓

Setting for maximum absorbance of standard 408 nm

Control sample prepared?* ✓

Any solids in sample removed through Whatman No. 41 filter paper? N/A

Absorbance measured at optimum wavelength used for the standards, using the blank solution as a zero reference? ✓

All analytical data recorded on checklist and laboratory form? ✓

* Most significant items/parameters to be checked.

Figure 5.3. Posttest operations.

Table 5.1. ACTIVITY MATRIX FOR SAMPLE ANALYSIS

Characteristic	Acceptance limits	Frequency and method of measurement	Action if requirements are not met
Control sample analysis (recommended)	Agree within 15% of the working standards for each sample	Compare control sample analysis to working standards analysis	Redo field and control samples and/ or seek assistance with analytical technique
Field sample analysis	No sample volume lost, or final results corrected	Compare liquid level to mark before analysis	Void sample
	Working standard analyzed simultaneously with field sample	Use same solutions and techniques used for control samples	As above
	No absorbance readings outside working standard solution concentration	Dilute sample and blank with equal amounts of deionized distilled water	Dilute and reanalyze
Data recording	All pertinent data recorded on Figs. 5.1 and 5.2	Visually check	Supply missing data

6.0 CALCULATIONS

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

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

6.1 Nomenclature

The following nomenclature is used in the calculations.

A = Absorbance of sample.

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

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

K_c = Spectrophotometer calibration factor.

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

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

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

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

T_f = Final absolute temperature of flask, K (°R).

T_i = Initial absolute temperature of flask, K (°R).

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

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

V_f = Volume of flask and valve, ml.

V_a = Volume of absorbing solution, 25 ml.

6.2 Calculations

The following are the equations used with example calculation forms Figures 6.1A and 6.1B to calculate the concentration of nitrogen oxides.

6.2.1 Sample Volume - Calculate the sample volume on a dry basis at standard conditions (760 mm (29.92 in.) Hg and 293K (528°R)) by using the following equation.

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

$$= K_1(V_f - 25 \text{ ml}) \left(\frac{P_f}{T_f} - \frac{P_i}{T_i}\right) \qquad \text{Equation 6-1}$$

where

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

$K_1 = 17.64 \ \frac{°R}{in.\ Hg}$ for English units.

6.2.2 Total µg of NO_2 Per Sample - Calculate the total µg of NO_2 per sample by using Equation 6-2.

$$m = 2\ K_c A F \quad . \qquad \text{Equation 6-2}$$

where

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

6.2.3 Sample Concentration - Calculate the sample concentration on a dry basis at standard conditions using Equation 6-3.

$$C = K_2 \left[\frac{m}{V_{sc}}\right] \qquad \text{Equation 6-3}$$

where

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

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

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Sample Volume

V_f = 2013 ml, P_f = 27.64 in. Hg, T_f = 533 °R

P_i = 0.59 in. Hg, T_i = 532. °R

$$V_{sc} = 17.64\ (V_f - 25)\left[\frac{P_f}{T_f} - \frac{P_i}{T_i}\right] = 1780 \text{ ml}$$ Equation 6-1

Total μg NO_2 Per Sample

K_c = 528., A = 0.743 OD, F = 1.00 Equation 6.2

$m = 2K_c\ AF$ = 785. μg of NO_2

Sample Concentration

$$C = 6.243 \times 10^{-5}\left[\frac{m}{V_{sc}}\right] = 2.75 \times 10^{-5} \text{ lb/dscf}$$

Figure 6.1A. Nitrogen oxide calculation form (English units).

Sample Volume

V_f = 2013. ml, P_f = 702.0 mm Hg, T_f = 295.2 K

P_i = 12.0 mm Hg, T_i = 295.5 K

$$V_{sc} = 0.3858\ (V_f - 25)\left[\frac{P_f}{T_f} - \frac{P_i}{T_i}\right] = 1775.\ \text{ml}$$ Equation 6-1

Total µg NO_2 Per Sample

K_c = 528., A = 0.743 OD, F = 1.00

$m = 2K_c\ AF$ = 784. µg of NO_2. Equation 6-2

Sample Concentration

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

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

Table 6.1 ACTIVITY MATRIX FOR CALCULATIONS

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

7.0 MAINTENANCE

The normal use of emission-testing equipment subjects it to corrosive gases, extremes in temperature, vibration, and shock. Keeping the equipment in good operating order over an extended period of time requires knowledge of the equipment and a routine maintenance program which should be performed quarterly or upon improper functioning of the apparatus. It is suggested that the vacuum pump be disassembled and cleaned yearly. A summary of the components with maintenance procedures is presented in Table 7.1 at the end of this section. The following procedures are not required, but are recommended to increase the reliability of the equipment.

7.1 Pumps

Several types of pumps are used in the present commercial sampling trains. The two most common are the fiber vane pump with in-line oiler and the diaphragm pump. The fiber vane pump requires a periodic check of the oiler jar. The oil should be translucent. During the yearly disassembly or if the fiber vane pump starts to run erratically, the head should be removed and the fiber vanes changed. The diaphragm pump will show a leak when the diaphragm needs changing. If the diaphragm pump runs erratically, it is usually due to a bad diaphragm (causing leakage) or to malfunctions in the valves. The valves should be cleaned annually by complete disassembly of the pump.

7.2 Shipping Containers

Since the majority of the sampling train is glassware, the shipping containers are very important for protection and safety. All shipping containers should be inspected quarterly for their condition, and repaired or modified to assure the safety of the equipment.

Table 7.1 ACTIVITY MATRIX FOR MAINTENANCE

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

8.0 AUDITING PROCEDURE

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

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

1. Audit of the analytical phase of Method 7.

2. Audit of data processing for both Methods.

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

8.1 Performance Audits

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

8.1.1 Pretest Audit of Analytical Phase Using Aqueous Ammonium Sulfate (Optional) - The pretest audit described in this section can be used to determine the proficiency of the analyst and the standardization of solutions in the Method 7 analysis and should be performed at the discretion of the agency auditor, the laboratory supervisor, source test company, or quality assurance officer. The analytical phase of Method 7 can be audited with the use of aqueous potassium nitrate samples provided to the testing laboratory before the enforcement source test. Aqueous potassium nitrate samples may be prepared by the procedure described in Section 3.6.5 on control sample preparation.

The pretest audit provides the opportunity for the testing laboratory to check the accuracy of its analytical procedure. This audit is especially recommended for a laboratory with little or no experience with the Method 7 analysis procedure described in this Handbook.

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

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

Equation 8-1

$$RE = \frac{C_d - C_a}{Ca} \times 100$$

where:

C_d = Determined audit sample concentration, mg/dsm^3.

C_a = Actual audit sample concentration, mg/dsm^3.

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

The two audit samples and the compliance samples should be

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

Calculate the concentrations in mg/dsm^3 using the specified sample volume in the audit instructions. (Note: Indication of acceptable results may be obtained immediately by reporting the audit results in mg/dsm^3 and compliance results in total mg NO_2/sample by telephone to the responsible enforcement agency.) Include the results of both audit samples, their identification numbers, and the analyst's name with the results of the compliance determination samples in appropriate reports to the EPA regional office or the appropriate enforcement agency. Include this information with subsequent compliance analyses for the same enforcement agency during the 30-day period.

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

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

8.1.3 Audit of Data Processing - Calculation errors are prevalent in Method 7.[3,4,5] Data processing errors can be determined by auditing the recorded data on the field and laboratory forms. The original and audit (check) calculations should agree within round-off error; if not, all of the remaining data should be checked. The data processing may also be audited by providing the testing laboratory with specific data sets (exactly as would appear in the field), and by requesting that the data calculation be completed and that the results be

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

8.2 Systems Audit

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

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

1. Inform the testing team of the results of pretest audits, specifying any area(s) that need special attention or improvement.

2. Observe procedures and techniques of the field team during sample collection.

3. Check/verify records of apparatus calibration checks and quality control used in the laboratory analysis of control samples from previous source tests, where applicable.

4. Record the results of the audit and forward them with comments to the team management so that appropriate corrective action may be initiated.

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

1. Setting up and leak testing the sampling train.

2. Preparing the absorbing solution and adding it to the collection flasks.

3. Collecting the sample.

4. Sample absorption, recovery, and preparation for shipment.

5. The spectrophotometer calibration should be checked for every series of analyses. The calculated concentration values should not differ from the actual concentrations by more than 7 percent for three of the four standards.

Figure 8.1 is a suggested checklist for the auditor.

Yes	No	Comment	
			Presampling preparation
___	___	_____	1. Information concerning combustion effluents that may act as interferents
___	___	_____	2. Plant operation parameters variation
___	___	_____	3. Calibration of the flask and valve volume---three determinations
___	___	_____	4. Absorbing reagent preparation
			On-site measurements
___	___	_____	5. Leak testing of sampling train
___	___	_____	6. Preparation and pipetting of absorbing solution into sampling flask
			Postsampling (Analysis and Calculation)
___	___	_____	7. Control sample analysis
___	___	_____	8. Sample aliquotting techniques
___	___	_____	9. Evaporation and chemical treatment of sample
___	___	_____	10. Spectrophotometric technique a. Preparation of standard nitrate samples b. Measurement of absorbance, including blanks c. Calibration factor (± 7 percent for 3 of 4 standards) d. Wavelength and absorbance, including blanks e. Check for calibration of instrument wavelength (once every six months)
___	___	_____	11. Audit results (± 10%) a. Use of computer program b. Independent check of calculations
			Comments

Figure 8.1. Method 7 checklist to be used by auditors.

Table 8.1 ACTIVITY MATRIX FOR AUDITING PROCEDURE

Audit	Acceptance Limits	Frequency and method of measurement	Action if requirements are not met
Spectrophotometer analysis using reference samples of dilute KNO	Measured RE of the pretest audit samples should be less than ± 10% for both audit results (optional)	Frequency: As considered necessary by the testing firm Method: Measure reference samples and compare their true value	Review operating technique and/or calibration curve check
	Measured RE of the audit samples should be less than ± 10% for both audit samples (required)	Frequency: Once during every enforcement source test* (required) Method: Measure audit samples and compare their true values	Review operating technique and/or calibration curve check and repeat the analysis of the audit and field samples
Data processing errors (recommended)	Original and check calculations agree within round-off error	Frequency: Once during every enforcement source test* Method: Independent calculations starting with recorded data on Figures 4.1 and 5.1	Check and correct all data for the audit period represented by the sampled data
Systems audit--observance of technique (recommended)	Operational technique as described in this section of the Handbook	Frequency: Once during every enforcement source test* until experience gained, then every fourth test Method: Observation of techniques assisted by audit checklist, Fig. 8.1	Explain to team their deviations from recommended techniques and note on Fig. 8.1

*As defined here, a source test for enforcement comprises a series of runs at one source. Source tests for purposes other than enforcement (e.g., a research project) may be audited at a lower frequency.

9.0 RECOMMENDED STANDARDS FOR ESTABLISHING TRACEABILITY

To achieve data of desired quality, two essential considerations are necessary: (1) the measurement process must be in a state of statistical control at the time of the measurement and (2) the systematic errors, when combined with the random variation (errors or measurement), must result in an acceptable uncertainty. As evidence in support of good quality data, it is necessary to perform quality control checks and independent audits of the measurement process; to document these data; and to use materials, instruments, and measurement procedures that can be traced to an appropriate standard of reference.

Data must be routinely obtained by repeat measurements of standard reference samples (primary, secondary, and/or working standards) and the establishment of a condition of process control. The working calibration standards should be traceable to standards of higher accuracy, such as that below.

Class-S weights (made to NBS specifications) are recommended for the analytical balance calibration. See Section 3.6.2 for details on balance calibration checks.

10.0 REFERENCE METHOD *

METHOD 7—DETERMINATION OF NITROGEN OXIDE EMISSIONS FROM STATIONARY SOURCES

1. *Principle and Applicability*

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

1.2 Applicability. This method is applicable to the measurement of nitrogen oxides emitted from stationary sources. The range of the method has been determined to be 2 to 400 milligrams NO_x (as NO_2) per dry standard cubic meter, without having to dilute the sample.

2. *Apparatus*

2.1 Sampling (see Figure 7-1). Other grab sampling systems or equipment, capable of measuring sample volume to within ±2.0 percent and collecting a sufficient sample volume to allow analytical reproducibility to within 5 percent, will be considered acceptable alternatives, subject to approval of the Administrator, U.S. Environmental Protection Agency. The following equipment is used in sampling:

2.1.1 Probe. Borosilicate glass tubing, sufficiently heated to prevent water condensation and equipped with an in-stack or out-stack filter to remove particulate matter (a plug of glass wool is satisfactory for this purpose). Stainless steel or Teflon [1] tubing may also be used for the probe. Heating is not necessary if the probe remains dry during the purging period.

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

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

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

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

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

2.1.6 Vacuum Gauge. U-tube manometer, 1 meter (35 in.), with 1-mm (0.1-in.) divisions, or other gauge capable of measuring pressure to within ±2.5 mm Hg (0.10 in. Hg).

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

2.1.8 Squeeze Bulb. One-way.

2.1.9 Volumetric Pipette. 25 ml.

2.1.10 Stopcock and Ground Joint Grease. A high-vacuum, high-temperature chlorofluorocarbon grease is required. Halocarbon 25-5S has been found to be effective.

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

2.2 Sample Recovery. The following equipment is required for sample recovery:

2.2.1 Graduated Cylinder. 50 ml with 1-ml divisions.

2.2.2 Storage Containers. Leak-free polyethylene bottles.

2.2.3 Wash Bottle. Polyethylene or glass.

2.2.4 Glass Stirring Rod.

2.2.5 Test Paper for Indicating pH. To cover the pH range of 7 to 14.

2.3 Analysis. For the analysis, the following equipment is needed:

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

2.3.2 Porcelain Evaporating Dishes. 175- to 250-ml capacity with lip for pouring, one for each sample and each standard. The Coors No. 45003 (shallow form, 195 ml) has been found to be satisfactory. Alternatively, polymethyl pentene beakers (Nalge No. 1203, 150 ml), or glass beakers (150 ml) may be used. When glass beakers are used, etching of the beakers may cause solid matter to be present in the analytical step; the solids should be removed by filtration (see Section 4.3).

2.3.3 Steam Bath. Low-temperature steam or thermostatically controlled hot plate kept below 95° C (200° F) are acceptable alternatives.

2.3.4 Dropping Pipette or Dropper. Three required.

2.3.5 Polyethylene Policeman. One for each sample and each standard.

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

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

2.3.8 Spectrophotometer. To measure absorbance at 410 nm.

2.3.9 Graduated Pipettes. 10 ml with 0.1-ml divisions.

2.3.10 Test Paper for Indicating pH. To cover the pH range of 7 to 14.

2.3.11 Analytical Balance. To measure to within 0.1 mg.

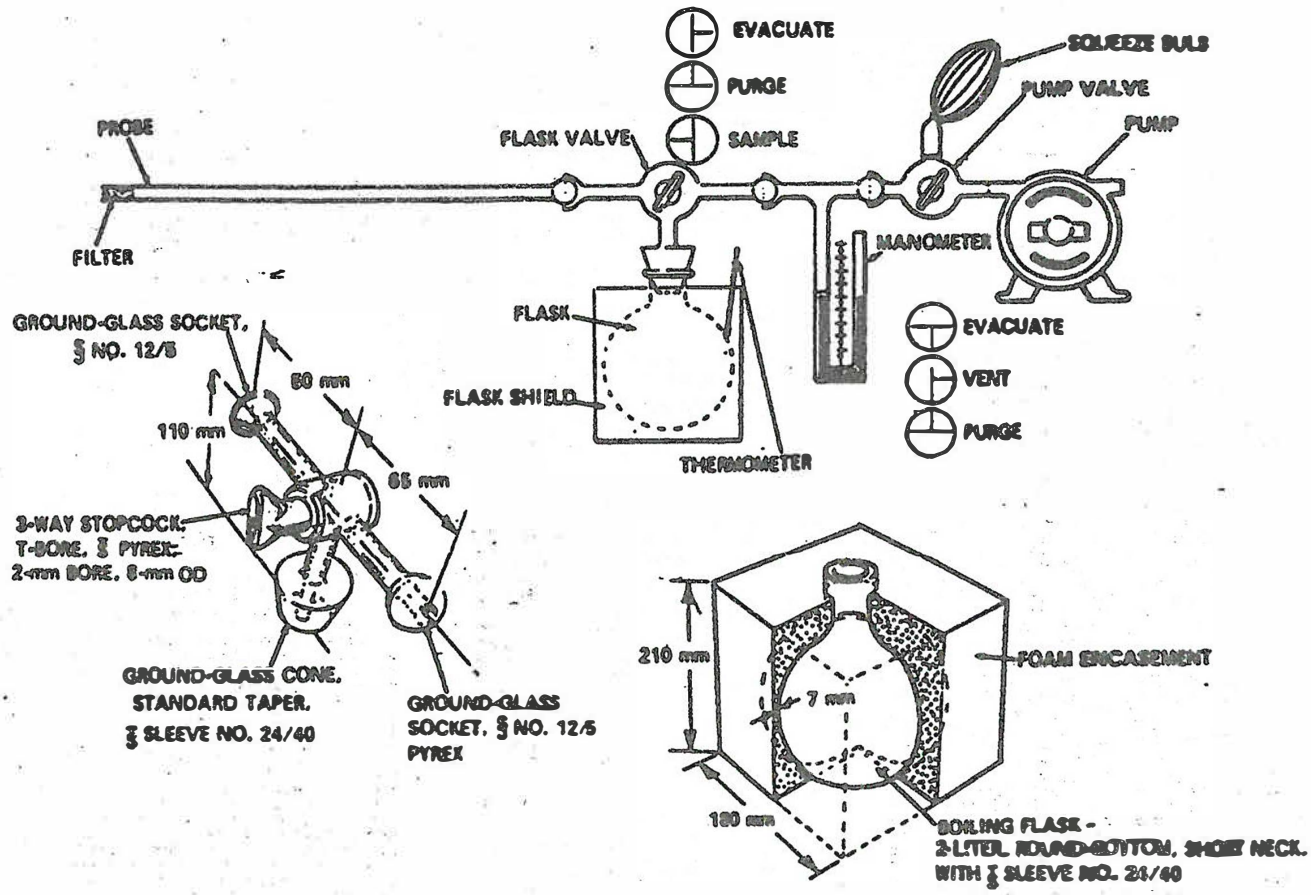

Figure 7-1. Sampling train, flask valve, and flask.

*40 CFR 60, July 1, 1978

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3. *Reagents*

Unless otherwise indicated, it is intended that all reagents conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available; otherwise, use the best available grade.

3.1 Sampling. To prepare the absorbing solution, cautiously add 2.8 ml concentrated H_2SO_4 to 1 liter of deionized, distilled water. Mix well and add 6 ml of 3 percent hydrogen peroxide, freshly prepared from 30 percent hydrogen peroxide solution. The absorbing solution should be used within 1 week of its preparation. Do not expose to extreme heat or direct sunlight.

3.2 Sample Recovery. Two reagents are required for sample recovery:

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

3.2.2 Water. Deionized, distilled to conform to ASTM specification D1193-74, Type 3. At the option of the analyst, the $KMnO_4$ test for oxidizable organic matter may be omitted when high concentrations of organic matter are not expected to be present.

3.3 Analysis. For the analysis, the following reagents are required:

3.3.1 Fuming Sulfuric Acid. 15 to 18 percent by weight free sulfur trioxide. HANDLE WITH CAUTION.

3.3.2 Phenol. White solid.

3.3.3 Sulfuric Acid, Concentrated, 95 percent minimum assay. HANDLE WITH CAUTION.

3.3.4 Potassium Nitrate. Dried at 105 to 110° C (220 to 230° F) for a minimum of 2 hours just prior to preparation of standard solution.

3.3.5 Standard KNO_3 Solution. Dissolve exactly 2.198 g of dried potassium nitrate (KNO_3) in deionized, distilled water and dilute to 1 liter with deionized, distilled water in a 1,000-ml volumetric flask.

3.3.6 Working Standard KNO_3 Solution. Dilute 10 ml of the standard solution to 100 ml with deionized distilled water. One milliliter of the working standard solution is equivalent to 100 μg nitrogen dioxide (NO_2).

3.3.7 Water. Deionized, distilled as in Section 3.2.2.

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

4. *Procedure*

4.1 Sampling.

4.1.1 Pipette 25 ml of absorbing solution into a sample flask, retaining a sufficient quantity for use in preparing the calibration standards. Insert the flask valve stopper into the flask with the valve in the "purge" position. Assemble the sampling train as shown in Figure 7-1 and place the probe at the sampling point. Make sure that all fittings are tight and leak-free, and that all ground glass joints have been properly greased with a high-vacuum, high-temperature chlorofluorocarbon-based stopcock grease. Turn the flask valve and the pump valve to their "evacuate" positions. Evacuate the flask to 75 mm Hg (3 in. Hg) absolute pressure, or less. Evacuation to a pressure approaching the vapor pressure of water at the existing temperature is desirable. Turn the pump valve to its "vent" position and turn off the pump. Check for leakage by observing the manometer for any pressure fluctuation. (Any variation greater than 10 mm Hg (0.4 in. Hg) over a period of 1 minute is not acceptable, and the flask is not to be used until the leakage problem is corrected. Pressure in the flask is not to exceed 75 mm Hg (3 in. Hg) absolute at the time sampling is commenced.) Record the volume of the flask and valve (V_f), the flask temperature (T_f), and the barometric pressure. Turn the flask valve counterclockwise to its "purge" position and do the same with the pump valve. Purge the probe and the vacuum tube using the squeeze bulb. If condensation occurs in the probe and the flask valve area, heat the probe and purge until the condensation disappears. Next, turn the pump valve to its "vent" position. Turn the flask valve clockwise to its "evacuate" position and record the difference in the mercury levels in the manometer. The absolute internal pressure in the flask (P_i) is equal to the barometric pressure less the manometer reading. Immediately turn the flask valve to the "sample" position and permit the gas to enter the flask until pressures in the flask and sample line (i.e., duct, stack) are equal. This will usually require about 15 seconds; a longer period indicates a "plug" in the probe, which must be corrected before sampling is continued. After collecting the sample, turn the flask valve to its "purge" position and disconnect the flask from the sampling train. Shake the flask for at least 5 minutes.

4.1.2 If the gas being sampled contains insufficient oxygen for the conversion of NO to NO_2 (e.g., an applicable subpart of the standard may require taking a sample of a calibration gas mixture of NO in N_2), then oxygen shall be introduced into the flask to permit this conversion. Oxygen may be introduced into the flask by one of three methods: (1) Before evacuating the sampling flask, flush with pure cylinder oxygen, then evacuate flask to 75 mm Hg (3 in. Hg) absolute pressure or less; or (2) inject oxygen into the flask after sampling; or (3) terminate sampling with a minimum of 50 mm Hg (2 in. Hg) vacuum remaining in the flask, record this final pressure, and then vent the flask to the atmosphere until the flask pressure is almost equal to atmospheric pressure.

4.2 Sample Recovery. Let the flask set for a minimum of 16 hours and then shake the contents for 2 minutes. Connect the flask to a mercury filled U-tube manometer. Open the valve from the flask to the manometer and record the flask temperature (T_f), the barometric pressure, and the difference between the mercury levels in the manometer. The absolute internal pressure in the flask (P_f) is the barometric pressure less the manometer reading. Transfer the contents of the flask to a leak-free polyethylene bottle. Rinse the flask twice with 5-ml portions of deionized, distilled water and add the rinse water to the bottle. Adjust the pH to between 9 and 12 by adding sodium hydroxide (1 N), dropwise (about 25 to 35 drops). Check the pH by dipping a stirring rod into the solution and then touching the rod to the pH test paper. Remove as little material as possible during this step. Mark the height of the liquid level so that the container can be checked for leakage after transport. Label the container to clearly identify its contents. Seal the container for shipping.

4.3 Analysis. Note the level of the liquid in container and confirm whether or not any sample was lost during shipment; note this on the analytical data sheet. If a noticeable amount of leakage has occurred, either void the sample or use methods, subject to the approval of the Administrator, to correct the final results. Immediately prior to analysis, transfer the contents of the shipping container to a 50-ml volumetric flask, and rinse the container twice with 5-ml portions of deionized, distilled water. Add the rinse water to the flask and dilute to the mark with deionized, distilled water; mix thoroughly. Pipette a 25-ml aliquot into the porcelain evaporating dish. Return any unused portion of the sample to the polyethylene storage bottle. Evaporate the 25-ml aliquot to dryness on a steam bath and allow to cool. Add 2 ml phenoldisulfonic acid solution to the dried residue and triturate thoroughly with a polyethylene policeman. Make sure the solution contacts all the residue. Add 1 ml deionized, distilled water and four drops of concentrated sulfuric acid. Heat the solution on a steam bath for 3 minutes with occasional stirring. Allow the solution to cool, add 20 ml deionized, distilled water, mix well by stirring, and add concentrated ammonium hydroxide, dropwise, with constant stirring, until the pH is 10 (as determined by pH paper). If the sample contains solids, these must be removed by filtration (centrifugation is an acceptable alternative, subject to the approval of the Administrator), as follows: filter through Whatman No. 41 filter paper into a 100-ml volumetric flask; rinse the evaporating dish with three 5-ml portions of deionized, distilled water; filter these three rinses. Wash the filter with at least three 15-ml portions of deionized, distilled water. Add the filter washings to the contents of the volumetric flask and dilute to the mark with deionized, distilled water. If solids are absent, the solution can be transferred directly to the 100-ml volumetric flask and diluted to the mark with deionized, distilled water. Mix the contents of the flask thoroughly, and measure the absorbance at the optimum wavelength used for the standards (Section 5.2.1), using the blank solution as a zero reference. Dilute the sample and the blank with equal volumes of deionized, distilled water if the absorbance exceeds A_4, the absorbance of the 400 μg NO_2 standard (see Section 5.2.2).

5. *Calibration*

5.1 Flask Volume. The volume of the collection flask-flask valve combination must be known prior to sampling. Assemble the flask and flask valve and fill with water, to the stopcock. Measure the volume of water to ±10 ml. Record this volume on the flask.

5.2 Spectrophotometer Calibration.

5.2.1 Optimum Wavelength Determination. For both fixed and variable wavelength spectrophotometers, calibrate against standard certified wavelength of 410 nm, every 6 months. Alternatively, for variable wavelength spectrophotometers, scan the spectrum between 400 and 415 nm using a 200 μg NO_2 standard solution (see Section 5.2.2). If a peak does not occur, the spectrophotometer is probably malfunctioning, and should be repaired. When a peak is obtained within the 400 to 415 nm range, the wavelength at which this peak occurs shall be the optimum wavelength for the measurement of absorbance for both the standards and samples.

5.2.2 Determination of Spectrophotometer Calibration Factor K_c. Add 0.0, 1.0, 2.0, 3.0, and 4.0 ml of the KNO_3 working standard solution (1 ml=100 μg NO_2) to a series of five porcelain evaporating dishes. To each, add 25 ml of absorbing solution, 10 ml deionized, distilled water, and sodium hydroxide (1N), dropwise, until the pH is between 9 and 12 (about 25 to 35 drops each). Beginning with the evaporation step, follow the analysis procedure of Section 4.3, until the solution has been transferred to the 100 ml volumetric flask and diluted to the mark. Measure the absorbance of each solution, at the optimum wavelength, as determined in Section 5.2.1. This calibration procedure must be repeated on each day that samples are analyzed. Calculate the spectrophotometer calibration factor as follows:

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

Equation 7-1

where:

K_c = Calibration factor
A_1 = Absorbance of the 100-μg NO_2 standard
A_2 = Absorbance of the 200-μg NO_2 standard
A_3 = Absorbance of the 300-μg NO_2 standard
A_4 = Absorbance of the 400-μg NO_2 standard

5.3 Barometer. Calibrate against a mercury barometer.

5.4 Temperature Gauge. Calibrate dial thermometer against mercury-in-glass thermometers.

5.5 Vacuum Gauge. Calibrate mechanical gauges, if used, against a mercury manometer such as that specified in 2.1.6.

5.6 Analytical Balance. Calibrate against standard weights.

6. *Calculations*

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

6.1 Nomenclature.

A = Absorbance of sample.
C = Concentration of NO_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 in gas sample, μg.
P_f = Final absolute pressure of flask, mm Hg (in. Hg).
P_i = Initial absolute pressure of flask, mm Hg (in. Hg).
P_{std} = Standard absolute pressure, 760 mm Hg (29.92 in. Hg).
T_f = Final absolute temperature of flask, °K (°R).
T_i = Initial absolute temperature of flask, °K (°R).
T_{std} = Standard absolute temperature, 293° K (535° R).
V_{sc} = Sample volume at standard conditions (dry basis), ml.
V_f = Volume of flask and valve, ml.
V_s = 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.

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

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

Equation 7-2

where:

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

$$= 17.64\,\frac{°R}{\text{in. Hg}} \text{ for English units}$$

6.3 Total μg NO_2 per sample.

$$m = 2\,K_c\,A\,F$$

Equation 7-3

NOTE.—If other than a 25-ml aliquot is used for analysis, the factor 2 must be replaced by a corresponding factor.

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

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

Equation 7-4

where:

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

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

7. *Bibliography*

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Amendments to Reference Method 8; Correction*

In Method 7 of Appendix A, Sections 2.3.2, 2.3.7, 4.2, 4.3, 5.2.1, 5.2.2, 6 and 7 are amended as follows:

1. In Section 2.3.2, a semicolon replaces the comma between the words "step" and "the."

2. In Section 2.3.7, the phrase "(one for each sample)" in the first line is corrected to read "(one for each sample and each standard)."

3. In Section 4.2, the letter "n" in the seventh line is corrected to read "in."

4. In Section 4.3, the word "poylethylene" in the seventeenth line is corrected to read "polyethylene."

5. In Section 5.2.1, delete the entire section and insert the following:

Optimum Wavelength Determination. Calibrate the wavelength scale of the spectrophotometer every 6 months. The calibration may be accomplished by using an energy source with an intense line emission such as a mercury lamp, or by using a series of glass filters spanning the measuring range of the spectrophotometer. Calibration materials are available commercially and from the National Bureau of Standards. Specific details on the use of such materials should be supplied by the vendor; general information about calibration techniques can be obtained from general reference books on analytical chemistry. The wavelength scale of the spectrophotometer must read correctly within ± 5 nm at all calibration points; otherwise, the spectrophotometer shall be repaired and recalibrated. Once the wavelength scale of the spectrophotometer is in proper calibration, use 410 nm as the optimum wavelength for the measurement of the absorbance of the standards and samples.

Alternatively, a scanning procedure may be employed to determine the proper measuring wavelength. If the instrument is a double-beam spectrophotometer, scan the spectrum between 400 and 415 nm using a 200 μg NO_2 standard solution in the sample cell and a blank solution in the reference cell. If a peak does not occur, the spectrophotometer is probably malfunctioning and should be repaired. When a peak is obtained within the 400 to 415 nm range, the wavelength at which this peak occurs shall be the optimum wavelength for the measurement of absorbance of both the standards and the samples. For a single-beam spectrophotometer, follow the scanning procedure described above, except that the blank and standard solutions shall be scanned separately. The optimum wavelength shall be the wavelength at which the maximum difference in absorbance between the standard and the blank occurs.

6. In Section 5.2.2, delete the first seven lines and insert the following:

Determination of Spectrophotometer Calibration Factor K. Add 0.0 ml, 2 ml, 4 ml, 6 ml, and 8 ml of the KNO_2 working standard solution (1 ml = 100 μg NO_2) to a series of five 50-ml volumetric flasks. To each flask, add 25 ml of absorbing solution, 10 ml deionized, distilled water, and sodium hydroxide (1 N) dropwise until the pH is between 9 and 12 (about 25 to 35 drops each). Dilute to the mark with deionized, distilled water. Mix thoroughly and pipette a 25-ml aliquot of each solution into a separate porcelain evaporating dish.

7. In Section 6.1, the word "Hass" in the tenth line is corrected to read "Mass."

8. In Section 7, the word "Vna" in (1) is corrected to read "Van." The word "drtermination" in (6) is corrected to read "Determination."

*Federal Register, Vol. 43, No. 57-March 23, 1978

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11.0 REFERENCES

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2. Buchanan, J. W. and D. E. Wagoner. Guidelines for Development of a Quality Assurance Program, Determination of Nitrogen Oxide Emissions from Stationary Sources. EPA.

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12. Fuerst, R. G., R. L. Denny, and M. R. Midgett. A Summary of Interlaboratory Source Performance Surveys for EPA Reference Methods 6 and 7-1977. Available from U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory (MD-77), Research Triangle Park, N.C. 27711.

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12.0 DATA FORMS

Blank data forms are provided on the following pages for the convenience of the Handbook user. Each blank form has the customary descriptive title centered at the top of the page. However, the section-page documentation in the top right-hand corner of each page has been replaced with a number in the lower right-hand corner that will enable the user to identify and refer to a similar filled-in form in a text section. For example, Form M7-1.2, indicates that the form is Figure 1.2 in Section 3.6.1 of the Method 7 Handbook. Future revisions of these forms, if any, can be documented by 1.2A, 1.2B, etc. Twelve of the blank forms listed below are included in this section. Four are in the Method Highlights subsection as shown by the MH following the form number.

Form	Title
1.2	Procurement log
2.1	Optimum Wavelength Determination Data Form
2.2	Analytical Balance Calibration Form
3.1 (MH)	Pretest Checklist
3.2 (MH)	Pretest Preparations
4.1A and 4.1B	Nitrogen Oxide Field Data Form (English and metric units)
4.2A and 4.2B	NO_x Sample Recovery and Integrity Data Form (English and metric units)
4.3 (MH)	On-site Measurements
5.1	Standard Solution and Control Sample Analytical Data Form
5.2	NO_x Laboratory Data Form
5.3 (MH)	Posttest Operations
6.1A and 6.1B	Nitrogen Oxide Calculation Form (English and metric units)
8.1	Method 7 Checklist to be Used by Auditors

PROCUREMENT LOG

Item description	Qty.	Purchase order number	Vendor	Date		Cost	Disposition	Comments
				Ord.	Rec.			

OPTIMUM WAVELENGTH DETERMINATION DATA FORM

Spectrophotometer number _____ Date _____

Calibrated by _____ Reviewed by _____

Spectrophotometer setting, nm	Absorbance of standard OD[a]	Absorbance of blank OD[b]	Actual absorbance of OD[c]
399 400 401			
402 403 404			
405 406 407			
408 409 410			
411 412 413			
414 415 416			

[a] Absorbance of the 200 µg NO_2 standard in a single beam spectrophotometer.

[b] Absorbance of the blank in a single-beam spectrophotometer.

[c] For a single-beam spectrophotometer -- absorbance of the standard minus absorbance of the blank. For a double beam spectrophotometer -- absorbance of the 200 µg NO_2 standard with the blank in the reference cell.

Spectrophotometer setting for maximum actual absorbance of standard _____ nm.

If the maximum actual absorbance occurs at a spectrophotometer setting of $\leq$399 or $\geq$416 nm, the spectrophotometer must be repaired or recalibrated.

ANALYTICAL BALANCE CALIBRATION FORM

Balance name _____ Number _____

Classification of standard weights _____

Date	0.5000 g	1.0000 g	10.000 g	50.0000 g	100.0000 g	Analyst

NITROGEN OXIDE FIELD DATA FORM
(English units)

Plant _____ City _____

Sample location _____ Date _____

Operator _____ Barometric pressure (P_{bar}) _____ in. Hg

Sample number	Sample point location	Sample time 24-hr	Probe temperature, °F	Flask and valve number	Volume of flask and valve (V_F), ml	Initial pressure in. Hg			Initial temperature	
						Leg A_i	Leg B_i	P_i [a]	°F (t_i)	°R (T_i) [b]

[a] $P_i = P_{bar} - (A_i + B_i)$.

[b] $T_i = t_i + 460°F$.

NITROGEN OXIDE FIELD DATA FORM
(metric units)

Plant _____ City _____

Sample location _____ Date _____

Operator _____ Barometric pressure (P_{bar}) _____ mm Hg

Sample number	Sample point location	Sample time 24-hr	Probe temperature, °C	Flask and valve number	Volume of flask and valve (V_F), ml	Initial pressure mm Hg			Initial temperature	
						Leg A_i	Leg B_i	P_i [a]	°C (t_i)	°K (T_i) [b]

[a] $P_i = P_{bar} - (A_i + B_i)$.

[b] $T_i = t_i + 273°C$.

NO_x SAMPLE RECOVERY AND INTEGRITY DATA FORM
(English units)

Plant _____ Date _____

Sample recovery personnel _____ Barometric pressure, (P_{bar}) _____ in. Hg

Person with direct responsibility for recovered samples _____

Sample number	Final pressure, in. Hg			Final temperature,		Sample recovery time, 24-h	pH adjusted 9 to 12	Liquid level marked	Samples stored in locked container
	Leg A_f	Leg B_f	P_f [a]	^oF (t_f)	^oR (T_f)[b]				

$P_f = P_{bar} - (A_f + B_f)$. $T_f = t_f + 460^oF$.

Lab person with direct responsibility for recovered samples _____

Date recovered samples received _____ Analyst _____

All samples identifiable?_____ All liquids at marked level?_____

Remarks _____

Signature of lab sample trustee _____

NO_x SAMPLE RECOVERY AND INTEGRITY DATA FORM
(metric units)

Plant _____ Date _____

Sample recovery personnel _____ Barometric pressure, (P_{bar}) _____ mm Hg

Person with direct responsibility for recovered samples _____

Sample number	Final pressure, mm Hg			Final temperature,		Sample recovery time, 24-hr	pH adjusted 9 to 12	Liquid level marked	Samples stored in locked container
	Leg A_f	Leg B_f	P_f	^oC (t_f)	K (T_f)				

$P_f = P_{bar} - (A_f + B_f)$. $T_f = t_f + 273^oC$.

Lab person with direct responsibility for recovered samples _____

Date recovered samples received _____ Analyst _____

All samples identifiable?_____ All liquids at marked level?_____

Remarks _____

Signature of lab sample trustee _____

STANDARD SOLUTION AND CONTROL SAMPLE ANALYTICAL DATA FORM

Plant _____ Date _____

Analyst _____ Optimum wavelength _____ nm

Blank used as reference? _____

Sample number	Sample, µg	Working solution	Control sample	Measured, absorbance, OD	Calculated absorbance,[a] OD	Absorbance comparison error,[b] %
A1	100	x			-	-
A2	200	x			-	-
A3	300	x			-	-
A4	400	x			-	-
S1	100		x			
S2	200		x			
S3	300		x			
						Avg[c]

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

[a] Calculated absorbance: $OD = (\mu g)/K_c$ i.e., S1 calculated absorbance = $100/K_c$.

[b] Absorbance comparison errors:

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

[c] Average of absolute values.

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NO_x LABORATORY DATA FORM

Plant _____ Run number(s) _____

Date samples received _____ Date analyzed _____

Aliquot factor _____ Samples analyzed by _____

Blank absorbance _____ Date reviewed by _____

Calibration factor (K_c) _____ Date of review _____

Sample number	Sample absorbance, A	Dilution factor, F	Total mass of NO_x as NO_2 in sample, m

m = 2 K_c AF, Note: If other than a 25 ml aliquot is used for analysis, the factor 2 must be replaced by a corresponding factor.

NITROGEN OXIDE CALCULATION FORM
(English units)

Sample Volume

V_f = _ _ _ _ ml, P_f = _ _._ _ in. Hg, T_f = _ _ _ ^{o}R

P_i = _ _._ _ in. Hg, T_i = _ _ _. ^{o}R

$$V_{sc} = 17.64\ (V_f - 25)\ \left[\frac{P_f}{T_f} - \frac{P_i}{T_i}\right] = \text{_ _ _ _ ml}$$ Equation 6.1

Total µg NO_2 Per Sample

K_c = _ _ _ _., A = _._ _ _ OD, F = _ _._ _ Equation 6.2

$m = 2K_c\ AF$ = _ _ _ _. µg of NO_2

Sample Concentration

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

NITROGEN OXIDE CALCULATION FORM
(metric units)

Sample Volume

V_f = _ _ _ _. ml, P_f = _ _ _._ mm Hg, T_f = _ _ _._ K

P_i = _ _ _._ mm Hg, T_i = _ _ _._ K

$$V_{sc} = 0.3858\ (V_f - 25)\left[\frac{P_f}{T_f} - \frac{P_i}{T_i}\right] = \_\_\_\_. \text{ ml} \quad \text{Equation 6-1}$$

Total µg NO_2 Per Sample

K_c = _ _ _ _., A = _._ _ _ OD, F = _ _._ _

$$m = 2K_c\ AF = \_\_\_\_. \text{ µg of } NO_2. \quad \text{Equation 6-2}$$

Sample Concentration

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

METHOD 7 CHECKLIST TO BE USED BY AUDITORS

Presampling Preparation

Yes	No		
___	___	1.	Information concerning combustion effluents that may act as interferents
___	___	2.	Plant operation parameters variation
___	___	3.	Calibration of the flask and valve volume--- three determinations
___	___	4.	Absorbing reagent preparation

On-site Measurements

___	___	5.	Leak testing of the sampling train
___	___	6.	Preparation and pipetting of absorbing solution into sampling flask

Postsampling (Analysis and Calculation)

___	___	7.	Control sample analysis
___	___	8.	Sample aliquotting technique
___	___	9.	Evaporation and chemical treatment of sample
___	___	10.	Spectrophotometric technique
			a. Preparation of standard nitrate samples
			b. Measurement of absorbance, including blanks
			c. Calibration factor
			d. Wavelength and absorbance, including blanks
___	___	11.	Calculation procedure and checks
			a. Use of computer program
			b. Independent check of calculations

Comments