Section 3.15

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

(Alkaline-Permanganate - Ion Chromatographic Method)

OUTLINE

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SUMMARY

For EPA Method 7D[1], an integrated, metered sample is extracted via a heated probe postioned at a point within the duct or stack. The sample is passed through a series of 3 restricted orifice impingers each containing an absorbing solution of sodium hydroxide (NaOH) and potassium permanganate ($KMnO_4$). The absorbing solution reacts with nitrogen oxides in the effluent gas to form nitrate ion, NO_3^-, and nitrite ion, NO_2^-. Nitrogen oxides (NO_x) are the sum of nitric oxide (NO) and nitrogen dioxide (NO_2) which are usually 19 to 1 by weight in the emission stream. The collected sample is allowed to sit for 36 hours prior to analysis in order for the NO_2^- to react completely to NO_3^-. Ion chromatography is then used to quantify the NO_3^- which is functionally related to the NO_x concentration of the effluent sample.

The absorbing solution also reacts with carbon dioxide, CO_2, in the effluent sample. Therefore, EPA Method 3 determinations of CO_2 must be conducted with Method 7D in order to correct the Method[2] 7D volumetric data for the volume of CO_2 absorbed.

Ammonia, NH_3, interferes with Method 7D by causing NO_x results to be biased high. Method 7D results can be corrected for the bias using data from concurrent determinations of NH_3.

Collection of the NO is presumed to involve oxidation - reduction reactions in which the NO is oxidized sequentially to NO_2^- and then to NO_3^-. The half reactions for the formation of NO_2^- are:[2]

$$MnO_4^- + 2H_2O + 3e^- = MnO_2 + 4OH^- \qquad \text{Reaction S-1}$$

$$3NO + 6OH^- = 3NO_2^- + 3H_2O + 3e^- \qquad \text{Reaction S-2}$$

and the overall reaction is:

$$3NO + MnO_4^- + 2OH^- = 3NO_2^- + MnO_2 + H_2O \qquad \text{Reaction S-3}$$

The half reactions for the formation of NO_3^- are:

$$3NO_2^- + 6OH^- = 3NO_3^- + 3H_2O + 6e^- \qquad \text{Reaction S-4}$$

$$2MnO_4^- + 4H_2O + 6e^- = 2MnO_2 + 8OH^- \qquad \text{Reaction S-5}$$

and the overall reaction is:

$$3NO_2^- + 2MnO_4^- + H_2O = 3NO_3^- + 2MnO_2 + 2OH^- \qquad \text{Reaction S-6}$$

The sum of Reactions S-3 and S-6 describes the reaction of NO to NO_3^-:

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$$NO + MnO_4^- = NO_3^- + MnO_2 \qquad \text{Reaction S-7}$$

The rate of the reaction of NO to NO_2^- is controlled by the solubility of NO. It takes approximately 36 hours for the reaction of NO_2^- to NO_3^- to reach completion; the factors controlling this reaction are unknown.

Absorption of NO_2 is also presumed to involve an oxidation-reduction reaction. In contrast to NO, NO_2 is rather reactive; thus, it is reasonable to show NO_2 reacting directly to NO_3^-. The half reactions are:

$$3NO_2 + 6OH^- = 3NO_3^- + 3H_2O + 3e^- \qquad \text{Reaction S-8}$$

$$MnO_4^- + 2H_2O + 3e^- = MnO_2 + 4OH^- \qquad \text{Reaction S-9}$$

and the overall reaction is:

$$3NO_2 + MnO_4^- + 2OH^- = 3NO_3^- + MnO_2 + H_2O \qquad \text{Reaction S-10}$$

The absorption of CO_2 involves the simple acid-base reaction with OH^- to form bicarbonate ion, HCO_3^-:

$$CO_2 + OH^- = HCO_3^- \qquad \text{Reaction S-11}$$

In the strongly basic absorbing solution, the bicarbonate ion reacts further to carbonate ion, $CO_3^=$:

$$HCO_3^- + OH^- = H_2O + CO_3^= \qquad \text{Reaction S-12}$$

Method 7D is applicable to the measurement of NO_x emitted from sources in the following categories:

(a) fossil-fuel-fired steam generators subject to 40 CFR Part 60, Subpart D;

(b) electric utility steam generating units subject to 40 CFR Part 60, Subpart Da; and

(c) nitric acid plants subject to 40 CFR Part 60, Subpart G.

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 lower limit of detectability (with NO_x defined as NO_2) is approximately 13 mg NO_2/m^3 (7 ppm NO_2) when sampling is conducted at a flow rate of 500 cc/min for 1 hour. The method's upper analytical limit has not been established; however, results of field evaluations have shown that NO_x can be collected quantitatively at concentrations of 1,782 mg NO_2/m^3 (932 ppm NO_2) when sampling is conducted at a flow rate of 500 cc/min for 1 hour.

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The method description which follows is based on the method[1] that was promulgated on September 27, 1984.

Section 3.15.10 contains a copy of Method 7D, and blank data forms are provided in Section 3.15.12 for the convenience of the Handbook user.

METHOD HIGHLIGHTS

Section 3.15 contains the required procedure for sampling and analyzing emissions of nitrogen oxides from stationary sources using Method 7D.[1] For the method, an integrated sample is taken from a point in the duct or stack using a heated probe constructed of borosilicate glass, stainless steel, or Teflon™. The effluent sample stream is passed through a series of three restricted orifice impingers, each containing 200 ml of a 4.0% (w/w) $KMnO_4$ and 2.0% (w/w) NaOH solution, termed "alkaline permanganate solution." The alkaline permanganate solution quantitatively removes NO_x, CO_2, and SO_2 from the effluent sample stream and converts these to ions: NO_2^- and NO_3^-, $CO_3^=$, and $SO_4^=$, respectively. Sampling is conducted at a measured flow rate between 400 and 500 cc/min for 60 minutes. The measured flow rate is on a moisture- and CO_2-free basis, and consequently, when the method is applied to effluents from combustion processes, the measured flow rate will be less than the sampling flow rate. In addition, sampling for CO_2 must be conducted using Method 3 in conjunction with Method 7D in order to correct the volumetric data for the volume of CO_2 absorbed.

After acquisition, the sample is allowed to sit for a minimum of 36 hours to ensure that the NO_2^- has been quantitatively reacted to NO_3^-. Sample preparation entails destruction of the excess permanganate and filtration of the solid, manganese reaction product, manganese dioxide (MnO_2). NO_x as NO_3^- is quantified using ion chromatography (IC).

Ion chromatography is a relatively recent analytical development. The reader is referred to the literature for detailed descriptions of the subject.[3-12] Small, et al.,[3] 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 material and are therefore separated into discrete bands. The separated ions are then passed through a post-separation suppressor device 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.,[12] 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 7D, 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.

The critical aspects of the method 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 has been performed for Method 7D and the results exhibit accuracy and precision similar to that of Method 7.[13]

The approporiate blank data forms at the end of this section may be removed from the Handbook and used in the pretest, on-site, and in posttest operations. Each form has a subtitle to assist the user in finding a similar filled-in form in the method description. 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 3.15.1 (Procurement of Apparatus and Supplies) gives specifications, criteria, and design features for the required equipment and materials. The sampling apparatus of Method 7D has design features similar to those of Method 6. Section 3.15.1 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 3.15.2 (Calibration of Apparatus) describes the

required calibration procedures and considerations for the Method 7D sampling equipment (essentially the same as Method 6) and for the ion chromatograph (the same as for Method 7A). Required accuracies for each component are also included. A pretest checklist (Figure 2.5, Section 3.15.2) or a similar form should be used to summarize the calibration and other pertinent pretest data. 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 3.15.3 (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 6 and Method 3. A pretest preparation form (Figure 3.1, Section 3.15.3) can be used as an equipment checkout and packing list. The method of packing and the use of the described packing containers should help protect the equipment, but neither is required by Method 7D.

Activity matrices for the calibration of equipment and the presampling operations (Tables 2.1 and 3.1) summarize the activities.

3. On-Site Measurements

Section 3.15.4 (On-Site Measurements) contains step-by-step procedures for sample collection and for sample recovery. Sample collection is similar to Method 6, with the exception that the alkaline permanganate solution is placed in restriced orifice impingers and the CO_2 content of the stack gas must be determined to correct the sample volume for the CO_2 removed by the sampling train. The on-site measurement checklist (Figure 4.4, Section 3.15.4) provides the tester with a quick method of checking the on-site requirements. Table 4.1 provides an activity matrix for all on-site activities.

4. Posttest Operations

Section 3.15.5 (Postsampling Operations) gives the posttest equipment procedures and a step-by-step analytical procedure for determination of NO_x, expressed as NO_2. The posttest operations form (Figure 5.4, Section 3.15.5) 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 a control sample is required prior to the analysis of the field samples. This analysis of independently prepared, known standards will provide the laboratory with quality control checks on the accuracy and precision of the analytical techniques. Strict adherence to the Method 7D analytical procedures must be observed.

Section 3.15.6 (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 3.15.7 (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, and 7.1) summarize all postsampling, calculation, and maintenance activities.

5. Auditing Procedure

Section 3.15.8 (Auditing Procedures) provides a description of necessary activities for conducting performance and system audits. The performance audit of the analytical phase can be conducted using audit samples supplied by the Quality Assurance Division, Environmental Monitoring Systems Laboratory, U. S. Environmental Protection Agency. 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 audits.

Section 3.15.9 (Recommended Standards for Establishing Traceability) provides the primary standard to which the analysis data should be traceable. The primary standard is sodium nitrate ($NaNO_3$).

6. References

Section 3.15.10 contains the promulgated Method 7D; Section 3.15.11 contains the references cited throughout the text; and Section 3.15.12 contains copies of data forms recommended for Method 7D.

PRETEST SAMPLING CHECKS
(Method 7D, Figure 2.5)

Date _____ Calibrated by _____

Meter box number _____

Dry Gas Meter*

Pretest calibration factor (Y) = _____ (within 2% of average factor for each calibration run).

Rotameter

Pretest calibration factor (Y_r) or setting = _____ (between 400 and 500 cc/min).

Dry Gas Meter Thermometer

Was a pretest temperature correction made? ___yes ___no

If yes, temperature correction _____ (within 3°C (5.4°F) of reference values for calibration and within 6°C (10.8°F) of reference values for calibration check).

Barometer

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

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*Most significant items/parameters to be checked.

PRETEST PREPARATIONS
(Method 7D, Figure 3.1)

Apparatus check	Acceptable Yes	Acceptable No	Quantity required	Ready Yes	Ready No	Loaded and packed Yes	Loaded and packed No
Probe Type liner Glass _____ Stainless steel _____ Other _____ Heated properly* Leak checked							
Filter Glass wool Other _____							
Glassware Restricted orifice impinger Size _____ Type _____							
Meter System Leak-free pumps* Rate meter* Dry gas meter*							
CO_2 Measurement Orsat _____ Fyrite _____							
Reagents Water Alkaline permanganate* Silica gel							
Other Barometer Drying tube							

*Most significant items/parameters to be checked.

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ON-SITE MEASUREMENTS
(Method 7D, Figure 4.4)

Sampling

Impinger contents properly selected , measured, and placed in impingers?* _____

Impinger Contents/Parameters*

1st: 200 ml of $KMnO_4$/NaOH _____

2nd: 200 ml of $KMnO_4$/NaOH _____

3rd: 200 ml of $KMnO_4$/NaOH _____

Drying tube: 6-16 mesh indicating type silica gel _____

Probe heat at proper level?* _____

Crushed ice around impingers? _____

Pretest leak check at 250 mm (10 in.) Hg? _____

Leakage rate? _____

Check of rotameter setting? _____

Probe placed at proper sampling point? _____

Flow rate constant at approximately 450 cc/min?* _____

CO_2 concentration measured?* _____

Posttest leak check at 250 mm (10 in.) Hg?* _____

Leakage rate?* _____

Sample Recovery

Contents of impingers placed in polyethylene bottles? _____

Fluid level marked?* _____

Sample containers sealed and identified?* _____

*Most significant items/parameters to be checked.

POSTTEST OPERATIONS
(Method 7D, Figure 5.4)

Reagents

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

Stock standard solution (potassium nitrate) less than 2 months old? _____

Sample Preparation

Has liquid level noticeably changed?* _____

Original volume _____ Corrected volume _____

Analysis

Standard calibration curve prepared?* _____

Reagent blanks made from absorbing solution? _____

_____

Same injection volume for both standards and samples? _____

Duplicate sample values agree within 5 percent of their mean?

_____

Audit sample analytical results within 10 percent of true value?

_____

All analytical data recorded on checklist and laboratory form?

_____

_____

* Most significant items/parameters to be checked.

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1.0 PROCUREMENT OF APPARATUS AND SUPPLIES

The procurement of appropriate apparatus and supplies enables quality results to be obtained from Method 7D. This section provides the user with information which complements the two sections of Method 7D, entitled "Apparatus" and "Reagents." The information is offered in the form of guidance and includes the following:

- Procedures for use in checking whether apparatus conforms with the requirements of the Method 7D and corrective actions for when it does not (Table 1.1 at the end of this section summarizes these procedures and also contains recommended corrective actions).

- Background information which can explain why specific apparatus and reagents are required, and therefore, what limits may exist for alternatives or deviations.

- Practical information pertinent to the selection and use of apparatus and reagents.

- Safety considerations.

Persons responsible for the initial procurement of apparatus and supplies may find a procurement log helpful in ensuring that all the necessary items are acquired and are in good working order. A procurement log can be used to record the descriptive title of the equipment, the quantity, an identification number (if appropriate), and the results of acceptance checks. An example procurement log is shown by Figure 1.1, a blank copy of this form is contained in Section 3.15.12 for the Handbook user. Calibration data obtained during acceptance checks also should be recorded in a calibration log book; see Section 2.0.

1.1 Sampling Apparatus

Figure 1.2 shows the sampling train for Method 7D. It should be noted that this sampling train is very similar to that used for Method 6. Several of the components and their use are identical, including:

- Needle Valve
- Drying Tube
- Vacuum Pump
- Parts of the Metering System

This subsection addresses the specifications needed for procurement purposes for all components of the sampling train and associated apparatus.

1.1.1 Sampling Probe - Method 7D specifies that sampling

Item description	Qty.	Purchase order number	Vendor	Date Ord.	Date Rec.	Cost	Disposition	Comments
Meter Box (Method 6)	1	77A131	ARC Technology	1/4/85	11/21/84	$1700	Calibrated; ready for use	Calibrated by RS 1/22/84
Restricted Orifice Impingers	14	Custom made	Fragile Glassware	1/4/84	2/10/84	$600	OK	—

Figure 1.1. Example of a procurement log.

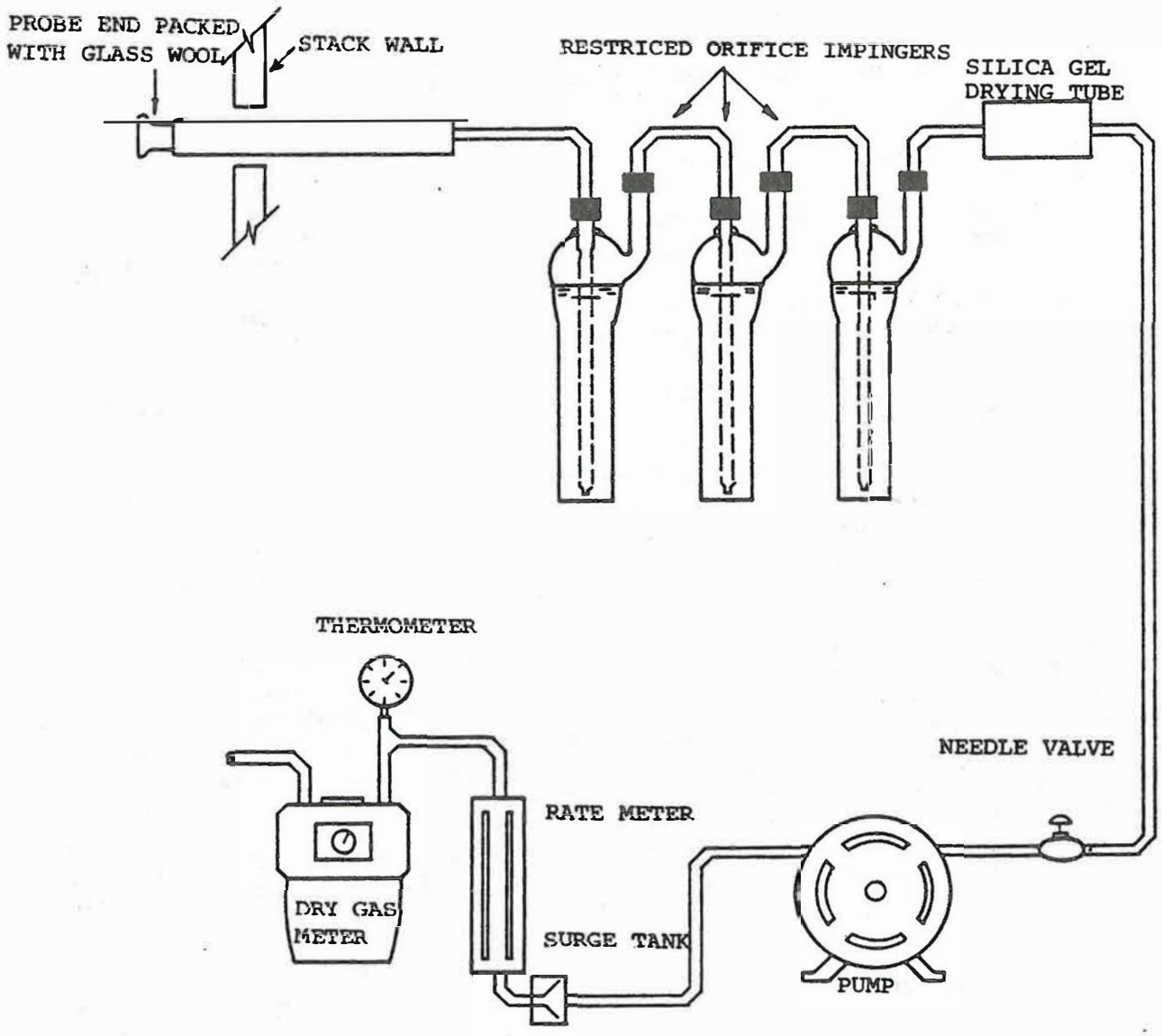

Figure 1.2. Method 7D sampling train.

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probes are to be constructed of borosilicate glass. The method also states that probes made of either stainless steel or Teflon™ are acceptable. Quartz probes (for example Vycor™) may be used for sampling when effluent temperatures exceed 480° (900°F).

The function of the probe is rather simple: to transport a representative effluent sample, cleaned of particulate matter, to the impinger train. To perform this function, the probe should:

(a) hold a filter to remove particulate matter, including sulfuric acid mist;

(b) be constructed of a material that is unreactive toward NO_x;

(c) be free from leaks;

(d) be sufficiently long to enable samples to be acquired from the specified points(s) within the stack or duct;

(e) have provisions for being heated in order to prevent condensation of water vapor in the effluent sample; and

(f) be designed to connect to the inlet of the impinger train.

The three materials identified above are unreactive toward NO_x. The appropriate length for the probe is determined primarily by its intended application which will depend upon regulatory requirements and the dimensions of the stack or duct where the measurements are to be made.

Sampling probes are generally provided with electrical heating systems consisting of a nichrome wire which is wrapped around the probe. The probe and heating system are, for protection, placed within a tightly fitting tube, referred to as a sheath. The heating system should be capable of preventing condensation of water vapor in the effluent sample stream during sampling. Condensation is not desired, because water absorbs NO_2 and lowers NO_x results. Additionally, if a stainless steel probe is used, condensation will promote corrosion which shortens probe lifetime and makes cleaning difficult.

It is recommended that probes be performance checked before initial use in the field to ensure that condensation can be prevented. The probe should first be visually checked for cracks or breaks and then checked for leaks according to the procedure described in Section 3.15.3 of this Handbook. Then the probe heating system should be checked as follows:

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

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

3. Start the pump, and adjust the needle valve until a flow rate of between 400 and 500 cc/min is achieved.

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

The connection between the probe's outlet and the impinger train may be a simple fitting or an additional length of tubing. Any connection should be leak-free. In addition, the connection should be constructed of borosilicate glass, stainless steel, or Teflon™, and therefore, like the probe be unreactive toward NO_x. Lastly, if tubing is used, provisions should exist to prevent condensation of water vapor upstream of the impinger train during sampling. A heating system for the connection is not required if the probe's heating system can supply enough heat to the effluent sample.

1.1.2 Restricted Orifice Impingers - The sampling train requires the use of three restricted orifice impingers connected in series. Figure 1.3 shows one of these impingers, which are commercially available.

Impinger design is important to obtain quality results.[13] The restricted orifice impinger is specifically designed to promote the complete collection of NO, which is relatively unreactive. Two design features are important: (a) the length of the liquid column, and (b) the size of the impinger's stem tip. The impingers used for Method 7D are narrower than Greenburg-Smith impingers in order to provide a greater depth of absorbing reagent and, hence, to increase the reaction time of the sample gas in the absorbing reagent. Because of the narrow opening of the stem tip, the effluent sample is introduced into the absorbing reagent as smaller bubbles. Smaller bubbles promote the reaction of NO because of their greater surface-to-volume ratio and thus, greater exposure to the absorbing reagent.

Impingers with stem tips restricted to less than 1.5 mm internal diameter are easily plugged by reaction products. The problem typically affects only the first impinger of the sampling train because: (a) most of the NO_x and CO_2, and (b) all the sulfur dioxide, if present, are reacted there. The plugging problem can be minimized by making the length of the capillary tubing as short as practical. Plugging also can be minimized by keeping stem tips clean. Reaction products in the stem tips can

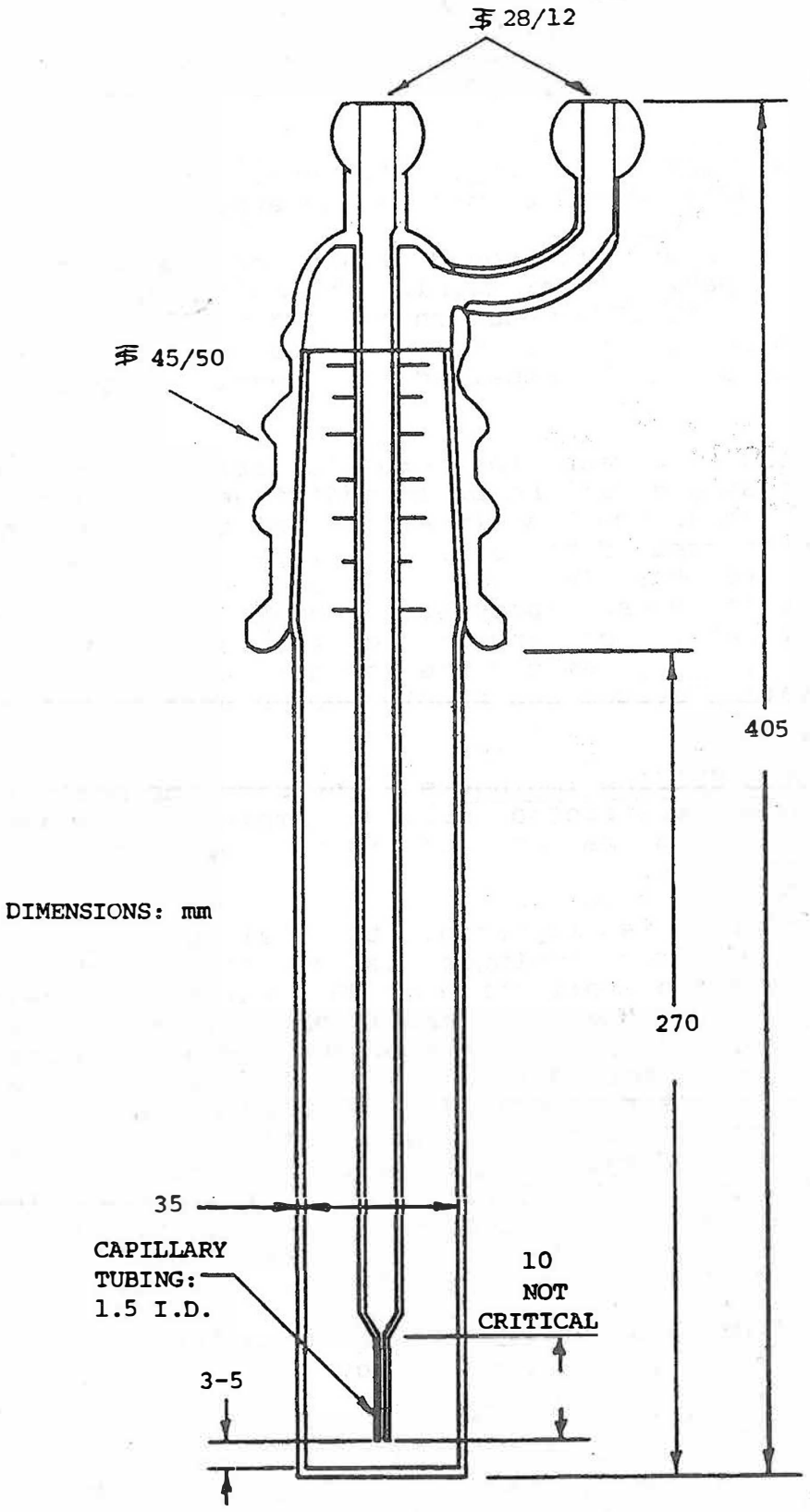

Figure 1.3. Restricted orifice impinger.

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be removed by immersion in either 3 percent by volume hydrogen peroxide solution [3% (v/v) H_2O_2 (aq)] or 3M hydrochloric acid solution [HCl (aq)]. CAUTION: Chlorine (Cl_2) gas is evolved during the use of the HCl; therefore, cleaning operations should be conducted in a fume hood. The H_2O_2 solution is identical to the absorbing solution used for Method 6.

It is recommended that each impinger upon receipt be checked visually for damage, such as breaks or cracks, and for manufacturing flaws, such as poorly shaped connections.

Other nonspecified collection absorbers and sampling flow rates may be used, subject to the approval to the Administrator, but collection efficiency must be shown to be at least 99% for each of three test runs and must be documented in the emission test report. For efficiency testing, an extra absorber must be added and analyzed separately and must not contain more than 1% of the total NO_x. Three Greenburg-Smith design impingers may be sufficient to provide adequate collection efficiency.

1.1.3 Vacuum Pump - The vacuum pump should be capable of maintaining a flow rate of approximately 400 to 500 cc/min for pump inlet vacuums up to 250 mm (10 in.) Hg with the pump outlet near standard pressure, [i.e., 760 mm (29.92 in.) Hg]. The pump must be leak free when running and pulling a vacuum (inlet plugged) of 250 mm (10 in.) Hg. Two types of vacuum pumps are commonly used: either a modified sliding fiber vane pump or a diaphragm pump. For safety reasons, the pump should be equipped with a three-wire electrical cord.

To check the pump for leaks, install a vacuum gauge in the pump inlet line. Plug the inlet line, and run the pump until the vacuum gauge reads 250 mm (10 in.) Hg of vacuum. Clamp the pump outlet line, and turn off the pump; the vacuum reading should remain stable for 30 seconds.

1.1.4 Volume Meter - The dry gas meter must be capable of measuring total volume with an accuracy to within 2%, calibrated at the selected flow rate (between 400 and 500 cc/min), and must be equipped with a temperature gauge (dial thermometer, or equivalent) capable of measuring the gas temperature to within 3°C (5.4°F).

A new dry gas meter may be checked for damage visually and by performing a calibration according to Section 3.5.2 of this Handbook. Any dry gas meter that is damaged, behaves erratically, or does not give readings within ±2% of the selected flow rate for each calibration run is unsatisfactory. Also upon receipt, the meter should be calibrated over a varying flow range to see whether there is any effect on the calibration.

Dry gas meters that are equipped with temperature compensa-

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tion must be calibrated over the entire range of temperatures that the meter encounters under actual field conditions. The calibration must contain at least one data point at each 10°F interval. All temperatures that are to be used in the field must be within 2% of the calibrated value.

The wet test meter used to check the dry gas meter should be calibrated using the primary displacement technique explained in Section 3.5.2 of this Handbook. The wet test meter must have a capacity of at least 0.0003 m^3/min (0.1 ft^3/min) with an accuracy of ±2%; otherwise at the higher flow rates, the water will not be level and this possibly will result in an incorrect reading.

1.1.5 Rotameter - A rotameter, or its equivalent, with a range of 0 to 1 L/min is used to monitor the sampling flow rate. The rotameter is checked against the calibrated dry gas meter with which it is to be used or against a wet test meter. The rotameter flow setting of about 450 cc/min should be determined.

Changes in pressure, density, and viscosity of the sample gas will affect the calibrated sample rate. However, since sampling is performed at a constant rate, which need not be isokinetic, these changes do not affect the sample volume measured by the dry gas meter.

1.1.6 Needle Valve - A metering valve with conveniently sized fittings is required in the sampling train to adjust and control the sample flow rate. It is recommended that the needle valve be placed on the vacuum side of the pump.

1.1.7 Drying Tube - The drying tube should be packed with 6- to 16-mesh indicating-type silica gel, or equivalent, to dry the sample gas and to protect the pump and the meter. A drying tube can be made by filling a 10-mm polyethylene tube with silica gel and packing glass wool in each end to hold the silicia gel and protect the sampling system. Plastic tubing can be utilized in any connections downstream of the impinger train without affecting the sampling results. The drying tube should have a minimum capacity of 30 to 50 g of silica gel and should be visually checked before use for proper size and for damage.

If the silica gel has been used previously, it must be dried at 175°C (350°F) for 2 hours. New silica gel may be used as received. Other types of desiccants may be used subject to approval of the Administrator.

1.1.8 Metering System - For ease of use, the metering system--which contains the dry gas meter, thermometer(s), vacuum pump, needle valve, and rotameter--can be assembled into one unit (meter box). After a meter box has been either constructed or purchased, then positive and negative pressure leak checks should be performed.

The positive pressure leak check, similar to the procedure described in Method 5 (Section 3.4) of this Handbook, is performed as follows:

1. Attach rubber tubing and inclined manometer, as shown in Figure 1.3 of Section 3.4.1.

2. Shut off the needle valve, and apply positive pressure to the system by blowing into the rubber tubing until the inclined manometer or magnehelic gauge reads from 12.5 to 17.5 cm (5 to 7 in.) H_2O.

3. Pinch off the tube, and observe the manometer for 1 minute. A loss of pressure indicates a leak of the apparatus in the meter box.

After the meter box apparatus has passed the positive leak check, then the negative leak check should be performed as follows:

1. Attach the vacuum gauge at the inlet to the drying tube, and pull a 250 mm (10 in.) Hg vacuum.

2. Pinch or clamp the outlet of the flow meter. This can be accomplished by closing the optional shutoff valve if employed.

3. Turn off the pump. Any deflection noted in the vacuum reading within 30 seconds indicates a leak.

4. Carefully release the vacuum gauge before releasing the flow meter end.

If either of these checks detects a leak that cannot be corrected, the meter box must be rejected and/or returned to the manufacturer.

The dry gas meter must be equipped with a temperature gauge (dial thermometer or equivalent). It is recommended that upon receipt this be checked visually for damage, such as dents or a bent stem. The thermometer should read within 3°C (5.4°F) of the true value when checked at two different ambient temperatures against a mercury-in-glass thermometer that conforms to ASTM E-1 No. 63C or 63F. The two ambient temperatures used to calibrate the thermometer must differ by a minimum of 10°C (18°F). Damaged thermometers that cannot be calibrated are to be rejected.

1.1.9 Barometer - A mercury, aneroid, or other barometer capable of measuring atmospheric pressure to within 2.5 mm (0.1 in.) Hg may be used. However, in many cases, the barometric pressure can be obtained from a nearby National Weather Service Station, in which case the station value (which is the absolute

barometric pressure) should be requested. The tester should be aware that the pressure is normally corrected to sea level by the weather station; the uncorrected readings should be obtained. An adjustment for differences in elevation of the weather station and the sampling location is applied at a rate of -2.5 mm Hg/30 m (-0.1 in. Hg/100 ft) of elevation increase, or vice versa for elevation decrease.

Accuracy can be ensured by checking the field barometer against a mercury-in-glass barometer or its equivalent. If the field barometer cannot be adjusted to agree with the mercury-in-glass barometer, it is not acceptable.

1.1.10 Vacuum Gauge - At least one 760-mm (29.92-in.) Hg gauge is necessary to leak check the sampling train. An acceptable vacuum gauge, when checked in a parallel leakless system with a mercury U-tube manometer at 250-mm (10-in.) Hg vacuum, will agree within 25 mm (1.0 in.) Hg.

1.2 Sample Recovery Apparatus

1.2.1 Wash Bottles - Two 500-ml polyethylene or glass wash bottles are needed for quantitative recovery of collected samples.

1.2.2 Storage Bottles - One 1-L polyethylene bottle is required to store each collected sample. An additional polyethylene bottle is necessary to retain a blank for each absorbing solution used in testing. Wash and storage bottles should be visually checked for damage. CAUTION: Each storage bottle seal should be checked prior to use to ensure that leakage will not occur.

1.2.3 Funnel and Stirring Rods - The analyst may find a glass funnel and glass stirring rods are helpful in transferring the absorbing reagent to and from the restricted orifice impingers. The flow of absorbing reagent can be controlled by pouring along the glass stirring rod.

1.3 Apparatus for Sample Preparation and Analysis

1.3.1 Magnetic Stirrer with Magnetic Stirring Bars - The magnetic stirrer and stirring bars are used for the removal of excess permanganate ion. The stirring bars should be Teflon™-coated owing to the corrosiveness of the alkaline-permanganate solution. Stirring bars having dimensions 25 mm by 10 mm are recommended. Smaller stirring bars can be expected to be less efficient because of the resistance offered by the absorbing reagent, which is relatively viscous.

Manual stirring is acceptable; however, being tedious and laborious, it is not recommended.

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1.3.2 Filtering Flask - One filtering flask having a 500-ml capacity is needed to filter the liquid sample after the excess permanganate ion has been removed.

1.3.3 Buchner Funnel - The Buchner funnel is used with the filtering flask for the filtering operations. A convenient size funnel is one with a 75-mm internal diameter. The analyst may wish to attach a section of Teflon™ tubing to the funnel's spout in order to prevent loss of sample via the side arm of the flask during filtration. The use of a trap located between the filtering flask and the vacuum source is also recommended in order to prevent inadvertant sample losses. Upstream tubing connections for the trap should be Teflon™.

1.3.4 Filter - Whatman GF/C glass microfiber discs are used in the Buchner funnel. For the funnel size recommended above, the applicable disc diameter is 7.0 cm. This filter is specified because it performs well on materials having a small particle size. The material filtered from the sample is primarily manganese dioxide which exists in very small particles when suspended in water.

In general, other types of filters are unsuitable owing either to clogging or to their inability to filter the manganese dioxide particles effectively. The analyst should note that particulate matter must be removed from the sample in order to avoid damage to syringes and the ion chromatograph.

1.3.5 Vacuum Source - A vacuum source is needed for the filtering operations. Either a water aspiration system or a vacuum pump can be used. If a vacuum pump is used, it should be protected by a trap installed at an upstream position.

1.3.6 Funnel and Stirring Rods - The analyst may find a funnel and glass stirring rods are helpful in transfering the sample aliquot to the Erlenmeyer flask prior to removal of the excess permanganate ion.

1.3.7 Volumetric Flask - One volumetric flask having the Class-A designation and a 250-ml capacity is needed for each sample and blank. As a practical matter, samples should be stored in the flasks for a minimum period of time owing to the fact that hydroxide ions (OH^-) will attack the glass and can also cause frozen ground-glass fittings.

1.3.8 Pipettes - A 50-ml Class-A pipette is needed for taking a sample aliquot. A 5-ml pipet is usually used for adding (not quantitatively) hydrogen peroxide to the sample aliquot in order to remove excess permanganate ion. Because hydroxide ion (OH^-), which is present in the sample, can attack glass, it is recommended that analysts rinse pipettes with water immediately after use on samples. If Quality Assurance Audit Samples are to be analyzed, additional pipettes (Class-A) may be needed.

1.3.9 Erlenmeyer Flasks - Erlenmeyer flasks having a 250-ml capacity are used for operations involving the removal of excess permanganate ion in the samples.

1.3.10 Ion Chromatograph - An ion chromatograph (IC) is used for analyzing the samples. The instrument should, at a minimum, have the components described below.

Columns - The IC should be equipped with an ion separator column capable of resolving nitrate ion (NO_3^-) from sulfate ion ($SO_4^=$), which may be found in samples acquired at fossil-fuel-fired steam generators. In addition, it should be capable of detecting and resolving nitrite ion (NO_2^-). Either suppressed or nonsuppressed IC's may be used provided that performance meets the above criteria. Suppressed IC's should be equipped with an acid (H^+) suppressor column in addition to the anion separator column. Suppressor columns (fiber preferred over packed bed) are generally produced as proprietory items; however, an acceptable column can be made 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 - 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.

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

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

1.4.1 Sampling - For sampling, the following are needed.

Absorbing solution - The absorbing solution is prepared by dissolving 40.0 g potassium permanganate ($KMnO_4$) and 20.0 g

sodium hydroxide (NaOH) in 940 ml of water. The solution's concentration is 4.0 percent (w/w) $KMnO_4$, 2.0 percent (w/w) NaOH. CAUTION: Extreme care should be taken in handling the $KMnO_4$ reagent and the absorbing solution. $KMnO_4$ is a strong oxidant and is incompatible with substances containing carbon such as paper, fabric, and human tissue. It is recommended that eye protection be worn when handling the absorbing solution. Skin exposed to the absorbing solution should be washed with plenty of water and until the exposed area no longer exhibits a soapy feeling.

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°C	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 (3.15) 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 presence of trace quantities of nitrate in the water will be negated. Therefore, a water blank correction is not necessary in the development of the calibration curve.

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

Water - See Subsection 1.4.1 above.

Hydrogen Peroxide - Five (5) percent (v/v) hydrogen peroxide (H_2O_2) is used which is prepared by mixing 1 part 30% (v/v) H_2O_2 with 5 parts water.

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Reagent Blank - The reagent blank may be prepared by dissolving 2.4 g $KMnO_4$ and 1.2 g NaOH in 96 ml water. Alternatively, the blank may be prepared by diluting 60 ml of the absorbing reagent to 100 ml using water.

Potassium Nitrate (KNO_3) Standard Solution - The following procedure is observed to prepare the KNO_3 standard solution.

1. Dry an adequate amount of KNO_3 at 110°C for about 2 hours; then transfer to a desiccator, and allow to cool to laboratory temperature.

2. Using an analytical balance, accurately weigh 9 to 10 g of the dried KNO_3 to the nearest 0.1 mg.

3. Transfer the KNO_3 to a suitable container, such as a beaker, dissolve the KNO_3 in water, and transfer all of the KNO_3 solution to a 1-L volumetric flask.

4. Dilute the KNO_3 solution to the 1-L mark with water.

The NO_3^- concentration of the standard solution is calculated from the mass of KNO_3 using the following relationship:

$$\text{Concentration } (\mu g/ml) \text{ of } NO_3^- = \text{Mass of } KNO_3 \text{ (g)} \left(\frac{10^3\ \mu g \cdot L}{g \cdot ml}\right)\left(\frac{62.01\ g/mol\ NO_3^-}{101.10\ g/mol\ KNO_3}\right)$$

Method 7D states that the KNO_3 standard solution is stable for 2 months without preservative at laboratory conditions. Novice analysts should note that certain microbes feed on NO_3^- solutions with the consequence for Method 7D being that NO_x results will be biased high. For this reason, standard solutions should be disposed of after 2 months.

Eluent Solution - For IC's involving the suppressed technique, an eluent solution being 3×10^{-3} M $NaHCO_3$ and 2.4×10^{-3} M Na_2CO_3 has proved adequate for Method 7D applications. This eluent is prepared by taking 1.008 g $NaHCO_3$ and 1.018 g Na_2CO_3 and dissolving them in 4 L water.

Other eluents may be used provided that they are capable of resolving NO_3^- from $SO_4^=$ and other ions which may be present in samples.

Quality Assurance Audit Samples - Quality Assurance Audit Samples are required to be analyzed in conjunction with field samples. The audit samples for Method 7D are essentially the same as those described in Method 7, Section 3.3.9. Because the analytical range for Method 7D differs from that for Method 7, analysts requesting audit samples should specify that samples be applicable to Method 7D.

Table 1.1. ACTIVITY MATRIX FOR PROCUREMENT OF APPARATUS AND SUPPLIES

Apparatus and supplies	Acceptance limits	Frequency and method of measurement	Action if requirements are not met
Sampling probe with heating system	Capable of maintaining 100°C (212°F) exit air at flow rate of 500 cc/min	Visually check and run heating system checkout	Repair, or return to supplier
Restricted orifice impingers	Standard stock glass; ensure that dimensions conform with specifications	Visually check upon receipt for breaks or leaks	Return to manufacturer
Vacuum pump	Capable of maintaining flow rate of 400 to 500 cc/min; leak free at 250 mm (10 in.) Hg	Check upon receipt for leaks and capacity	As above
Dry gas meter	Capable of measuring total volume within 2% at a flow rate of 500 cc/min	Check for damage upon receipt, and calibrate (Sec. 3.15.2) against wet test meter	Reject if damaged, behaves erratically, or cannot be properly adjusted
Wet test meter	Capable of measuring total volume within 2% at a flow rate of 500 cc/min	Upon assembly, leak check all connections, and check calibration by liquid displacement	As above
Rotameter	Within 5% of manufacturer's calibration curve (recommended)	Check upon receipt for damage, and calibrate (Sec. 3.15.2) against wet test meter	Recalibrate, and construct a new calibration curve
Drying tube	Minimum capacity of 30 to 50 g of silica gel	Visually check upon receipt for damage and proper size	Return to supplier

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Table 1.1 (continued)

Apparatus and supplies	Acceptance limits	Frequency and method of measurement	Action if requirements are not met
Thermometers	Within 1°C (2°F) true value in the range of 0°C to 25°C (32° to 77°F) for impinger and within 3°C (5.4°F) for dry gas meter thermometer	Check upon receipt for damage (i.e., dents and bent stem), and calibrate (Sec. 3.15.2) against mercury-in-glass thermometer	Return to supplier if unable to calibrate
Barometer	Capable of measuring atmospheric pressure to within 2.5 mm (0.1 in.) Hg calibrate	Check against mercury-in-glass barometer or equivalent (Sec. 3.5.2)	Determine correction factor, or reject if difference is more than 2.5 mm
Vacuum gauge	0 to 760 mm (0 to 29.92 in.) Hg range, ±25 mm (1.0 in.) Hg accuracy at 250 mm (10 in.) Hg	Check against U-tube mercury manometer upon receipt	Adjust, or return to supplier
Wash bottles	Polyethylene or glass, 500-ml	Visually check for damage upon receipt	Replace, or return to supplier
Storage bottles	Polyethylene, 1-L	Visually check for damage upon receipt, and be sure that caps seal properly	As above
Pipettes and volumetric flasks	Glass, Class-A	Upon receipt, check for stock number, cracks, breaks, and manufacturer flaws	As above
Water	Must conform to ASTM-D1193-82, Type III	Check each lot or specify type when ordering	As above

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Table 1.1 (continued)

Apparatus and supplies	Acceptance limits	Frequency and method of measurement	Action if requirements are not met
Stopcock grease	High vacuum, high temperature chlorofluorocarbon grease	Visually check upon receipt	Return to supplier, and note in procurement log
Analytical balance	Capable of measuring to ±0.1 mg	Check with standard weights upon receipt and before each use	Replace, or return to manufacturer
Ion Chromatograph			
1. Columns	1. Capable of giving nitrate ion peaks with baseline separation	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
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, repair, replace, or return to manufacturer; check tubing of ion chromatograph for leaks or obstructions; check flow meter performance
3. Flow gauges	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

(continued)

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Table 1.1 (continued)

Apparatus and supplies	Acceptance limits	Frequency and method of measurement	Action if requirements are not met
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 record responses for manual integration	5. Check during analyses	5. Consult operator's manual; adjust speed
Hydrogen peroxide	30% aqueous solution, ACS reagent grade	Check each lot, or specify type when ordering	Replace or return to manufacturer
Potassium 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
Sodium hydroxide	ACS reagent grade	As above	As above
Potassium permanganate	ACS reagent grade	As above	As above

2.0 CALIBRATION OF APPARATUS

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

The calibration procedures and considerations addressed in this section are those which are unique to Method 7D. The sampling phase of Method 7D involves the use of equipment that is essentially the same as that used for Method 6. The analysis phase of Method 7D entails the use of an ion chromatograph, an instrument that also is used for Method 7A. The Handbook user should note that: (a) the standard used for Method 7A is sodium nitrate ($NaNO_3$), while for Method 7D the standard used is potassium nitrate (KNO_3); and (b) sulfate ion ($SO_4^=$) peaks in ion chromatograms for Method 7D will have a lesser tendancy to overlap and therefore to interfere with nitrate (NO_3^-) peaks because $SO_4^=$ will exist at a lower concentration because it originates only from sulfur oxides in the effluent.

2.1 Metering System

2.1.1. Wet Test Meter - The wet test meter must be calibrated and have the proper capacity. For Method 7D, the wet test meter should have a capacity of at least 1 L/min. No upper limit is placed on the capacity; however, the wet test meter dial should make at least one complete revolution at the specified flow rate for each of the three independent calibrations.

Wet test meters are calibrated by the manufacturer to an accuracy of ±2%. Calibration of the wet test meter must be checked initially upon receipt and yearly thereafter.

The following liquid positive displacement technique can be used to verify and adjust, if necessary, the accuracy of the wet test meter to ±2%:

1. Level the wet test meter by adjusting the legs until the bubble on the level located on the top of the meter is centered.

2. Adjust the water volume in the meter so that the pointer in the water level gauge just touches the meniscus.

3. Adjust the water manometer to zero by moving the scale or by adding water to the manometer.

4. Set up the apparatus and calibration system as shown in Figure 2.1.

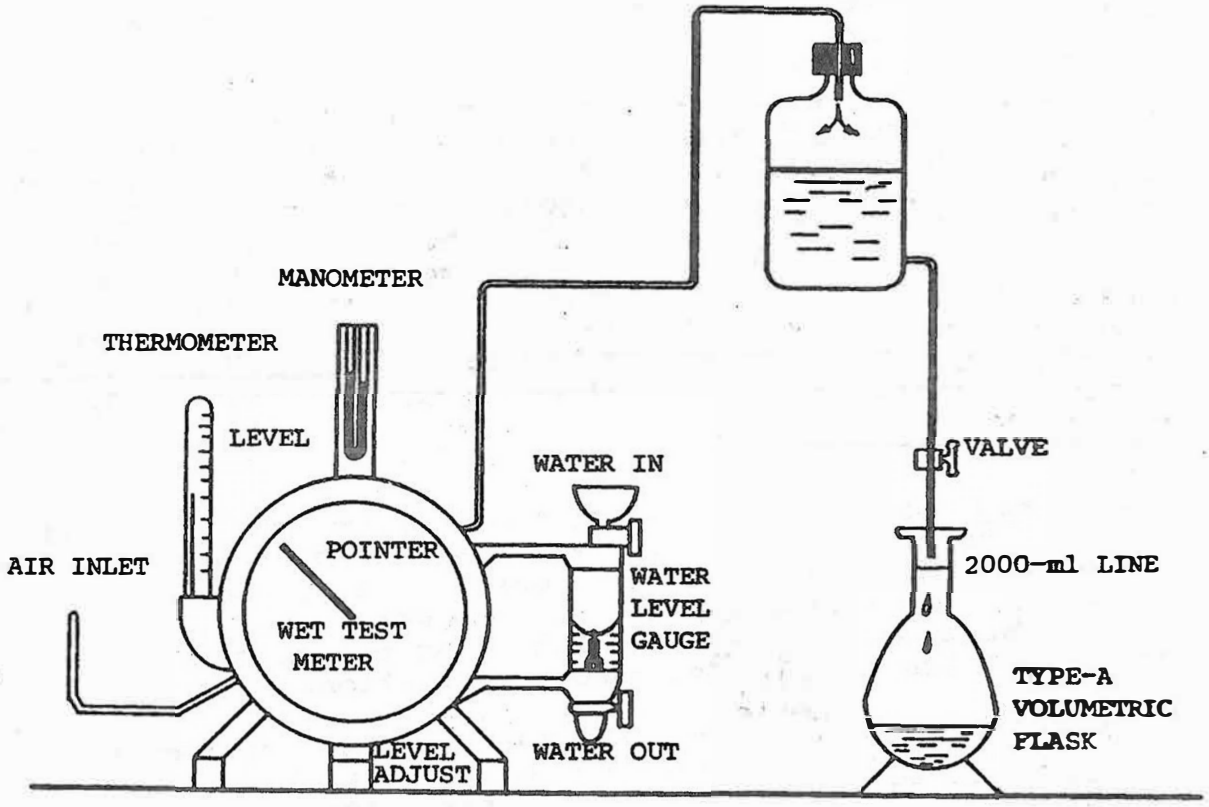

Figure 2.1. Calibration check apparatus for wet test meter.

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a. Fill the rigid-wall 5-gal jug with water to below the air inlet tube. Put water in the impinger or saturator, and allow both to equilibrate to room temperature (about 24 hours) before use.

b. Start water siphoning through the system, and collect the water in a 1-gal container, located in place of the volumetric flask.

5. Check operation of the meter as follows:

a. If the manometer is reading <10 mm (0.4 in.) H_2O, the meter is in proper working condition. Continue to step 6.

b. If the manometer reading is >10 mm (0.4 in.) H_2O, the wet test meter is defective. If the wet test meter is defective, and if the defects(s) (e.g., bad connections or joints) cannot be found and corrected, return it to the manufacturer for repair.

6. Continue the operation until the 1-gal container is almost full. Plug the inlet to the saturator. If no leak exists, the flow of liquid to the gallon container should stop. If the flow continues, correct for leaks. Turn the siphon system off by closing the valve, and unplug the inlet to the wet test meter.

7. Read the initial volume (V_i) from the wet test meter dial, and record on the wet test meter calibration log, Figure 2.2.

8. Place a clean, dry volumetric flask (Class-A) under the siphon tube, open the pinch clamp, and fill the volumetric flask to the mark. The volumetric flask must be large enough to allow at least one complete revolution of the wet test meter with not more than two fillings of the volumetric flask.

9. Start the flow of water, and record the maximum wet test meter manometer reading during the test after a constant flow of liquid is obtained.

10. Carefully fill the volumetric flask, and shut off the liquid flow at the 2-L mark. Record the final volume shown on the wet test meter.

11. Steps 7 through 10 must be performed three times.

Since the water temperature in the wet test meter and reservoir has been equilibrated to the ambient temperature and the pressure in the wet test meter will equilibrate with the water reservoir after the water flow is shut off, the air volume can be compared directly with the liquid displacement volume.

Wet test meter serial number 43-246 Date 2/21/84

Range of wet test meter flow rate 0-120 L/min

Volume of test flask V_s = 2.00 L

Satisfactory leak check? yes

Ambient temperature of equilibrate liquid in wet test meter and reservoir 74°F

Test number	Manometer reading, [a] mm H_2O	Final volume (V_f), L	Initial volume (V_i), L	Total volume, (V_m) [b] L	Flask volume (V_s), L	Percent error, [c] %
1	5	1.99	0	1.99	2.00	0.5
2	5	2.00	0	2.00	2.00	0
3	5	2.00	0	2.00	2.00	0

[a]Must be less than 10 mm (0.4 in.) H_2O.

Calculations:

[b]$V_m = V_f - V_i$.

[c]% error = $100 (V_m - V_s)/V_s$ = 0.5 (±1%).

Roy Doster Signature of calibration person

Figure 2.2. Wet test meter calibration log.

Any temperature or pressure difference would be less than measurement error and would not affect the final calculations.

The error should not exceed ±1%; if this error magnitude is exceeded, check all connections within the test apparatus for leaks, and gravimetrically check the volume of the standard flask. Repeat the calibration procedure, and if the tolerance level is not met, adjust the liquid level within the meter (see the manufacturer's manual) until the specifications are met.

2.1.2 Sample Metering System - The sample metering system, consisting of the drying tube, needle valve, pump, rotameter, and dry gas meter, is initially calibrated by stringent laboratory methods before it is used in the field. The calibration is then rechecked after each field test series. This recheck requires less effort than the initial calibration. When a recheck indicates that the calibration factor has changed, the tester must again perform the complete laboratory procedure to obtain the new calibration factor. After the meter is recalibrated, the metered sample volume is multiplied by the calibration factor (initial or recalibrated) that yields the lower gas volume for each test run.

Initial Calibration - The metering system should be calibrated when first purchased and at any time the posttest check yields a calibration factor that does not agree within 5% of the pretest calibration factor. A calibrated wet test meter (properly sized, with ±1% accuracy) should be used to calibrate the metering system.

The metering system should be calibrated in the following manner before its initial use in the field.

1. Leak check the metering system (drying tube, needle valve, pump, rotameter, and dry gas meter) as follows:

   a. Temporarily attach a suitable rotameter (e.g., 0-40 cm^3/min) to the outlet of the dry gas meter, and place a vacuum gauge at the inlet to the drying tube.

   b. Plug the drying tube inlet. Pull a vacuum of at least 250 mm (10 in.) Hg.

   c. Note the flow rate as indicated by the rotameter.

   d. A leak of <0.02 L/min must be recorded or leaks must be eliminated.

   e. Carefully release the vacuum gauge before turning off pump.

2. Assemble the apparatus, as shown in Figure 2.3, with the wet test meter replacing the drying tube and impingers; that is, connect the outlet of the wet test meter to the inlet side of the needle valve and the inlet side of the wet test meter to a saturator which is open to the atmosphere. Note: Do not use a drying tube.

3. Run the pump for 15 minutes with the flow rate set at 450 cc/min to allow the pump to warm up and to permit the interior surface of the wet test meter to become wet.

4. Collect the information required in the forms provided, Figure 2.4A (English units) or 2.4B (metric units), using sample volumes equivalent to at least five revolutions of the dry test meter. Three independent runs must be made.

5. Calculate Y_i for each of the three runs using Equation 2-1. Record the values in the form (Figure 2.4A or 2.4B).

$$Y_i = \frac{V_w \left(P_m + \frac{D_m}{13.6}\right) (t_d + 460^\circ F \text{ or } 273^\circ C)}{V_d P_m (t_w + 460^\circ F \text{ or } 273^\circ C)} \quad \text{Equation 2-1}$$

where:

Y_i = ratio for each run of volumes measured by the wet test meter and dry gas meter, dimensionless calibration factor,

V_w = volume measured by wet test meter, m^3 (ft^3),

P_m = barometric pressure at the meters, mm (in.) Hg,

D_m = pressure drop across the wet test meter, mm (in.) H_2O,

t_d = average temperature of dry gas meter, $^\circ C$ ($^\circ F$),

V_d = volume measured by the dry gas meter, m^3 (ft^3), and

t_w = temperature of wet test meter, $^\circ C$ ($^\circ F$).

6. Adjust and recalibrate or reject the dry gas meter if one or more values of Y_i fall outside the interval $\bar{Y} \pm 0.02\bar{Y}$, where $\bar{Y}$ is the average for three runs. Otherwise, the $\bar{Y}$ (calibration factor) is acceptable and is to be used for future checks and subsequent test runs. The completed form should be forwarded to the supervisor for approval, and then filed in the calibration log book.

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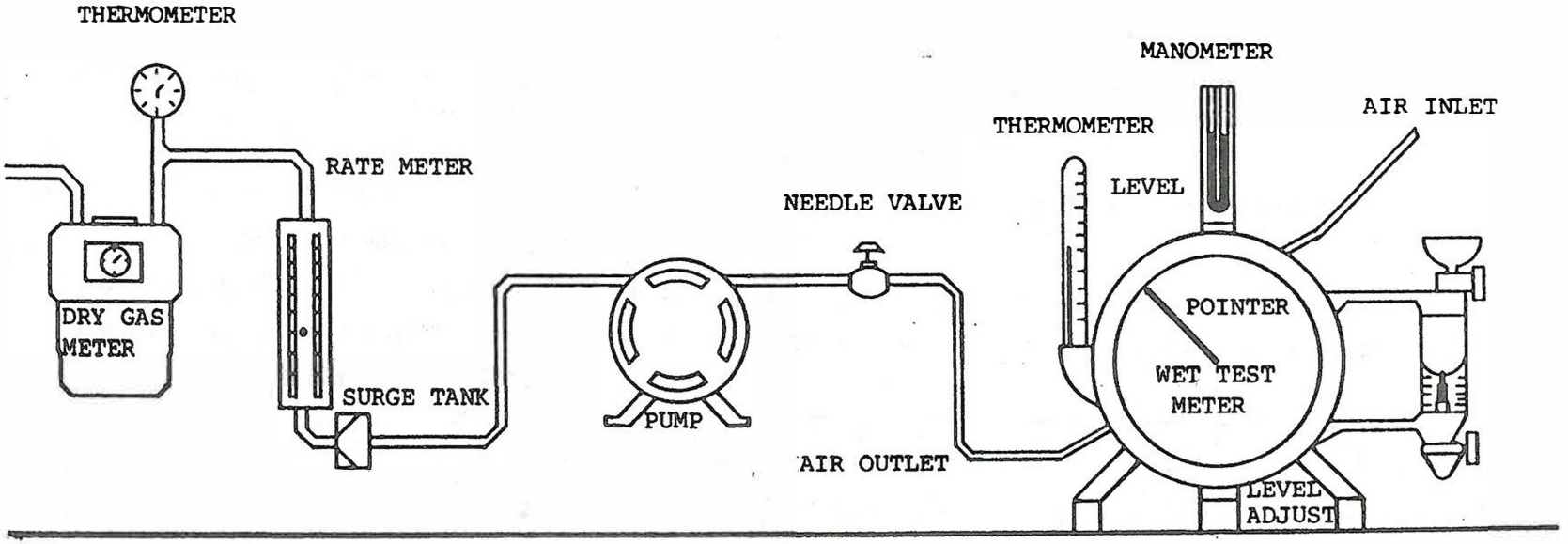

Figure 2.3. Sample metering system calibration setup.

Date 2/22/84 Calibrated by Roy Doster Meter box number EE-1 Wet test meter number 101-A

Barometer pressure, P_m = 29.41 in. Hg Dry gas meter temperature correction factor NA °F

Wet test meter pressure drop (D_m),[a] in. H_2O	Rotameter setting (R_s), ft^3/min	Wet test meter gas volume (V_m),[b] ft^3	Dry test meter gas volume (V_d),[b] ft^3 Initial	Dry test meter gas volume (V_d),[b] ft^3 Final	Wet test meter gas temp (t_w), °F	Inlet gas temp (t_{d_i}), °F	Dry test meter Outlet gas temp (t_{d_o}), °F	Dry test meter Average gas temp (t_d),[c] °F	Dry test meter Time of run (θ),[d] min	Dry test meter Average ratio (Y_i),[e]	(Y_{r_i}),[f]
0.25	0.016	1.058	725.613	726.672	72	80	78	79	68	1.013	0.986
0.25	0.016	1.059	728.961	730.021	72	82	80	81	68	1.017	0.990
0.25	0.016	1.061	732.098	733.158	72	84	80	82	68	1.020	0.994

[a] D_m expressed as negative number.

[b] Volume passing through meter. Dry gas volume is minimum for at least five revolutions of the meter.

[c] The average of t_{d_i} and t_{d_o} if using two thermometers; the actual reading if using one thermometer.

[d] The time it takes to complete the calibration run.

[e] With Y defined as the average ratio of volumes for the wet test and the dry test meters, $Y_i = Y \pm 0.02\ Y$ for calibration and $Y_i = Y \pm 0.05\ Y$ for the posttest checks; thus,

$$Y_i = \frac{V_w\ (t_d + 460^\circ F)\ \left[P_m + (D_m/13.6)\right]}{V_d\ (t_w + 460^\circ F)\ (P_m)} \quad \text{(Eq. 1)} \qquad \text{and} \qquad Y = \frac{Y_1 + Y_2 + Y_3}{3} = 1.017. \quad \text{(Eq. 2)}$$

[f] With Y_r defined as the average ratio of volumetric measurement by wet test meter to rotameter. Tolerance $Y_r = 1 \pm 0.05$ for calibration and $Y \pm 0.1$ for posttest checks.

$$Y_{r_i} = \frac{V_w\ (t_d + 460^\circ F)\ \left[P_m + (D_m/13.6)\right]}{\theta\ (t_w + 460^\circ F)\ (P_m)\ (R_s)} \quad \text{(Eq. 3)} \qquad \text{and} \qquad Y_r = \frac{Y_1 + Y_2 + Y_3}{3} = 0.990. \quad \text{(Eq. 4)}$$

Figure 2.4A. Dry gas meter calibration data form (English units).

Date 2/22/84 Calibrated by Roy Doster Meter box number EE-1 Wet test meter number 101-A

Barometer pressure, P_m = 748 in. Hg Dry gas meter temperature correction factor NA °C

Wet test meter pressure drop (D_m),[a] mm H_2O	Rotameter setting (R_s), cc/min	Wet test meter gas volume (V_m),[b] L	Dry test meter gas volume (V_d),[b] L		Wet test meter gas temp (t_w), °C	Inlet gas temp (t_{d_1}), °C	Dry test meter				(Y_{r_1}),[f]
			Initial	Final			Outlet gas temp (t_{d_o}), °C	Average gas temp (t_d),[c] °C	Time of run (θ),[d] min	Average ratio (Y_1),[e]	
6.4	450	29.958	105.631	135.618	22	27	26	26.5	68	1.015	0.995
6.4	450	29.987	140.362	170.377	22	28	27	27.5	68	1.018	0.999
6.4	450	30.043	181.619	211.634	22	29	28	28.5	68	1.024	1.004

[a] D_m expressed as negative number.

[b] Volume passing through meter. Dry gas volume is minimum for at least five revolutions of the meter.

[c] The average of t_{d_1} and t_{d_o} if using two thermometers; the actual reading if using one thermometer.

[d] The time it takes to complete the calibration run.

[e] With Y defined as the average ratio of volumes for the wet test and the dry test meters, Y_1 = Y ±0.02 Y for calibration and Y_1 = Y ±0.05 Y for the posttest checks; thus,

$$Y_1 = \frac{V_w\,(t_d + 273^\circ C)\left[P_m + (D_m/13.6)\right]}{V_d\,(t_w + 273^\circ C)\,(P_m)} \quad \text{(Eq. 1)} \qquad \text{and} \qquad Y = \frac{Y_1 + Y_2 + Y_3}{3} = 1.019. \quad \text{(Eq. 2)}$$

[f] With Y_r defined as the average ratio of volumetric measurement by wet test meter to rotameter. Tolerance Y_r = 1 ±0.05 for calibration and Y ±0.1 for posttest checks.

$$Y_{r_1} = \frac{V_w\,(t_d + 273^\circ C)\left[P_m + (D_m/13.6)\,1000\right]}{\theta\,(t_w + 273^\circ C)\,(P_m)\,(R_s} \quad \text{(Eq. 3)} \qquad \text{and} \qquad Y_r = \frac{Y_1 + Y_2 + Y_3}{3} = 0.999. \quad \text{(Eq. 4)}$$

Figure 2.4B. Dry gas meter calibration data form (metric units).

Posttest Calibration Check - After each field test series, conduct a calibration check as in Subsection 2.1.2 with the following exceptions:

1. The leak check is not conducted because a leak may have been corrected that was present during testing.

2. Three or more revolutions of the dry gas meter may be used.

3. Only two independent runs need be made.

4. If a temperature-compensating dry gas meter was used, the calibration temperature for the dry gas meter must be within 6°C (10.8°F) of the average meter temperature observed during the field test series.

When a lower meter calibration factor is obtained as a result of an uncorrected leak, the tester should correct the leak and then determine the calibration factor for the leakless system. If the new calibration factor changes the compliance status of the facility in comparison to the lower factor, either include this information in the report or consult with the Administrator for reporting procedures. If the calibration factor does not deviate by >5% from the initial calibration factor Y (determined in Subsection 2.1.2), then the dry gas meter volumes obtained during the test series are acceptable. If the calibration factor does deviate by >5%, recalibrate the metering system as in Subsection 2.1.2; for the calculations, use the calibration factor (initial or recalibration) that yields the lower gas volume for each test run.

2.2 Thermometer

The thermometer(s) on the dry gas meter inlet used to measure the metered sample gas temperature should be initially compared with a mercury-in-glass thermometer that meets ASTM E-1 No. 63C or 63F specifications:

1. Place the dial type or an equivalent thermometer and the mercury-in-glass thermometer in a hot water bath, 40°C to 50°C (104° to 122°F). Compare the readings after the bath stabilizes.

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

3. The dial type or equivalent thermometer is acceptable if (1) values agree within 3°C (5.4°F) at both points (steps 1 and 2 above) or (2) if the temperature differentials at both points are within 3°C (5.4°F) and the temperature differential is taped to the thermometer and recorded on the meter calibration form (Figure 2.4A or 2.4B).

4. Prior to each field trip, compare the temperature reading of the mercury-in-glass thermometer at room temperature with that of the thermometer that is part of the metering system. If the values or the corrected values are not within 6°C (10.8°F) of each other, replace or recalibrate the meter thermometer.

2.3 Rotameter

Method 7D recommends (optional) that the tester calibrate the rotameter prior to each test. Before being sent to the field, the rotameter should be cleaned and maintained according to the manufacturer's instructions. For this reason, it is recommended (optional) that the calibration curve and/or rotameter markings be checked upon receipt and then routinely checked with the posttest metering system check. The rotameter may be calibrated as follows:

1. Ensure that the rotameter has been cleaned as specified by the manufacturer and is not damaged.

2. Use the manufacturer's calibration curve and/or markings on the rotameter for the initial calibration. Calibrate the rotameter as described in the metering system calibration of Subsection 2.1.2, and record the data on the calibration form (Figure 2.4A or 2.4B).

3. Use the rotameter for testing if the pretest calculated calibration is within 450 +25 cc/min. If, however, the calibration point is not within 5%, determine a new flow rate setting, and recalibrate the system until the proper setting is determined.

4. Check the rotameter calibration with each posttest metering system check. If the rotameter check is within 10% of the 450 cc/min setting, the rotameter is acceptable. If, however, the check is not within 10% of the flow setting, disassemble and clean the rotameter, and perform a full recalibration.

2.4 Barometer

The field barometer should be adjusted initially and before each test series to agree within 2.5 mm (0.1 in.) Hg with a mercury-in-glass barometer or with the pressure value reported from a nearby National Weather Service Station and corrected for elevation. The tester should be aware that the pressure readings are normally corrected to sea level. The uncorrected readings should be obtained. The correction for the elevation difference between the weather station and the sampling point should be applied at a rate of -2.5 mm Hg/30 m (-0.1 in. Hg/100 ft) elevation increase, or vice versa for elevation decrease.

The calibration checks should be recorded on the pretest sampling form (Figure 2.5).

2.5 Analytical Balance

The analytical balance used to weigh the reagents for the nitrate stock standard should be calibrated by the following procedure:

1. Zero the balance.

2. Place a 5-g Class-S weight on the balance. Record the balance reading for the 5-g weight.

3. Place a 10-g Class-S weight on the balance. Record the balance reading for the 10-g weight.

4. The balance readings for the 5-g and 10-g weights must be within 2 mg of the actual weights.

5. If the balance readings are greater than ±2 mg either of the actual weights, repair the balance or contact the balance manufacturer.

2.6 Ion Chromatograph System

2.6.1 Performance Check of the Ion Chromatograph - Method 7D states that the instrument used for analysis should provide adequate resolution of NO_3^- and should be able to resolve and detect nitrite ion (NO_2^-). It is recommended that the instrument be performance checked prior to initial use to ensure that the instrument can meet the above criteria.

Method 7D does not quantify the criteria for acceptable instrument performance. The numerical limits and procedures given below are offered from a purely technical viewpoint. Their observance should ensure that the instrument conforms with the method, but should not be interpreted as a requirement. The preliminary considerations follow.

Conductivity Detector - Prior to its initial use, the conductivity detector of the ion chromatograph should be calibrated by the method described in the operator's manual. After this initial calibration, a quality control sample should be analyzed to check the detector response. A quality control sample should be analyzed immediately after the initial calibration curve for each analytical run and the concentration compared to the values obtained for the same QC sample in the past. If the control limits are exceeded, the analysis must be stopped until the problem is found.

Integrator - Many ion chromatographs are equipped with elec-

Date 2/22/84 Calibrated by Roy Doster

Meter box number EE-1

Dry Gas Meter*

Pretest calibration factor = 1.020 (within 2% of average factor for each calibration run).

Rotameter

Pretest calibration factor (Y_r) or setting = 1.00 (between 400 and 500 cc/min).

Dry Gas Meter Thermometer

Was a pretest temperature correction made? ___yes X no

If yes, temperature correction _____ (within 3°C (5.4°F) of reference values for calibration and within 6°C (10.8°F) of reference values for calibration check).

Barometer

Was the pretest field barometer reading correct? X yes __ no (within 2.5 mm (0.1 in.) Hg of mercury-in-glass ~~barometer).~~

*Most significant items/parameters to be checked.

Figure 2.5. Pretest sampling checks.

tronic integrators which, if properly used, give results of greater accuracy and precision than manual techniques. (Manual techniques include quantification based upon measuring: (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 and weighing it on a balance, and (e) peak area by planimetry.) However, an electronic integrator is a potential source of error if integration parameters are not set up correctly. For example, when the Hewlett Packard 3390A Recording Integrator is used in the peak area mode, the processes of recognizing and integrating peaks in the data signal depend upon the values chosen for PK WD and THRSH. If these two parameters are mismatched to each other or to the data signal, peaks will be missed by the integrator. The appropriate sections of the operator's manual should be read carefully before selecting and setting integrator parameters.

Electronic integrators, used in the peak height mode, have been demonstrated to give equally good results as the peak area mode, and therefore, many laboratories have chosen to use this simpler method.

The performance of the integrator in either mode should be checked using a quality control sample as described above. A second check of the integrator's performance can be made by comparing its results to those obtained manually. If the integrator is functioning properly, results should agree within 5 percent.

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, 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 NO_3^- peak from the other ion peaks should be achieved. A source of $SO_4^=$ in a sample may be sulfur dioxide present in the effluent stream sample. Figures 2.6a and 2.6b 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 analyst is encouraged to check the performance of the ion chromatograph system before analyzing samples in order to ensure that baseline separation of NO_3^- is attainable.

The ion chromatograph can be performance checked using a solution containing NO_3^- and $SO_4^=$ for compliance purposes or a solution containing NO_3^-, NO_2^-, and $SO_4^=$ if the nitrate is to

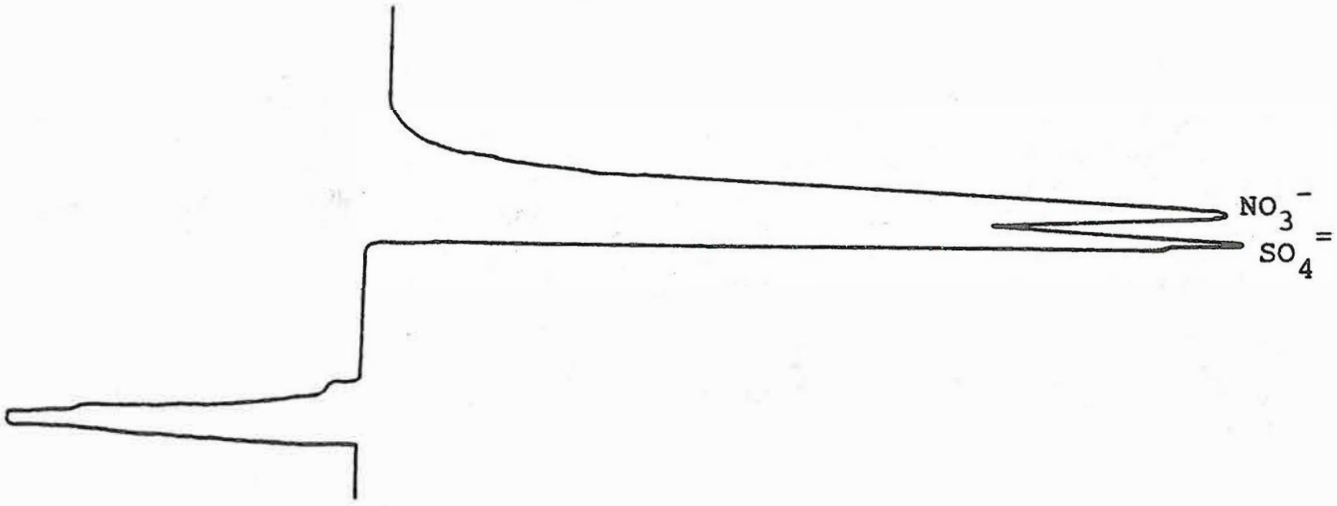

Figure 2.6a. Example chromatogram having overlapping peaks.

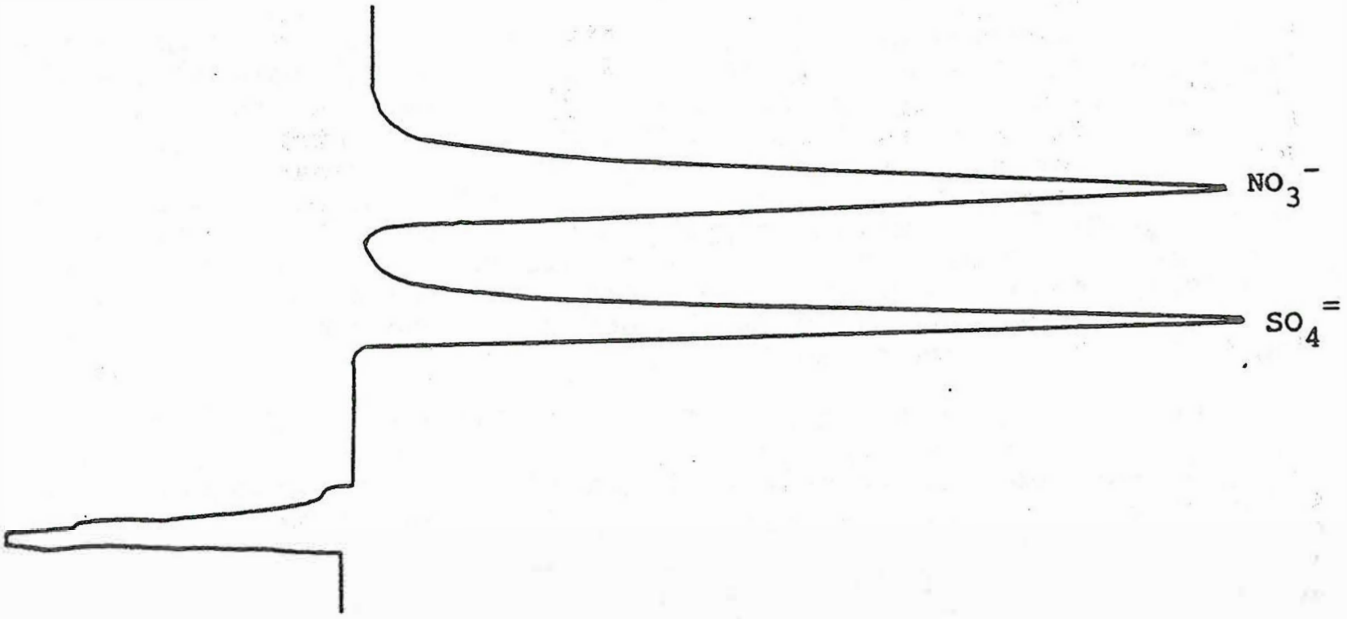

Figure 2.6b. Example chromatogram showing baseline separation of peaks.

be quantified. A solution that will provide rigorous conditions involves the use of KNO_3 working standard solution (described in Section 3.15.5, page 3) and NO_2^- (if applicable) and $SO_4^=$ solutions, the preparation of which are addressed below.

The $SO_4^=$ solution is prepared as follows: Weigh out 0.231 of sodium sulfate (Na_2SO_4), and transfer it to a beaker. Dissolve the Na_2SO_4 in water, quantitatively transfer the solution to a 250-ml volumetric flask, and finally, dilute to the mark with water.

The concentration of the solution is 625 µg $SO_4^=$/ml. Sodium sulfate (Na_2SO_4) is a component of the pusher solution in the Orsat apparatus used for Method 3. It is not special and has been chosen because of its probable availability. Other $SO_4^=$ reagents can be used.

If the nitrite is to be quantified, then separation of the nitrate peak should also be checked. To prepare the NO_2^- stock solution, first weigh out 52.5 mg sodium nitrite ($NaNO_2$) and transfer it to a beaker. Dissolve the $NaNO_2$ in water, quantitatively transfer it to a 250-ml volumetric flask, and finally, dilute to the mark with water. To prepare the NO_2^- working solution, pipet 10.0 ml of the stock solution into a 100-ml volumetric flask, and dilute to volume with water. The concentration of the working solution is 14 µg NO_2^-/ml.

To prepare the performance check solution, pipet 10 ml of the KNO_3 working standard solution, 8 ml of the $SO_4^=$ solution, and 1 ml of the NO_2^- working solution (if applicable) into a 200-ml volumetric flask, and dilute to the mark with water.

The concentration of NO_3^- in the performance check sample is 7.5 µg NO_3^-/ml, which corresponds to a NO_x level around the emission standard for coal-fired boilers subject to 40 CFR Part 60, Subparts D or Da. This correspondence also is based on the assumptions that sampling is conducted for one hour at 500 ml/min and that the effluent sample is 12% (v/v) CO_2.

The $SO_4^=$ concentration of the performance check sample is 25 µg $SO_4^=$/ml, which corresponds to an SO_2 level of roughly 1000 ppm (for a one-hour sample acquired at 500 ml/min and containing 12% (v/v) CO_2). This concentration level should be more than adequate for situations involving the application of Method 7D to sources subject to 40 CFR Part 60, Subpart D; thus, it is recommended that analysts decrease the $SO_4^=$ concentration in proportion to the SO_2 levels expected for the effluent. For example, if the effluent concentration of SO_2 were 500 ppm, 5 ml (rather than 10 ml) of the $SO_4^=$ solution would be used in

preparing the performance check sample. For applications upstream of flue gas desulfurization systems at sources subject to 40 CFR Part 60, Subpart Da, the opposite situation may exist, and it is recommended that the concentration of $SO_4^=$ be increased accordingly.

The NO_2^- concentration of the performance check solution is 0.07 µg NO_2^-/ml. This corresponds to 6 ppm NO_2 for a one-hour sample acquired at 500 ml/min and containg 12% (v/v) CO_2.

The performance check solution should be analyzed with the calibration standards during the initial check of the ion chromatograph's calibrations. The same experimental conditions should be observed for the solution and the standards. Figure 2.7 provides an example chromatogram that shows where the NO_2^-, NO_3^-, and $SO_4^=$ can be expected to elute.

2.6.2 Preparation of Calibration Curve - Method 7D gives general instructions for preparing the calibration curve for the ion chromatograph. Accordingly, the method requires that:

(a) at least four calibration standards be prepared;

(b) the concentration range of the calibration standards cover the concentration range of the samples being analyzed;

(c) the calibration standards be prepared from the KNO_3 standard solution using pipettes having volumes 1.0 ml or greater;

(d) the calibration standards be analyzed and the results be interpreted in the same manner as for the samples being analyzed;

(e) the results of the analyses of the calibration standards (in units of either peak height or peak area) should be plotted versus the standards' concentrations (in units of µg NO_3^-/ml);

(f) the plotted points define a linear relation;

(g) the calibration equation be determined from the points using linear regression; and

(h) the calibration standards be analyzed twice in order to compensate for any drift in the response of the ion chromatograph.

The method leaves to the analyst details including:

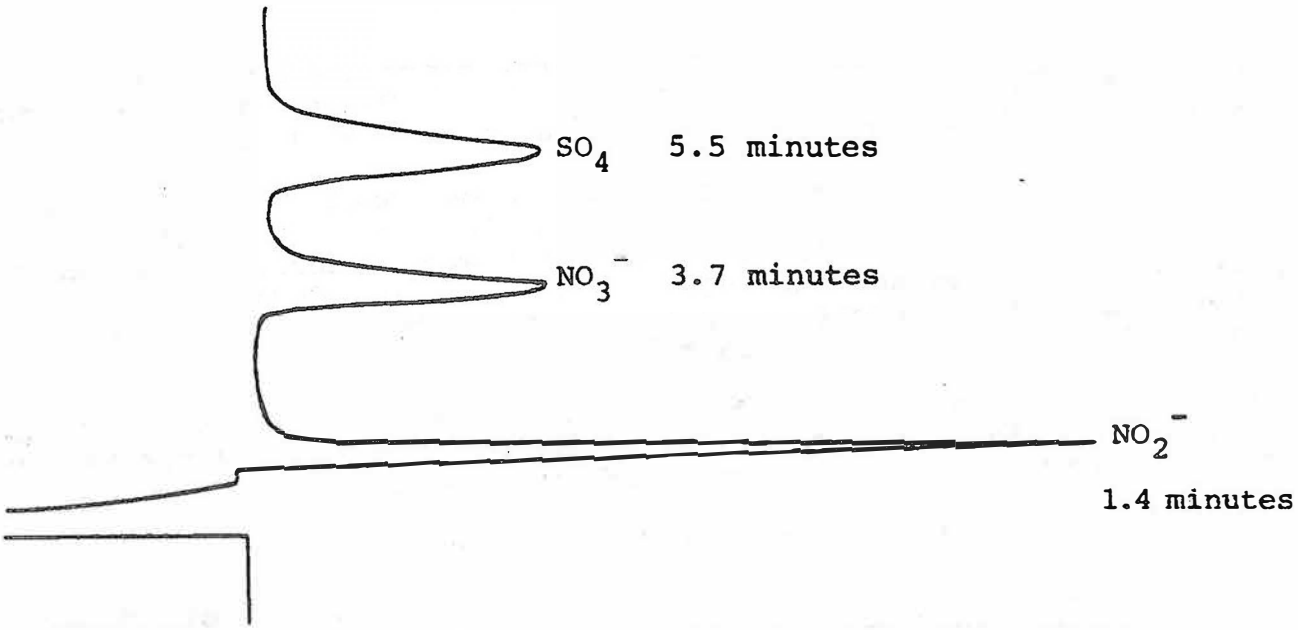

Figure 2.7. Chromatogram showing resolution of nitrite, nitrate, and sulfate peaks.

(a) the concentration values for the individual calibration standards;

(b) the degree of linearity of the calibration curve that will ensure quality results; and

(c) the procedure to be used to compensate results for the ion chromatograph's drift.

Concentration values for calibration standards - The step-by step-procedures for preparing the calibration standards and preparing the calibration curve are given in Section 3.15.5.

Table 2.1. ACTIVITIY MATRIX FOR CALIBRATION OF EQUIPMENT

Apparatus	Acceptance Limits	Frequency and method of measurement	Action if requirements are not met
Wet test meter	Capacity of at least 2 L/min and an accuracy within 1.0%	Calibrate initially and then yearly by liquid displacement	Adjust until specifications are met, or return to manufacturer
Dry gas meter	$Y_i = Y \pm 0.02Y$ at a flow rate of about 450 cc/min	Calibrate vs. wet test meter initially and when the posttest check is not within $Y \pm 0.05$	Repair and then recalibrate, or replace
Dry gas meter thermometer	Within $3^{\circ}C$ ($5.4^{\circ}F$) of true value	Calibrate each initially as a separate component against a mercury-in-glass thermometer; after train is assembled before each field test, compare with mercury-in-glass thermometer	Adjust, determine a constant correction fact or reject
Rotameter	Clean and maintain according to manufacturer's instructions (required); calibrate to $\pm 5\%$ (recommended)	Initially and after each field trip	Adjust and recalibrate, or reject
Barometer	Within 2.5 mm (0.1 in.) Hg of mercury-in-glass barometer or of weather station value	Calibrate initially using a mercury-in-glass barometer; check before and after each field test	Adjust to agree with certified barometer
Analytical balance	Weight within 2 mg of standard weights (Class-S)	Use standard weight before preparation of working solution	Repair or return to manufacturer

(continued)

Table 2.1. (continued)

Apparatus	Acceptance Limits	Frequency and method of measurement	Action if requirements are not met
Ion chromatograph	Calibrate prior to each set of sample analyses	With each set of field samples; calibration standards prepared from potassium nitrate	Interpret data using another technique; e.g., if using peak height, change to peak area; analyze additional calibration standards; calibrate conductivity detector; consult operator's manual

3.0 PRESAMPLING OPERATIONS

The quality assurance activities for presampling preparation are summarized in Table 3.1 at the end of this section. See Section 3.0 of this Handbook for details on preliminary site visits.

3.1 Apparatus Check and Calibration

Figure 3.1 or a similar form is recommended to aid the tester in preparing an equipment checklist, status report form, and packing list.

3.1.1 Sampling Train - The schematic for the NO_x sampling train is given in Figure 1.2. Commercial models of this system are available. Each individual or fabricated train must be in compliance with the specifications in Method 7D, Section 3.15.10.

3.1.2 Probe - The probe should be cleaned internally by brushing first with tap water, then with deionized distilled water, and finally with acetone. Allow the probe to dry in the air. In extreme cases, the glass or stainless steel liner can be cleaned with stronger reagents; the objective is to leave the liner free from contaminants. The probe's heating system should be checked to see whether it is operating properly. The probe must be leak free when sealed at the inlet or tip and checked for leaks at a vacuum of 250 mm (10 in.) Hg with the meter box. Any leaks should be corrected. The liner should be sealed inside the metal sheath to prevent diluent air from entering the source since most stacks are under negative pressure.

3.1.3 Restricted Orifice Impingers and Glass Connectors - All glassware should be cleaned with detergent and tap water, and then with reagent water. Any items that do not pass a visual inspection for cracks or breakage must be repaired or discarded.

3.1.4 Drying Tubes - Drying tubes should be packed with 6- to 16-mesh silica gel and sealed at both ends.

3.1.5 Valve and Rotameter - Prior to each field trip or at any sign of erratic behavior, the flow control valve and rotameter should be cleaned according to the maintenance procedure recommended by the manufacturer.

3.1.6 Pump - The vacuum pump and oiler should be serviced as recommended by the manufacturer, every 3 months, or every 10th test (whichever comes first), or upon erratic behavior (nonuniform or insufficient pumping action).

3.1.7 Dry Gas Meter - A dry gas meter calibration check should be made in accordance with the procedure in Section 3.15.2. An acceptable posttest check from the previous test is sufficient.

Apparatus check	Acceptable Yes	Acceptable No	Quantity required	Ready Yes	Ready No	Loaded and packed Yes	Loaded and packed No
Probe	✓		4	✓		✓	
Type liner							
Glass ✓							
Stainless steel ___							
Other ___							
Heated properly*	✓						
Leak checked	✓						
Filter	✓		Small box	✓		✓	
Glass wool							
Other ___							
Glassware							
Restriced orifice impinger	✓		14	✓		✓	
Size ___							
Type ___							
Meter System							
Leak-free pumps*	✓		2	✓		✓	
Rate meter*	✓		1	✓		✓	
Dry gas meter*	✓		1	✓		✓	
CO_2 Measurement							
Orsat ✓	✓		2	✓		✓	
Fyrite ___							
Reagents							
Water	✓		2 gal	✓		✓	
Potassium permanganate*	✓		2 gal	✓		✓	
Silica gel	✓		5 #	✓		✓	
Other							
Barometer	✓		1	✓		✓	
Drying tube	✓		6	✓		✓	

* Most significant items/parameters to be checked.

Figure 3.1. Pretest preparations.

3.1.8 Thermometers - The thermometers should be compared with the mercury-in-glass thermometer at room temperature prior to each field trip.

3.1.9 Barometer - The field barometer should be compared with the mercury-in-glass barometer or with a National Weather Service Station reading prior to each field trip.

3.1.10 CO_2 Analysis - Method 3 sampling apparatus should be leak checked, and the reagents should be checked to ensure freshness (see Section 3.2 of this Handbook).

3.2 Reagents for Sampling

The following reagents are needed during the sampling phase of Method 7D:

3.2.1 Water - Deionized distilled water should conform to ASTM specification D1193-82, Type III (see Subsection 1.4.1 for detailed specifications).

3.2.2 Potassium Permanganate/Sodium Hydroxide ($KMnO_4$/NaOH) Solution - Dissolve 40.0 g of $KMNO_4$ and 20.0 g of NaOH in 940 ml of water.

3.3 Packaging Equipment for Shipment

Equipment should be packed in rigid containers to protect it against rough handling during shipping and field operations.

3.3.1 Probe - The inlet and outlet of the probe must be sealed and protected from breakage. A suggested container is a wooden case lined with polyethylene foam or other suitable packing material; the case should have separate compartments for individual devices. The case should be equipped with handles or eye hooks that can withstand hoisting, and should be rigid to prevent bending or twisting during shipping and handling.

3.3.2 Impingers, Connectors, and Assorted Glassware - All impingers and glassware should be packed in a rigid container and protected by polyethylene foam or other suitable packing material. Individual compartments for glassware help to organize and protect each item. The impinger train may be charged and assembled in the laboratory if sampling is to be performed within 24 hours.

3.3.3 Drying Tubes and Volumetric Glassware - A rigid container lined with polyethylene foam material protects drying tubes and assorted volumetric glassware.

3.3.4 Meter Box - The meter box, which contains the valve, rotameter, vacuum pump, dry gas meter, and thermometer(s), should

be packed in a rigid shipping container unless its housing is strong enough to protect components during travel. Additional pump oil should be packed if oil is required for operation. It is advisable to ship a spare meter box in case of equipment failure.

3.3.5 Wash Bottles and Storage Containers - Storage containers and miscellaneous glassware should be packed in a rigid foam-lined container. Samples being transported in the containers should be protected from extremely low ambient temperatures (below freezing).

Table 3.1. ACTIVITY MATRIX FOR PRESAMPLING OPERATIONS

Operation	Acceptance limits	Frequency and method of measurement	Action if requirements are not met
Probe	1. Probe liner free of contaminants	1. Clean probe internally by brushing with tap water, then deionized distilled water, then acetone; allow to dry in air before test	1. Retrace cleaning procedure and assembly
	2. Probe leak free at 250 mm (10 in.) Hg	2. Visually check for cracks before test	2. Replace
	3. No moisture condensation	3. Check out heating system initially and when moisture appears during testing	3. Repair or replace
Restricted orifice impingers and glass connectors	Clean and free of breaks, cracks, etc.	Clean with detergent, tap water, and then with deionized distilled water	Repair or discard
Flow control valve and rotameter	Clean and without sign of erratic behavior (ball not moving)	Clean prior to each field trip or upon erratic behavior	Repair or return to manufacturer
Vacuum pump	Maintain sampling rate of 400 to 500 cc/min at a vacuum up to 250 mm (10 in.) Hg	Service every 3 mo. or upon erratic behavior; check oiler jars every 10th test	As above
Dry gas meter	Clean and within 2% of calibration factor	Calibrate according to Section 3.15.2; check for excess oil if oiler is used	As above
CO_2 analyzer	Leak-free and fresh reagents	Leak check, and check reagents	As above

(continued)

Table 3.1 (continued)

Operation	Acceptance limits	Frequency and method of measurement	Action if requirements are not met
Reagents			
Sampling	Requires all ACS grade reagents	Prepare and store in sealed containers	Prepare new reagent
Sample recovery	Requires water on site	Quantity sufficient to recover sample after testing and clean impingers prior to testing	Prepare new reagent
Package Equipment for Shipment			
Probe	Protect with polyethylene foam	Prior to each shipment	Repack
Impingers, connectors, and assorted glassware	Pack in rigid containers with polyethylene foam	As above	As above
Drying tubes, volumetric glassware	Sturdy container lined with foam	As above	As above
Meter box	Meter box case and/or container to protect components, pack spare meter box and oil	As above	As above
Wash bottles and storage containers	Pack in rigid foam-lined container	As above	As above
Samples	Protect from extreme cold (below freezing)	As above	As above

4.0 ON-SITE MEASUREMENTS

On-site activities include transporting the equipment to the test site, unpacking and assembling, sampling for nitrogen oxides, and recording the data. The quality assurance activities are summarized in Table 4.1 at the end of this section.

4.1 Transport of Equipment to the Sampling Site

The most efficient means of transporting the equipment from ground level to the sampling site (often above ground level) should be decided during the preliminary site visit or by prior correspondence. Care should be taken to prevent damage to the equipment or injury to test personnel during the moving. A laboratory area should be designated for preparing the absorbing reagents, charging the impingers, and sample recovery.

4.2 Preliminary Measurements and Setup

Method 7D outlines the procedure for determining the concentration of nitrogen oxides in the gas stream. The accuracy of the equipment that has been transported to the sampling site and that may have been handled roughly can be determined by making a one-point check of the rotameter reading against the dry gas meter reading at the test site. Use Equation 3 in Figure 2.4A or 2.4B, and substitute dry gas meter readings in place of wet test meter readings (i.e., $V_d = V_w$). Y_{ri} should bebetween 0.9 and 1.1; if not, the meter box has lost its rate or volume calibration. The tester can still use the meter box, but the data should not be released for decision making until a post-test recalibration has been made. If the dry gas meter calibration factor did change, the dry gas meter volumes may have to be corrected. Record the test identification number on the sampling data form, Figure 4.1.

4.3 Sampling

The on-site sampling includes the following steps:

1. Preparation and/or addition of the absorbing reagents to the impingers.

2. Setup of the sampling train.

3. Connection to the electrical service.

4. Preparation of the probe (leak check of entire sampling train and addition of particulate filter).

5. Check of rotameter setting.

6. Insertion of the probe into the stack.

Plant name Acme Power Plant City Coal Bend MT
Location Boiler No. 3 Date 3/15/84
Operator Ken Loder Sample no. AP-1
Probe length/material Glass - 4ft. Probe setting 250°F
Meter box no. EE-1 Meter factor (Y) 1.02
Sampling point location(s) 1.35m from Port A Bar press mm (in.) Hg 29.41
Rotameter setting 450cc/min Rotameter check? 459cc/min (OK)
Initial leak check? 0.004 L/min @250 mm Hg Final leak check? 0.006 L/min @250 mm Hg
CO_2 concentration (1) 14.8 (2) 15.0 (3) 14.7 avg 14.833

Sampling time, min	Clock time 24 h	Dry gas meter readings L (ft^3)	Sample flow rate setting, cc/min (ft^3/min)	Sample volume metered, L (ft^3) (V_m)	Percent deviation,[a] %	Dry gas meter temp, °C (°F)
0	1100	140.215	—	—	—	—
5	1105	142.461	450	2.246	-0.22	72
10	1110	144.701	450	2.240	-0.49	74
15	1115	146.958	450	2.257	+0.27	74
20	1120	149.202	450	2.244	-0.31	75
25	1125	151.454	450	2.252	+0.04	76
30	1130	153.699	450	2.245	-0.27	76
35	1135	155.953	450	2.254	+0.13	78
40	1140	158.222	450	2.269	+0.80	78
45	1145	160.480	450	2.258	+0.31	78
50	1150	162.728	450	2.248	-0.13	79
55	1155	164.982	450	2.254	+0.13	78
60	1200	167.226	450	2.244	-0.31	79
Total 60		Total 27.011		V_m avg 2.251	Avg dev -0.42	Avg 76.4

[a] Percent deviation = $\frac{V_m - V_m \text{ avg}}{V \text{ avg}} \times 100$ (must be less than 10 percent).

Figure 4.1. Field sampling data form for NO_x.

7. Sealing of the port.

8. Check of the temperature of the probe.

9. Sampling.

10. Measuring the CO_2 concentration.

11. Recording of the data in Figure 4.1.

A final leak check of the train is always performed after sampling.

4.3.1 Preparation and/or Addition of Absorbing Reagents to Collection System - Absorbing reagents can be prepared on site, if necessary, according to the directions in Subsection 1.4.1.

1. Use a pipette or a graduated cylinder to introduce 200 ml of alkaline permanganate ($KMnO_4$/NaOH) solution into each of the three impingers.

2. Place in the sampling train a drying tube that has new or regenerated silica gel.

4.3.2 Assembling the Sampling Train - After assembling the sampling train as shown in Figure 1.2, perform the following:

1. Adjust probe heater to operating temperature. Place crushed ice and water around the impingers.

2. Leak check the sampling train just prior to use at the sampling site (not mandatory) by temporarily attaching a rotameter (capacity of 0 to 40 cc/min) to the outlet of the dry gas meter and placing a vacuum gauge at or near the probe inlet. Plug the probe inlet, pull a vacuum of at least 250 mm (10 in.) Hg, and note the flow rate indicated by the rotameter. A leakage rate $\leq$ 2% of the average sampling rate is acceptable. Note: Carefully release the probe inlet plug before turning off the pump. It is suggested (but not mandatory) that the pump be leak checked separately, either prior to or after the sampling run. If prior to the run, the pump leak check shall precede the leak check of the sampling train. If after, the pump leak check shall follow the train leak check. To leak check the pump, proceed as follows. Disconnect the drying tube from the probe impinger assembly. Pull a vacuum of 250 mm (10 in.) Hg. Plug or pinch off the outlet of the flow meter, and then turn off the pump. The vacuum should remain stable for at least 30 seconds.

3. Place a loosely packed filter of glass wool in the end of the probe, and connect the probe to the first impinger.

4.3.3 Rotameter Setting Check (Optional) - After leak checking the sampling train, disconnect the probe from the first impinger,

and connect the filter (optional). The filter is a tube containing approximately 20 g of 5-Angstrom molecular sieve to remove the NO_x from the ambient air. Start the pump, and adjust the flow to the rotameter setting to be used during the sampling run. After the flow has stablized, start measuring the volume sampled, as recorded by the dry gas meter and the sampling time. Collect sufficient volume to measure accurately the flow rate, and calculate the flow rate. The average flow rate must be less than 500 cc/min for the sample to be valid; therefore, it is recommended that the flow rate be checked as above prior to each run. Record the sampling rate on the data form.

4.3.4 Sampling (Constant Rate) - Sampling is performed at a constant rate of between 400 and 500 cc/min as indicated by the rotameter during the entire sampling run. The procedure is as follows:

1. Record the initial dry gas meter readings, barometer reading, and other data as indicated in Figure 4.1. Double check the dry gas meter reading.

2. Position the tip of the probe at the sampling point, connect the probe to the first impinger, and start the pump. Warning: If the stack is under a negative pressure of >250 mm (10 in.) H_2O while disconnected from the impinger, the probe should be positioned at the sampling point, the sample pump turned on, and then the probe immediately connected to the impinger to prevent the impinger solutions from being siphoned backwards.

3. Adjust the sample flow to the preselected flow rate (400 to 500 cc/min) as indicated by the rotameter.

4. Maintain a constant rate within 10% during the entire sampling run, and take readings (dry gas meter, temperatures at dry gas meter, and rate meter) at least every 5 minutes.

5. Refer to emission standards for minimum sampling time and/or volume. (For example, the Federal standard for fossil fuel-fired steam generators specifies a minimum sampling time of 60 minutes; for relative accuracy tests, when the SO_2 concentration is greater than 1200 ppm, the sampling time should be 30 minutes.) A quick calculation can be made after half the sampling time to guarantee that the sampling rate will not exceed 500 cc/min.

6. During sampling, measure the CO_2 content of the stack gas near the sampling point using Method 3. The single-point grab sampling procedure is adequate, provided the measurements are made at least three times (near the start, midway, and before theend of a run) and provided the average CO_2 concentration is computed. An Orsat (which is highly recommended) or Fyrite

analyzer may be used for this analysis. The results should be recorded on the data form (Figure 4.1).

7. Turn off the pump at the conclusion of each run, remove the probe from the stack, and record the final readings. Warning: Again, if the stack is under negative pressure, disconnect the probe first, and turn off the pump immediately thereafter.

8. Conduct a leak check, as described in Subsection 4.3.2 (mandatory).

9. Calculate the sampling rate. The sample volume (ΔV_m) for each point should be within 10% of the average sampling volume for all points, and the average sampling rate for the test should be less than 500 cc/min. If the average sampling rate exceeds 500 cc/min, the sample collection efficiency may be affected.

4.4 Sample Recovery

Method 7D requires transfer of the impinger contents and the connector washings to a polyethylene storage container. This transfer should be done in the "laboratory" area to prevent contamination of the test sample.

After completing the final leak check, disconnect the impingers, and transport them to the cleanup area. Cap off the impinger section with the use of polyethylene or equivalent caps before transport to the cleanup area. Transfer the contents of the impingers into a labeled, leak-free polyethylene sample bottle. Rinse the three impingers a couple of times and the connecting tubes once with 3- to 15-ml portions of water. Add these washings to the same sample bottle, and mark the fluid level on the side. Place about 100 ml of the absorbing reagent ($KMnO_4$/NaOH) in a polyethylene bottle, and label it for use as a blank during sample analysis (once for each test). An example of a sample label is shown in Figure 4.2.

Plant Acme Power Plant City Coalbend, MT
Site Boiler No. 3 Sample type NO_x
Date 3/15/84 Run number AP-1
Front rinse ☐ Front filter ☐ Front solution ☐
Back rinse ☐ Back filter ☐ Back solution ☑
Solution $KMnO_4$/NaOH Level marked ✓
Volume: Initial 600 mL Final 642 mL
Cleanup by Ken Loder
Remarks:

Figure 4.2. Example of a sample label.

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4.5 Sample Logistics (Data) and Packing Equipment

The sampling and sample recovery procedures are followed until the required number of runs are completed. Log all data on the Sample Recovery and Integrity Data Form, Figure 4.3. If the impingers, and connectors are to be used in the next test, they should be rinsed with water, and a new drying tube should be inserted into the sampling trian. At the completion of the test:

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

2. Record all data collected during the field test in duplicate by using carbon paper or by using data forms and a field laboratory notebook. One set of data should be mailed to the base laboratory, given to another team member, or given to the Agency. Hand carrying the other set (not mandatory) can prevent a very costly and embarrassing mistake.

3. Examine all sample containers and sampling equipment for damage, and pack them for shipment to the base laboratory, being careful to label all shipping containers to prevent loss of samples or equipment.

4. Make a quick check of the sampling and sample recovery procedures using the data form, Figure 4.4.

Plant Acme Power Plant Sampling location Boiler No. 3

Field Data Checks

Sample recovery personnel Ken Loder

Person with direct responsibility for recovered samples _____

Sample number	Sample identification number	Date of recovery	Liquid level marked	Stored in locked container
1	AP-1	3/15/84	✓	✓
2				
3				
Blank				

Remarks Container checked for leaks

Signature of field sample trustee Ken Loder

Laboratory Data Checks

Lab person with direct responsibility for recovered samples E. Esks

Date recovered samples received 3/16/84

Analyst Scott Steinsberger

Sample number	Sample identification number	Date of analysis	Liquid level marked	Stored in locked container
1	AP-1	3/18/84	✓	✓
2				
3				
Blank				

Remarks _____

Signature of lab sample trustee Scott Steinsberger

Figure 4.3. Sample recovery and integrity data.

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Sampling

Impinger contents properly selected, measured, and placed in impingers?* ✓

Impinger Contents/Parameters*

1st: 200 ml of $KMnO_4$/NaOH ✓

2nd: 200 ml of $KMnO_4$/NaOH ✓

3rd: 200 ml of $KMnO_4$/NaOH ✓

Drying tube: 6- to 16-mesh silica gel ✓

Probe heat at proper level?* ✓

Crushed ice around impingers? no; not required

Pretest leak check at 250 mm (10 in.) Hg? ✓

Leakage rate? 0.004 L/min

Check of rotameter setting? 459 cc/min

Probe placed at proper sampling point? ✓

Flow rate constant at approximately 450 cc/min?* ✓

CO_2 concentration measured?* ✓

Posttest leak check at 250 mm (10 in.) Hg?* ✓

Leakage rate? 0.006 L/min

Sample Recovery

Contents of impingers placed in polyethylene bottles? ✓

Fluid level marked?* ✓

Sample containers sealed and identified?* ✓

* Most significant items/parameters to be checked.

Figure 4.4. On-site measurements.

1808

Table 4.1. ACTIVITY MATRIX FOR ON-SITE MEASUREMENT CHECKS

Activity	Acceptance limits	Frequency and method of measurement	Action if requirements are not met
Preparing and/or adding absorbing reagents	Add 200 ml of $KMnO_4$/NaOH to the impingers	Add 40.0 g of $KMnO_4$ and 20.0 g of NaOH to 940 ml of water	Reassemble collection system
Assembling the sampling train	1. Assemble to specifications in Fig. 1.2	1. Before each sampling run	1. Reassemble
	2. A leakage rate of $\leq$2% of the average sampling rate	2. Leak check before sampling (recommended) by attaching a rotameter to dry gas meter outlet, placing a vacuum gauge at or near probe inlet, and pulling a vacuum of $\geq$ 250 mm (10 in.) Hg	2. Correct the leak
Sampling (constant rate)	1. Within 10% of constant rate	1. Calculate % deviation for each sample using equation in Fig. 4.1	1. Repeat the sampling, or obtain acceptance from a representative of the Administrator
	2. Minimum acceptable time is 60 min and sampling rate less than 500 cc/min	2. Make a quick calculation prior to completion and an exact calculation after completion	2. As above
	3. Less than 2% leakage rate at 250 mm (10 in.) Hg	3. Leak check after sampling run (mandatory); use same procedure as above	3. As above
	4. Determine CO_2 content	4. Measure CO_2 content using Method 3	4. As above

(continued)

Table 4.1 (continued)

Activity	Acceptance limits	Frequency and method of measurement	Action if requirements are not met
Sample logistics (data) and packing of equipment	1. All data are recorded correctly	1. Visually check upon completion of each run and before packing	1. Complete the data form
	2. All equipment examined for damage and labeled for shipment	2. As above	2. Redo test if damage occurred during testing
	3. All sample containers properly labeled and packaged	3. Visually check upon completion of test	3. Correct when possible

5.0 POSTSAMPLING OPERATIONS

The postsampling operations for Method 7D include an apparatus check, a barometer check, sample preparation, and sample analysis by ion chromatography. The procedures for the apparatus check and the barometer check are the same as in Method 6. These procedures are detailed in Section 3.5.5 in the Quality Assurance Handbook for Air Pollution Measurement Systems, Volume III and are not discussed here. The procedures for sample preparation and sample analysis are described here. Table 5.1 provides a checklist summarizing the postsampling procedures.

5.1 Sample Preparation

Sample preparation should not be started until the required 36-hour conversion time has elapsed for complete conversion of NO_2^- to NO_3^-. When using Method 7D for relative accuracy testing of continuous emission monitors, the sample can be prepared immediately if the nitrite in the sample is quantitated using the procedures described in Section 5.2. The liquid level in the sample container should be checked to determine if sample has been lost during shipment. If a loss has occured, the appropriate steps should be taken to correct for the loss. The sample is prepared for ion chromatography by precipitating the excess permanganate as manganese dioxide (MnO_2). A 5% (v/v) hydrogen peroxide (H_2O_2) solution is used to reduce the permanganate to MnO_2. The MnO_2 precipitate is removed by vacuum filtration and the filtered solution is volumetrically diluted prior to chromatographic analysis.

5.1.1 Sample Loss Determination and Correction - Before preparing the sample, it must be allowed the full 36-hour conversion time. Compare the liquid level in the sample container to the mark on the container. If a noticeable amount of sample has been lost, use the following procedure for correcting the sample volume:

1. Mark the new level of liquid on the sample container.

2. Transfer the sample to a 1-liter volumetric flask (V_{soln}), and rinse the container with water.

3. Fill the sample container with water to the initial sample level. Transfer the water to a graduated cylinder, and determine the original sample volume (V_{soln_i}).

4. Fill the sample container with water to the final sample level. Transfer the water to a graduated cylinder, and determine the final sample volume (V_{soln_f}).

5. If V_{soln_f} is less than V_{soln_i}, correct the sample volume (V_{soln}) by using Equation 5-1:

$$V'_{soln} = V_{soln} \frac{V_{soln_i}}{V_{soln_f}}$$ Equation 5-1

where:

V'_{soln} = sample volume to be used for calculations, ml,

V_{soln} = volumetric flask volume, ml,

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

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

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

5.1.2 Permanganate Precipitation and Filtration - After the required 36-hour conversion period for the sample has elapsed and the sample container has been checked for sample loss, the sample can be quantitatively transfered to a 1-liter volumetric flask. (If the correction for sample loss has already been made, the sample should already be in a 1-liter volumetric flask.) The procedure for precipitating the excess permanganate is as follows:

1. Dilute the sample in a 1-liter volumetric flask (V_{soln}) to volume with reagent water, and mix well.

2. Take a 50-ml aliquot (V_a) of the sample from the 1-liter volumetric flask, and transfer the aliquot to a 250-ml Erlenmeyer flask containing a Teflon-coated stirring bar. If the NO_x concentration is low, a 100-ml aliquot may be taken to increase the instrument response.

3. Stir the sample as fast as possible without splashing any of the sample out of the flask.

4. Add a 5% H_2O_2 solution in 5-ml portions while stirring until the permanganate color disappears.

5. Stop stirring and allow the precipitated manganese dioxide to settle. If the solution is clear, then enough H_2O_2 has been added. If the permanganate color persists in the solution, then continue the H_2O_2 addition in 5-ml portions until a clear solution is produced after settling.

6. Assemble the Buchner funnel and filter flask. The spout of the Buchner funnel may be fitted with a length of Teflon tubing to minimize the probability of sample loss by aspiration during filtration.

7. Place a piece of GF/C filter paper (or an equivalent type of filter paper) in the Buchner funnel. Wet the paper with water, and seal the filter by applying a vacuum to the flask.

8. Quantitatively transfer the precipitated sample solution to the filter, and filter the solution. Wash the Erlenmeyer flask and the solid material on the filter with water four times, and collect the washings with the filtered solution.

9. Quantitatively transfer the filtered solution from the filter flask to a 250-ml volumetric flask (V_b). Dilute to volume with water.

10. Prepare a reagent blank by repeating steps 2 through 9 on a diluted sample of the alkaline-permanganate absorbing solution. Dilute 60 ml of the absorbing solution to 100 ml with water, and use 50 ml in step 2.

5.2 Sample Analysis by Ion Chromatography

For Method 7D, the basic components and the operation of the ion chromatograph are the same as for Method 7A. A discussion of the ion chromatograph can be found in Section 3.14.2 of Method 7A. The analyst should be familiar with the operater's manual for his particular ion chromatograph system. In this section, the preparation of calibration standards, the use of quality assurance audit samples, the analysis procedure, and the data reduction and reporting are described.

5.2.1 Preparation of Calibration Standards - The accuracy of the ion chromatographic analysis, as in any analysis, depends directly on the accuracy of the prepared calibration standards. The use of proper pipetting procedures, described in Method 7A, Section 3.14.5, and a properly dried, reagent grade standard are necessary to obtain quality results from the analysis. The preparation of the NO_3^- calibration standards is as follows:

1. Dry approximately 15 g of potassium nitrate (KNO_3) in an oven at 105° to 110°C for 2 hours. (Sodium nitrate can also be used provided the difference in the formula weight is considered in the subsequent calculations.) Allow the dried KNO_3 to cool to room temperature in a desiccator before weighing.

2. Calibrate an analytical balance with a 5-g Class-S calibration weight and a 10-g Class-S calibration weight to within 2 mg. Accurately weigh 9 to 10 g of dried KNO_3 to within 0.1 mg.

3. Dissolve in reagent water, and dilute to 1 liter in a Class-A volumetric flask. Calculate the exact NO_3^- concentration using the following formula:

$$\mu g\ NO_3^-/ml = g\ of\ KNO_3 \times 10^3 \frac{62.01}{101.1} \qquad \text{Equation 5-2}$$

The stock standard solution should be stable for 2 months if precautions, such as refrigeration, are used to prevent decomposition by nitrate-utilizing microorganisms.

4. Prepare a fresh working standard solution for each set of analyses by pipetting 5 ml of stock standard solution into a 200-ml Class-A volumetric flask. Dilute to volume with water.

5. Prepare a series of four calibration standards from the fresh working standard solution. Pipet 1.0 ml, 3.0 ml, 5.0 ml, and 10.0 ml into a series of four 100-ml Class-A volumetric flasks. Dilute to volume with reagent water. The concentration of the calibration standards made from a 9.7823 g KNO_3/liter (6000 $\mu g\ NO_3^-/ml$) stock standard solution would be 1.5, 4.5, 7.5, and 15.0 $\mu g\ NO_3^-/ml$.

The calibration standard concentrations cited above are used in the example employing Figure 5.1, the analytical data form for analysis of calibration standards.

The calibration standards for nitrite quantitation are prepared when Method 7D is used for relative accuracy testing of continuous emission monitors. A stock NO_2^- standard solution is (1) prepared with $NaNO_2$ of known purity or (2) analyzed before use. Do not oven dry the $NaNO_2$. Dissolve 52.5 mg of $NaNO_2$ in water and dilute to volume in a 250-ml Class-A volumetric flask. A series of four calibration standards with NO_2^- concentrations of 1.4, 4.2, 7.0, and 14.0 g NO_2^-/ml are prepared by pipetting 1.0, 3.0, 5.0, and 10 ml of stock NO_2^- standard into four 100-ml Class-A volumetric flasks. The NO_2^- calibration standards are diluted to volume with water.

5.2.2 Quality Assurance Audit Samples - The accuracy of the calibration standards can be assessed by analyzing nitrate standard solutions prepared by an outside laboratory with the concentrations unknown to the analyst. For making compliance determinations, a set of two Quality Assurance Audit Samples are obtained from the U. S. Environmental Protection Agency, Environmental Monitoring Systems Laboratory, Quality Assurance Division, Source Branch, Mail Drop 77A, Research Triangle Park, NC 27711. (The analyst should notify the Quality Assurance Officer or the responsible enforcement agency at least 30 days in advance of the need for quality assurance samples. The analyst must also specify that the quality assurance samples are for Method 7D.) The concentrations of the quality assurance samples determined by the analyst must be within 10% of the actual concentrations of the same samples.

Plant Acme Power Plant Location Boiler No. 3

Date 3/18/84 Analyst S. Steinsberger

Standard identifier	Standard concentration (x) (µg/ml NO_3^-)	Instrument response (y) peak height or area count mm				Predicted standard concentration (P) (µg/ml NO_3^-)	Deviation (%)
		1	2	3	Avg		
Std 1	1.5	20	20	22	20.7	1.54	+2.7
Std 2	4.5	65	59	61	61.7	4.55	-1.1
Std 3	7.5	99	98	103	100.0	7.36	-1.9
Std 4	15.0	198	210	206	204.7	15.05	+0.3

Equation for Linear Calibration Curve, Average Response as a Function of Standard Concentration

$y = mx + b = (13.6175)\,x + (-0.2497)$

where:

y = instrument response (mm or area count) = 20.7

m = calibration curve slope $\frac{\text{mm or area count}}{\mu g\ NO_3^-/ml}$ = 13.6175

x = standard concentration (µg NO_3^-/ml) = 1.5

b = I = intercept term (mm or area count) = -0.2497

Predicted Standard Concentration (P)

$$P\ (\mu g\ NO_3^-/ml) = \frac{\text{Average Instrument Response (y) - Intercept (I)}}{\text{Calibration Curve Slope (m)}}$$

$$P\ (\text{for first standard}) = \frac{(20.7) - (-0.2497)}{13.6175} = 1.54\ \mu g\ NO_3^-/ml$$

Deviation

$$\text{Deviation (\%)} = \frac{P\ (\mu g\ NO_3^-/ml) - x\ (\mu g\ NO_3^-/ml)}{x\ (\mu g\ NO_3^-/mL)} \times 100\%$$

$$\text{Deviation (of first set of standards)} = \frac{(1.54) - (1.5)}{1.5} \times 100\% = 2.7\ \%$$

Figure 5.1. Analytical data form for analyses of calibration standards.

5.2.3. Ion Chromatographic Analysis - The selection of the ion chromatographic conditions depends on the particular ion chromatograph system available to the analyst. The selection of eluents for ion chromatography depends on the method of detection used. For suppressed ion chromatography the following conditions have been used successfully:

1. A 0.003M $NaHCO_3$/0.0024M Na_2CO_3 eluent solution is prepared by dissolving 1.008 g of $NaHCO_3$ and 1.018 of Na_2CO_3 in water and diluting to 4 liters.

2. The full-scale detection range is set at 3 μMHO, and a 0.5-ml sample loop is used.

3. A flow rate of 2.5 ml/min gives a NO_3^- retention time of approximately 15 minutes depending on the type of column used.

Non-suppressed ion chromatography and ion-pairing chromatography may also be used provided baseline separation of NO_3^- and $SO_4^=$ separation and detection of NO_2^- are obtained (see Figure 5.2). Packed-bed suppression columns are not recommended for quantifying NO_2^- when using Method 7D for relative accuracy testing.

The recommended procedure for the ion chromatographic analysis is as follows:

1. Establish a stable baseline. Inject a sample of water, and observe the chromatogram to see whether any NO_3^- elutes. Repeat the water injection until NO_3^- is not observed on the chromatogram. If, after 5 injections, a NO_3^- peak is still seen, the water source should be checked for contamination.

2. Inject samples in the following order: calibration standards, reagent blank, field samples, calibration standards, reagent blank, field samples, calibration standards. The injection volumes for all the standards and samples should be the same.

3. The chromatograms should be documented with the sample identification, injection point, injection volume, nitrate retention time, eluent flow rate, detector sensitivity setting, and recorder chart speed.

4. Manually measure the NO_3^- peak height or determine the NO_3^- peak area with an electronic integrator.

5.2.4 Data Reduction and Reporting - The details of the data reduction procedure are discussed in Section 3.15.6. The procedures for calculating a response factor from the calibration standards by linear regression and for calculating the % deviation on each standard from the predicted value are as follows:

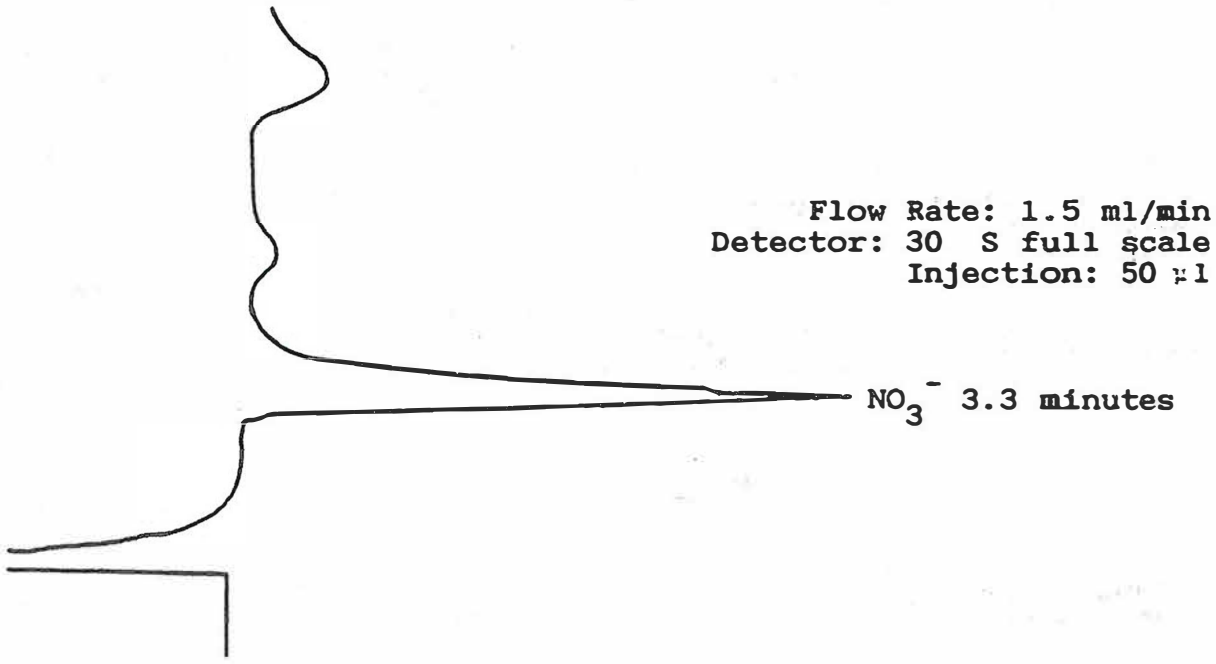

Figure 5.2. Example of chromatogram having adequate documentation.

1. Use the analytical data form (see Figure 5.1) for calculating the linear regression equation based on the calibration standards.

2. Record the calculated concentrations for the four calibration standards (x) on the data sheet. Determine the average value for the instrument response (y) for NO_3^- (peak height or area under the peak) from the three determinations for each of the four calibration standards.

3. Plot the average values for the instrument response for the calibration standards against the corresponding calculated concentrations of the calibration standards. Draw a smooth curve through the points without forcing the curve through zero. The curve should be linear.

4. Determine the slope (m) and the intercept term (b or I) for the linear calibration curve by linear regression. Many scientific calculators are capable of performing linear regression.

5. Calculate the predicted standard concentration (P) for each calibration standard using the following equation:

Equation 5-3

$$P(\mu g/ml\ NO_3^-) = \frac{\text{Average Instrument Response (y) - Intercept (I)}}{\text{Calibration Curve Slope (m)}}$$

6. Calculate the percent deviation of each calibration standard (x) from the predicted value using the following equation (optional):

Equation 5-4

$$\% \text{ Deviation} = \frac{P\ (\mu g\ NO_3^-/ml) - x\ (\mu g\ NO_3^-ml)}{x\ (\mu g\ NO_3^-/ml)} \times 100$$

If any standard deviates from the standard curve by more than $\pm$7%, the problem should be investigated.

The concentration of the field samples, the reagent blank, and the quality assurance samples are calculated by the same procedure used to calculate the predicted values for the calibration standards. Use the data form shown in Figure 5.3 for the analysis of field samples. The procedure is as follows:

1. Determine the instrument response factor for the sample and calculate the sample concentration using Equation 5-3. Calculate the average value for the two determinations made on each sample.

Date samples received 3/16/84 Date samples analyzed 3/18/84
Plant Acme Power Plant Run number(s) AP-1, 2, & 3
Location Coalbend, MT Analyst S. Steinsberger
Calibration curve slope (m) 13.6175 Intercept term (I) -0.2497

Field sample number	Analysis number	Instrument response (y) (mm or area counts)	Concentration of analysis sample (µg/ml NO_3^-)	Average Concentration of analysis sample (µg/ml NO_3^-)	Deviation (%)
AP-1	1st 2nd	79 mm 78 mm	5.8 5.7	S = 5.75	0.87
AP-2	1st 2nd	64 mm 62 mm	4.7 4.6	S = 4.65	1.1
AP-3	1st 2nd	72 mm 70 mm	5.3 5.2	S = 5.25	0.95
Field Blank	1st 2nd	5 mm 5 mm	0.39 0.39	B = 0.39	NA

$$\text{Concentration of Analysis Sample } (\mu g\ NO_3^-/ml) = \frac{\text{Instrument Response (y) - Intercept (I)}}{\text{Calibration Curve Slope (m)}}$$

$$\text{Concentration (of first sample)} = \frac{(79) - (-0.2497)}{13.6175} = 5.8$$

$$\text{Deviation (\%)} = \frac{\text{Sample Concentration - Average Concentration}}{\text{Average Concentration}} \times 100\%$$

$$\text{Deviation (of first standard set)} = \frac{(5.8) - (5.75)}{5.75} \times 100\% = 0.87$$

Figure 5.3. NO_x laboratory data form for analyses of field samples.

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2. Calculate the percent deviation of the concentration measured for each individual sample from the average of the concentrations measured for the duplicate samples using the following equation:

Equation 5-5

$$\% \text{ Deviation} = \frac{\text{Sample Concentration - Average Concentration}}{\text{Average Concentration}} \times 100$$

The percent deviation for a sample must be within 5% of the average value before the analysis can be considered valid.

The data reduction procedures described above for NO_3^- analysis can be used for NO_2^- analysis when using Method 7D for relative accuracy testing of continuous emission monitors.

The main parameters of the analytical procedures may be checked during or after the analysis, using the posttest operations form (Figure 5.4).

Reagents

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

Stock standard solution (potassium nitrate) less than 2 months 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 (optional)? Yes

Reagent blanks made from absorbing solution? Yes

Same injection volume for both standards and samples? ✓

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

Audit sample analytical results within 10 percent of true value? Yes

All analytical data recorded on checklist and laboratory form? Yes

* Most significant items/parameters to be checked.

Figure 5.4. Posttest operations.

Table 5.1. ACTIVITY MATRIX FOR SAMPLE ANALYSIS

Characteristics	Acceptance Limits	Frequency and method of measurement	Action if requirements are not met
Sample Preparation			
1. Conversion time	36 hour minimum	Determine sample age	Hold sample in container for 36 hours minimum time
2. Sample loss	Noticeable amount	Compare sample level to mark on container	Correct by procedure in Section 5.1.1
3. Permanganate precipitation	Absence of purple permanganate color	Between each 5 ml portion of 5% H_2O_2 solution	Continue adding 5 ml portions of 5% H_2O_2
4. Permanganate filtration	Absence of solids in the filtrate	After filtration is complete	Refilter
Calibration Standards Preparation			
1. ACS grade KNO_3	15 g dry KNO_3	Oven dry at 105° to 110°C for 2 hours; cool in desiccator	High bias will occur if standard contains moisture; redry KNO_3
2. Stock standard solution	9 to 10 g of KNO_3 accurately weighed to 0.1 mg; dilute to 1 liter; store refrigerated	Calibrate analytical balance	Biases will occur with poor pipetting or improper storage; remake standard
3. Calibration standards	Standard range to cover sample range; maximum allowed deviation of individual standard from the predicted value is +7% (optional)	Use recommended volumes of stock standard solution; calculate deviation (optional) using Equation 5-4	Invalid analysis; remake and rerun calibration standards

(continued)

Table 5.1. (continued)

Characteristics	Acceptance Limits	Frequency and method of measurement	Action if requirements are not met
Ion Chromatograph Analysis			
1. Sample injection device	Absence of KNO_3 on chromatogram of water injection	Inject reagent water up to four times	Check water source for contamination
2. Sample analysis	Individual sample replicates within 5% of average	Calculate deviation using Equation 5-5	Invalidate analysis reanalyze samples
3. Chromatogram documentation	Include sample identification, injection point, injection volume, NO_3^- retention time, eluent flow rate, detector sensitivity setting, and chart speed	Visually check	Supply missing information
4. Quality assurance	Analytical results must be within 10% of actual value	Report results to agency with sample identification	Invalidate analysis; repeat preparation of sample; prepare new standards

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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 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 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 ones shown in Figure 6.1A and 6.1B, following the nomenclature list.

6.1 Nomenclature

The following nomenclature is used in the calculations:

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

Y = dry gas meter calibration factor, dimensionless,

P_{bar} = barometric pressure, mm (in.) Hg,

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

T_m = average dry gas meter absolute temperature, ^{o}K (^{o}R),

T_{std} = standard absolute temperature, 293^{o}K (528^{o}R),

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

S = analysis of sample, µg NO_3^-/ml,

B = analysis of blank, µg NO_3^-/ml,

m = mass of NO_x as NO_2 in sample, µg,

C = concentration of NO_x as NO_2, dry basis, mg/dscm (lb/dscf), and

X = CO_2 correction factor.

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6.2 Calculations

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

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) using Equation 6-1.

$$V_{m(std)} = V_m (X) Y \frac{T_{std}}{T_m} \frac{P_{bar}}{P_{std}} = K_1 (X) Y \frac{V_m P_{bar}}{T_m} \qquad \text{Equation 6-1}$$

where:

X = correction factor for CO_2 collection, $\frac{100}{100 - \%CO_2 \text{ v/v}}$,

K_1 = 0.3858 $\frac{°K}{mmHg}$ for metric units, or

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

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

$$m = (S - B)\ 250 \times \frac{1000}{50} \times \frac{46.01}{62.01} = 3710\ (S - B) \qquad \text{Equation 6-2}$$

where:

250 = volume of prepared sample, ml,

46.01 = molecular weight of NO_2^-,

62.01 = molecular weight of NO_3^-,

1000 = total volume of $KMnO_4$ solution, ml, and

50 = aliquot $KMnO_4$ / NaOH solution, ml.

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

$$C = K_2 \frac{m}{V_{m(std)}} \qquad \text{Equation 6-3}$$

where:

K_2 = 10^{-3} mg/µg for metric units, or

K_2 = 2.205×10^{-9} lb/µg for English units.

Sample Volume

V_m = 0.9539 dcf, Y = 1.020, X = 1.174,
P_{bar} = 29.41 in. Hg, T_m = 536.5 °R

$$V_{m(std)} = 17.64 \times Y \frac{V_m P_{bar}}{T_m} = 1.105 \text{ dscf}$$ Equation 6-1

Total µg NO_2 Per Sample

S = 5.75 µg/ml, B = 0.39 µg/ml

$$m = 3710 (S - B) = 19886 \text{ µg of } NO_2$$ Equation 6-2

Sample Concentration

$$C = 2.205 \times 10^{-9} \frac{m}{V_{m(std)}} = 3.968 \times 10^{-5} \text{ lb/dscf}$$ Equation 6-3

Sample Concentration in ppm

$$\text{ppm } NO_2 = 8.375 \times 10^6 \, C = 332 \text{ ppm } NO_2$$ Equation 6-4

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

Sample Volume

V_m = 0.0 2 7 0 1 1 m^3, Y = 1.0 2 0, X = 1.1 7 4,

P_{bar} = 7 4 7 mm Hg, T_m = 2 9 7.7 °K

$$V_{m(std)} = 0.3858 \times Y \frac{V_m P_{bar}}{T_m} = 0.0\ 3\ 1\ 3\ 1 \text{ dscm}$$ Equation 6-1

Total µg NO_2 Per Sample

S = 5.7 5 µg/ml, B = 0.3 9 µg/ml

$m = 3710 (S - B)$ = 1 9 8 8 6 µg of NO_2 Equation 6-2

Sample Concentration

$$C = 10^{-3} \frac{m}{V_{m(std)}} = 6\ 3\ 5.1 \text{ mg } NO_2/\text{dscm}$$ Equation 6-3

Sample Concentration in ppm

ppm NO_2 = 0.5228 C = 3 3 2 ppm NO_2 Equation 6-4

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

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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 calculations	Check and correct all data
Document and report results	All data available; calculations correct within round-off error	For each sample, examine the data form	Complete the data, or void the sample

7.0 MAINTENANCE

The normal use of emission-testing equipment subjects it to corrosive gases, extremes in temperature, vibration, and shock. Keeping the equipment in good operating order over an extended period of time requires knowledge of the equipment and a program of routine maintenance which is performed quarterly or after 2830 L (100 ft^3) of operation, whichever is greater. In addition to the quarterly maintenance, a yearly cleaning of the entire meter box is recommended. Maintenance procedures for the various components are summarized in Table 7.1 at the end of the section. The following procedures are not required, but are recommended to increase the reliability of the equipment.

7.1 Pump

In the present commercial sampling train, several types of pumps are used; 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. Its contents should be translucent; the oil should be changed if not translucent. Use the oil specified by the manufacturer. If none is specified, use SAE-10 nondetergent oil. Whenever the fiber vane pump starts to run erratically or during the yearly disassembly, the head should be removed and the fiber vanes changed. Erratic operation of the diaphragm pump is normally due to either a bad diaphragm (causing leakage) or to malfunctions of the valves, which should be cleaned annually by complete disassembly.

7.2 Dry Gas Meter

The dry gas meter should be checked for excess oil or corrosion of the components by removing the top plate every 3 months. The meter should be disassembled and all components cleaned and checked whenever the rotation of the dials is erratic, whenever the meter will not calibrate properly over the required flow rate range, and during the yearly maintenance.

7.3 Rotameter

The rotameter should be disassembled and cleaned according to the manufacturer's instructions using only recommended cleaning fluids every 3 months or upon erratic operation.

7.4 Sampling Train

All remaining sampling train components should be visually checked every 3 months and completely disassembled and cleaned or replaced yearly. Many items, such as quick disconnects, should be replaced whenever damaged rather than checked periodically. Normally, the best procedure for maintenance in the field is to use another entire unit such as a meter box, sample box, or umbilical

cord (the hose that connects the sample box and meter box) rather than replacing individual components.

7.5 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.[14]

Table 7.1. ACTIVITY MATRIX FOR EQUIPMENT MAINTENANCE CHECKS

Apparatus	Acceptance limits	Frequency and method of measurement	Action if requirements are not met
Sample train control console	No erratic behavior	Routine maintenance performed quarterly; disassemble and clean yearly	Replace parts as needed
Fiber vane pump	In-line oiler free of leaks	Periodically check oiler jar; remove head and change fiber vanes	Replace as needed
Diaphragm pump	Leak-free valves functioning properly	Clean valves during yearly disassembly	Replace when leaking or malfunctioning
Dry gas meter	No excess oil, corrosion, or erratic rotation of the dial	Check every 3 mo. for excess oil or corrosion by removing the top plate; check valves and diaphragm yearly and whenever meter dial runs erratically or whenever meter will not calibrate	Replace parts as needed, or replace meter
Rotameter	Clean and no erratic behavior	Clean every 3 mo. or whenever ball does not move freely	Replace
Sampling train	No damage	Visually check every 3 mo.; completely disassemble and clean or replace yearly	If failure noted, use another entire meter box, sample box, or umbilical cord
Ion chromatograph	See owner's manual	See owner's manual	See owner's manual

10.0 REFERENCE METHOD*,**

Method 7D—Determination of Nitrogen Oxide Emissions From Stationary Sources

Alkaline-Permanganate/Ion Chromatographic Method

1. *Applicability, Principle, Interferences, Precision, Bias, and Stability.*

1.1 Applicability. The method is applicable to the determination of NO_x emissions from fossil-fuel fired steam generators, electric utility plants, nitric acid plants, or other sources as specified in the regulations. The lower detectable limit is similar to that for Method 7C. No upper limit has been established; however, when using the recommended sampling conditions, the method has been found to collect NO_x emissions quantitatively up to 1782 mg/NO_x/m^3, as NO_2 (932 pm NO_x).

1.2 Principle. An integrated gas sample is extracted from the stack and collected in alkaline-potassium permanganate solution; NO_x ($NO + NO_2$) emissions are oxidized to NO_3^-. Then NO_3^- is analyzed by ion chromatography.

1.3 Interferences. Possible interferences are SO_2 and NH_3. High concentrations of SO_2 could interfere because SO_2 consumes MnO_4^- (as does NO_x) and, therefore, could reduce the NO_x collection efficiency. However, when sampling emissions from a coal-fired electric utility plant burning 2.1-percent sulfur coal with no control of SO_2 emissions, collection efficiency was not reduced. In fact, calculations show that sampling 3000 ppm SO_2 will reduce the MnO_4^- concentration by only 5 percent if all the SO_2 is consumed in the first impinger.

NH_3 is slowly oxidized to NO_3^- by the absorbing solution. At 100 ppm NH_3 in the gas stream, an interference of 6 ppm NO_x (11 mg NO_2/m^3) was observed when the sample was analyzed 10 days after collection. Therefore, the method may not be applicable to plants using NH_3 injection to control NO_x emissions unless means are taken to correct the results. An equation has been developed to allow quantitation of the interference and is discussed in Citation 4 of the bibliography.

1.4 Precision and Bias. The method does not exhibit any bias relative to Method 7. The within-laboratory relative standard deviation for a single measurement was approximately 6 percent at 200 to 270 ppm NO_x.

1.5 Stability. Collected samples are stable for at least 4 weeks.

2. *Apparatus.*

2.1 Sampling and Sample Recovery. The sampling train is the same as in Figure 7C–1 of Method 7C. Component parts are the same as in Method 7C, Section 2.1.

2.2 Sample Preparation and Analysis.

2.2.1 Magnetic Stirrer. With 25- by 10-mm Teflon-coated stirring bars.

2.2.2 Filtering Flask. 500-ml capacity with sidearm.

2.2.3 Buchner Funnel. 75-mm ID. The spout equipped with a 13-mm ID by 90-mm long piece of Teflon tubing to minimize possibility of aspirating sample solution during filtration.

2.2.4 Filter Paper. Whatman GF/C, 7.0-cm diameter.

2.2.5 Stirring Rods.

2.2.6 Volumetric Flask. 250-ml.

2.2.7 Pipettes. Class A.

2.2.8 Erlenmeyer Flasks. 250-ml.

2.2.9 Ion Chromatograph. Equipped with an anion separator column to separate NO_3^-, a H^+ suppressor, and necessary auxiliary equipment. Nonsuppressed and other forms of ion chromatography mey also be used provided that adequate resolution of NO_3^- is obtained. The system must also be able to resolve and detect NO_2^-.

3. *Reagents.*

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

3.1 Sampling.

3.1.1 Water. Deionized distilled to conform to ASTM specification D 1193–74, Type 3 (incorporated by reference—see § 60.17).

3.1.2 Potassium Permanganate, 4.0 Percent (w/w), Sodium Hydroxide, 2.0 Percent (w/w). Dissolve 40.0 g of $KMnO_4$ and 20.0 g of NaOH in 940 ml of water.

3.2 Sample Preparation and Analysis.

3.2.1 Water. Same as in Section 3.1.1.

3.2.2 Hydrogen Peroxide. 5 Percent. Dilute 30 percent H_2O_2 1:5 (v/v) with water.

3.2.3 Blank Solution. Dissolve 2.4 g of $KMnO_4$ and 1.2 g of NaOH in 96 ml of water. Alternatively, dilute 60 ml of $KMnO_4$/NaOH solution to 100 ml.

3.2.4 KNO_3 Standard Solution. Dry KNO_3 at 110 ° C for 2 hours, and cool in a desiccator. Accurately weigh 9 to 10 g of KNO_3 to within 0.1 mg, dissolve in water, and dilute to 1 liter. Calculate the exact NO_3^- concentration from the following relationship:

$$\mu g\ NO_3^-/ml = g\ of\ KNO_3 \times 10^3 \times \frac{62.01}{101.10}$$

*Method 7C is reproduced in this section in addition to Method 7D since the latter refers extensively to Method 7C and Method 7C is not reproduced elsewhere in this Handbook.

** Federal Register, Volume 49, No. 189, September 27, 1984.

This solution is stable for 2 months without preservative under laboratory conditions.

3.2.5 Eluent. 0.003 M $NaHCO_3$/0.0024 M Na_2CO_3. Dissolve 1.008 g $NaHCO_3$ and 1.018 g Na_2CO_3 in water, and dilute to 4 liters. Other eluents capable of resolving nitrate ion from sulfate and other species present may be used.

3.2.6 Quality Assurance Audit Samples. This is the same as in Method 7, section 3.3.9. When requesting audit samples, specify that they be in the appropriate concentration range for Method 7D.

4. *Procedure.*

4.1 Sampling. This is the same as in Method 7C, Section 4.1.

4.2 Sample Recovery. This is the same as in Method 7C, Section 4.2.

4.3 Sample Preparation for Analysis. Note the level of liquid in the sample container, and determine whether any sample was lost during shipment. If a noticeable amount of leakage has occurred, the volume lost can be determined from the difference between initial and final solution levels, and this value can then be used to correct the analytical result. Quantitatively transfer the contents to a 1-liter volumetric flask, and dilute to volume.

Sample preparation can be started 36 hours after collection. This time is necessary to ensure that all NO_2^- is converted to NO_3^-. Take a 50-ml aliquot of the sample and blank, and transfer to 250-ml Erlenmeyer flasks. Add a magnetic stirring bar. Adjust the stirring rate to as fast a rate as possible without loss of solution. Add 5 percent H_2O_2 in increments of approximately 5 ml using a 5-ml pipette. When the $KMnO_4$ color appears to have been removed, allow the precipitate to settle, and examine the supernatant liquid. If the liquid is clear, the H_2O_2 addition is complete. If the $KMnO_4$ color persists, add more H_2O_2, with stirring, until the supernatant liquid is clear. Note.—The faster the stirring rate, the less volume of H_2O_2 that will be required to remove the $KMnO_4$.) Quantitatively transfer the mixture to a Buchner funnel containg GF/C filter paper, and filter the precipitate. The spout of the Buchner funnel should be equipped with a 13-mm ID by 90-mm long piece of Teflon tubing. This modification minimizes the possibility of aspirating sample solution during filtration. Filter the mixture into a 500-ml filtering flask. Wash the solid material four times with water. When filtration is complete, wash the Teflon tubing, quantitatively transfer the filtrate to a 250-ml volumetric flask, and dilute to volume. The sample and blank are now ready for NO_3 analysis.

4.4 Sample Analysis. The following chromatographic conditions are recommended: 0.003 M $NaHCO_3$/0.0024 M Na_2CO_3 eluent solution. (3.2.5), full scale range 3 μMHO; sample loop, 0.5 ml; flow rate, 2.5 ml/min. These conditions should give a NO_3^- retention time of approximately 15 minutes (Figure 7D-1).

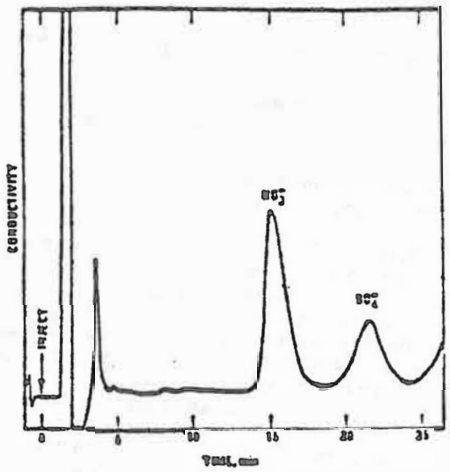

Figure 7D-1. Ion chromatograph of a prepared sample

Establish a stable baseline. Inject a sample of water, and determine if any NO_3^- appears in the chromatogram. If NO_3^- is present, repeat the water load/injection procedure approximately five times; then re-inject a water sample, and observe the chromatogram. When no NO_3^- is present, the instrument is ready for use. Inject calibration standards. Then inject samples and a blank. Repeat the injection of the calibration standards (to compensate for any drift in response of the instrument). Measure the NO_3 peak height or peak area, and determine the sample concentration from the calibration curve.

4.5 Audit analysis. This is the same as in Method 7, Section 4.4

5. *Calibration.*

5.1 Dry Gas Metering System (DGM).

5.1.1 Initial Calibration. Same as in Method 6, Section 5.1.1. For detailed instructions on carrying out this calibration, it is suggested that Section 3.5.2 of Citation 3 in the bibliography be consulted.

5.1.2 Post-Test Calibration Check. Same as in Method 6, Section 5.1.2.

5.2 Thermometers for DGM and Barometer. Same as in Method 6, Section 5.2 and 5.4, respectively.

5.3 Calibration Curve for Ion Chromatograph. Dilute a given volume (1.0 ml or greater) of the KNO_3 standard solution to a convenient volume with water, and use this solution to prepare calibration standards. Prepare at least four standards to cover the range of the samples being analyzed. Use pipettes for all additions. Run standards as instructed in Section 4.4. Determine peak height or area, and plot the individual values versus concentration in μg NO_3^-/ml. Do not force the curve through zero. Draw a smooth curve through the points. The curve should be linear. With the linear curve, use linear regression to determine the calibration equation.

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6. *Calculations.*

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

6.1 Sample Volume, Dry Basis, Corrected to Standard Conditions. Same as in Method 7C, Section 6.1.

6.2 Total μg NO_2 Per Sample.

$$m = (S-B) \times 250 \times \frac{1000}{50} \times \frac{46.01}{62.01} = 3710\,(S-B) \quad \text{(Eq. 7D-1)}$$

Where:

m = Mass of NO_x, as NO_2, in sample, μg.
S = Analysis of sample, μg NO_3^-/ml.
B = Analysis of blank, μg NO_3^-/ml.
250 = Volume of prepared sample, ml.
46.01 = Molecular weight of NO_2^-.
62.01 = Molecular weight of NO_3^-.
1000 = Total volume of $KMnO_4$ solution, ml.
50 = Aliquot $KMnO_4$/NaOH solution, ml.

6.3 Sample Concentration.

$$C = K_2 \frac{m}{V_{m(std)}}$$

Where:

C = Concentration of NO_x as NO_2, dry basis, mg/dscm.
$K_2 = 10^{-3}$ mg/μg.
$V_{m(std)}$ = Dry gas volume measured by the dry gas meter, corrected to standard conditions, dscm.

6.4 Conversion Factors.

1.0 ppm NO = 1.247 mg NO/m^3 at STP.
1.0 ppm NO_2 = 1.912 mg NO_2/m^3 at STP.
1 $ft^3 = 2.832 \times 10^{-2}$ m^3.

7. *Quality Control.*

Quality control procedures are specified in Sections 4.1.3 (flow rate accuracy) and 4.5 (audit analysis accuracy) of Method 7C.

8. *Bibliography.*

1. Margeson, J.H., W.J. Mitchell, J.C. Suggs, and M.R. Midgett. Integrated Sampling and Analysis Methods for Determining NO_x Emissions at Electric Utility Plants. U.S. Environmental Protection Agency, Research Triangle Park, N.C. Journal of the Air Pollution Control Association. *32*:1210–1215. 1982.

2. Memorandum and attachment form J.H. Margeson, Source Branch, Quality Assurance Division, Environmental Monitoring Systems Laboratory, to The Record, EPA. March 30, 1983. NH_3 Interference in Methods 7C and 7D.

3. Quality Assurance Handbook for Air Pollution Measurement Systems. Volume III—Stationary Source Specific Methods. U.S. Environmental Protection Agency. Research Triangle Park, N.C. Publication No. EPA–600/4–77–027b. August 1977.

4. Margeson, J.H., et al. An Integrated Method for determining NO_x Emissions at Nitric Acid Plants. Manuscript submitted to Analytical Chemistry. April 1984.

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Method 7C—Determination of Nitrogen Oxide Emissions From Stationary Sources

Alkaline-Permanganate/Colorimetric Method

1. *Applicability, Principle, Interferences, Precision, Bias, and Stability.*

1.1 Applicability. The method is applicable to the determination of NO_x emissions from fossil-fuel fired steam generators, electric utility plants, nitric acid plants, or other sources as specified in the regulations. The lower detectable limit is 13 mg NO_x/m^3, as NO_2 (7 ppm NO_x) when sampling at 500 cc/min for 1 hour. No upper limit has been established; however, when using the recommended sampling conditions, the method has been found to collect NO_x emissions quantitatively up to 1,782 mg NO_x/m^3, as NO_2 (932 ppm NO_x).

1.2 Principle. An integrated gas sample is extracted from the stack and collected in alkaline-potassium permanganate solution; NO_x ($NO + NO_2$) emissions are oxidized to NO_3^- and NO_2^-. The NO_3^- is reduced to NO_2^- with cadmium, and the NO_2^- is analyzed colorimetrically.

1.3 Interferences. Possible interferences are SO_2 and NH_3. High concentrations of SO_2 could interfere because SO_2 consumes MnO_4^- (as does NO_x) and, therefore, could reduce the NO_x collection efficiency. However, when sampling emissions from a coal-fired electric utility plant burning 2.1-percent sulfur coal with no control of SO_2 emissions, collection efficiency was not reduced. In fact, calculations show that sampling 3000 ppm SO_2 will reduce the MnO_4^- concentration by only 5 percent if all the SO_2 is consumed in the first impinger.

NH_3 is slowly oxidized to NO_3^- by the absorbing solution. At 100 ppm NH_3 in the gas stream, an interference of 6 ppm NO_x (11 mg NO_2/m^3) was observed when the sample was analyzed 10 days after collection. Therefore, the method may not be applicable to plants using NH_3 injection to control NO_x emissions unless means are taken to correct the results. An equation has been developed to allow quantitation of the interference and is discussed in Citation 5 of the bibliography.

1.4 Precision and Bias. The method does not exhibit any bias relative to Method 7. The within-laboratory relative standard deviation for a single measurement is 2.8 and 2.9 percent at 201 and 268 ppm NO_x, respectively.

1.5 Stability. Collected samples are stable for at least 4 weeks.

2. *Apparatus.*

2.1 Sampling and Sample Recovery. The Sampling train is shown in Figure 7C-1, and component parts are discussed below. Alternative apparatus and procedures are allowed provided acceptable accuracy and precision can be demonstrated.

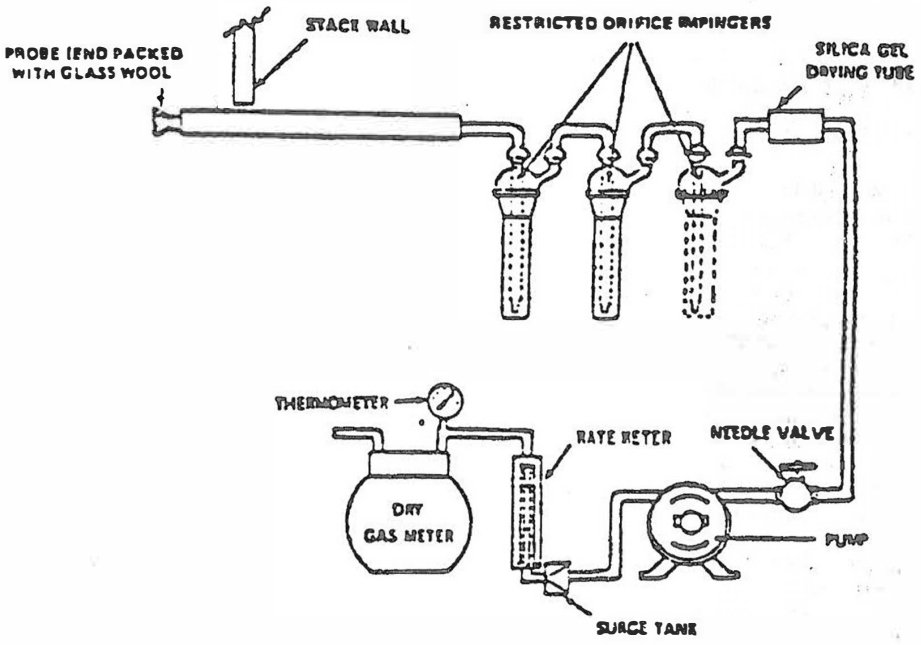

Figure 7C-1. NO_x sampling train

2.1.1 Probe. Borosilicate glass tubing, sufficiently heated to prevent water condensation and equipped with an in-stack or out-stack filter to remove particulate matter (a plug of glass wool is satisfactory for this purpose). Stainless steel or Teflon tubing may also be used for the probe. (Note: Mention of trade names or specific products does not constitute endorsement by the U.S. Environmental Protection Agency.)

2.1.2 Impingers. Three restricted-orifice glass impingers, having the specifications given in Figure 7C-2, are required for each sampling train. The impingers must be connected in series with leak-free glass connectors. Stopcock grease may be used, if necessary, to prevent leakage. (The impingers can be fabricated by a glass blower until they become available commercially.)

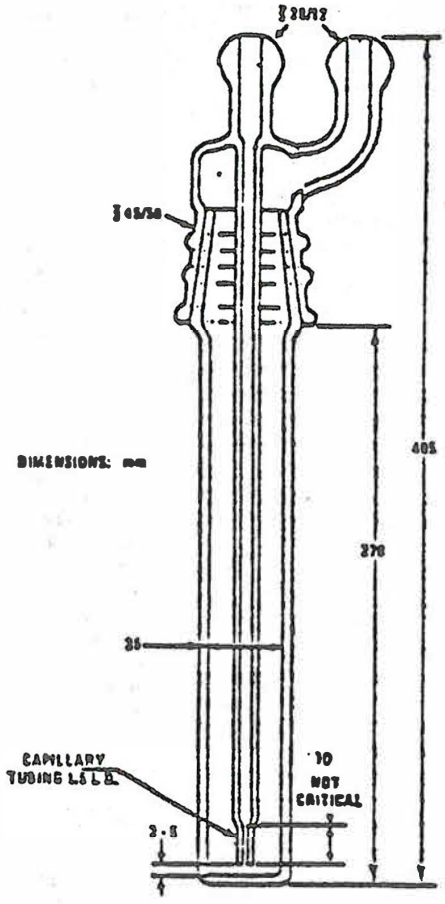

Figure 7C-2. Restricted orifice impinger

2.1.3 Glass Wool, Stopcock Grease, Drying Tube, Valve, Pump, Barometer, and Vacuum Gauge and Rotameter. Same as in Method 6, Sections 2.1.3, 2.1.4, 2.1.6, 2.1.7, 2.1.8, 2.1.11, and 2.1.12, respectively.

2.1.4 Rate Meter. Rotameter, or equivalent, accurate to within 2 percent at the selected flow rate between 400 and 500 cc/min. For rotameters, a range of 0 to 1 liter/min is recommended.

2.1.5 Volume Meter. Dry gas meter capable of measuring the sample volume, under the sampling conditions of 400 to 500 cc/min for 60 minutes within an accuracy of 2 percent.

2.1.6 Filter. To remove NO_2 from ambient air, prepared by adding 20 g of a 5-angstrom molecular sieve to a cylindrical tube, e.g., a polyethylene drying tube.

2.1.7 Polyethylene Bottles. 1-liter, for sample recovery.

2.1.8 Funnel and Stirring Rods. For sample recovery.

2.2 *Sample Preparation and Analysis.*

2.2.1 Hot Plate. Stirring type with 50- by 10-mm Teflon-coated stirring bars.

2.2.2 Beakers. 400-, 600-, and 1000-ml capacities.

2.2.3 Filtering Flask. 500-ml capacity with side arm.

2.2.4 Buchner Funnel. 75-mm ID, with spout equipped with a 13-mm ID by 90-mm long piece of Teflon tubing to minimize possibility of aspirating sample solution during filtration.

2.2.5 Filter Paper. Whatman GF/C, 7.0-cm diameter.

2.2.6 Stirring Rods.

2.2.7 Volumetric Flasks. 100-, 200- or 250-, 500-, and 1000-ml capacity.

2.2.8 Watch Glasses. To cover 600- and 1,000-ml beakers.

2.2.9 Graduated Cylinders. 50- and 250-ml capacities.

2.2.10 Pipettes. Class A

2.2.11 pH Meter. To measure pH from 0.5 to 12.0

2.2.12 Burette. 50-ml with a micrometer type stopcock. (The stopcock is Catalogue No. 8225-t-05, Ace Glass, Inc., Post Office Box 996, Louisville, Kentucky 50201.) Place a glass wool plug in bottom of burette. Cut off burette at a height of 43 cm from the top of plug, and have a glass blower attach a glass funnel to top of burette such that the diameter of the burette remains essentially unchanged. Other means of attaching the funnel are acceptable.

2.2.13 Glass Funnel. 75-mm ID at the top.

2.2.14 Spectrophotometer. Capable of measuring absorbance at 540 nm. One-cm cells are adequate.

2.2.15 Metal Thermometers. Bimetallic thermometers, range 0 to 150 °C.

2.2.16 Culture Tubes. 20- by 150-mm. Kimax No. 45048.

2.2.17 Parafilm "M." Obtained from American Can Company, Greenwich, Connecticut 06830.

2.2.18 CO_2 Measurement Equipment. Same as in Method 3.

3. *Reagents.*

Unless otherwise indicated, all reagents should 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.

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3.1 Sampling.

3.1.1 Water. Deionized distilled to conform to ASTM specification D 1193–74, Type 3 (incorporated by reference—see § 60.17).

3.1.2 Potassium Permanganate, 4.0 percent (w/w), Sodium Hydroxide, 2.0 percent (w/w). Dissolve 40.0 g of $KMnO_4$ and 20.0 g of NaOH in 940 ml of water.

3.2 Sample Preparation and Analysis.

3.2.1 Water. Same as in Section 3.1.1.

3.2.2 Sulfuric Acid. Concentrated H_2SO_4.

3.2.3 Oxalic Acid Solution. Dissolve 48 g of oxalic acid $[(COOH)_2 \cdot 2H_2O]$ in water, and dilute to 500 ml. Do not heat the solution.

3.2.4 Sodium Hydroxide, 0.5 N. Dissolve 20 g of NaOH in water, and dilute to 1 liter.

3.2.5 Sodium Hydroxide, 10 N. Dissolve 40 g of NaOH in water and dilute to 100 ml.

3.2.6 Ethylenediamine Tetraacetic Acid (EDTA) Solution, 6.5 Percent. Dissolve 6.5 g of EDTA (disodium salt) in water, and dilute to 100 ml. Solution is best accomplished by using a magnetic stirrer.

3.2.7 Column Rinse Solution. Add 20 ml of 6.5 percent EDTA solution to 960 ml of water, and adjust the pH to 11.7 to 12.0 with 0.5 N NaOH.

3.2.8 Hydrochloric Acid (HCl), 2 N. Add 86 ml of concentrated HCl to a 500-ml volumetric flask containing water, dilute to volume, and mix well. Store in a glass-stoppered bottle.

3.2.9 Sulfanilamide Solution. Add 20 g of sulfanilamide (melting point 165 to 167 °C) to 700 ml of water. Add, with mixing, 50 ml concentrated phosphoric acid (85 percent), and dilute to 1000 ml. This solution is stable for at least 1 month, if refrigerated.

3.2.10 N-(1-Naphthyl)-Ethylenediamine Dihydrochloride (NEDA) Solution. Dissolve 0.5 g of NEDA in 500 ml of water. An aqueous solution should have one absorption peak at 320 nm over the range of 260 to 400 nm.

NEDA, showing more than one absorption peak over this range, is impure and should not be used. This solution is stable for at least 1 month if protected from light and refrigerated.

3.2.11 Cadmium. Obtained from Matheson Coleman and Bell, 2909 Highland Avenue, Norwood, Ohio 45212, as EM Laboratories Catalogue No. 2001. Prepare by rinsing in 2 N HCl for 5 minutes until the color is silver-grey. Then rinse the cadmium with water until the rinsings are neutral when tested with pH paper. CAUTION: H_2 is liberated during preparation. Prepare in an exhaust hood away from any flame.

3.2.12 $NaNO_2$ Standard Solution. Nominal Concentration, 100 μg NO_2^-/ml. Desiccate $NaNO_2$ overnight. Accurately weigh 1.4 to 1.6 g of $NaNO_2$ (assay of 97 percent $NaNO_2$ or greater), dissolve in water, and dilute to 1 liter. Calculate the exact NO_2^- concentration from the following relationship:

$$\mu g\ NO_2^-/ml = g\ of\ NaNO_2 \times \frac{purity,\ \%}{100} \times 10^3 \times \frac{46.01}{69.01}$$

This solution is stable for at least 6 months under laboratory conditions.

3.2.13 KNO_3 Standard Solution. Dry KNO_3 at 110 °C for 2 hours, and cool in a desiccator.

Accurately weigh 9 to 10 g of KNO_3 to within 0.1 mg, dissolve in water, and dilute to 1 liter. Calculate the exact NO_3^- concentration from the following relationship:

$$\mu g\ NO_3^-/ml = g\ of\ KNO_3 \times 10^3 \times \frac{62.01}{101.10}$$

This solution is stable for 2 months without preservative under laboratory conditions.

3.2.14 Spiking Solution. Pipette 7 ml of the KNO_3 standard into a 100-ml volumetric flask, and dilute to volume.

3.2.15 Blank Solution. Dissolve 2.4 g of $KMnO_4$ and 1.2 g of NaOH in 96 ml of water. Alternatively, dilute 60 ml of $KMnO_4$/NaOH solution to 100 ml.

3.2.16 Quality Assurance Audit Samples. Same as in Method 7, Section 3.3.9. When requesting audit samples, specify that they be in the appropriate concentration range for Method 7C.

4. *Procedure.*

4.1 Sampling.

4.1.1 Preparation of Collection Train. Add 200 ml of $KMnO_4$/NaOH solution (3.1.2) to each of three impingers, and assemble the train as shown in Figure 7C–1. Adjust probe heater to a temperature sufficient to prevent water condensation.

4.1.2 Leak-Check Procedure. A leak-check prior to the sampling run should be carried out; a leak-check after the sampling run is mandatory. Carry out the leak-check(s) according to Method 6, Section 4.1.2.

4.1.3 Check of Rotameter Calibration Accuracy (Optional). Disconnect the probe from the first impinger, and connect the filter (2.1.6). Start the pump, and adjust the rotameter to read between 400 and 500 cc/min. After the flow rate has stabilized, start measuring the volume sampled, as recorded by the dry gas meter (DGM), and the sampling time. Collect enough volume to measure accurately the flow rate, and calculate the flow rate. This average flow rate must be less than 500 cc/min for the sample to be valid; therefore, it is recommended that the flow rate be checked as above prior to each test.

4.1.4 Sample Collection. Record the initial DGM reading and barometric pressure. Determine the sampling point or points according to the appropriate regulations, e.g., Section 60.46(c) of 40 CFR Part 60. Position the tip of the probe at the sampling point, connect the probe to the first impinger, and start the pump. Adjust the sample flow to a value between 400 and 500 cc/min. CAUTION: HIGHER FLOW RATES WILL PRODUCE LOW RESULTS. Once adjusted, maintain a constant flow rate during the entire sampling run. Sample for 60 minutes. For relative accuracy (RA) testing of continuous emission monitors, the minimum sampling time is 1 hour, sampling 20 minutes

at each traverse point. [Note.—When the SO_2 concentration is greater than 1200 ppm, the sampling time may have to be reduced to 30 minutes to eliminate plugging of the impinger orifice with MnO_2. For RA tests with SO_2 greater than 1200 ppm, sample for 30 minutes (10 minutes at each point)]. Record the DGM temperature, and check the flow rate at least every 5 minutes. At the conclusion of each run, turn off the pump, remove probe from the stack, and record the final readings. Divide the sample volume by the sampling time to determine the average flow rate. Conduct a leak-check as in Section 4.1.2. If a leak is found, void the test run, or use procedures acceptable to the Administrator to adjust the sample volume for the leakage.

4.1.5 CO_2 Measurement. During sampling, measure the CO_2 content of the stack gas near the sampling point using Method 3. The single-point grab sampling procedure is adequate, provided the measurements are made at least three times—near the start, midway, and before the end of a run and the average CO_2 concentration is computed. The Orsat or Fyrite analyzer may be used for this analysis.

4.2 Sample Recovery. Disconnect the impingers. Pour the contents of the impingers into a 1-liter polyethylene bottle using a funnel and a stirring rod (or other means) to prevent spillage. Complete the quantitative transfer by rinsing the impingers and connecting tubes with water until the rinsings that are clear to light pink, and add the rinsings to the bottle. Mix the sample, and mark the solution level. Seal and identify the sample container.

4.3 Sample Preparation for Analysis. Prepare a cadmium reduction column as follows: Fill the burette (2.2.12) with water. Add freshly prepared cadmium slowly with tapping until no further settling occurs. The height of the cadmium column should be 39 cm. When not in use, store the column under rinse solution (3.2.7). [Note.—The column should not contain any bands of cadmium fines. This may occur if regenerated column is used and will greatly reduce the column lifetime.]

Note the level of liquid in the sample container, and determine whether any sample was lost during shipment. If a noticeable amount of leakage has occurred, the volume lost can be determined from the difference between initial and final solution levels, and this value can then be used to correct the analytical result. Quantitatively transfer the contents to a 1-liter volumetric flask, and dilute to volume.

Take a 100-ml aliquot of the sample and blank (unexposed $KMnO_4$/NaOH) solutions, and transfer to 400-ml beakers containing magnetic stirring bars. Using a pH meter, add concentrated H_2SO_4 with stirring until a pH of 0.7 is obtained. Allow the solutions to stand for 15 minutes. Cover the beakers with watch glasses, and bring the temperature of the solutions to 50 °C. Keep the temperature below 60 °C. Dissolve 4.8 g of oxalic acid in a minimum volume of water, approximately 50 ml, at room temperature. Do not heat the solution. Add this solution slowly, in increments, until the $KMnO_4$ solution becomes colorless. If the color is not completely removed, prepare some more of the above oxalic acid solution, and add until a colorless solution is obtained. Add an excess of oxalic acid by dissolving 1.8 g of oxalic acid in 50 ml of water, and add 6 ml of this solution to the colorless solution. If suspended matter is present, add concentrated H_2SO_4 until a clear solution is obtained.

Allow the samples to cool to near room temperature, being sure that the samples are still clear. Adjust the pH to 11.7 to 12.0 with 10 N NaOH. Quantitatively transfer the mixture to a Buchner funnel containing GF/C filter paper, and filter the precipitate. Filter the mixture into a 500-ml filtering flask. Wash the solid material four times with water. When filtration is complete, wash the Teflon tubing, quantitatively transfer the filtrate to a 500-ml volumetric flask, and dilute to volume. The samples are now ready for cadmium reduction. Pipette a 50-ml aliquot of the sample into a 150-ml beaker, and add a magnetic stirring bar. Pipette in 1.0 ml of 6.5 percent EDTA solution, and mix.

Determine the correct stopcock setting to establish a flow rate of 7 to 9 ml/min of column rinse solution through the cadmium reduction column. Use a 50-ml graduated cylinder to collect and measure the solution volume. After the last of the rinse solution has passed from the funnel into the burette, but before air entrapment can occur, start adding the sample, and collect it in a 250-ml graduated cylinder. Complete the quantitative transfer of the sample to the column as the sample passes through the column. After the last of the sample has passed from the funnel into the burette, start adding 60 ml of column rinse solution, and collect the rinse solution until the solution just disappears from the funnel. Quantitatively transfer the sample to a 200-ml volumetric flask (250-ml may be required), and dilute to volume. The samples are now ready for NO_3^- analysis. [Note.— Both the sample and blank should go through this procedure. Additionally, two spiked samples should be run with every group of samples passed through the column. To do this, prepare two additional 50-ml aliquots of the sample suspected to have the highest NO_3^- concentration, and add 1 ml of the spiking solution to these aliquots. If the spike recovery or column efficiency (see 6.2.1) is below 95 percent, prepare a new column, and repeat the cadmium reduction].

4.4 Sample Analysis. Pipette 10 ml of sample into a culture tube. [Note.—Some test tubes give a high blank NO_3^- value but culture tubes do not.] Pipette in 10 ml of sulfanilamide solution and 1.4 ml of NEDA solution. Cover the culture tube with parafilm, and mix the solution. Prepare a blank in the same manner using the sample from treatment of the unexposed $KMnO_4$/NaOH solution (3.1.2). Also, prepare a calibration standard to check the slope of the calibration curve. After a 10-minute color development interval, measure the absorbance at 540 nm against water. Read μg NO_3^-/ml from the calibration curve. If the

absorbance is greater than that of the highest calibration standard, pipette less than 10 ml of sample and enough water to make the total sample volume 10 ml, and repeat the analysis. Determine the NO_2 concentration using the calibration curve obtained in Section 5.3.

4.5 Audit Analysis. This is the same as in Method 7, Section 4.4.

5. *Calibration.*

5.1 Dry Gas Metering System (DGM).

5.1.1 Initial Calibration. Same as in Method 6, Section 5.1.1. For detailed instructions on carrying out this calibration, it is suggested that Section 3.5.2 of Citation 4 in the bibiography be consulted.

5.1.2 Post-Test Calibration Check. Same as in Method 6, Section 5.1.2.

5.2 Thermometers for DGM and Barometer. Same as in Method 6, Sections 5.2 and 5.4, respectively.

5.3 Calibration Curve for Spectrophotometer. Dilute 5.0 ml of the $NaNO_2$ standard solution to 200 ml with water. This solution nominally contains 25 µg NO_2^-/ml. Use this solution to prepare calibration standards to cover the range of 0.25 to 3.00 µg NO_2^-/ml. Prepare a minimum of three standards each for the linear and slightly nonlinear (described below) range of the curve. Use pipettes for all additions.

Run standards and a water blank as instructed in Section 4.4. Plot the net absorbance vs µg NO_2^-/ml. Draw a smooth curve through the points. The curve should be linear up to an absorbance of approximately 1.2 with a slope of approximately 0.53 absorbance units/µg NO_2^-/ml. The curve should pass through the origin. The curve is slightly nonlinear from an absorbance of 1.2 to 1.6.

6. *Calculations.*

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

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

$$V_{m(std)} = V_m Y X \frac{T_{std}}{T_m} \frac{P_{bar}}{P_{std}} = K_1 Y X \frac{V_m P_{bar}}{T_m} \qquad \text{(Eq. 7C-1)}$$

Where:

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

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

Y = Dry gas meter calibration factor.

X = Correction factor for CO_2 collection.

$$= \frac{100}{100 - \%CO_2 (v/v)}$$

P_{bar} = Barometric pressure, mm Hg.

P_{std} = Standard absolute pressure, 760 mm Hg.

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

T_{std} = Standard absolute temperature, 293 °K.

K_1 = 0.3858 °K/mm Hg.

6.2 Total µg NO_2 Per Sample.

6.2.1 Efficiency of Cadmium Reduction Column. Calculate this value as follows:

$$E = \frac{(x - y) \cdot 200}{s \times 1.0 \times \frac{46.01}{62.01}} = \frac{269.6\ (x - y)}{s}$$

(Eq. 7C-2)

Where:

E = Column efficiency, unitless.

x = Analysis of spiked sample, µg NO_2^-/ml.

y = Analysis of unspiked sample, µg NO_2^-/ml.

200 = Final volume of sample and blank after passing through the column, ml

s = Concentration of spiking solution, µg NO_2/ml.

1.0 = Volume of spiking solution added, ml.

46.01 = µg NO_2^-/µmole.

62.01 = µg NO_2^-/µmole.

6.2.2 Total µg NO_2.

$$m = \frac{(S-B)}{E} \times 200 \times \frac{500}{50} \times \frac{1000}{100} = \frac{(2 \times 10^4)(S-B)}{E}$$

(Eq. 7C-3)

Where:

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

S = Analysis of sample, µg NO_2^-/ml.

B = Analysis of blank, µg NO_2^-/ml.

500 = Total volume of prepared sample, ml.

50 = Aliquot of prepared sample processed through cadmium column, ml.

100 = Aliquot of $KMnO_4$/NaOH solution, ml.

1000 = Total volume of $KMnO_4$/NaOH solution ml.

6.3 Sample Concentration.

$$C = K_2 \frac{m}{V_{m(std)}}$$

Where:

C = Concentration of NO_x as NO_2, dry basis, mg/dscm.

$K_2 = 10^{-3}$ mg/µg.

6.4 Conversion Factors.

1.0 ppm NO = 1.247 mg NO/m^3 at STP.

1.0 ppm NO_2 = 1.912 mg NO_2/m^3 at STP.

1 ft^3 = 2.832 × 10^{-2} m^3.

7. *Quality Control.*

Quality control procedures are specified in Sections 4.1.3 (flow rate accuracy); 4.3 (cadmium column efficiency); 4.4 (calibration curve accuracy); and 4.5 (audit analysis accuracy).

8. *Bibliography.*

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11.0 REFERENCES

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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 of other sections 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 M7D-1.1 indicates that the form is Figure 1.1 in Section 3.15.1 of the Method 7D section. Future revisions of these forms, if any, can be documented by 1.2A, 1.2B, etc. Twelve of the blank forms listed below are included in this section. Four are in the Method Highlights subsection as shown by the MH following the form number.

Form	Title
1.1	Procurement Log
2.2	Wet Test Meter Calibration Log
2.4A and 2.4B	Dry Gas Meter Calibration Data Form (English and Metric Units)
2.5 (MH)	Pretest Sampling Checks
3.1 (MH)	Pretest Preparations
4.1	Field Sampling Data Form for NO_x
4.2	Sample Label
4.3	Sample Recovery and Integrity Data
4.4 (MH)	On-Site Measurements
5.1	Analytical Data Form for Analyses of Calibration Standards
5.3	NO_x Laboratory Data Form for Analyses of Field Samples
5.4 (MH)	Posttest Operations
6.1A and 6.1B	Nitrogen Oxide Calculation Form (English and Metric Units)
8.1	Method 7D Checklist to be Used by Auditors

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PROCUREMENT LOG

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

WET TEST METER CALIBRATION LOG

Wet test meter serial number _____ Date _____

Range of wet test meter flow rate _____

Volume of test flask V_s = _____

Satisfactory leak check? _____

Ambient temperature of equilibrate liquid in wet test meter and reservoir _____

Test number	Manometer reading,[a] mm H_2O	Final volume (V_f), L	Initial volume (V_i), L	Total volume, (V_m)[b] L	Flask volume (V_s), L	Percent error,[c] %
1						
2						
3						

[a]Must be less than 10 mm (0.4 in.) H_2O.

Calculations:

[b]$V_m = V_f - V_i$.

[c]% error = $100 (V_m - V_s)/V_s$ = _____ (±1%).

_____ Signature of calibration person

DRY GAS METER CALIBRATION FORM (ENGLISH UNITS)

Date _____ Calibrated by _____ Meter box number _____ Wet test meter number _____

Barometer pressure, P_m = _____ in. Hg Dry gas meter temperature correction factor _____ ^oF

Wet test meter pressure drop (D_m),[a] in. H_2O	Rotameter setting (R_s), ft^3/min	Wet test meter gas volume (V_m),[b] ft^3	Dry test meter gas volume (V_d),[b] ft^3		Wet test meter gas temp (t_w), ^oF	Inlet gas temp (t_{d_i}), ^oF	Dry test meter				(Y_{r_i}),[f]
			Initial	Final			Outlet gas temp (t_{d_o}), ^oF	Average gas temp (t_d),[c] ^oF	Time of run (θ),[d] min	Average ratio (Y_i),[e]	

[a] D_m expressed as negative number.

[b] Volume passing through meter. Dry gas volume is minimum for at least five revolutions of the meter.

[c] The average of t_{d_i} and t_{d_o} if using two thermometers; the actual reading if using one thermometer.

[d] The time it takes to complete the calibration run.

[e] With Y defined as the average ratio of volumes for the wet test and the dry test meters, $Y_i = Y \pm 0.02\ Y$ for calibration and $Y_i = Y \pm 0.05\ Y$ for the posttest checks; thus,

$$Y_i = \frac{V_w\ (t_d + 460^oF)\ \left[P_m + (D_m/13.6)\right]}{V_d\ (t_w + 460^oF)\ (P_m)} \quad \text{(Eq. 1)} \qquad \text{and} \qquad Y = \frac{Y_1 + Y_2 + Y_3}{3} = \_\_\_\_\_. \quad \text{(Eq. 2)}$$

[f] With Y_r defined as the average ratio of volumetric measurement by wet test meter to rotameter. Tolerance $Y_r = 1 \pm 0.05$ for calibration and $Y \pm 0.1$ for posttest checks.

$$Y_{r_i} = \frac{V_w\ (t_d + 460^oF)\ \left[P_m + (D_m/13.6)\right]}{0\ (t_w + 460^oF)\ (P_m)\ (R_s)} \quad \text{(Eq. 3)} \qquad \text{and} \qquad Y_r = \frac{Y_1 + Y_2 + Y_3}{3} = \_\_\_\_\_. \quad \text{(Eq. 4)}$$

DRY GAS METER CALIBRATION DATA FORM (METRIC UNITS)

Date _____ Calibrated by _____ Meter box number _____ Wet test meter number _____

Barometer pressure, P_m = _____ in. Hg Dry gas meter temperature correction factor _____ ^oC

Wet test meter pressure drop (D_m),[a]	Rotameter setting (R_s),	Wet test meter gas volume (V_m),[b]	Dry test meter gas volume (V_d),[b] L		Wet test meter gas temp (t_w),	Inlet gas temp (t_{d_i}),	Dry test meter				(Y_{r_i}),[f]
							Outlet gas temp (t_{d_o}),	Average gas temp (t_d),[c]	Time of run (θ),[d]	Average ratio (Y_i),[e]	
mm H_2O	cc/min	L	Initial	Final	^oC	^oC	^oC	^oC	min		

[a] D_m expressed as negative number.

[b] Volume passing through meter. Dry gas volume is minimum for at least five revolutions of the meter.

[c] The average of t_{d_i} and t_{d_o} if using two thermometers; the actual reading if using one thermometer.

[d] The time it takes to complete the calibration run.

[e] With Y defined as the average ratio of volumes for the wet test and the dry test meters, $Y_i = Y \pm 0.02\ Y$ for calibration and $Y_i = Y \pm 0.05\ Y$ for the posttest checks; thus,

$$Y_i = \frac{V_w\ (t_d + 273^oC)\ \left[P_m + (D_m/13.6)\right]}{V_d\ (t_w + 273^oC)\ (P_m)} \quad \text{(Eq. 1)} \qquad \text{and} \qquad Y = \frac{Y_1 + Y_2 + Y_3}{3} = \_\_\_\_\_. \quad \text{(Eq. 2)}$$

[f] With Y_r defined as the average ratio of volumetric measurement by wet test meter to rotameter. Tolerance $Y_r = 1 \pm 0.05$ for calibration and $Y \pm 0.1$ for posttest checks.

$$Y_{r_i} = \frac{V_w\ (t_d + 273^oC)\ \left[P_m + (D_m/13.6)\ 1000\right]}{0\ (t_w + 273^oC)\ (P_m)\ (R_s} \quad \text{(Eq. 3)} \qquad \text{and} \qquad Y_r = \frac{Y_1 + Y_2 + Y_3}{3} = \_\_\_\_\_. \quad \text{(Eq. 4)}$$

FIELD SAMPLING DATA FORM FOR NO_x

Plant name _____ City _____

Location _____ Date _____

Operator _____ Sample no. _____

Probe length/material _____ Probe setting _____

Meter box no. _____ Meter factor (Y) _____

Sampling point location(s) _____ Bar press mm (in.) Hg _____

Rotameter setting _____ Rotameter check? _____

Initial leak check? _____ Final leak check? _____

CO_2 concentration (1) _____ (2) _____ (3) _____ avg _____

Sampling time, min	Clock time 24 h	Dry gas meter readings L (ft^3)	Sample flow rate setting, cc/min (ft^3/min)	Sample volume metered, L (ft^3) (V_m)	Percent deviation,[a] %	Dry gas meter temp, °C (°F)
Total		Total		V_m avg	Avg dev	Avg

[a] Percent deviation = $\frac{V_m - V_{m\ avg}}{V_{avg}} \times 100$ (must be less than 10 percent).

SAMPLE LABEL

Plant _____ City _____
Site _____ Sample type _____
Date _____ Run number _____
Front rinse ☐ Front filter ☐ Front solution ☐
Back rinse ☐ Back filter ☐ Back solution ☐
Solution _____ Level marked _____
Volume: Initial _____ Final _____
Cleanup by _____

Remarks: _____

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SAMPLE RECOVERY AND INTEGRITY DATA

Plant _____ Sampling location _____

Field Data Checks

Sample recovery personnel _____

Person with direct responsibility for recovered samples _____

Sample number	Sample identification number	Date of recovery	Liquid level marked	Stored in locked container
1				
2				
3				
Blank				

Remarks _____

_____

Signature of field sample trustee _____

Laboratory Data Checks

Lab person with direct responsibility for recovered samples _____

Date recovered samples received _____

Analyst _____

Sample number	Sample identification number	Date of analysis	Liquid level marked	Stored in locked container
1				
2				
3				
Blank				

Remarks _____

_____

Signature of lab sample trustee _____

(1873 1875 1877

ANALYTICAL DATA FORM FOR ANALYSES OF CALIBRATION STANDARDS

Plant _____ Location _____

Date _____ Analyst _____

Standard identifier	Standard concentration (x) ($\mu g/ml\ NO_3^-$)	Instrument response (y) peak height or area count mm				Predicted standard concentration (P) ($\mu g/ml\ NO_3^-$)	Deviation (%)
		1	2	3	Avg		
Std 1							
Std 2							
Std 3							
Std 4							

Equation for Linear Calibration Curve, Average Response as a Function of Standard Concentration

$y = mx + b = (\_\_\_\_\_)\ x + (\_\_\_\_\_)$

where:

y = instrument response (mm or area count) = _____

m = calibration curve slope $\frac{\text{mm or area count}}{\mu g\ NO_3^-/ml}$ = _____

x = standard concentration ($\mu g\ NO_3^-/ml$) = _____

b = I = intercept term (mm or area count) = _____

Predicted Standard Concentration (P)

$$P\ (\mu g\ NO_3^-/ml) = \frac{\text{Average Instrument Response (y) - Intercept (I)}}{\text{Calibration Curve Slope (m)}}$$

$$P\ (\text{for first standard}) = \frac{(\_\_\_\_\_) - (\_\_\_\_\_)}{\_\_\_\_\_} = \_\_\_\_\_\ \mu g\ NO_3^-/ml$$

Deviation

$$\text{Deviation (\%)} = \frac{P\ (\mu g\ NO_3^-/ml) - x\ (\mu g\ NO_3^-/ml)}{x\ (\mu g\ NO_3^-/mL)} \times 100\%$$

$$\text{Deviation (of first set of standards)} = \frac{(\_\_\_\_\_) - (\_\_\_\_\_)}{\_\_\_\_\_} \times 100\% = \_\_\_\_\_\ \%$$

1874 1857 1857

NO_x LABORATORY DATA FORM FOR ANALYSES OF FIELD SAMPLES

Date samples received _____ Date samples analyzed _____

Plant _____ Run number(s) _____

Location _____ Analyst _____

Calibration curve slope (m) _____ Intercept term (I) _____

Field sample number	Analysis number	Instrument response (y) (mm or area counts)	Concentration of analysis sample ($\mu g/ml\ NO_3^-$)	Average Concentration of analysis sample ($\mu g/ml\ NO_3^-$)	Deviation (%)
	1st 2nd			S =	
	1st 2nd			S =	
	1st 2nd			S =	
Field Blank	1st 2nd			B =	

$$\text{Concentration of Analysis Sample } (\mu g\ NO_3^-/ml) = \frac{\text{Instrument Response (y) - Intercept (I)}}{\text{Calibration Curve Slope (m)}}$$

$$\text{Concentration (of first sample)} = \frac{(\_\_\_\_\_) - (\_\_\_\_\_)}{\_\_\_\_\_} = \_\_\_\_\_$$

$$\text{Deviation (\%)} = \frac{\text{Sample Concentration - Average Concentration}}{\text{Average Concentration}} \times 100\%$$

$$\text{Deviation (of first standard set)} = \frac{(\_\_\_\_\_) - (\_\_\_\_\_)}{\_\_\_\_\_} \times 100\% = \_\_\_\_\_$$

(1875) (1885) (1886)

NITROGEN OXIDE CALCULATION FORM (ENGLISH UNITS)

Sample Volume

V_m = __.__ __ __ __ dcf, Y = __.__ __ __, X = __.__ __ __,
P_{bar} = __ __.__ __ in. Hg, T_m = __ __ __.__ ^{o}R

$$V_{m(std)} = 17.64 \times Y \frac{V_m P_{bar}}{T_m} = \_\_.\_\_ \_\_ \_\_ \text{ dscf} \qquad \text{Equation 6-1}$$

Total µg NO_2 Per Sample

S = __ __ __ µg/ml, B = __ __ __ µg/ml

$$m = 3710 (S - B) = \_\_ \_\_ \_\_ \_\_ \_\_ \ \mu g \text{ of } NO_2 \qquad \text{Equation 6-2}$$

Sample Concentration

$$C = 2.205 \times 10^{-9} \frac{m}{V_{m(std)}} = \_\_ \_\_ \_\_ \_\_ \times 10^{-5} \text{ lb/dscf} \qquad \text{Equation 6-3}$$

Sample Concentration in ppm

$$ppm\ NO_2 = 8.375 \times 10^{6} C = \_\_ \_\_ \_\_ \_\_ \text{ ppm } NO_2 \qquad \text{Equation 6-4}$$

(1876) (1855) (1857)

NITROGEN OXIDE CALCULATION FORM (METRIC UNITS)

Sample Volume

V_m = 0.0 _ _ _ _ _ m^3, Y = _._ _ _, X = _._ _ _,

P_{bar} = _ _ _ mm Hg, T_m = _ _ _._ ^oK

$$V_{m(std)} = 0.3858 \times Y \frac{V_m P_{bar}}{T_m} = 0.0 \_ \_ \_ \_ \text{ dscm}$$ Equation 6-1

Total µg NO_2 Per Sample

S = _ _ _ µg/ml, B = _ _ _ µg/ml

$$m = 3710 (S - B) = \_ \_ \_ \_ \_ \text{ µg of } NO_2$$ Equation 6-2

Sample Concentration

$$C = 10^{-3} \frac{m}{V_{m(std)}} = \_ \_ \_ \_ \text{ mg } NO_2/\text{dscm}$$ Equation 6-3

Sample Concentration in ppm

$$\text{ppm } NO_2 = 0.5228 \, C = \_ \_ \_ \_ \text{ ppm } NO_2$$ Equation 6-4

(1877) ~~1856~~ (1857)

METHOD 7D CHECKLIST TO BE USED BY AUDITORS

Yes	No	Comment	OPERATION
			PRESAMPLING PREPARATION
___	___	_____	1. Knowledge of process conditions
___	___	_____	2. Calibration of pertinent equipment, in particular, the dry gas meter and rotameter, prior to each field test
			ON-SITE MEASUREMENTS
___	___	_____	3. Leak-testing of sampling train after sample run
___	___	_____	4. Preparation of absorbing solution and its addition to impingers
___	___	_____	5. Constant sampling at less than 500 cc/min
___	___	_____	6. Measurement of CO_2 content
___	___	_____	7. Recording of pertinent process conditions during sample collection
___	___	_____	8. Maintaining the probe at a given temperature
			POSTSAMPLING
___	___	_____	9. Control sample analysis - accuracy and precision
___	___	_____	10. Sample aliquotting techniques
___	___	_____	11. Ion chromatographic technique
			a. Preparation of standard nitrate samples (pipetting) b. Calibration factor ($\pm$7 % for all standards, optional) c. Adequate peak separation
___	___	_____	12. Audit results ($\pm$10%)
			a. Use of computer program b. Independent check of calculations
			COMMENTS

(1878) (1853) 1855