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## **METHOD 7A—DETERMINATION OF NITROGEN OXIDE EMISSIONS FROM STATIONARY SOURCES (ION CHROMATOGRAPHIC 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 5, and Method 7.

### *1.0 Scope and Application*

#### 1.1 Analytes.

| <b>Analyte</b>  | <b>CAS No.</b> | <b>Sensitivity</b> |
|---|----------------|--------------------|
| Nitrogen oxides (NO <sub>x</sub> ), as NO <sub>2</sub> , including: |                |                    |
| Nitric oxide (NO)   | 10102-43-9     |                    |
| Nitrogen dioxide (NO <sub>2</sub> )                                 | 10102-44-0     | 65-655 ppmv        |

1.2 Applicability. This method is applicable for the determination of NO<sub>x</sub> emissions from stationary sources.

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*

A grab sample is collected in an evacuated flask containing a dilute sulfuric acid-hydrogen peroxide absorbing solution. The nitrogen oxides, excluding nitrous oxide (N<sub>2</sub>O), are oxidized to nitrate and measured by ion chromatography.

### *3.0 Definitions [Reserved]*

### *4.0 Interferences*

Biased results have been observed when sampling under conditions of high sulfur dioxide concentrations. At or above 2100 ppm SO<sub>2</sub>, use five times the H<sub>2</sub>O<sub>2</sub> concentration of the Method 7 absorbing solution. Laboratory tests have shown that high concentrations of SO<sub>2</sub> (about 2100 ppm) cause low results in Method 7 and 7A. Increasing the H<sub>2</sub>O<sub>2</sub> concentration to five times the original concentration eliminates this bias. However, when no SO<sub>2</sub> is present, increasing the concentration by five times results in a low bias.

## 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 burns as thermal burns.

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

5.2.2 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 in Method 7, section 6.1.

6.2 Sample Recovery. Same as in Method 7, section 6.2, except the stirring rod and pH paper are not needed.

6.3 Analysis. For the analysis, the following equipment and supplies are required. Alternative instrumentation and procedures will be allowed provided the calibration precision requirement in section 10.1.2 can be met.

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

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

6.3.3 Analytical Balance. To measure to within 0.1 mg.

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

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

experimenting with alternative columns that may offer more efficient separation. When using guard columns with the stronger reagent to protect the separation column, the analyst should allow rest periods between injection intervals to purge possible sulfate buildup in the guard column.

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

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

6.3.4.4 Conductivity Detector.

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

### *7.0 Reagents and Standards*

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

7.1 Sample Collection. Same as Method 7, section 7.1.

7.2 Sample Recovery. Same as Method 7, section 7.1.1.

7.3 Analysis. The following reagents and standards are required for analysis:

7.3.1 Water. Same as Method 7, section 7.1.1.

7.3.2 Stock Standard Solution, 1 mg NO<sub>2</sub>/ml. Dry an adequate amount of sodium nitrate (NaNO<sub>3</sub>) at 105 to 110 °C (221 to 230 °F) for a minimum of 2 hours just before preparing the standard solution. Then dissolve exactly 1.847 g of dried NaNO<sub>3</sub> in water, and dilute to 1 liter in a volumetric flask. Mix well. This solution is stable for 1 month and should not be used beyond this time.

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

7.3.4 Eluent Solution. Weigh 1.018 g of sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>) and 1.008 g of sodium bicarbonate (NaHCO<sub>3</sub>), and dissolve in 4 liters of water. This solution is 0.0024 M Na<sub>2</sub>CO<sub>3</sub>/0.003 M NaHCO<sub>3</sub>. Other eluents appropriate to the column type and capable of resolving nitrate ion from sulfate and other species present may be used.

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

8.1 Sampling. Same as in Method 7, section 8.1.

8.2 Sample Recovery. Same as in Method 7, section 8.2, except delete the steps on adjusting and checking the pH of the sample. Do not store the samples more than 4 days between collection and analysis.

### 9.0 Quality Control

| Section | Quality control measure        | Effect   |
|---------|--------------------------------|--|
| 10.1    | Ion chromatographn calibration | Ensure linearity of ion chromatograph response to standards. |

### 10.0 Calibration and Standardizations

#### 10.1 Ion Chromatograph.

10.1.1 Determination of Ion Chromatograph Calibration Factor S. Prepare a series of five standards by adding 1.0, 2.0, 4.0, 6.0, and 10.0 ml of working standard solution (25 µg/ml) to a series of five 50-ml volumetric flasks. (The standard masses will equal 25, 50, 100, 150, and 250 µg.) Dilute each flask to the mark with water, and mix well. Analyze with the samples as described in section 11.2, and subtract the blank from each value. Prepare or calculate a linear regression plot of the standard masses in µg (x-axis) versus their peak height responses in millimeters (y-axis). (Take peak height measurements with symmetrical peaks; in all other cases, calculate peak areas.) From this curve, or equation, determine the slope, and calculate its reciprocal to denote as the calibration factor, S.

10.1.2 Ion Chromatograph Calibration Quality Control. If any point on the calibration curve deviates from the line by more than 7 percent of the concentration at that point, remake and reanalyze that standard. This deviation can be determined by multiplying S times the peak height response for each standard. The resultant concentrations must not differ by more than 7 percent from each known standard mass (*i.e.*, 25, 50, 100, 150, and 250 µg).

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

10.3 Barometer. Calibrate against a mercury barometer.

10.4 Temperature Gauge. Calibrate dial thermometers against mercury-in-glass thermometers. An alternative mercury-free thermometer may be used if the thermometer is, at a minimum, equivalent in terms of performance or suitably effective for the specific temperature measurement application.

10.5 Vacuum Gauge. Calibrate mechanical gauges, if used, against a mercury manometer such as that specified in section 6.1.6 of Method 7.

10.6 Analytical Balance. Calibrate against standard weights.

### 11.0 Analytical Procedures

### 11.1 Sample Preparation.

11.1.1 Note on the analytical data sheet, the level of the liquid in the container, and whether any sample was lost during shipment. If a noticeable amount of leakage has occurred, either void the sample or use methods, subject to the approval of the Administrator, to correct the final results. Immediately before analysis, transfer the contents of the shipping container to a 50-ml volumetric flask, and rinse the container twice with 5 ml portions of water. Add the rinse water to the flask, and dilute to the mark with water. Mix thoroughly.

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

### 11.2 Analysis.

11.2.1 Prepare a standard calibration curve according to section 10.1.1. Analyze the set of standards followed by the set of samples using the same injection volume for both standards and samples. Repeat this analysis sequence followed by a final analysis of the standard set. Average the results. The two sample values must agree within 5 percent of their mean for the analysis to be valid. Perform this duplicate analysis sequence on the same day. Dilute any sample and the blank with equal volumes of water if the concentration exceeds that of the highest standard.

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.

### *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  $\text{NO}_x$  as  $\text{NO}_2$ .

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  $\text{NO}_2$  may be calculated as ppm  $\text{NO}_2$  at standard conditions as follows:

$$\text{ppm NO}_2 = 0.5228C \quad \text{Eq. 7A-2}$$

Where:

0.5228=ml/mg  $\text{NO}_2$ .

### *13.0 Method Performance*

13.1 Range. The analytical range of the method is from 125 to 1250 mg  $\text{NO}_x/\text{m}^3$  as  $\text{NO}_2$  (65 to 655 ppmv), and higher concentrations may be analyzed by diluting the sample. The lower detection limit is approximately 19 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]*

