Section 3.14

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

(Grab Sampling - Ion Chromatographic Method)

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-liter round bottom borosilicate flask containing 25 ml of dilute sulfuric acid-hydrogen peroxide absorbing reagent. The nitrogen oxides, NO and NO_2, react with the absorbing reagent to form nitrate ion which is analyzed by ion chromatography (IC). The method does not respond to nitrous oxide, N_2O.

The reactions that describe absorption of the NO_x are distinct for NO and NO_2. The common feature of the reactions is the formation of nitrate, NO_3^-, as nitric acid, HNO_3.

The absorption of NO involves an oxidation-reduction reaction where the oxidizing agent is the acidic hydrogen peroxide solution. The two half reactions are:

$$3H_2O_2 + 6H^+ + 6e^- = 6H_2O$$

and

$$2NO + 4H_2O = 2NO_3^- + 9H^+ + 6e^-;$$

and the overall reaction is:

$$2NO + 3H_2O_2 = 2NO_3^- + 2H^+ + 2H_2O.$$

The absorption of NO_2 presumably involves the reaction with water to form nitric acid and NO. NO_2 reacts with water to form nitric acid and nitrous acid, HNO_2:

$$2NO_2 + H_2O = HNO_3 + HNO_2.$$

The nitrous acid is unstable and decomposes:

$$3HNO_2 = 2NO + HNO_3 + H_2O.$$

The observed reaction is the sum of the two reactions above:

$$3NO_2 + H_2O = 2HNO_3 + NO.$$

Absorption of NO_2 proceeds faster than absorption of NO because NO_2 is more soluble in solution, where reaction occurs. In this respect, it should be noted that absorption of NO is quickened as a consequence of reaction with oxygen also present within the flask:

$$2NO + O_2 = 2NO_2.$$

If the gas being sampled contains insufficient oxygen for the conversion of NO to NO_2, then oxygen should be introduced into the flask by one of three methods: (1) before evacuating the sampling

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flask, flush it with pure cylinder oxygen, and then evacuate the 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.

Method 7A is applicable to the measurement of nitrogen oxides emitted from stationary sources. It may be used as an alternative to Method 7 (as defined in 40 CFR Part 60.8(b)) to determine compliance if the stack concentration is within the analytical range. The analytical range of the method is from 125 to 1250 mg NO_x, expressed as NO_2, per dry standard cubic meter (65 to 655 ppm). Higher concentrations may be analyzed by diluting the sample. The lower detection limit is approximately 19 mg/m^3 (10 ppm), but may vary among instruments.

The method description which follows is based on the method that was promulgated on December 8, 1983.

Section 3.14.10 contains a copy of Method 7A,[1] and blank data forms are provided in Section 3.14.12 for the convenience of the Handbook user.

Note: Because of similarities between Method 7A and Method 7 sampling equipment and procedures, in most cases only the differences in Method 7A are presented in detail in this section (3.14). However, all tasks are shown in the activity matrices and data sheets needed to perform Method 7A are included, whether or not differences occur in the written descriptions. Other Method 7A procedures are referenced to the corresponding description in Section 3.6, Method 7. This is done for both time savings to the reader and cost savings to the Government.

METHOD HIGHLIGHTS

Section 3.14 (Method 7A) describes the required procedure for sampling and analyzing of nitrogen oxides emissions from stationary sources. For the method, a grab sample is extracted from a point in the stack, and collected in a previously evacuated flask containing a sulfuric acid-hydrogen peroxide absorbing solution. With the exception of nitrous oxide, the nitrogen oxides are oxidized to nitrate which is analyzed by ion chromatography (IC). Results are expressed as concentrations of nitrogen dioxide (NO_2). The applicable regulation should be consulted to determine whether additional measurements, such as velocity or O_2 determinations, are required.

The absorbing reagent for EPA Method 7A has a sulfuric acid concentration one-tenth that of EPA Method 7. In all other respects, the sampling train and sampling procedures of EPA Method 7A are identical to those of EPA Method 7. Sample preparation involves only dilution to reach a measurable concentration range for the ion chromatograph.

Ion chromatography is a relatively recent analytical development. The reader is referred to the literature for detailed descriptions of the subject.[2-12] Small, et al.,[2] developed the technique using the principles of ion exchange chromatography and conductimetric detection. Previous attempts to use this type of detection were unsuccessful because of the presence of the background electrolyte used for elution of the ionic species. Small, et al., used a novel combination of resins to separate the ions of interest and neutralize the eluent from the background.

The aqueous sample is introduced into a fixed-volume sample loop by using a plastic syringe. Once injected, the sample is carried through a separation column at different rates according to their relative affinities for the resin and the eluent and are therefore separated into discrete bands. The separated ions are then passed through a post-separation suppressor device, a source of hydrogen ion (H^+), which converts the eluent ions into a less conducting weak acid while converting the analyte ions into a highly conducting form. This permits the use of a conductivity cell as a very sensitive detector of all ionic species.

Gjerde, et al.,[11] described a modified ion chromatographic method that eliminates the need for a suppressor device. Anions are separated on a column containing an anion-exchange resin with a low exchange capacity. Because of the low capacity, a very dilute solution of an aromatic organic acid salt may be used as the eluent. The conductance of the eluent is sufficiently low that no suppression is needed.

For Method 7A, either suppressed or non-suppressed IC may be used. The basic ion chromatograph will have the following components:

(a) sample injection device,

(b) anion separation column,

(c) anion suppressor column, either packed bed or fiber type (not required for non-suppressed IC),

(d) conductivity detector, and

(e) recorder.

Two critical aspects of Method 7A are (a) the measurement of the gaseous sample volume, and (b) the preparation of the calibration standards for the ion chromatograph. Analysts are advised to observe specified procedures carefully at these points of the method. Analysts performing the method should be well trained in the use of the ion chromatograph.

Collaborative testing of EPA Method 7A has not been performed. However, from a technical standpoint, it can be expected that EPA Method 7A will exhibit accuracy and precision as good as, if not better than, EPA Method 7.

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 7A, Figure 3.1) to assist the user in finding a similar completed form in the method description (Section 3.14.3). On the blank and filled-in forms, the items/parameters that can cause the most significant errors are designated with an asterisk.

1. Procurement of Apparatus and Supplies

Section 3.14.1 (Procurement of Apparatus and Supplies) gives specifications, criteria, and design features for the required equipment and materials. The sampling apparatus for Method 7A has the same design features as that of Method 7. Section 3.14.1 can be used as a guide for procurement and initial checks of equipment and supplies. The activity matrix (Table 1.1) at the end of the section is a summary of the details given in the text and can be used as a quick reference.

2. Pretest Preparations

Section 3.14.2 (Calibration of Apparatus) addresses the required calibration procedures and considerations for the Method 7A sampling equipment (same as Method 7) and analytical equipment (the ion chromatograph). Required accuracies for each component are also included. A pretest sampling checklist (Figure 3.1 in Section 3.14.3) or a similar form should be used to summarize the calibration and other pertinent pretest data. 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 personnel involved in calibration activities.

Section 3.14.3 (Presampling Operations) provides the tester with a guide for equipment and supplies preparation for the field test. With the exception of the preparation of certain reagents, these are the same as for Method 7. A pretest preparation form (Figure 3.2, Section 3.14.3) 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 Method 7A.

Activity matrices for the calibration of equipment and the presampling operations (Tables 2.2 and 3.1) summarize the activities.

3. On-Site Measurements

Section 3.14.4 (On-Site Measurements) contains step-by-step procedures for sample collection and for sample recovery. Sample collections are the same as for Method 7; sample recovery procedures differ slightly from Method 7 in that the sample pH does not have to be checked and adjusted. The on-site checklist (Figure 4.3, Section 3.14.4) provides the tester with a quick method of checking the on-site 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-hour sample residence time in the flask must be observed. Table 4.1 provides an activity matrix for all on-site activities.

4. Posttest Operations

Section 3.14.5 (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 operations form (Figure 5.1, Section 3.14.5) provides 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 calibration standards is conducted in conjunction with the analysis of the field samples. Strict adherence to Method 7A analytical procedures must be observed.

Section 3.14.6 (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 chances of calculation error.

Section 3.14.7 (Maintenance) provides the tester with a guide for a maintenance program. This program is not required, but should reduce equipment malfunctions. Activity matrices (Tables 5.1, 6.1,

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and 7.1) summarize all postsampling, calculation, and maintenance activities.

5. Auditing Procedure

Section 3.14.8 (Auditing Procedure) provides a description of necessary activities for conducting performance and system audits. When Method 7A is used to demonstrate compliance with an EPA pollutant emission standard, a performance audit is required to be conducted of the analytical phase of the method. The data processing procedures and a checklist for a systems audit are also included in this section. Table 8.1 is an activity matrix for conducting the performance and system audits.

Section 3.14.9 (Recommended Standards for Establishing Traceability) provides the primary standard to which the analysis data should be traceable.

6. References

Section 3.14.10 contains the promulgated Method 7A; Section 3.14.11 contains the references cited throughout the text; and Section 3.14.12 contains copies of data forms recommended for Method 7A.

PRETEST SAMPLING CHECKS

(Method 7A, 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 7A, 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 Water Absorbing solution*							
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 7A, 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?* _____

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 water and rinse added to bottle containing sample? _____

_____

* Most significant items/parameters to be checked.

** Note that absorbing solution for Method 7A is different from that of Method 7.

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POSTTEST OPERATIONS
(Method 7A, Figure 5.1)

Reagents

Sodium nitrate dried at 105° to 110°C for a minimum of 2 hours before use? _____

Stock standard solution (sodium nitrate) less than 1 month old? _____

Sample Preparation

Has liquid level noticeably changed?* _____

Original volume _____ Corrected volume _____

Analysis

Standard calibration curve prepared?* _____

All calibration points within 7 percent of linear calibration curve?* _____

Reagent blanks made from absorbing solution or eluent solution? _____

Same injection volume for both standards and samples? _____

Duplicate sample values agree within 5 percent of their mean? _____

All analytical data recorded on checklist and laboratory form? _____

_____

* Most significant items/parameters to be checked.

1.0 PROCUREMENT OF APPARATUS AND SUPPLIES

A schematic of the sampling train used for Method 7A is shown in Figure 1.1. The train and sampling procedures are identical to those for Method 7. The sample recovery procedures and equipment are also identical, with the exception that there is no need to check and adjust the pH of the samples. The analytical procedures and equipment involved are different.

Specifications, criteria, and/or design features are given in this section to aid in the selection of equipment or any components that are different from those in Section 3.6.1. Procedures and limits (where applicable) for acceptance checks are also given. 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% may be acceptable, subject to approval.

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 provided in Section 3.14.12 for the convenience of the Handbook user. Calibration data generated in the acceptance check are to be recorded in the calibration log book.

The following equipment is that which is specified in Method 7A and has not already been described in Section 3.6.1 for Method 7. Table 1.1 at the end of this section summarizes quality assurance activities for the procurement and acceptance of all apparatus and supplies for Method 7A including the equipment described in Section 3.6.1.

1.1 Analysis

For the analysis, the following equipment is needed. Alternative instrumentation (and corresponding procedures) will be allowed, provided the calibration precision discussed in Section 3.14.2 and acceptable accuracy can be met.

1.1.1 Volumetric Pipets - Class-A volumetric pipets are required. For making up the calibration standards, pipets of the following sizes are needed: one 1-ml, one 2-ml, one 4-ml, one 6-ml, and one 10-ml. Enough 5-ml pipets are needed for preparing calibration standards, blanks, and samples.

1.1.2 Volumetric Flasks - Two Class-A 50-ml volumetric flasks are needed for each sample, and one Class-A 50-ml volumetric flask is needed for each standard and each blank. Also required are Class-A 200-ml and Class-A 1000-ml sizes. Additional volumetric flasks (50-ml) may be required for audit samples and for dilution of samples having concentrations in excess of the highest standard.

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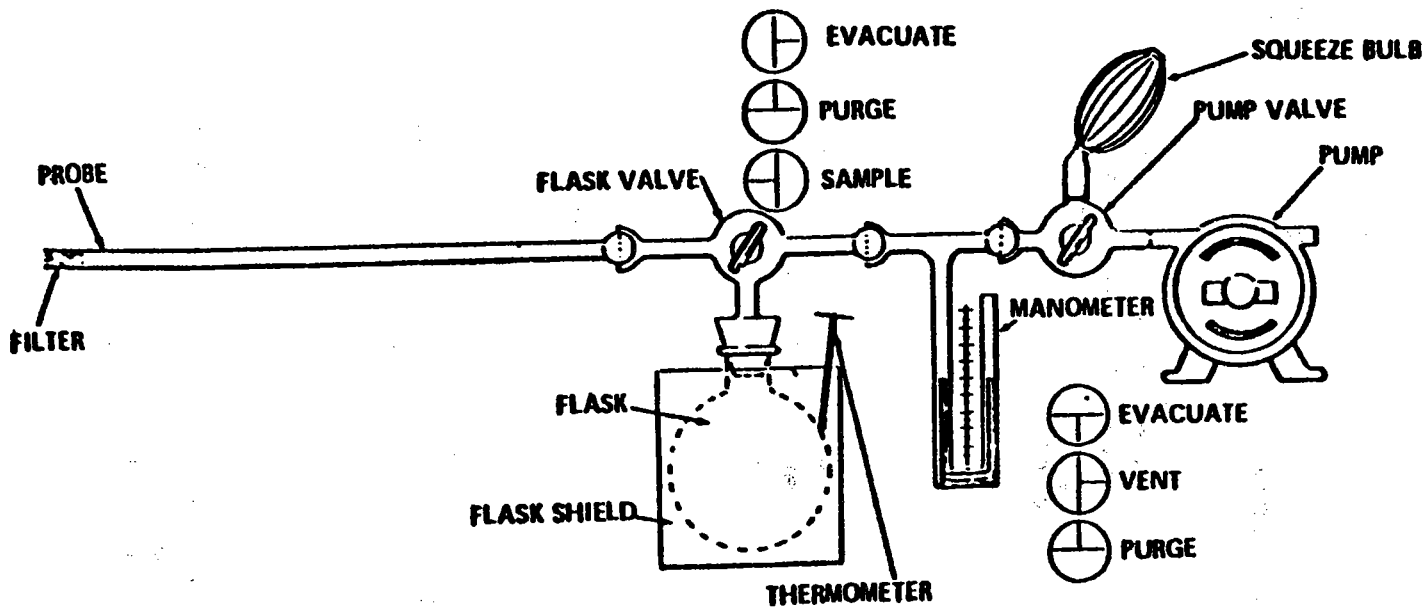

Figure 1.1. Method 7A evacuated flask sampling train.

(4.8)

Item description	Qty.	Purchase order number	Vendor	Date		Cost	Disposition	Comments
				Ord.	Rec.			
2120i Automated Ion Chromatograph	1	1035	Dionex	1/2/85	1/15/85	$10,000	Calibrated; ready for use 1/22/85	RRS

Figure 1.2. Example of a procurement log.

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

1.1.4 Ion Chromatograph - The ion chromatograph should, at a minimum, have the components described below.

Sample Injection Device - This device must be capable of delivering a reproducible volume of sample to the ion chromatograph.

Columns - The ion chromatograph should have an anion separator column capable of giving duplicate results within 5 percent of mean value and of resolving the nitrate ion from sulfate ion and from other species present. Both the Dionex HPIC-ASC fast run anion column for suppressed IC and the Wescan 269-029 Anion/R Column for non-suppressed IC have been demonstrated to give acceptable separation. If suppressed IC is to be used, an anion suppressor column is required. The Dionex AFS anion fiber suppressor (recommended) or ASC-1 general purpose suppressor may be used. Suppressor columns are generally produced as proprietary items; however, one can be made in the laboratory using the resin available from BioRad Company, 32nd and Griffin Streets, Richmond, California.

Pump - The pump must be capable of maintaining a steady eluent flow as required by the system.

Flow Gauges - These must be capable of measuring the specified eluent flow rate. It is recommended that the gauge be calibrated upon receipt.

Conductivity Detector with Temperature Compensation - It should be capable of giving responses that can be integrated with a precision of ± 5 percent. It is recommended that the detector be calibrated according to manufacturer's procedures prior to initial use.

Recorder - It should be compatible with the output voltage of the detector.

1.2 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 grade available.

1.2.1 Sampling - To prepare the absorbing solution, cautiously add 2.8 ml concentrated H_2SO_4 to a 100-ml flask containing water (see specifications in Subsection 1.2.3 below), and dilute to volume with mixing. Add 10 ml of this solution, along with 6 ml of 3%

hydrogen peroxide that has been freshly prepared from 30% hydrogen peroxide, to a 1-liter flask. Dilute to volume with water (see Subsection 1.2.3), and mix well. The absorbing solution must be used within 1 week of its preparation and, if possible, within 24 hours. Store in a dark-colored bottle. Do not expose to extreme heat or direct sunlight. Refrigerate the 30% hydrogen peroxide solution. Note: The H_2SO_4 content of this absorbing solution is 10 times less than that used for Method 7. The solution is prepared in this manner to avoid interference from sulfate ions during the analysis by IC.

1.2.2 Sample Recovery - Use ASTM D1193-82, Type III water (see Subsection 1.2.3) for sample recovery and in making various solutions. 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.

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

Water - Water should be used which conforms with ASTM specification D1193-82, Type III. Type III water is prepared by distillation, ion exchange, reverse osmosis, or a combination thereof, followed by polishing with a 0.45 µm membrane filter. The specifications for Type III water are shown below.

Specifications for ASTM D1193-82, Type III Water

Total matter, max., (mg/L)	1.0
Electrical conductivity, max., (µmho/cm) at 25°C	1.0
Electrical resistivity, min., (µmho/cm) at 25°	1.0
pH at 25°C	6.2 to 7.5
Minimum color retention time of $KMnO_4$, (min)	10
Maximum soluble silica, (µg/L)	10

Note: Mention of "water" anywhere in this Section (3.14) refers to ASTM D1193-82, Type III water as described above. By using water from the same source for making reagents, calibration standards, and eluents for the ion chromatograph, the effects of trace quantities of nitrate in the water will be negated with regard to sample analysis. Therefore, a water blank correction is not necessary in the development of the calibration curve.

Sodium Nitrate - Dry an adequate amount of sodium nitrate ($NaNO_3$) at 105° to 110°C for a minimum of 2 hours just prior to preparing the standard solution. (The analyst should note that potassium nitrate, KNO_3, is used in EPA Method 7; KNO_3 is an acceptable alternative for Method 7A.)

Stock Standard Solution, 1 mg NO_2/ml - To prepare, dissolve exactly 1.847 g of dried $NaNO_3$ (or 2.198 g of dried KNO_3) in water, and dilute to 1 liter in a volumetric flask; mix well. This solution is stable for 1 month and should not be used beyond this time.

The use of old solution may cause results to be biased high. Solutions are readily contaminated by microorganisms that feed on nitrate ion. Unquantified loss of nitrate ion from the standard solution causes the high bias.

Working Standard Solution, 25 µg NO_2/ml - Dilute 5 ml of the standard solution to 200 ml with water in a volumetric flask, and mix well.

Eluent Solution - Use an eluent appropriate to the column type and capable of resolving nitrate ion from sulfate and other species present. The following eluents have been demonstrated to give acceptable separation:

Suppressed IC -- 0.0024M Na_2CO_3/0.003M $NaHCO_3$. To prepare, weigh 1.018 g of sodium carbonate (Na_2CO_3) and 1.008 g of sodium bicarbonate ($NaHCO_3$), and dissolve in 4 liters of water.

Non-Suppressed IC -- 0.007M p-hydroxybenzoic acid, pH 8.4. To prepare, weigh 3.867 g p-hydroxybenzoic acid, and dissolve in 4 liters of water. Adjust to pH 8.4 with lithium hydroxide.

Quality Assurance Audit Samples - Same as required by Method 7 (Section 3.6.8).

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TABLE 1.1. ACTIVITY MATRIX FOR PROCUREMENT OF APPARATUS AND SUPPLIES

Apparatus/ supplies	Acceptance criteria	Frequency and method of measurement	Action if requirements are not met
Probe	Borosilicate glass stainless steel, or Teflon tubing capable of removing moisture condensation	Upon receipt, visually check for cracks or flaws and heating capability	Return to supplier, and note in procurement log
Collection flask	Two-liter borosilicate glass round bottom, short neck w/24/40 standard taper opening	Upon receipt, visually check, and leak check	As above
Flask valve	Borosilicate glass T-bore stopcock w/24/40 standard taper male joint (joint connection to be made by glassblower)	Visually check upon receipt	As above
Temperature gauge	Dial-type, capable of measuring from -5° to $+50^{\circ}C$ within $1^{\circ}C$	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-, 4-, 5-, 6-, 10-, 25-ml Class-A glass and graduated 5-ml	As above	As above

(continued)

Table 1.1 (continued)

Apparatus/ supplies	Acceptance criteria	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
Analytical balance	Capable of measuring to ±0.1 mg	Check with standard weights upon receipt and before each use	Replace or return to manufacturer
Volumetric cylinders	50-ml (Class-A) with 1-ml divisions	As above	As above
Ion Chromatograph 1. Columns	1. Capable of giving nitrate ion peaks with baseline separation; capable of giving duplicate results within 5 percent of mean value	1. Check during analyses	1. Consult operator's manual; regenerate suppressor column; clean separator column; check performance of components below; replace column(s) if above actions are unsuccessful

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Table 1.1 (continued)

Apparatus/ supplies	Acceptance criteria	Frequency and method of measurement	Action if requirements are not met
2. Pump	2. Capable of delivering eluent at constant and repeatable flow rate	2. Check during analyses by monitoring flow rate	2. Consult operator's manual; oil, clean, rerepair, replace, or return to manufacturer; check tubing of ion chromatograph for leaks or obstructions; check flow meter performance
3. Flow control	3. Capable of giving repeatable indications of eluent flow rate	3. Check calibration and repeatability upon receipt	3. Consult operator's manual; adjust, repair, replace, or return to manufacturer; check pump performance
4. Conductivity detector	4. Capable of giving responses which can be manually or electronically integrated within a precision of 5 percent	4. Calibrate according to manufacturer's instructions prior to use	4. Consult operator's manual; Repair, replace, or return to manufacturer
5. Recorder	5. As above, if used to record responses for manual integration	5. Check during analyses	5. Consult operator's manual; adjust speed
Water	Meets ASTM D1193-82; Type III	Check each lot, or specify type when ordering	Replace, or return to manufacturer

(continued)

Table 1.1 (continued)

Apparatus/ supplies	Acceptance criteria	Frequency and method of measurement	Action if requirements are not met
Sulfuric acid	Concentrated, ACS reagent grade	As above	As above
Hydrogen peroxide	30% aqueous solution, ACS reagent grade (store refrigerated)	As above	As above
Sodium nitrate	ACS reagent grade	As above	As above
Sodium carbonate	ACS reagent grade	As above	As above
Sodium bicarbonate	ACS reagent grade	As above	As above
p-Hydroxybenzoic acid	ACS reagent grade	As above	As above

2.0 CALIBRATION OF APPARATUS

Calibration of apparatus is one of the most important functions in maintaining data quality. It is highly recommended that a laboratory log book of all calibrations be maintained. Calibration procedures for the collection flasks, field barometer, thermometers, vacuum gauge, and analytical balance used in Method 7A are the same as those described for Method 7 (see Section 3.6.2) and are not duplicated in this section; a form, however, for use in the analytical balance calibration is shown in Figure 2.1. Detailed calibration procedures for the ion chromatograph system are described in this section. Table 2.2 at the end of this section summarizes the quality assurance activities for all calibrations in Method 7A including those described in Section 3.6.2.

2.1 Ion Chromatograph System

For Method 7A, the calibration of the ion chromatograph (IC) system, except for the initial calibration of the conductivity detector, is conducted in conjunction with analysis of the field samples. Specifically, the field samples are analyzed twice in between three analyses of the ion chromatograph calibration standards; the exact sequence is discussed in detail in Section 3.14.5. The three analyses of the calibration standards are used to prepare a calibration curve that is used to determine a calibration factor for calculating the concentration of nitrogen oxides in the field samples. It is, however, highly recommended that the analyst conduct a preliminary calibration of the IC any time the system is set up for analysis of NO_x field samples. For this reason, the full discussion of the analysis of calibration standards and preparation of the calibration curve is presented in this section. Also addressed in this section are preliminary considerations in preparing the IC system for use and other considerations for ensuring quality data.

2.1.1 Preliminary Considerations

Conductivity Detector - Prior to its initial use, the conductivity detector of the ion chromatograph must be calibrated by the method described in the operator's manual.

Recorder - A strip chart recorder compatible with the output voltage range of the conductivity detector may be used to record the ion chromatogram. Manual measurement techniques that can be used for quantitation of the chromatogram include (a) peak height, (b) peak area by triangulation, (c) peak area by multiplying peak height times the peak width at half-height, (d) peak area by cutting out the peak from the chromatogram and weighing it on an analytical balance, and (e) peak area by planimetry.

The use of an electronic integrator, if available, is recommended for greater accuracy and precision. The electronic integrator can be used in the peak area mode when the integration parameters are set up

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
2/25/85	0.5504	0.998	10.0002	50.0006	100.0004	BLT

Figure 2.1. Analytical balance calibration form.

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properly. The key integration parameters for peak area determination concern the identification of the beginning and end of a peak and the placement of the baseline under the peak. Analysts should carefully read the operator's manual and understand the selection and set up of the integration parameters for their particular integrator. The electronic integrator can also be used in the peak height mode provided that the peaks are symmetrical and an acceptable standard calibration curve can be generated without any calibration point deviating from the line by more than 7 percent (see Subsection 2.1.3 of this section).

Sample Injection Device Contamination Check - The analyst is encouraged to check the sample injection device for contamination by injecting water before the calibration standards are analyzed. Contaminants will appear as peaks on the chromatogram. Repeated injections of water should be used to remove contaminants from the sample injection device. If certain peaks remain after several injections of water then the water may be contaminated and should be replaced.

Separation of Nitrate, NO_3^- - To ensure accurate results from the ion chromatographic analysis, baseline separation of the nitrate ion (NO_3^-) peak from the other ion peaks should be achieved. For Method 7A, the separation of the NO_3^- peak from the sulfate ion ($SO_4^=$) peak is of major concern. The $SO_4^=$ originates primarily from the sulfuric acid absorbing reagent. A second source of $SO_4^=$ in a sample may be sulfur dioxide present in the effluent stream sample. Figures 2.2a and 2.2b show two chromatograms, one having overlapping NO_3^- and $SO_4^=$ peaks, and the other having baseline separation of the NO_3^- and $SO_4^=$ peaks. The sulfuric acid concentration in the absorbing reagent used for Method 7A is 10 times less than that for Method 7 to minimize the problem of adequately separating NO_3^- from $SO_4^=$.

The analyst is encouraged to check the performance of the ion chromatograph system before analyzing samples in order to ensure baseline separation of NO_3^- is attainable. A test for baseline separation of NO_3^- can be made by preparing a performance check sample and analyzing during the recommended preliminary calibration as follows:

1. Pipet 10.0 ml of the 25 μg NO_2/ml working standard solution into a 50-ml volumetric flask.

2. Into the same volumetric flask, pipet 5 ml of absorbing reagent.

3. Dilute with water to the mark.

4. Analyze this performance check sample with calibration standards in the same manner as described for field samples (see Subsections 5.1.4, 2.1.2, and 2.1.3).

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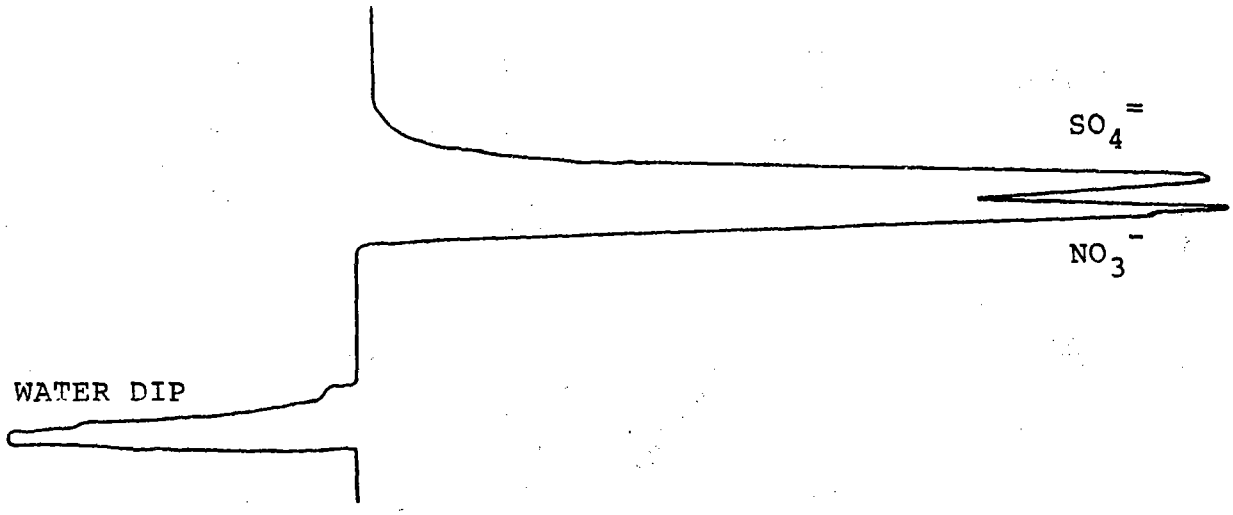

Figure 2.2a. Example chromatogram having overlapping peaks.

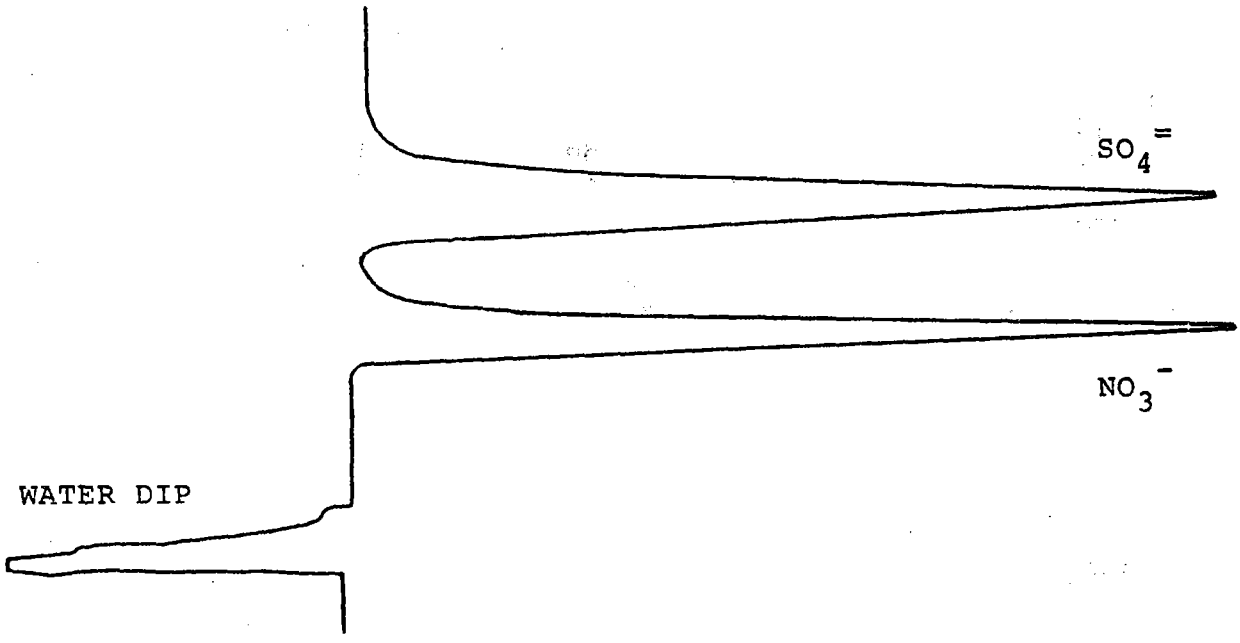

Figure 2.2b. Example chromatogram showing baseline separations of peaks.

The analyst should check the chromatogram of the performance check sample for baseline separation. If the baseline separation is marginal for the performance check sample and the samples have NO_3 concentrations close to that of the highest standard (5 μg NO_2/ml), the analyst should closely monitor subsequent field sample chromatograms to ensure that results are not adversely affected by deterioration of the ion chromatograph column or varying performance of the ion chromatograph.[13]

The final aspect of the performance check involves a precision assessment. The result from the analysis of the performance check sample should agree within 5 percent of the value for the 5 μg NO_2/ml calibration standard data point.

2.1.2 Preparation of Calibration Standards - The preparation of the calibration standards is perhaps the most critical aspect of the Method 7A analysis, since the quality of sample results will only be as good as the quality of the calibration. The steps observed in the preparation of the calibration standards are detailed below.

Stock Standard Solution

1. Dry approximately 5 g ACS-grade sodium nitrate ($NaNO_3$) in an oven at 105° to 110°C for at least 2 hours prior to use. Drying of the $NaNO_3$ is necessary to prevent NO_x results from being biased high because of absorbed moisture.

2. Calibrate the analytical balance using a 2-g Class-S calibration weight (see Figure 2.1 for an example form). The balance reading should agree within 2 mg of the Class-S calibration weight. Corrective actions should be taken if this agreement is not achieved.

3. Allow the dried $NaNO_3$ to cool to room temperature in a desiccator. When the reagent has cooled, weigh out 1.847 g to ±0.002 g. Cooling is required to prevent weighing errors originating from convection currents. Storage of the $NaNO_3$ in the desiccator ensures that moisture will not be adsorbed.

4. Place weighed $NaNO_3$ in a 1-liter Class-A volumetric flask and dissolve in exactly 1 liter of water. Label the flask accordingly:

$NaNO_3$(aq)
Stock Standard
for EPA Method 7A
(1 mg NO_2/ml)
Date
Analyst's Initials

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The solution is stable for one month and should not be used beyond that time. After about one month, there is increased risk that the reagent will be contaminated by microorganisms that feed on nitrate. The use of such contaminated reagents will cause NO_x results to be biased high.

Working Standard Solution

5. Pour about 25 ml of stock standard solution into a clean, dry beaker.

6. Using a 5-ml Class-A pipet, pipet 5 ml of stock standard solution into a 200-ml Class-A volumetric flask. Dilute to the calibration mark with water, and mix well.

   This solution is the Working Standard; its nitrate content represents a concentration of 25 µg NO_2/ml. The working standard solution is prepared fresh for each set of analyses.

Calibration Standards

7. Prepare a series of five calibration standards by pipetting 1.0, 2.0, 4.0, 6.0, and 10.0 ml of working standard solution (25 µg/ml) into a series of five 50-ml Class-A volumetric flasks. The standard masses will equal 25, 50, 100, 150, and 250 µg NO_2, respectively. Dilute to the mark with either water or eluent solution, and mix well.

   The choice of diluent is determined by practical considerations. If the "water dip" (see Figure 2.2) is expected to interfere with the nitrate peak of the chromatogram, then eluent should be used as the diluent since this will minimize the "water dip." Note: Whichever diluent is used, it is important for the analyst to use the same diluent for the field samples, the calibration standards, and the blank, as specified in the Federal Register.

2.1.3 Preparation and Validation of the Calibration Curve - Method 7A specifies the determination of a calibration factor, S, which is used to calculate the concentration of NO_x in the field samples. S is defined as the reciprocal of the slope of the calibration curve, which is determined by preparing or calculating a linear regression plot of the standard masses of the calibration standards (µg) versus instrument response (peak height or area). Determination of S does not take into account the y-intercept, if present, of the calibration curve.

The first subsection that follows describes the calibration procedures and the determination of the calibration factor as specified in Method 7A. The second subsection offers an alternative approach acceptable to the Administrator, for conducting the calibration

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calculations that utilize the non-zero y-intercept, if present. This approach is based on the calibration procedures of Method 7D and involves the determination of a calibration equation. A data form which can be used with both approaches is presented in Figure 2.3.

Determination of the Calibration Factor (S) - The determination of the calibration factor, S, involves the three steps presented below.

1. Analyze each of the calibration standards (25, 50, 100, 150, and 250 μg NO_2) three times using the ion chromatograph. Document chromatograms (see Subsection 5.1.4) and record the results on the analytical data form for calibration standards (Figure 2.3). Average the three responses for each of the five standards.

2. Use the average response for the five calibration standards to calculate the slope of the calibration curve, graphically, by least squares, or by linear regression. To calculate the slope graphically, plot the instrument response (peak height or area count) on the y-axis against the corresponding NO_2 standard concentration value on the x-axis. Draw a "best-fit" line between the points and determine the slope of the line. Least squares (a method acceptable to the Administrator) can be hand calculated and is shown in Figure 2.3. To calculate the slope by linear regression, use the NO_2 standards as the independent variable (x-axis) and the corresponding instrument response as the dependent variable (y-axis).

3. The calibration factor, S, is calculated as the reciprocal of the slope of the calibration curve, determined from the "best-fit" line or the linear regression equation. Any y-intercept is ignored.

4. The calibration factor, S, and therefore, the curve must be validated. Using the calibration factor for calculation, the predicted sample mass for each calibration standard is compared with the known value for that standard. The predicted sample mass must not deviate from the known standard concentration by more than 7%. The quantity "μg NO_2 Predicted" is calculated using the calibration factor (S) and the detector response (H), in millimeters or integrator response, as shown in Equation 2-1.

Equation 2-1

$$\mu g\ NO_2\ \text{Predicted} = S\ (\mu g/mm) \times \text{Detector Response H}\ (mm)$$

The deviation of each predicted sample mass from the known mass is calculated using Equation 2-2.

Equation 2-2

$$\text{Deviation}\ (\%) = \frac{\mu g\ NO_2\ \text{Predicted} - \mu g\ NO_2\ \text{Standard}}{\mu g\ NO_2\ \text{Standard}} \times 100\%$$

Plant pre-test calibration Location _____

Date 1/22/85 Analyst E. Estes

Was an integrator used? ___ yes ✓ no

Was the intercept (I) used for calculations? ___ yes ✓ no

Were all points within 7 percent of calculated value? ✓ yes ___ no

Sample Identifier	Sample Mass ($\mu g\ NO_2$)	Integrator Response or Peak Height (mm) H				Predicted Sample Mass ($\mu g\ NO_2$)	Deviation (%)
		1	2	3	Avg		
Std 1	25	6.1	6.4	6.2	6.23	25.36	+1.46
Std 2	50	12.5	12.9	13.0	12.80	52.11	+4.23
Std 3	100	25.3	24.9	25.5	25.23	102.72	+2.72
Std 4	150	38.1	39.1	38.6	38.60	157.15	+4.77
Std 5	250	60.1	59.9	59.6	59.87	243.75	−2.50

Predicted Sample Mass using Least Squares to Calculate Calibration Factor (S) with Zero Intercept

$$S = \frac{S_1H_1 + S_2H_2 + S_3H_3 + S_4H_4 + S_5H_5}{H_1^2 + H_2^2 + H_3^2 + H_4^2 + H_5^2}$$

$$S = \frac{(25)(6.23) + (50)(12.80) + (100)(25.23) + (150)(38.60) + (250)(59.87)}{(6.23)^2 + (12.80)^2 + (25.23)^2 + (38.60)^2 + (59.87)^2}$$

$S = 4.0713\ \mu g\ NO_2/mm$

Predicted Sample Mass ($\mu g\ NO_2$)

$\mu g\ NO_2 = H \times S = (6.23) \times (4.0713) = 25.36$ Equation 2-1

Predicted Sample Mass using Linear Regression to Calculate Calibration Factor (S) and Non-Zero Intercept (I)

$y = mx + b$; $m =$ _____; $b =$ _____;

$x = \frac{1}{m}(y - b)$; $\frac{1}{m} = S = \frac{1}{\_\_\_} =$ _____;

$y = H$; and $b = I$ (Intercept) = _____.

Predicted Sample Mass ($\mu g\ NO_2$)

$\mu g\ NO_2 = S(H - I)$ Equation 2-4

$\mu g\ NO_2$ at 25 μg standard = _____(____ - ____) = _____

Figure 2.3. Analytical data form for analysis of calibration standards.

This calculation is performed for each calibration standard using the average of the three response measurements. If any point (known concentration of standard) deviates from the line (predicted concentration) by more than ±7 percent, that standard should be remade and reanalyzed.

Linear regression using a hand-held calculator is recommended to obtain the slope (and equation) for the calibration curve. Inexpensive calculators are available which have linear regression programs that are quick and simple to use. Graphical techniques are relatively simple matters when all the calibration data points lie on or close to the line. However, when deviations from linearity occur, the placement of the "best-fit" line becomes ambiguous because the data points are not evenly distributed.

Determination of the Calibration Equation - As discussed previously, Method 7A directs that the calibration factor, S, be used to calculate the field sample analytical results. In cases where the calibration curve does not pass through the origin, the procedure of Method 7A could give biased results for both the field samples and the linearity check since the equation for the calibration curve will contain an intercept term not taken into account in the calculations. Accordingly, this section offers an alternative calibration approach adapted from Method 7D. The approach involves determination of a calibration equation which takes into account both the slope of the calibration curve and any y-intercept term and which is used in calculating the NO_x concentration of field samples.

Derive the linear calibration equation or curve using linear regression. The calibration equation should be expressed in the following form:

$$y = m x + b \qquad \text{Equation 2-3}$$

where

m = slope of the linear calibration curve, which is equal to the reciprocal of the calibration factor, 1/S, and

b = y-intercept of linear calibration curve which will be referred to as "I" for purposes of later calculations.

As discussed in the previous section, Method 7A requires that none of the calibration data points deviate from the calibration curve by more than 7 percent of the concentration at that point. Method 7A (Section 5.2.3) states that deviations can be determined by multiplying the calibration factor S times the peak height response for each standard. When the calibration equation with intercept is used, the quantity "μg NO_2 Predicted" is computed using the following equation:

$$\mu g\ NO_2\ \text{Predicted} = S\ (\mu g/mm) \left(\text{Detector Response H (mm)} - I\ (mm) \right) \qquad \text{Equation 2-4}$$

As before, calculation of the % deviation from the line is accomplished using Equation 2-2. If any deviation is greater than 7%, the corresponding standard should be remade and reanalyzed. If this does not result in improved results, other approaches are discussed in the following subsection "Other Considerations."

2.1.4 Other Considerations - Method 7A requires that if any calibration standard point deviates from the standard calibration curve by more than 7%, then that corresponding calibration standard is to be remade and reanalyzed. This corrective action may not always reduce the calibration point deviations below 7%. Some potential causes for deviation of the calibration points from the calibration curve include (a) improper pipetting procedures used to prepare calibration standards, (b) improper technique for manual sample injection into the ion chromatograph, (c) inaccurate measurement of the ion chromatograph response, and (d) non-linear detector response. Table 2.1 shows the precisions for calibration operations for Method 7A.

TABLE 2.1. TARGET PRECISIONS FOR CALIBRATION OPERATIONS OF METHOD 7A

Operation	Precision Target (%)
Pipetting	1
Introduction of Samples into Ion Chromatograph	<1
Measurement Response	
o Peak Height	1-4
o Triangulation	4
o Height X Width at Half-Height	3
o Electronic Integration	<0.5

Pipetting Procedure and Pipetting Errors - In preparing the calibration standards, pipetting is the most critical step. Serious errors can originate from poor pipetting technique. In general, errors will appear as high biased NO_x results. The correct pipetting procedure is described below.[14]

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The pipet should be inspected before use and checked to ensure that the tip is not chipped. The pipet should be replaced if a chip is observed.

The pipet should be rinsed with the reagent to be pipetted and checked for cleanliness before use as follows. Approximately 2 ml of reagent is drawn into the pipet, which is then rotated and tilted in order to expose the inner surface to the solution. The rinse solution is then allowed to drain freely from the pipet into a beaker assigned for waste. If the pipet is clean, the analyst will observe, after about 10 seconds, that all the rinse solution will have drained from the pipet with the exception of a small quantity remaining in the tip. If this is not observed, either the pipet should be cleaned, or another pipet should be obtained. The rinse and check for cleanliness should be performed at least once.

For the actual pipetting, reagent is drawn into the pipet until the liquid meniscus is above the calibration mark. The pipet is then withdrawn from the solution and the end is wiped with a laboratory tissue. Next, the pipet is brought to a vertical position and its tip is brought to touch the inside of the beaker assigned for waste. The liquid in the pipet is then allowed to drain slowly until the meniscus coincides with the calibration mark.

The pipet is then transferred to the appropriate container and, with the pipet in a vertical position and its tip touching the inside wall of the container, the liquid is allowed to drain freely into the container. The pipet's tip should be kept in contact with the wall for roughly 10 seconds after the liquid has apparently drained. The pipet is then removed from the container without disturbing the small amount of liquid remaining in the tip.

It is important to recognize that Class-A pipets are calibrated in a manner which accounts for the drainage time and the liquid remaining in the tip. If dirty pipets are used or if the proper draining technique is not observed, NO_x results will be biased high. Low biases will occur if the liquid remaining in the pipet tip is blown out into the receiving container. The significance of these biases depends on the size of the pipet involved. For example, the error with a dirty 25-ml pipet may be undetectable, while the error for a 1-ml pipet can easily exceed 10 percent.

The precision of the pipetting operation can be checked gravimetrically using water. The technique involves pipetting a known volume of water into a tared container and determining the weight of the water. The precision of the pipetting operation is estimated from the results of several repetitions.

The procedure for manually injecting a sample into the ion chromatograph can be a source of error when analyzing calibration standards, field samples, and QA samples. For fixed loop injection systems, considerable variation can result from injecting the sample

into the loop too fast, resulting in the sample loop not being completely filled. A slow, deliberate injection of the sample into the loop will completely fill the loop. The precision of the injection procedure can be checked by performing repetitive analyses on a single sample.

Chromatogram Quantitation - The choice of quantitation methods for the ion chromatograms can also be a source of error when analyzing calibration standards, field samples, and QA samples. As shown in Table 2.1, measurement of the detector response by manual methods has a higher degree of imprecision compared to measurement by electronic integration. Method 7A states that peak height measurement can be used provided the peaks are symmetrical and the required 7% deviation of calibration points from the standard calibration curves can be met. The peak height measurement method, even with symmetrical peaks, may not produce a linear standard caliration curve because the peak width of the higher concentration standards will typically be wider than the peak width of the lower concentration standards. Figure 2.4 shows the difference in the linearity of ion chromatographic calibration curves using the peak area mode and the peak height mode. The dead volume of the ion chromatograph system, particularly suppressed ion chromatograph systems, can also affect the peak width. Quantitation by peak area measurement will eliminate the biases caused by widening peaks provided the peak area measurement is done properly. The use of an electronic integrator in the peak area mode for ion chromatograms with baseline separation of the nitrate peak will produce the most precise calibration curves and subsequent accurate analyses of field samples and QA samples.

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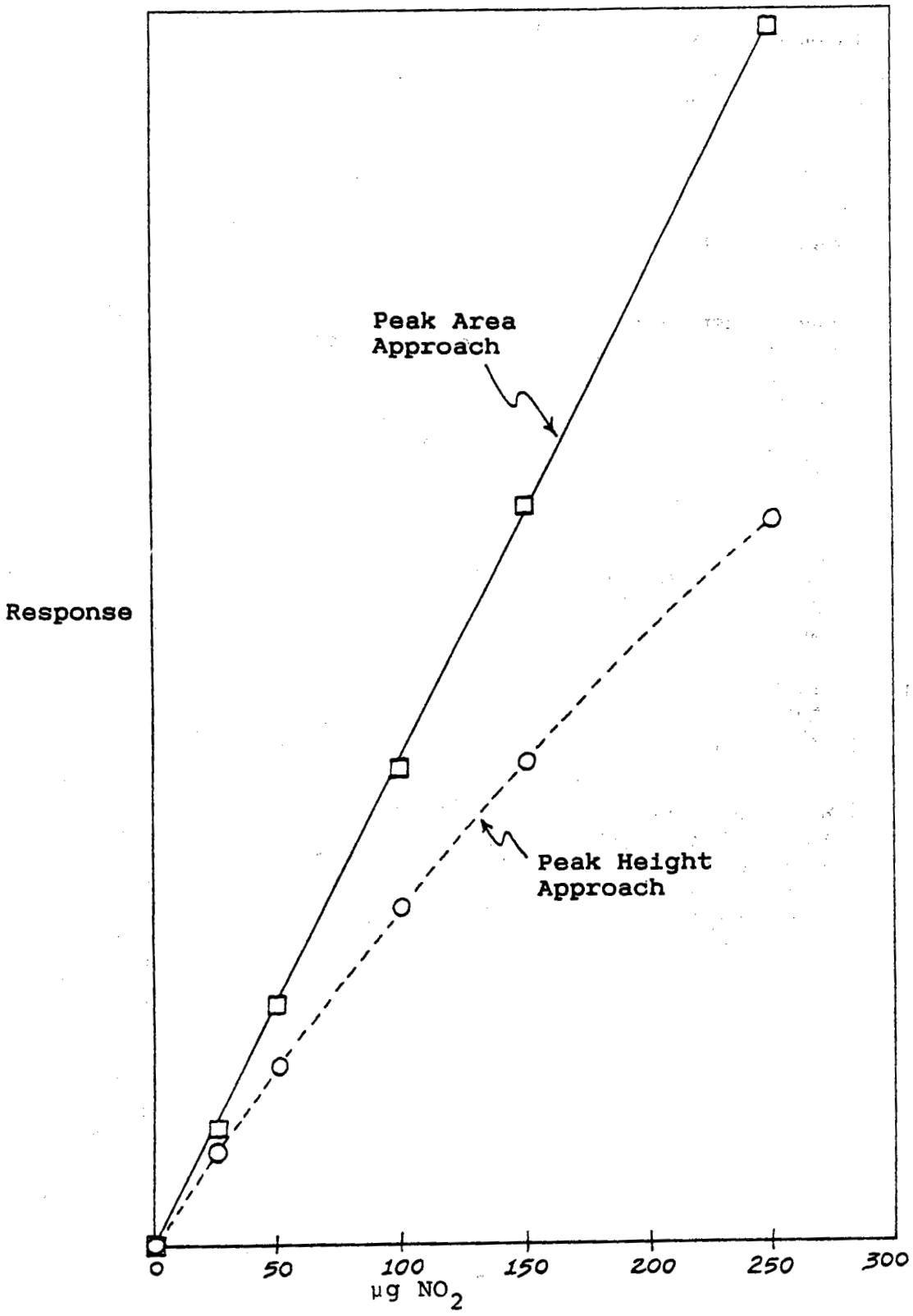

Figure 2.4. Linear and non-linear ion chromatographic calibration curves.

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TABLE 2.2. 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
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
Ion chromatograph	Calibration curve should be linear; data points for calibration standards must not deviate from the linear calibration curve by more than ±7 percent	With each set of field samples; calibration standards prepared from sodium nitrate	Interpret data using another technique: e.g., if using peak height, change to peak area; conduct additional analyses of calibration standards; calibrate conductivity detector; consult operator's manual

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3.0 PRESAMPLING OPERATIONS

This section addresses the preparation and packing of supplies and equipment needed for the sampling. The pretest preparation form (Figure 3.1) can be used as an equipment checklist. Many presampling operations for Method 7A are identical to those for Method 7. This section will only discuss the operations that are different; however all quality assurance activities for Method 7A presampling operations are summarized in Table 3.1 at the end of this section including those described in Section 3.6.3. See Section 3.0 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 sampling checks form (Figure 3.1) summarizes equipment calibration. The pretest preparations 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.

3.2 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. See Subsection 1.2.3 of Section 3.14.1 for water specifications.

3.2.1 Sampling - The absorbing reagent is prepared by adding 2.8 ml of concentrated sulfuric acid (H_2SO_4) to a 100-ml flask containing water and diluting to volume with mixing. Add 10 ml of this solution, along with 6 ml of 3% hydrogen peroxide (H_2O_2) that has been freshly prepared from a 30 percent solution, to a 1-liter flask. Dilute to volume with water, and mix well. Prepare fresh absorbing solution weekly, and avoid exposure to extreme heat or to direct sunlight, as these will cause the hydrogen peroxide to decompose. If the reagent must be shipped to the field, it is advisable that the absorbing reagent be prepared fresh on-site.

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

Date 2/25/85 Calibrated by RRS

Flask Volume

Flask volume 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.) 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							
Glass liner clean	✓		3	✓		✓	
Heated properly*	✓						
Leak checked	✓						
Collection Flask							
Clean	✓		14	✓		✓	
Leak checked	✓						
Temperature gauge	✓						
Evacuation System							
Leak-free pumps	✓		2	✓		✓	
Manifold and tubing	✓		3	✓		✓	
U-tube manometer	✓		2	✓		✓	
Barometer	✓		1	✓		✓	
Reagents							
Water	✓		1 liter	✓		✓	
Absorbing solution*	✓		1 liter	✓		✓	
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.

Stock standard solution - Dissolve exactly 1.847 g of dried sodium nitrate ($NaNO_3$) [or 2.198 g of dried potassium nitrate (KNO_3)] in water, and dilute to 1 liter in a volumetric flask; mix well. Prepare fresh after 1 month.

Working standard solution - Dilute 5 ml of the standard solution to 200 ml with water in a volumetric flask, and mix well. Note: One ml of the working standard solution is equivalent to 25 g of nitrogen dioxide.

Eluent solution - Weigh 1.018 g of sodium carbonate ($NaCO_3$) and 1.008 g of sodium bicarbonate ($NaHCO_3$), and dissolve in 4 liters of water. Other eluents may be used (see Subsection 1.4.3).

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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	Replace
	2. Heating properly if equipped with heating system	2. As above	Replace or repair
	3. Leak free	3. Pressure <380 mm (15 in.) Hg	Replace or repair
Collection flask	Clean; volume within 10 ml	Before each test, clean with strong detergent and hot tap water, and rinse with tap water and then ASTM Type III 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 Reagent			
Sulfuric acid concentrated	Final concentration: 0.28 ml/liter	Prepare fresh absorbing solution weekly; use graduated pipette	Make up new solution
Hydrogen peroxide, 3%	6 ml/liter		
Water	Deionized distilled to ASTM specifications D 1193-82, Type III		Prepare fresh for each analysis period

(continued)

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TABLE 3.1. (continued)

Characteristic	Acceptance limits	Frequency and method of measurement	Action if requirements are not met
Analytical Reagents			
Stock standard solution	1. 1.847 ±0.001 g $NaNO_3$ ACS reagent grade into a 1-liter volumetric flask (Class-A)	1. On makeup of solution use analytical balance	1. Make up new solution
	2. Stored for less than 1 month	2. Date solution	2. As above
Working standard solution	5 ml of stock solution into 200-ml volumetric flask (Class-A)	On makeup of solution, use Class A pipet and proper technique	As above
Eluent solution	1.018 g ± 0.001 g of $NaCO_3$ and 1.008 g ± 0.002 g of $NaHCO_3$ in 4 liters	On makeup of solution, use analytical balance	As above
Packing Equipment for Shipment			
Probe	Rigid container lined with polyethylene foam	Prior to each shipment	Repack
Collection flasks and valves	Rigid container lined with polyethylene foam	As above	As above
Evacuation system, temperature gauges, vacuum lines, and reagents	Sturdy case lined with polyethylene foam	As above	As above
Evacuation pump	Shipping container or housing designed for travel	As above	As above

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4.0 ON-SITE MEASUREMENTS

The on-site activities include transporting equipment to the test site, unpacking and assembling the equipment, confirming duct measurements and traverse points (if volumetric flow rate is to be determined), determining the molecular weight of the stack gas, sampling for oxides of nitrogen, and recording the data. These activities are the same as for Method 7 (Section 3.6.4), with the exception of a portion of the sample recovery procedures as described below. Blank data forms can be found in Section 3.14.12 for the convenience of the Handbook user. Table 4.1 at the end of this section summarizes the quality assurance activities relative to all on-site measurements in Method 7A, including those described in Section 3.6.12.

4.1 Sampling

On-site sampling procedures for Method 7A are the same as those for Method 7. See Subsection 4.3 of Section 3.6.4 for detailed descriptions of sampling procedures. For convenience, examples of completed field data forms for Method 7 are reproduced in this section (Figures 4.1A and 4.1B); blank copies are provided in Section 3.14.12.

4.2 Sample Recovery

Sample recovery procedures should be performed as described for Method 7 (Section 3.6.4), with the exception that the steps for checking and adjusting the pH of the sample should be deleted (note changes in Figures 4.2A, 4.2B, and 4.3).

A 16-hour minimum sample absorption period is required as in Method 7. Samples should be recovered within 4 days of collection.[15] As currently written, the method states that the samples should be stored no more than 4 days between collection and analysis. However, a recent study[16] utilizing samples from nitric acid plants and power plants indicates that the storage period between recovery and collection may be extended to 30 days.

Plant Acme Power Plant City Coalbend, Montana

Sample location ESP Outlet, Boiler #1 Date 2/27/85

Operator GBO 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	E-13	2013	13.6	13.7	2.54	73	533
AP-2	B-10	0745	210	EE-10	2010	13.7	13.8	2.34	73	533
AP-3	C-10	0801	210	EE-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 Coalbend, Montana

Sample location ESP Outlet, Boiler #1 Date 2/27/85

Operator GBO 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 in. Hg			Initial temperature	
						Leg A_i	Leg B_i	P_i[a]	°C (t_i)	°R(T_i)[b]
AP-1	B-11	0733	100	EE-13	2013	372	371	17.2	22.2	295.2
AP-2	B-10	0745	100	EE-10	2010	373	370.5	16.7	21.2	294.2
AP-3	C-10	0801	100	EE-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).

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Plant Acme Power Plant Date 2/27/85

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

Person with direct responsibility for recovered samples M.E. Jackson

Sample number	Final pressure, in. Hg			Final temperature,		Sample recovery time, 24-h	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	✓	✓

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

Lab person with direct responsibility for recovered samples _____

Date recovered samples received 3/1/85 Analyst E. Estes

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

Remarks _____

Signature of lab sample trustee P. Grohse

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

Plant Acme Power Plant Date 2/27/85

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

Person with direct responsibility for recovered samples M.E. Jackson

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

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

Lab person with direct responsibility for recovered samples _____

Date recovered samples received 3/1/85 Analyst E. Estes

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

Remarks _____

Signature of lab sample trustee P. Grohse

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

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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 in. Hg/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?* ✓

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 water, and rinse added to bottle containing sample? ✓

* Most significant items/parameters to be checked.
** Note that absorbing solution for Method 7A is different from that of Method 7.

Figure 4.3. On-site measurements.

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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; repeat 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 <10 mm (0.4 in.) Hg/min	As above	Check all joints and valves for source of leak
Sample recovery	Shake flask for 5 min		
	Let flask set for a minimum of 16 h, but no more than 4 days	During each sample collection, use manometer and Celsius thermometer	Reject sample, rerun test
	Shake flask for 2 min		
	Determine flask pressure and temperature		
	Mark sample level on container		
	Record data on data form (Fig. 4.2)		
Sample logistics	Properly label all containers, etc.	Visually check each sample	Complete the labeling
	Record all data on field data forms	As above	Complete the data records

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5.0 POSTSAMPLING OPERATIONS

The postsampling operations include checks on (a) the apparatus used in the field to quantify sample volumes (volume, temperature, and pressure measurements), and (b) analyses of the samples collected and forwarded to the base laboratory. If the laboratory receives the samples in the sample flasks, laboratory personnel will have to complete the sample recovery procedures referred to in Section 3.6.4.

The postsampling checks on the sample collection train are the same as for Method 7 (Section 3.6.5). The analytical procedures for Method 7A are different from Method 7 and are discussed below. Figure 5.1 is a checklist for all Method 7A posttest operations. Table 5.1 at the end of this section summarizes the quality assurance activities for all postsampling operations for Method 7A including those described in Section 3.6.5.

5.1 Analysis (Base Laboratory)

Calibration of the ion chromatograph, including preparation of the calibration standards and preparation of the field samples is of primary importance to a precise and accurate analysis. For Method 7A, the calibration of the IC is conducted in conjunction with analysis of the field samples (and quality assurance samples). This section presents the steps for analysis of the field samples including preparation of samples, field blanks, and use of quality assurance samples. The relationship between analysis of the field samples and preparation of the calibration curve is addressed. However, because a calibration and performance check of the IC prior to conducting any NO_x analyses is highly recommended, the detailed discussion of the IC calibration is presented in Section 3.14.2. Therefore, the analyst should use Section 3.14.2 in association with this section (3.14.5) in conducting the analysis. In particular, the analyst is encouraged to review the discussion of pipetting errors (see Subsection 2.1.4). Upon completion of each step of the preparation of the calibration curve and of each sample analysis, the data should be entered on the proper data form.

5.1.1 Preparation of Field Samples - Check the level of the liquid in the sample container and confirm whether any sample was lost during shipment; note this on a data form such as that shown in Figure 5.1. 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 before analysis prepare each field sample. The following steps detail sample preparation operations.

1. With the aid of a funnel, transfer the contents of the sampling flask to a 50-ml Class-A volumetric flask.

2. Add approximately a 5-ml portion of water to the sampling flask, replace the stopcock (ensuring that it is in the

Reagents

Sodium nitrate dried at 105° to 110°C for a minimum of 2 hours before use? ✓

Stock standard solution (sodium nitrate) less than 1 month old? ✓

Sample Preparation

Has liquid level noticeably changed?* No

Original volume _____ Corrected volume _____

Analysis

Standard calibration curve prepared?* ✓

All calibration points within 7 percent of linear calibration curve?* Yes

Reagent blanks made from absorbing solution? ✓

Same injection volume for both standards and samples? ✓

Duplicate sample values agree within 5 percent of their mean? Yes

All analytical data recorded on checklist and laboratory form? Yes

* Most significant items/parameters to be checked.

Figure 5.1. Posttest operations.

GMC

closed position), and rinse the interior by shaking and rotating the flask. Transfer the rinse to the volumetric flask. Repeat the rinse with another 5-ml portion of water, and add this rinse to the volumetric flask also.

3. Reassemble the sampling flask and place the stopcock in the closed position to prevent contamination during storage prior to reuse.

4. Using water, dilute the contents of the volumetric flask to the mark. Mix the contents of the flask well.

5. Using a 5-ml Class-A pipet, pipet a 5-ml aliquot of the sample into another 50-ml Class-A volumetric flask. This aliquot is diluted to the mark with either water or eluent solution. Mix the contents of the flask well.

The diluent used must be the same as that used for the calibration standards. (See Subsection 2.1.2 Preparation of Calibration Standards.)

5.1.2 Preparation of Reagent Blank - The reagent blank is prepared in essentially the same manner as the field samples. The difference in procedure occurs at the first step. In preparing the reagent blank, 25 ml of absorbing reagent is transferred to a 50-ml Class-A volumetric flask. A 25-ml pipet may be used for measuring and dispensing the reagent solution; however, the use of a graduated cylinder will give results of acceptable accuracy and precision. After introducing the absorbing reagent into the volumetric flask, add water to the mark, and mix the contents of the flask well. The remaining steps for preparing the reagent blank are identical to those of Step 5 under Preparation of Field Samples.

The reagent blank is used to adjust the analytical results of the field samples for matrix effects of the absorbing reagent and the water. (The sample matrix is simply the medium that contains the substance to be analyzed, which in this case is nitrate.) Because ion chromatography involves separation of the ions prior to detection and quantification, the potential for the sample matrix to interfere with the analysis is small. For Method 7A, matrix effects can arise from the presence of (a) nitrate contaminant in either the absorbing reagent or the water, or (b) a contaminating substance appearing on the chromatogram at about the same time as the nitrate peak. In practice, the ion chromatogram should exhibit no significant response at that point where nitrate should appear. Nevertheless, since data are adjusted for the reagent blank, quality results can be obtained even if contamination exists. The presence of contamination, however, indicates the need for greater quality control in connection with reagent integrity.[17]

5.1.3 Quality Assurance Audit Samples - The quality of analytical results can be assessed by analyzing nitrate standard solutions

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prepared by an independent laboratory. For such standard solutions, or quality assurance audit samples, the concentrations are known to the control agency (the auditor) but are unknown to the analyst.

Subsection 3.3.5 of the Federal Register promulgation of Method 7A (see Section 3.14.10) requires the analysis of quality assurance audit samples as described in Method 7. This means that when Method 7A is used to demonstrate compliance with an EPA pollutant emission standard (specified in 40 CFR Part 60), a performance audit must be conducted on the analytical phase of the method. Nitrate samples in glass vials must be obtained for this performance audit from the Quality Assurance Management Office at each EPA Regional Office or from the responsible enforcement agency. The addresses of the EPA Regional Quality Assurance Coordinators are shown in Table 5.1 of Section 3.0.5 of this Handbook.

The concentration of each audit sample measured by the analyst must agree within 10 percent (relative error) of the actual audit concentration. The relative error is calculated using the following equation:

Equation 5-1

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

where

C_d = Determined audit sample concentration, mg/dscm, and

C_a = Actual audit sample concentration, mg/dscm.

5.1.4 Analysis of Calibration Standards, Reagent Blank, Field Samples, and Quality Assurance Samples - Field samples should be recovered within 4 days of sample collection.[15] As currently written, the method states that the samples should be stored no more than 4 days between collection and analysis. However, a recent study[16] utilizing samples from nitric acid plants and power plants indicates that the storage period between recovery and collection may be extended to 30 days. Sample analysis using an ion chromatograph is a straightforward operation provided that the instrument has been properly set up (see Section 3.14.2). All samples (calibration standards, reagent blank, field samples, and quality assurance samples) should be introduced into the ion chromatograph using the same procedure. Sample introduction involves filling a constant volume sample loop using a syringe or automatic sampling device. Sample loops give extremely repeatable injection volumes; however, the volumes that identify sample loop capacity are not necessarily accurate. Nevertheless, accurate results can be obtained without having accurately known sample loop volumes, provided that the same sample loop is used for injecting field samples and calibration standards. With this procedure, any inaccuracy in the injection volume is accounted for by the calibration.

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Ion chromatographic analysis of calibration standards, field samples, reagent blank, and quality assurance samples are performed in five phases during the same day, alternating between the calibration standards and unknown samples to account for instrument calibration drift. These phases are shown in the schedule below. When Method 7A is used to demonstrate compliance with an EPA pollutant emission standard, the quality assurance audit samples described in Subsection 5.1.3 must be analyzed with the field samples.

Phase	Activity
1	First analysis of all calibration standards.
2	First analysis of all field samples, reagent blank, and quality assurance samples, if applicable.
3	Second analysis of all calibration standards.
4	Second analysis of field samples, reagent blank, and quality assurance samples, if applicable.
5	Third analysis of all calibration standards.

The calibration standards are analyzed in triplicate; the field samples, reagent blank, and quality assurance samples in duplicate. Replication of analyses increases the accuracy and precision of the results. Each chromatogram obtained from the analysis should be documented with the following information:

- sample identification,
- injection point,
- injection volume,
- nitrate retention time,
- sulfate retention time,
- eluent flow rate,
- detector sensitivity setting, and
- recorder chart speed.

Figure 5.2 shows an example chromatogram having acceptable documentation. The injection volume, eluent flow rate, detector sensitivity setting, and the recorder chart speed need to be documented only once for the series of chromatograms if these analytical parameters remain constant over the course of the Method 7A analysis.

Retention time is the elapsed time between when the sample is introduced into the ion chromatograph and when the peak of interest

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Field Sample: AP-1

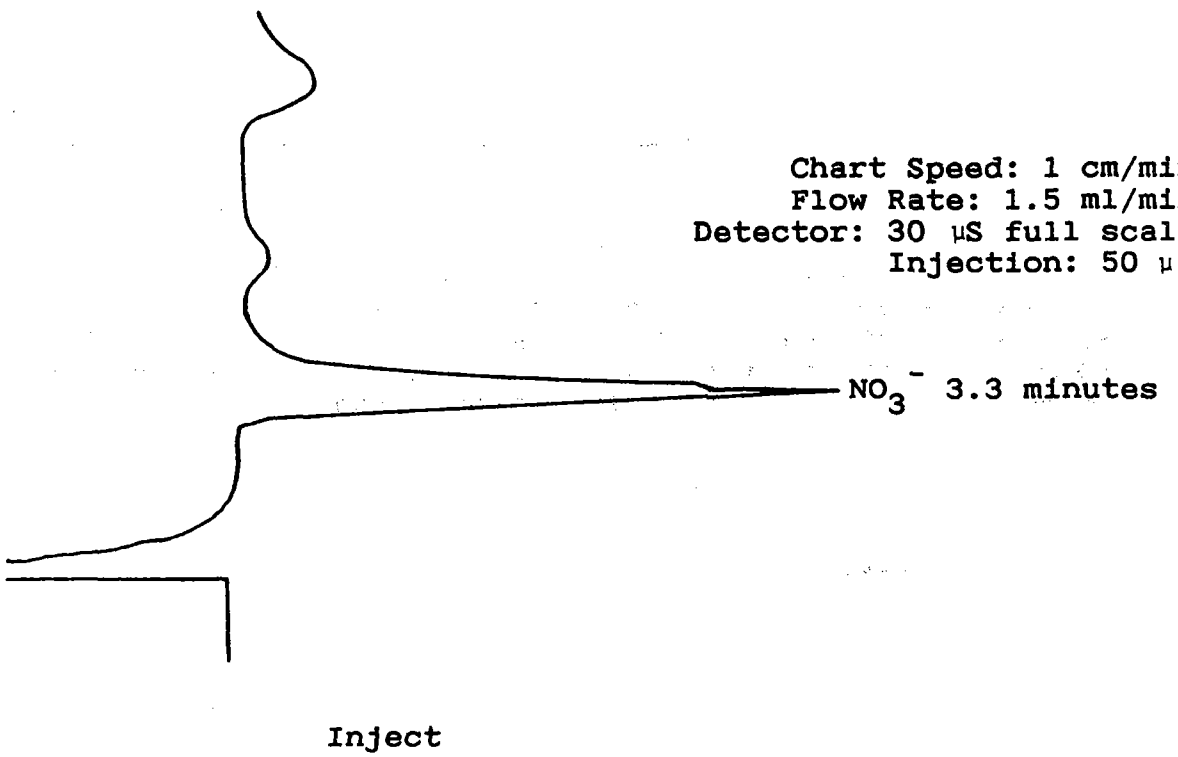

Figure 5.2. Example of chromatogram having adequate documentation.

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occurs. Peaks on the chromatogram may be qualitatively identified by retention time. Retention times can be easily computed from chromatograms provided that the injection point is indicated clearly and the chart speed is known. Identification of the injection point is necessary because a chromatogram's trace will not show when injection occurred.

Record the results for the calibration standards, the field samples, and reagent blank on the appropriate analytical data form (Figures 5.3 and 5.4, respectively). As discussed in Subsection 2.1.3 and shown in Figure 5.3, the percent deviation from the calibration curve of the average response value for each calibration standard must be calculated and must be within 7 percent. A detailed discussion of preparation of the calibration curve and calculation of the calibration factor (S) is found in 3.14.2. The example data in Figure 5.3 shows the use of linear regression to calculate S and a non-zero intercept; the example data in Figure 2.3 shows calculation of S with a zero intercept using least squares. Equation 2-1 or 2-4 along with Equation 2-2 (repeated below) are used to calculate the percent deviation using either a zero intercept (Eq. 2-1) or a non-zero intercept (Eq. 2-4).

Equation 2-1

$$\mu g\ NO_2\ \text{Predicted} = S\ (\mu g/mm) \times \text{Detector Response H}\ (mm)$$

Equation 2-4

$$\mu g\ NO_2\ \text{Predicted} = S\ (\mu g/mm) \left(\text{Detector Response H}\ (mm) - I\ (mm)\right)$$

Equation 2-2

$$\text{Deviation}\ (\%) = \frac{\mu g\ NO_2\ \text{Predicted} - \mu g\ NO_2\ \text{Standard}}{\mu g\ NO_2\ \text{Standard}} \times 100\%$$

For the analyses of the field samples, average the two response values of each sample (see Figure 5.4). The calculated average should have units consistent with those of the calibration curve, for example, units of peak height, peak area, etc. The pair of response values for each sample must each agree within 5 percent of their mean for the analysis to be valid. For this computation, the following equation is used:

Equation 5-2

$$\text{Deviation}\ (\%) = \frac{\text{Instrument Response} - \text{Mean Response}}{\text{Mean Response}} \times 100\%$$

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Plant Acme Power Plant Location Coolbend, Montana

Date March 1, 1985 Analyst E. Estes

Was an integrator used? ✓ yes ___ no

Was the intercept (I) used for calculations? ✓ yes ___ no

Were all points within 7 percent of calculated value? ✓ yes ___ no

Sample Identifier	Sample Mass ($\mu g\ NO_2$)	Integrator Response or Peak Height (mm) H				Predicted Sample Mass ($\mu g\ NO_2$)	Deviation (%)
		1	2	3	Avg		
Std 1	25	8.3	8.4	8.4	8.37	23.30	−6.8
Std 2	50	14.3	14.4	14.2	14.30	48.81	−2.4
Std 3	100	26.5	26.2	26.9	26.53	101.42	+1.4
Std 4	150	38.0	39.0	39.3	38.77	154.06	+2.7
Std 5	250	59.9	60.0	61.5	60.47	247.40	−1.0

Predicted Sample Mass using Least Squares to Calculate Calibration Factor (S) with Zero Intercept

$$S = \frac{S_1H_1 + S_2H_2 + S_3H_3 + S_4H_4 + S_5H_5}{H_1^2 + H_2^2 + H_3^2 + H_4^2 + H_5^2}$$

$$S = \frac{(\_\_\_)(\_\_\_) + (\_\_\_)(\_\_\_) + (\_\_\_)(\_\_\_) + (\_\_\_)(\_\_\_) + (\_\_\_)(\_\_\_)}{(\_\_\_)^2 + (\_\_\_)^2 + (\_\_\_)^2 + (\_\_\_)^2 + (\_\_\_)^2}$$

$S =$ _____ $\mu g\ NO_2/mm$

Predicted Sample Mass ($\mu g\ NO_2$)

$\mu g\ NO_2 = H \times S =$ (____) x (_____) = _____ Equation 2-1

Predicted Sample Mass using Linear Regression to Calculate Calibration Factor (S) and Non-Zero Intercept (I)

$y = mx + b$; $m =$ 0.2325 ; $b =$ 2.9518 ;

$x = \frac{1}{m}(y - b)$; $\frac{1}{m} = S = \frac{1}{0.2325} =$ 4.3013 ;

$y = H$; and $b = I$ (Intercept) = 2.9518.

Predicted Sample Mass ($\mu g\ NO_2$)

$\mu g\ NO_2 = S(H - I)$ Equation 2-4

$\mu g\ NO_2$ at 25 μg standard = 4.301 (8.37 - 2.952) = 23.30

Figure 5.3. Analytical data form for analysis of calibration standards.

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Date samples received 3/1/85 Date samples analyzed 3/1/85
Plant Acme Power Plant Run number(s) AP-1, 2, 3, 4, 5, 6
Location Coalbend, Montana Analyst E. Estes
Calibration factor (S) 4.301 Intercept (I), if applicable 2.952
Reagent blank values: 0.0 1st, 0.0 2nd, 0.0 Avg

Field Sample Number	Analysis Number	Instrument Response (mm)	Mean Instrument Response (mm)	Percent Deviation (μg NO_2)	Mean Instrument Response Blank Corrected (H)	Dilution Factor (F)	Mass of Field Sample (μg NO_2)
AP-1	1st	28.9	29.55	2.2	29.55	1	114.4
	2nd	30.2					
AP-2	1st	23.7	23.1	2.6	23.1	1	86.7
	2nd	22.5					

Deviation of two samples, (%) = $100 \times \frac{|A_1 - A_2|}{A_1 + A_2}$ (must be less than 5%)

$$= 100 \left(\frac{|28.9 - 30.2|}{28.9 + 30.2} \right) = 2.2$$

Mass of field sample without intercept (μg NO_2) = S x H x F

= ____ x ____ x ____ = _____

Mass of field sample with intercept (μg NO_2) = S (H - I) F

= 4.031 (29.55 - 2.952) 1 = 114.4

Figure 5.4. Analytical data form for analysis of field samples.

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The reagent blank is analyzed at the same time as the field samples. The average blank corrected instrument response (H) is determined by subtracting the blank value from the average instrument response for each sample. The blank corrected instrument response (H), the dilution factor (F), and the calibration factor (S) [with intercept (I) if necessary] are then used to calculate the mass of NO_2 per sample as shown in Figure 5.4.

Table 5.1. ACTIVITY MATRIX FOR SAMPLE ANALYSIS

Characteristic	Acceptance Limits	Frequency and method of measurement	Action if requirements are not met
Calibration standards	Data points for calibration standards must not deviate from the linear calibration curve by more than ±7%	Conduct for all analyses of field samples and calibration standards	Remake and reanalyze standards for data points that do not meet criteria; interpret data using another technique (e.g. peak area instead of peak height); strictly observe pipetting technique; use calibration factor with y-intercept for calculations; calibrate conductivity detector
Field sample	Results from duplicate analyses must be within 5 percent of mean value	Conduct for all analyses of field samples	Repeat duplicate analysis, and strictly observe correct pipetting technique; seek assistance with analytical technique
	No results exceeding value for calibration standard having largest concentration	Applicable to all analyses of field samples; determined by visual inspection	Dilute blank and and affected field sample with equal volumes of water and repeat analyses of both
Performance audit of analytical phase	See Section 3.14.8	See Section 3.14.8	See Section 3.14.8
Data recording	All pertinent data recorded on Figs. 5.1, 5.2, 5.3, and 5.4	Visually check	Supply missing data

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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.

6.1 Nomenclature

The following nomenclature is used in the calculations:

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, ^oK (^oR),

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

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

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

V_f = volume of flask and valve, ml,

V_a = volume of absorbing solution, 25 ml,

H = sample peak height or area (blank should be subtracted out), mm,

F = dilution factor (required only if additional sample dilution was needed to reduce the concentration into the range of calibration),

C = sample concentration of NO_x as NO_2, mg/dscm,

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S = calibration factor, μg/mm, and

I = intercept term from calibration equation, mm.

6.2 Calculations

The following four Subsections outline the procedures for calculating the concentration of nitrogen oxides in samples. Subsection 6.2.1 presents the equation for calculating the sample volume on a dry basis at standard conditions.

Subsection 6.2.2 presents the equation for calculating the sample concentration of nitrogen oxides as it appears in Method 7A. This equation utilizes the calibration factor, S, determined during the calibration of the ion chromatograph (see Subsection 2.1.3 of Section 3.14.2). Subsection 6.2.3 offers an alternative approach acceptable to the Administrator for calculating the sample concentration of nitrogen oxides utilizing the calibration factor, S, and the intercept term, I, from the calibration equation. This equation is determined following the procedures outlined in Method 7D for calibration of the ion chromatograph (see Subsection 2.1.3 of Section 3.14.2).

Subsection 6.2.4 presents a simple equation for converting sample concentration to parts per million. Examples of nitrogen oxide calculation forms are presented at the end of each section and should be used with the appropriate calculation methodology.

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

Equation 6-1

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

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

where

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

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

6.2.2 Sample Concentration Using the Calibration Factor, S - Calculate the sample concentration on a dry basis at standard conditions using the calibration factor, S, as shown in Equation 6-2 when the calibration factor S was calculated with no intercept. See Figures

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6.1A and 6.1B for examples of calculation forms for English and metric units, respectively.

Equation 6-2

$$C = \frac{HSF \times 10^4}{V_{sc}}$$

where

10^4 = 1:10 dilution times conversion factors of

$$\frac{mg}{10^3\ \mu g} \times \frac{10^6\ ml}{m^3}.$$

6.2.3 Sample Concentration Using the Calibration Equation and Factor, S - Calculate the sample concentration on a dry basis at standard conditions using the calibration factor and the intercept term for the calibration equation as shown in Equation 6-3. See Figures 6.1A and 6.1B for examples of calculation forms for English and metric units, respectively.

Equation 6-3

$$C = K_2 \frac{(H-I)\ SF \times 10^4}{V_{sc}}$$

where

K_2 = 1 for metric units, or

$K_2 = 6.243 \times 10^{-8}\ \frac{dscm/mg}{dscf/lb}$ for English units.

10^4 = 1:10 dilution times conversion factors of

$$\frac{mg}{10^3\ \mu g} \times \frac{10^6\ ml}{m^3}.$$

6.2.4 Sample Concentration in Parts-Per-Million - If desired, the concentration of NO_2 may be calculated as ppm NO_2 at standard conditions using Equation 6-4 as shown below.

Equation 6-4

$$ppm\ NO_2 = K_3\ C$$

where

$K_3 = 0.5228\ \frac{ppm\ NO_2}{mg\ NO_2/dscm}$ for metric units, or

$K_3 = 8.375 \times 10^6\ \frac{ppm\ NO_2}{lbs\ NO_2/dscf}$ 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

Equation 6-1

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

Sample Concentration

(No Intercept Used)

H = _ _ . _ _ mm, S = _ _ _ _ μg/mm,

F = _ _ _, V_{sc} = _ _ _ _ ml

Equation 6-2

$$C = 6.243 \times 10^{-8}\ \frac{HSF \times 10^4}{V_{sc}} = \_\_ . \_\_ \times 10^{-5} \text{ lbs } NO_2/\text{dscf}$$

(With Intercept Used)

H = 23.10 mm, I = 2.95 mm, S = 4.301 μg/mm,

F = 1.0, V_{sc} = 1780 ml

Equation 6-3

$$C = 6.243 \times 10^{-8}\ \frac{(H-I)SF \times 10^4}{V_{sc}} = 3.04 \times 10^{-5} \text{ lbs } NO_2/\text{dscf}$$

Sample Concentration in ppm

Equation 6-4

$$\text{ppm } NO_2 = 8.375 \times 10^6\ C = 255 \text{ ppm } NO_2$$

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

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Sample Volume

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

P_i = 15.0 mm Hg, T_i = 295.5 °K

Equation 6-1

$$V_{sc} = 0.3858\ (V_f - 25)\ \left(\frac{P_f}{T_f} - \frac{P_i}{T_i}\right) = 1785.\ \text{ml}$$

Sample Concentration

(No Intercept Used)

H = __.__ mm, S = ____ μg/mm

F = ___, V_{sc} = ____ ml

Equation 6-2

$$C = \frac{HSF \times 10^4}{V_{sc}} = \_.\_\_\_ \times 10^3\ \text{mg}\ NO_2/\text{dscm}$$

(With Intercept Used)

H = 23.10 mm, I = 2.95 mm, S = 4.301 μg/mm,

F = 1.0, V_{sc} = 1785 ml

Equation 6-3

$$C = \frac{(H-I)SF \times 10^4}{V_{sc}} = 0.485 \times 10^3\ \text{mg}\ NO_2/\text{dscm}$$

Sample Concentration in ppm

Equation 6-4

ppm NO_2 = 0.5228 C = 254 ppm NO_2

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

Table 6.1. ACTIVITY MATRIX FOR CALCULATIONS

Characteristics	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 checked 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

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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. As for Method 7, 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. These 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.

7.3 Ion Chromatograph

Maintenance activities and schedules for ion chromatographs are make and model specific. It is therefore recommended that the analyst consult the operator's manual for instructions relative to maintenance practices and procedures.

Guard columns, while not required, are recommended for use with the ion chromatograph in order to extend column lifetime.[18]

Table 7.1. ACTIVITY MATRIX FOR MAINTENANCE

Apparatus	Acceptance criteria	Frequency and method of measurement	Action if requirements are not met
Fiber vane pump	Oil translucent; pump leakless and capable of pulling a vacuum of less than 75 mm (3 in.) Hg absolute pressure	Check 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
Ion chromatograph	See owner's manual	See owner's manual	See owner's manual

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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 team and their standards and equipment. Routine quality assurance checks by a field team are necessary to generate 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[19,20,21] of Method 7, two specific performance audits are recommended:

1. Audit of the analytical phase of Method 7A.
2. Audit of data processing.

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

8.1 Performance Audits

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

8.1.1 Pretest Audit of Analytical Phase (Optional) - The pretest audit described in this section can be used to determine the proficiency of the analyst, the quality of the standard solutions in the Method 7A analysis, and the ability to perform the computations correctly. It 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 7A can be audited with the use of aqueous potassium or sodium nitrate samples. Aqueous sodium nitrate samples may be prepared using the same procedure described in Section 3.14.2 for calibration standard 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 7A analysis procedure described in this Handbook.

As an alternative to preparing their own audit samples for a pretest audit, a testing laboratory may, 30 days prior to the time of

the planned pretest audit, make a request to EPA's Environmental Monitoring Systems Laboratory, Quality Assurance Division, Source Branch, Mail Drop 77A, Research Triangle Park, North Carolina 27711 for known quality control samples. These samples are aqueous potassium nitrate samples (and not sodium nitrate samples).

The relative error for each of two samples should be within 10 percent of true value. The relative error (RE) is an indication of the bias that may be associated with the analytical phase of Method 7A. Calculate RE using Equation 8-1.

Equation 8-1

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

where

C_d = Determined audit sample concentration, mg/dscm, and

C_a = Actual audit sample concentration, mg/dscm.

8.1.2 Audit of Analytical Phase of the Field Test (Required) - As stated in Sections 3.3.9 and 4.4 of 40 CFR 60, Appendix A, Method 7 (49 FR 26522, 06/27/84), when the method is used for enforcement testing, the analyst must analyze two audit samples along with the field samples. The testing laboratory should notify the responsible agency requiring the performance test of the intent to test at least 30 days prior to the enforcement source test. The responsible agency will provide two audit samples to be analyzed along with the field samples from the enforcement source test. The purpose of this audit is to assess the data quality at the time of the analysis. If EPA is the agency requiring the performance test, the testing laboratory should notify the Quality Assurance Management Office in the respective EPA Regional Office. The addresses of the EPA Regional Quality Assurance Coordinators are shown in Table 5.1 of Section 3.0.5 of this Handbook.

The two audit samples and the compliance samples must be concurrently analyzed in the same manner to evaluate the technique of the analyst, the standards preparation, and computation skills. (Note: It is recommended that known quality control samples be analyzed prior to the compliance and audit sample analysis to indicate any problems. One source of these samples is the Source Branch listed in Subsection 8.1.1.) 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.

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Calculate the concentrations in mg/dscm 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/dscm 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 each audit sample measured by the analyst shall agree within 10 percent of the actual concentration. 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.

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. Other applications of Method 7A (i.e., Performance Specification Tests) should follow agency recommended or required procedures.

8.1.3 Audit of Data Processing - Calculation errors are prevalent in Method 7.[19,20,21] 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, 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 (if performed on-site) and adding it to the collection flasks.

3. Collecting the sample.

4. Sample absorption procedures, sample recovery, and preparation of samples for shipment.

Figure 8.1 is a suggested checklist for the auditor.

Yes	No	Comment	
			Presampling preparation
✓			1. Plant operation parameters variation
✓			2. Calibration of the flask and valve volume---three determinations
✓			3. Absorbing reagent preparation
			On-site measurements
✓			4. Leak testing of sampling train
✓			5. Preparation and introduction of absorbing solution into sampling flask
			Postsampling (Analysis and Calculation)
✓			6. Control sample analysis
✓			7. Sample aliquotting techniques
✓			8. Ion chromatographic technique
			a. Preparation of standard nitrate samples (pipetting) b. Calibration factor (± 7 percent for all standards) c. Duplicate sample values within 5 percent of their mean d. Adequate peak separation
✓			9. Audit results (± 10%)
			a. Use of computer program b. Independent check of calculations
			Comments

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

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Table 8.1. ACTIVITY MATRIX FOR AUDITING PROCEDURE

Audit	Acceptance Limits	Frequency and method of measurement	Action if requirements are not met
Performance audit of analytical phase	Measured RE of the audit samples shall be within 10% for both audit results	Frequency: Once during every enforcement source test* Method: Measure QA samples and report values to responsible agency	Review operating technique and/or calibration check
Data processing errors	Original and checked 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	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 te their deviations from recommended techniques, and note on Fig. 8.1

*As defined here, a source test for enforcement of the NSPS 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.

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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.

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.

Class-A volumetric flasks and pipets (made to NBS specifications) should be used in the preparation and transfer of solutions.

Audit samples (as discussed in Section 3.14.8) must be used to validate test results for compliance determination purposes and are recommended as an independent check on the measurement process when the method is performed for other purposes.

10.0 REFERENCE METHOD*

METHOD 7A—DETERMINATION OF NITROGEN OXIDE EMISSIONS FROM STATIONARY SOURCES—ION CHROMATOGRAPHIC METHOD

1. *Applicability and Principle.*

1.1 Applicability. This method applies to the measurement of nitrogen oxides emitted from stationary sources; it may be used as an alternative to Method 7 (as defined in 40 CFR Part 60.8(b)) to determine compliance if the stack concentration is within the analytical range. The analytical range of the method is from 125 to 1,250 mg NO_x/m^3 as NO_2 (65 to 655 ppm), and higher concentrations may be analyzed by diluting the sample. The lower detection limit is approximately 19 mg/m³ (10 ppm), but may vary among instruments.

1.2 Principle. A grab sample is collected in an evacuated flask containing a diluted sulfuric acid-hydrogen peroxide absorbing solution. The nitrogen oxides, except nitrous oxide, are oxidized to nitrate and measured by ion chromatography.

2. *Apparatus.*

2.1 Sampling. Same as in Method 7, Section 2.1.

2.2 Sampling Recovery. Same as in Method 7, Section 2.2, except the stirring rod and pH paper are not needed.

2.3 Analysis. For the analysis, the following equipment is needed. Alternative instrumentation and procedures will be allowed provided the calibration precision in Section 5.2 and acceptable audit accuracy can be met.

2.3.1 Volumetric Pipets. Class A; 1-, 2-, 4-, 5-ml (two for the set of standards and one per sample), 6-, 10-, and graduated 5-ml sizes.

2.3.2 Volumetric Flasks. 50-ml (two per sample and one per standard), 200-ml, and 1-liter sizes.

2.3.3 Analytical Balance. To measure to within 0.1 mg.

2.3.4 Ion Chromatograph. The ion chromatograph should have at least the following components:

2.3.4.1 Columns. An anion separation or other column capable of resolving the nitrate ion from sulfate and other species present and a standard anion suppressor column (optional). Suppressor columns are produced as proprietary items; however, one can be produced in the laboratory using the resin available from BioRad Company, 32nd and Griffin Streets, Richmond, California.

2.3.4.2 Pump. Capable of maintaining a steady flow as required by the system.

2.3.4.3 Flow Gauges. Capable of measuring the specified system flow rate.

2.3.4.4 Conductivity Detector.

2.3.4.5 Recorder. Compatible with the output voltage range of the detector.

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. An absorbing solution consisting of sulfuric acid (H_2SO_4) and hydrogen peroxide (H_2O_2) is required for sampling. To prepare the absorbing solution, cautiously add 2.8 ml concentrated H_2SO_4 to a 100-ml flask containing water (same as Section 3.2), and dilute to volume with mixing. Add 10 ml of this solution, along with 6 ml of 3 percent H_2O_2 that has been freshly prepared from 30 percent solution, to a 1-liter flask. Dilute to volume with water and mix well. This absorbing solution should be used within 1 week of its preparation. Do not expose to extreme heat or direct sunlight.

3.2 Sample Recovery. Deionized distilled water that conforms to American Society for Testing and Materials specification D 1193-74, Type 3, is required for sample recovery. 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 Water. Same as in Section 3.2.

3.3.2 Stock Standard Solution, 1 mg NO_x/ml. Dry an adequate amount of sodium nitrate ($NaNO_3$) at 105 to 110°C for a minimum of 2 hours just before preparing the standard solution. Then dissolve exactly 1.847 g of dried $NaNO_3$ in water, and dilute to 1 liter in a volumetric flask. Mix well. This solution is stable for 1 month and should not be used beyond this time.

3.3.3 Working Standard Solution, 25 μg/ml. Dilute 5 ml of the standard solution to 200 ml with water in a volumetric flask, and mix well.

3.3.4 Eluent Solution. Weight 1.018 g of sodium carbonate (Na_2CO_3) and 1.008 g of sodium bicarbonate ($NaHCO_3$), and dissolve in 4 liters of water. This solution is 0.0024 M Na_2CO_3/0.003 M $NaHCO_3$. Other eluents appropriate to the column type and capable of resolving nitrate ion from sulfate and other species present may be used.

3.35 Quality Assurance Audit Samples. Same as required in Method 7.

4. *Procedure.*

4.1 Sampling. Same as in Method 7, Section 4.1.

4.2 Sample. Recovery. Same as in Method 7, Section 4.2, except delete the steps on adjusting and checking the pH of the sample. Do not store the samples more than 4 days between collection and analysis.

* Federal Register, Volume 48, No. 237, December 8, 1983.

4.3 Sample. Preparation. Note the level of the liquid in the container and confirm whether 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 before analysis, transfer the contents of the shipping container to a 50-ml volumetric flask, and rinse the container twice with 5-ml portions of water. Add the rinse water to the flask, and dilute to the mark with water. Mix thoroughly.

Pipet a 5-ml aliquot of the sample into a 50-ml volumetric flask, and dilute to the mark with water. Mix thoroughly. For each set of determinations, prepare a reagent blank by diluting 5 ml of absorbing solution to 50 ml with water. (Alternatively, eluent solution may be used in all sample, standard, and blank dilutions.)

4.4 Analysis. Prepare a standard calibration curve according to Section 5.2. Analyze the set of standards followed by the set of samples using the same injection volume for both standards and samples. Repeat this analysis sequence followed by a final analysis of the standard set. Average the results.

The two sample values must agree within 5 percent of their mean for the analysis to be valid. Perform this duplicate analysis sequence on the same day. Dilute any sample and the blank with equal volumes of water if the concentration exceeds that of the highest standard.

Document each sample chromatogram by listing the following analytical parameters: injection point, injection volume, nitrate and sulfate retention times, flow rate, detector sensitivity setting, and recorder chart speed.

4.5 Audit Analysis. Same as required in Method 7.

5. *Calibration.*

5.1 Flask Volume. Same as in Method 7, Section 5.1.

5.2 Standard Calibration Curve. Prepare a series of five standards by adding 1.0, 2.0, 4.0, 6.0, and 10.0 ml of working standard solution (25 μg/ml) to a series of five 50-ml volumetric flasks. (The standard masses will equal 25, 50, 100, 150, and 250 μg.) Dilute each flask to volume with water, and mix well. Analyze with the samples as described in Section 4.4 and subtract the blank from each value. Prepare or calculate a linear regression plot to the standard masses in μg (x-axis) versus their peak height responses in millimeters (y-axis). (Take peak height measurements with symmetrical peaks; in all other cases, calculate peak areas.) From this curve, or equation, determine the slope, and calculate its reciprocal to denote as the calibration factor, S. If any point deviates from the line by more than 7 percent of the concentration at that point, remake and reanalyze that standard. This deviation can be determined by multiplying S times the peak height response for each standard. The resultant concentrations must not differ by more than 7 percent from each known standard mass (i.e., 25, 50, 100, 150, and 250 μg).

5.3 Conductivity Detector. Calibrate according to manufacturer's specifications prior to initial use.

5.4 Barometer. Calibrate against a mercury barometer.

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

5.6 Vacuum Gauge. Calibrate mechanical gauges, if used, against a mercury manometer such as that specified in Section 2.1.6 of Method 7.

5.7 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 Sample Volume. Calculate the sample volume V_m (in ml) on a dry basis, corrected to standard conditions, using Equation 7-2 of Method 7.

6.2 Sample Concentration of NO_x as NO_2. Calculate the sample concentration C (in mg/dscm) as follows:

$$C = \frac{HSF \times 10^4}{V_m} \qquad \text{Eq. 7A-1}$$

Where:

H = Sample peak height, mm

S = Calibration factor, μg/mm

F = Dilution factor (required only if sample dilution was needed to reduce the concentration into the range of calibration)

10^4 = 1:10 dilution times conversion factor of

$$\frac{mg}{10^3\ \mu g} \times \frac{10^6\ ml}{m^3}$$

If desired, the concentration of NO_2 may be calculated as ppm NO_2 at standard conditions as follows:

$$\text{ppm } NO_2 = 0.5228\ C \qquad \text{Eq. 7A-2}$$

Where:

0.5228 = ml/mg NO_2.

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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 M7A-1.2 indicates that the form is Figure 1.2 in Section 3.14.1 of the Method 7A section. Future revisions of these forms, if any, can be documented by 1.2A, 1.2B, etc. Eleven 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	Analytical Balance Calibration Form
2.3	Analytical Data Form for Analysis of Calibration Standards
3.1 (MH)	Pretest Sampling Checks
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 (MH)	Posttest Operations
5.4	Analytical Data Form for Analysis of Field Samples
6.1A and 6.1B	Nitrogen Oxide Calculation Form (English and metric units)
8.1	Method 7A Checklist to be Used by Auditors

PROCUREMENT LOG

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

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

ANALYTICAL DATA FORM FOR ANALYSIS OF CALIBRATION STANDARDS

Plant _____ Location _____

Date _____ Analyst _____

Was an integrator used? ___ yes ___ no

Was the intercept (I) used for calculations? ___ yes ___ no

Were all points within 7 percent of calculated value? ___ yes ___ no

Sample Identifier	Sample Mass ($\mu g\ NO_2$)	Integrator Response or Peak Height (mm) H				Predicted Sample Mass ($\mu g\ NO_2$)	Deviation (%)
		1	2	3	Avg		
Std 1	25						
Std 2	50						
Std 3	100						
Std 4	150						
Std 5	250						

Predicted Sample Mass using Least Squares to Calculate Calibration Factor (S) with Zero Intercept

$$S = \frac{S_1H_1 + S_2H_2 + S_3H_3 + S_4H_4 + S_5H_5}{H_1^2 + H_2^2 + H_3^2 + H_4^2 + H_5^2}$$

$$S = \frac{(\_\_\_)(\_\_\_) + (\_\_\_)(\_\_\_) + (\_\_\_)(\_\_\_) + (\_\_\_)(\_\_\_) + (\_\_\_)(\_\_\_)}{(\_\_\_)^2 + (\_\_\_)^2 + (\_\_\_)^2 + (\_\_\_)^2 + (\_\_\_)^2}$$

$S =$ _____ $\mu g\ NO_2/mm$

Predicted Sample Mass ($\mu g\ NO_2$)

$\mu g\ NO_2 = H \times S =$ (____) x (_____) = _____ Equation 2-1

Predicted Sample Mass using Linear Regression to Calculate Calibration Factor (S) and Non-Zero Intercept (I)

$y = mx + b$; $m =$ _____; $b =$ _____;

$x = \frac{1}{m}(y - b)$; $\frac{1}{m} = S = \frac{1}{\_\_\_} =$ _____;

$y = H$; and $b = I$ (Intercept) = _____.

Predicted Sample Mass ($\mu g\ NO_2$)

$\mu g\ NO_2 = S(H - I)$ Equation 2-4

$\mu g\ NO_2$ at 25 μg standard = _____(____ - ____) = _____

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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 in. Hg			Initial temperature	
						Leg A_i	Leg B_i	P_i [a]	°C(t_i)	°R(T_i) [b]

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

[b] $T_i = t_i + 273°C$.

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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	Liquid level marked	Samples stored in locked container
	Leg A_f	Leg B_f	P_f[a]	°F (t_f)	°R (T_f)[b]			

[a] $P_f = P_{bar} - (A_f + B_f)$. [b] $T_f = t_f + 460°F$.

Lab person with direct responsibility for recovered samples _____

Date recovered samples received _____ Analyst _____

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

Remarks _____

Signature of lab sample trustee _____

NO_x SAMPLE RECOVERY AND INTEGRITY DATA FORM (METRIC UNITS)

Plant _____ Date _____

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

Person with direct responsibility for recovered samples _____

Sample number	Final pressure, mm Hg			Final temperature,		Sample recovery time, 24-h	Liquid level marked	Samples stored in locked container
	Leg A_f	Leg B_f	P_f[a]	°C (t_f)	°K (T_f)[b]			

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

Lab person with direct responsibility for recovered samples _____

Date recovered samples received _____ Analyst _____

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

Remarks _____

Signature of lab sample trustee _____

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ANALYTICAL DATA FORM FOR ANALYSIS OF FIELD SAMPLES

Date samples received _____ Date samples analyzed _____

Plant _____ Run number(s) _____

Location _____ Analyst _____

Calibration factor (S) _____ Intercept (I), if applicable _____

Reagent blank values: _____ 1st, _____ 2nd, _____ Avg

Field Sample Number	Analysis Number	Instrument Response (mm)	Mean Instrument Response (mm)	Deviation (μg NO_2)	Mean Instrument Response Blank Corrected (H)	Dilution Factor (F)	Mass of Field Sample (μg NO_2)

Deviation of two samples, (%) $= 100 \times \frac{|A_1 - A_2|}{A_1 + A_2}$ (must be less than 5%)

$$= 100 \left(\frac{|\_\_\_ - \_\_\_|}{\_\_\_ + \_\_\_} \right) = \_\_\_$$

Mass of field sample without intercept (μg NO_2) = S x H x F

= ____ x ____ x ____ = _____

Mass of field sample with intercept (μg NO_2) = S (H - I) F

= _____ (_____ - _____) _____ = _____

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NITROGEN OXIDE CALCULATION FORM (ENGLISH UNITS)

Sample Volume

V_f = _ _ _ _ ml, P_f = _ _ . _ _ in. Hg, T_f = _ _ _ ^oR

P_i = _ _ . _ _ in. Hg, T_i = _ _ _ ^oR

Equation 6-1

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

Sample Concentration

(No Intercept Used)

H = _ _ . _ _ mm, S = _ _ _ _ µg/mm,

F = _ _ _, V_{sc} = _ _ _ _ ml

Equation 6-2

$$C = 6.243 \times 10^{-8}\ \frac{HSF \times 10^4}{V_{sc}} = \_\ \_\ .\ \_\ \_ \times 10^{-5}\ \text{lbs}\ NO_2/\text{dscf}$$

(With Intercept Used)

H = _ _ . _ _ mm, I = _ _ . _ _ mm, S = _ _ _ _ µg/mm,

F = _ _ _, V_{sc} = _ _ _ _ ml

Equation 6-3

$$C = 6.243 \times 10^{-8}\ \frac{(H-I)SF \times 10^4}{V_{sc}} = \_\ \_\ .\ \_\ \_ \times 10^{-5}\ \text{lbs}\ NO_2/\text{dscf}$$

Sample Concentration in ppm

Equation 6-4

$$\text{ppm}\ NO_2 = 8.375 \times 10^6\ C = \_\ \_\ \_\ \_\ \text{ppm}\ NO_2$$

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NITROGEN OXIDE CALCULATION FORM (METRIC UNITS)

Sample Volume

V_f = _ _ _ _ ml, P_f = _ _ _. _ mm Hg, T_f = _ _ _. _ ^oK

P_i = _ _ _. _ mm Hg, T_i = _ _ _. _ ^oK

Equation 6-1

$$V_{sc} = 0.3858\ (V_f - 25) \left(\frac{P_f}{T_f} - \frac{P_i}{T_i}\right) = \_\ \_\ \_\ \_.\ ml$$

Sample Concentration

(No Intercept Used)

H = _ _. _ _ mm, S = _ _ _ _ μg/mm

F = _ _ _, V_{sc} = _ _ _ _ ml

Equation 6-2

$$C = \frac{HSF \times 10^4}{V_{sc}} = \_.\ \_\ \_\ \_ \times 10^3\ mg\ NO_2/dscm$$

(With Intercept Used)

H = _ _ . _ _ mm, I = _ _ . _ _ mm, S = _ _ _ _ μg/mm,

F = _ _ _, V_{sc} = _ _ _ _ ml

Equation 6-3

$$C = \frac{(H-I)SF \times 10^4}{V_{sc}} = \_\ .\ \_\ \_\ \_ \times 10^3\ mg\ NO_2/dscm$$

Sample Concentration in ppm

Equation 6-4

$$ppm\ NO_2 = 0.5228\ C = \_\ \_\ \_\ \_\ ppm\ NO_2$$

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METHOD 7A CHECKLIST TO BE USED BY AUDITORS

Yes	No	Comment	
			Presampling preparation
___	___	_____	1. Plant operation parameters variation
___	___	_____	2. Calibration of the flask and valve volume---three determinations
___	___	_____	3. Absorbing reagent preparation
			On-site measurements
___	___	_____	4. Leak testing of sampling train
___	___	_____	5. Preparation and introduction of absorbing solution into sampling flask
			Postsampling (Analysis and Calculation)
___	___	_____	6. Control sample analysis
___	___	_____	7. Sample aliquotting techniques
___	___	_____	8. Ion chromatographic technique a. Preparation of standard nitrate samples (pipetting) b. Calibration factor (± 7 percent for all standards) c. Duplicate sample values within 5 percent of their mean d. Adequate peak separation
___	___	_____	9. Audit results (± 10%) a. Use of computer program b. Independent check of calculations
			Comments