

both standards and samples. Repeat this analysis sequence followed by a final analysis of the standard set. Average the results. The two sample values must agree within 5 percent of their mean for the analysis to be valid. Perform this duplicate analysis sequence on the same day. Dilute any sample and the blank with equal volumes of water if the concentration exceeds that of the highest standard.

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

11.3 Audit Sample Analysis. Same as Method 7, Section 11.4.

12.0 Data Analysis and Calculations

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

12.1 Sample Volume. Calculate the sample volume  $V_{sc}$  (in ml), on a dry basis, corrected to standard conditions, using Equation 7-2 of Method 7.

12.2 Sample Concentration of  $NO_x$  as  $NO_2$ .

12.2.1 Calculate the sample concentration  $C$  (in mg/dscm) as follows:

$$C = (H)(S)(F)(10^4)/V_{sc} \quad \text{Eq. 7A-1}$$

Where:

H=Sample peak height, mm.

S=Calibration factor,  $\mu\text{g}/\text{mm}$ .

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

$10^4=1:10$  dilution times conversion factor of ( $\text{mg}/10^3 \mu\text{g})(10^6 \text{ ml}/\text{m}^3)$ .

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

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

Where:

0.5228=ml/mg  $NO_2$ .

13.0 Method Performance

13.1 Range. The analytical range of the method is from 125 to 1250 mg  $NO_x/\text{m}^3$  as  $NO_2$

(65 to 655 ppmv), and higher concentrations may be analyzed by diluting the sample. The lower detection limit is approximately 19  $\text{mg}/\text{m}^3$  (10 ppmv), but may vary among instruments.

14.0 Pollution Prevention. [Reserved]

15.0 Waste Management. [Reserved]

16.0 References

1. Mulik, J.D., and E. Sawicki. Ion Chromatographic Analysis of Environmental Pollutants. Ann Arbor, Ann Arbor Science Publishers, Inc. Vol. 2, 1979.

2. Sawicki, E., J.D. Mulik, and E. Wittgenstein. Ion Chromatographic Analysis of Environmental Pollutants. Ann Arbor, Ann Arbor Science Publishers, Inc. Vol. 1, 1978.

3. Siemer, D.D. Separation of Chloride and Bromide from Complex Matrices Prior to Ion Chromatographic Determination. Anal. Chem. 52(12):1874-1877. October 1980.

4. Small, H., T.S. Stevens, and W.C. Bauman. Novel Ion Exchange Chromatographic Method Using Conductimetric Determination. Anal. Chem. 47(11):1801. 1975.

5. Yu, K.K., and P.R. Westlin. Evaluation of Reference Method 7 Flask Reaction Time. Source Evaluation Society Newsletter. 4(4). November 1979. 10 pp.

6. Stack Sampling Safety Manual (Draft). U.S. Environmental Protection Agency, Office of Air Quality Planning and Standard, Research Triangle Park, NC. September 1978.

17.0 Tables, Diagrams, Flowcharts, and Validation Data. [Reserved]

METHOD 7B—DETERMINATION OF NITROGEN OXIDE EMISSIONS FROM STATIONARY SOURCES (ULTRAVIOLET SPECTROPHOTOMETRIC METHOD)

NOTE: This method does not include all of the specifications (e.g., equipment and supplies) and procedures (e.g., sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 1, Method 5, and Method 7.

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS No.	Sensitivity
Nitrogen oxides ( $NO_x$ ), as $NO_2$ , including:		
Nitric oxide (NO) .....	10102-43-9	
Nitrogen dioxide ( $NO_2$ ) .....	10102-44-0	30-786 ppmv

1.2 Applicability. This method is applicable for the determination of NO<sub>x</sub> emissions from nitric acid plants.

1.3 Data Quality Objectives. Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

#### 2.0 Summary of Method

2.1 A grab sample is collected in an evacuated flask containing a dilute sulfuric acid-hydrogen peroxide absorbing solution; the NO<sub>x</sub>, excluding nitrous oxide (N<sub>2</sub>O), are measured by ultraviolet spectrophotometry.

3.0 Definition. [Reserved]

4.0 Interferences. [Reserved]

#### 5.0 Safety

5.1 This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and to determine the applicability of regulatory limitations prior to performing this test method.

5.2 Corrosive reagents. The following reagents are hazardous. Personal protective equipment and safe procedures are useful in preventing chemical splashes. If contact occurs, immediately flush with copious amounts of water at least 15 minutes. Remove clothing under shower and decontaminate. Treat residual chemical burn as thermal burn.

5.2.1 Hydrogen Peroxide (H<sub>2</sub>O<sub>2</sub>). Irritating to eyes, skin, nose, and lungs.

5.2.2 Sodium Hydroxide (NaOH). Causes severe damage to eyes and skin. Inhalation causes irritation to nose, throat, and lungs. Reacts exothermically with limited amounts of water.

5.2.3 Sulfuric Acid (H<sub>2</sub>SO<sub>4</sub>). Rapidly destructive to body tissue. Will cause third degree burns. Eye damage may result in blindness. Inhalation may be fatal from spasm of the larynx, usually within 30 minutes. May cause lung tissue damage with edema. 3 mg/m<sup>3</sup> will cause lung damage in uninitiated. 1 mg/m<sup>3</sup> for 8 hours will cause lung damage or, in higher concentrations, death. Provide ventilation to limit inhalation. Reacts violently with metals and organics.

#### 6.0 Equipment and Supplies

6.1 Sample Collection. Same as Method 7, Section 6.1.

6.2 Sample Recovery. The following items are required for sample recovery:

6.2.1 Wash Bottle. Polyethylene or glass.

6.2.2 Volumetric Flasks. 100-ml (one for each sample).

6.3 Analysis. The following items are required for analysis:

6.3.1 Volumetric Pipettes. 5-, 10-, 15-, and 20-ml to make standards and sample dilutions.

6.3.2 Volumetric Flasks. 1000- and 100-ml for preparing standards and dilution of samples.

6.3.3 Spectrophotometer. To measure ultraviolet absorbance at 210 nm.

6.3.4 Analytical Balance. To measure to within 0.1 mg.

#### 7.0 Reagents and Standards

NOTE: Unless otherwise indicated, all reagents are to 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.

7.1 Sample Collection. Same as Method 7, Section 7.1. It is important that the amount of hydrogen peroxide in the absorbing solution not be increased. Higher concentrations of peroxide may interfere with sample analysis.

7.2 Sample Recovery. Same as Method 7, Section 7.2.

7.3 Analysis. Same as Method 7, Sections 7.3.1, 7.3.3, and 7.3.4, with the addition of the following:

7.3.1 Working Standard KNO<sub>3</sub> Solution. Dilute 10 ml of the standard solution to 1000 ml with water. One milliliter of the working standard is equivalent to 10 µg NO<sub>2</sub>.

#### 8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Sample Collection. Same as Method 7, Section 8.1.

8.2 Sample Recovery.

8.2.1 Let the flask sit for a minimum of 16 hours, and then shake the contents for 2 minutes.

8.2.2 Connect the flask to a mercury filled U-tube manometer. Open the valve from the flask to the manometer, and record the flask temperature (T<sub>f</sub>), the barometric pressure, and the difference between the mercury levels in the manometer. The absolute internal pressure in the flask (P<sub>f</sub>) is the barometric pressure less the manometer reading.

8.2.3 Transfer the contents of the flask to a leak-free wash bottle. Rinse the flask three times with 10-ml portions of water, and add to the bottle. Mark the height of the liquid level so that the container can be checked for leakage after transport. Label the container to identify clearly its contents. Seal the container for shipping.

#### 9.0 Quality Control

Section	Quality control measure	Effect
10.1 .....	Spectrophotometer calibration .....	Ensures linearity of spectrophotometer response to standards.
11.4 .....	Audit sample analysis .....	Evaluates analytical technique and preparation of standards.

10.0 Calibration and Standardizations

Same as Method 7, Sections 10.2 through 10.5, with the addition of the following:

10.1 Determination of Spectrophotometer Standard Curve. Add 0 ml, 5 ml, 10 ml, 15 ml, and 20 ml of the KNO<sub>3</sub> working standard solution (1 ml=10 µg NO<sub>2</sub>) to a series of five 100-ml volumetric flasks. To each flask, add 5 ml of absorbing solution. Dilute to the mark with water. The resulting solutions contain 0.0, 50, 100, 150, and 200 µg NO<sub>2</sub>, respectively. Measure the absorbance by ultraviolet spectrophotometry at 210 nm, using the blank as a zero reference. Prepare a standard curve plotting absorbance vs. µg NO<sub>2</sub>.

NOTE: If other than a 20-ml aliquot of sample is used for analysis, then the amount of absorbing solution in the blank and standards must be adjusted such that the same amount of absorbing solution is in the blank

and standards as is in the aliquot of sample used.

10.1.1 Calculate the spectrophotometer calibration factor as follows:

$$K_c = \frac{\sum_{i=1}^n M_i A_i}{\sum_{i=1}^n A_i^2} \quad \text{Eq. 7B-1}$$

Where:

M<sub>i</sub>=Mass of NO<sub>2</sub> in standard i, µg.

A<sub>i</sub>=Absorbance of NO<sub>2</sub> standard i.

n=Total number of calibration standards.

10.1.2 For the set of calibration standards specified here, Equation 7B-1 simplifies to the following:

$$K_c = 50 \frac{A_1 + 2A_2 + 3A_3 + 4A_4}{A_1^2 + A_2^2 + A_3^2 + A_4^2} \quad \text{Eq. 7B-2}$$

10.2 Spectrophotometer Calibration Quality Control. Multiply the absorbance value obtained for each standard by the K<sub>c</sub> factor (reciprocal of the least squares slope) to determine the distance each calibration point lies from the theoretical calibration line. The difference between the calculated concentration values and the actual concentrations (i.e., 50, 100, 150, and 200 µg NO<sub>2</sub>) should be less than 7 percent for all standards.

11.0 Analytical Procedures

11.1 Sample Loss Check. Note the level of the liquid in the container, and confirm whether any sample was lost during shipment. Note this on the analytical data sheet. If a noticeable amount of leakage has occurred, either void the sample or use methods, subject to the approval of the Administrator, to correct the final results.

11.2 Sample Preparation. Immediately prior to analysis, transfer the contents of the shipping container to a 100-ml volumetric flask, and rinse the container twice with 5-ml portions of water. Add the rinse water to the flask, and dilute to mark with water.

11.3 Sample Analysis. Mix the contents of the flask thoroughly and pipette a 20 ml-ali-

quot of sample into a 100-ml volumetric flask. Dilute to the mark with water. Using the blank as zero reference, read the absorbance of the sample at 210 nm.

11.4 Audit Sample Analysis. Same as Method 7, Section 11.4, except that a set of audit samples must be analyzed with each set of compliance samples or once per analysis day, or once per week when averaging continuous samples.

12.0 Data Analysis and Calculations

Same as Method 7, Section 12.0, except replace Section 12.3 with the following:

12.1 Total µg NO<sub>2</sub> Per Sample.

$$m = 5 K_c A F \quad \text{Eq. 7B-3}$$

Where:

5=100/20, the aliquot factor.

NOTE: If other than a 20-ml aliquot is used for analysis, the factor 5 must be replaced by a corresponding factor.

13.0 Method Performance

13.1 Range. The analytical range of the method as outlined has been determined to be 57 to 1500 milligrams NO<sub>x</sub> (as NO<sub>2</sub>) per dry

standard cubic meter, or 30 to 786 parts per million by volume (ppmv) NO<sub>x</sub>.

14.0 *Pollution Prevention.* [Reserved]

15.0 *Waste Management.* [Reserved]

16.0 *References*

1. National Institute for Occupational Safety and Health. Recommendations for Occupational Exposure to Nitric Acid. In: Occupational Safety and Health Reporter. Washington, D.C. Bureau of National Affairs, Inc. 1976. p. 149.
2. Rennie, P.J., A.M. Sumner, and F.B. Basketter. Determination of Nitrate in Raw, Potable, and Waste Waters by Ultraviolet Spectrophotometry. *Analyst.* 104:837. September 1979.

17.0 *Tables, Diagrams, Flowcharts, and Validation Data.* [Reserved]

METHOD 7C—DETERMINATION OF NITROGEN OXIDE EMISSIONS FROM STATIONARY SOURCES (ALKALINE PERMANGANATE/COLORIMETRIC METHOD)

NOTE: This method does not include all of the specifications (e.g., equipment and supplies) and procedures (e.g., sampling and analytical) essential to its performance. Some material is incorporated by reference from other methods in this part. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 1, Method 3, Method 6 and Method 7.

1.0 *Scope and Application*

1.1 *Analytes.*

Analyte	CAS no.	Sensitivity
Nitrogen oxides (NO <sub>x</sub> ), as NO <sub>2</sub> , including:		
Nitric oxide (NO) .....	10102-43-9	ppmv
Nitrogen dioxide (NO <sub>2</sub> ) .....	10102-44-07	

1.2 *Applicability.* This method applies to the measurement of NO<sub>x</sub> emissions from fossil-fuel fired steam generators, electric utility plants, nitric acid plants, or other sources as specified in the regulations.

1.3 *Data Quality Objectives.* Adherence to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 *Summary of Method*

An integrated gas sample is extracted from the stack and passed through impingers containing an alkaline potassium permanganate solution; NO<sub>x</sub> (NO + NO<sub>2</sub>) emissions are oxidized to NO<sub>2</sub> and NO<sub>3</sub>. Then NO<sub>3</sub><sup>-</sup> is reduced to NO<sub>2</sub><sup>-</sup> with cadmium, and the NO<sub>2</sub><sup>-</sup> is analyzed colorimetrically.

3.0 *Definitions.* [Reserved]

4.0 *Interferences*

Possible interferents are sulfur dioxides (SO<sub>2</sub>) and ammonia (NH<sub>3</sub>).

4.1 High concentrations of SO<sub>2</sub> could interfere because SO<sub>2</sub> consumes MnO<sub>4</sub> (as does NO<sub>x</sub>) and, therefore, could reduce the NO<sub>x</sub> collection efficiency. However, when sampling emissions from a coal-fired electric utility plant burning 2.1 percent sulfur coal with no control of SO<sub>2</sub> emissions, collection efficiency was not reduced. In fact, calculations show that sampling 3000 ppm SO<sub>2</sub> will reduce the MnO<sub>4</sub> concentration by only 5 percent if all the SO<sub>2</sub> is consumed in the first impinger.

4.2 Ammonia (NH<sub>3</sub>) is slowly oxidized to NO<sub>3</sub><sup>-</sup> by the absorbing solution. At 100 ppm NH<sub>3</sub> in the gas stream, an interference of 6 ppm NO<sub>x</sub> (11 mg NO<sub>2</sub>/m<sup>3</sup>) was observed when the sample was analyzed 10 days after collection. Therefore, the method may not be applicable to plants using NH<sub>3</sub> injection to control NO<sub>x</sub> emissions unless means are taken to correct the results. An equation has been developed to allow quantification of the interference and is discussed in Reference 5 of Section 16.0.

5.0 *Safety*

5.1 *Disclaimer.* This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and to determine the applicability of regulatory limitations prior to performing this test method.

5.2 *Corrosive Reagents.* The following reagents are hazardous. Personal protective equipment and safe procedures are useful in preventing chemical splashes. If contact occurs, immediately flush with copious amounts of water for at least 15 minutes. Remove clothing under shower and decontaminate. Treat residual chemical burns as thermal burns.

5.2.1 *Hydrochloric Acid (HCl).* Highly toxic and corrosive. Causes severe damage to skin. Vapors are highly irritating to eyes, skin, nose, and lungs, causing severe damage. May cause bronchitis, pneumonia, or