

NITRIC OXIDE and NITROGEN DIOXIDE

6014

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|-----------------|-----------|-----------------|------------------|
| NO | MW: 30.01 | CAS: 10102-43-9 | RTECS: QX0525000 |
| NO ₂ | 46.01 | 10102-44-0 | QW9800000 |

METHOD: 6014, Issue 1

EVALUATION: FULL

Issue 1: 15 August 1994

OSHA : 25 ppm NO; C 1 ppm NO₂
NIOSH: 25 ppm NO; 1 ppm STEL NO₂
ACGIH: 25 ppm NO; 3 ppm TWA, 5 ppm STEL NO₂
 (1 ppm NO = 1.227 mg/m³ @ NTP)
 (1 ppm NO₂ = 1.882 mg/m³ @ NTP)

PROPERTIES: NO: gas; BP -151.7 °C; vapor density (air=1) 1.0
 NO₂: gas; MP -11.2 °C; BP 21 °C; vapor density (air=1) 2.83

SYNONYMS: NO: nitrogen monoxide
 NO₂: nitrogen peroxide; nitrogen tetroxide

| SAMPLING | | MEASUREMENT | |
|--|--|-----------------------------------|--|
| SAMPLER: | SORBENT TUBES (oxidizer + 2 triethanolamine-treated molecular sieve) | TECHNIQUE: | VISIBLE ABSORPTION SPECTROPHOTOMETRY |
| FLOW RATE: | NO: 0.025 L/min NO ₂ : 0.025 - 0.2 L/min | ANALYTE: | nitrite ion, NO ₂ ⁻ |
| VOL-MIN: | 1.5 L | EXTRACTION SOLUTION: | absorbing solution, 50 mL |
| -MAX: | 6 L | WAVELENGTH: | 540 nm |
| SHIPMENT: | routine | CALIBRATION: | standard solutions of NO ₂ ⁻ |
| SAMPLE STABILITY: | stable at least 7 days @ 25 °C [1,2] | RANGE: | 3 to 18 µg NO ₂ ⁻ per sample [1] |
| BLANKS: | 3 to 6 field blanks and 10 media blanks per set | ESTIMATED LOD: | 1 µg NO ₂ ⁻ per sample [3] |
| ACCURACY | | PRECISION (S_p): | NO: 0.061 [1]; NO ₂ : 0.026 [2] |
| RANGE STUDIED: | NO: 11-48 ppm [1]; NO ₂ : 2-12 ppm [2] (1.5-L samples) (3-L samples) | | |
| BIAS: | NO: 4.1% [1]; NO ₂ : -2% [2] | | |
| OVERALL PRECISION (S_{rT}): | NO: 0.083 [1]; NO ₂ : 0.063 [2] | | |
| ACCURACY: | NO: ± 20.4%; NO ₂ : ± 14.6% | | |

APPLICABILITY: The working range for NO is 1 to 50 ppm (1.3 to 61 mg/m³) for a 1.5-L air sample. The working range for NO₂ is 0.5 to 25 ppm (1 to 47 mg/m³) for a 3-L air sample. The lower sampling rate for NO is to allow collection of oxidized NO on the back sorbent section. At the lower rate, both NO and NO₂ may be determined simultaneously.

INTERFERENCES: Any compound that reacts with the colorimetric reagents will interfere.

OTHER METHODS: This method is based on that of Willey, et al. [4] and combines S321, S320, and P&CAM 231 in a revised format [3,5]. OSHA methods ID-182 and ID-190 use the same sampler, with measurement by ion chromatography [6].

REAGENTS:

1. Triethanolamine, TEA, reagent grade.
2. n-Butanol, reagent grade.
3. Phosphoric acid, H_3PO_4 , conc., reagent grade.*
4. N-(1-naphthyl)ethylenediaminedihydrochloride, NEDA.
5. Sodium nitrite, $NaNO_2$.
6. Absorbing solution: Dissolve 15.0 g triethanolamine in ca. 500 mL deionized water, add 0.5 mL n-butanol, and dilute to 1 L.
7. H_2O_2 solution, 0.02% (v/v): Dilute 0.2 mL of 30% H_2O_2 to 250 mL with deionized water.
8. Sulfanilamide solution: Dissolve 10 g sulfanilamide in 400 mL deionized water, add 25 mL conc. H_3PO_4 , and dilute to 500 mL.
9. NEDA solution: Dissolve 0.5 g N-(1-naphthyl)ethylenediamine dihydrochloride in 500 mL deionized water.
10. Calibration stock solution, 100 NO_2^- $\mu g/mL$: Dissolve 0.1500 g $NaNO_2$ in 1 L deionized water.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: Three glass tubes, 7-mm OD, flame-sealed ends with plastic caps, with glass wool retainers:
Tube A: 400 mg TEA-coated molecular sieve (type 13x, 30-40 mesh)
Tube B: 800 mg oxidizer (chromate) to convert NO to NO_2 .
Tube C: Same as Tube A.
Connect the tubes in series with flexible tubing. Position Tube C closest to the inlet of the sampling pump. Tubes are commercially available (SKC-226-40, or equivalent).
2. Personal sampling pump, 0.025 to 0.2 L/min, with flexible connecting tubing.
3. Spectrophotometer, UV-visible (540 nm), with cuvettes, 1-cm silica cuvettes.
4. Beakers, borosilicate, 100-mL.
5. Volumetric flasks, 50-mL and other convenient sizes.
6. Pipets, 1-, 5-, 10-mL and other convenient sizes.
7. Stopwatch.

SPECIAL PRECAUTIONS: Concentrated acid is corrosive to the skin and mucous membranes. Handle it only in a hood.

SAMPLING:

1. Calibrate the sampling pump with a representative sampler in line.
2. Immediately before sampling, break ends of sampler and attach to pump.
NOTE: Nitrogen dioxide collects on the first tube (Tube A), and is thereby separated from nitric oxide, which is oxidized by Tube B and then is collected on Tube C (adjacent to the sampling pump.)
3. Sample at an accurately known flow rate of 0.025 L/min \pm 5%.
NOTE: If nitric oxide is not to be determined, a flow rate of up to 0.2 L/min may be used.
4. Cap the sampler and pack securely for shipment. Submit adequate numbers of field blanks and media blanks to the laboratory.

SAMPLE PREPARATION:

5. Transfer the sorbent from Tube A and Tube C to separate 50-mL volumetric flasks. Discard glass wool plugs and oxidizer (Tube B).
6. Add absorbing solution to sample in 50-mL volumetric and bring to the mark.
7. Stopper flask and shake vigorously for 30 sec. Allow solids to settle.
8. Pipet 10 mL of extracted sample into a 50-mL volumetric flask.
NOTE: Start reagent blanks at this step.
9. Add 1.0 mL hydrogen peroxide solution, 10.0 mL sulfanilamide solution, and 1.4 mL NEDA solution. Mix thoroughly after each addition.
10. Allow 10 min for complete color development.

CALIBRATION AND QUALITY CONTROL:

11. Calibrate daily with at least six working standards to cover the range of 1 to 18 μg nitrite ion per 10-mL sample.
 - a. Analyze the working standards together with blanks and samples (steps 8 through 10 and steps 12 through 14).
 - b. Prepare a calibration graph [absorbance vs. μg NO_2^- per sample].

MEASUREMENT:

12. Set wavelength on the spectrophotometer to 540 nm.
13. Set to zero with reagent blank.
14. Transfer some of the sample solution from step 10 to a cuvette and record the absorbance.

CALCULATIONS:

15. From the calibration graph, determine the mass of NO_2^- in each Tube A, W_A (μg), and in the corresponding average blank, B_A (μg). Similarly, determine the mass of NO_2^- in each Tube C, W_C (μg), and average blank, B_C (μg).
16. Calculate the concentration, C_{NO_2} (mg/m^3) of NO_2 in the volume of air sampled, V (L), applying the conversion factor 0.63:

$$C_{\text{NO}_2} = \frac{(W_A - B_A)}{0.63 V}, \text{ mg}/\text{m}^3.$$

NOTE: The conversion factor 0.63 represents the number of moles of nitrite ion produced by 1 mole of nitrogen dioxide gas. For NO or NO_2 , gas concentrations above 10 ppm, use 0.5 as the conversion factor [7].

17. Calculate the concentration, C_{NO} (mg/m^3), of NO in the air volume sampled, V (L), applying the factor 0.652 ($\text{MW NO}/\text{MW NO}_2^-$) and the conversion factor 0.63:

$$C_{\text{NO}} = \frac{(W_C - B_C) \cdot 0.652}{0.63 V}, \text{ mg}/\text{m}^3.$$

EVALUATION OF METHOD:

Method S321, Nitric Oxide, was evaluated over the range of 11.1 to 47.7 ppm (13.8 to 58.5 mg/m^3) for 1.5-L samples, collected from dynamically generated test atmospheres [1,8]. The test concentration was verified with a direct reading instrument, Energetic Sciences Enolyzer. The 1.2 g oxidizer section was found adequate for a 60-min sampling time. NO samples had a mean recovery of 99.5% after 7 days storage at ambient temperature.

Method S320, Nitrogen Dioxide, was evaluated over the range 3.0 - 11.6 ppm (5.8 to 21.6 mg/m^3) using 3.9-L samples [2,7]. When an atmosphere at 84% RH containing 11.59 ppm NO_2 was sampled at 0.064 L/min, 1.0% breakthrough occurred after 60 min and 2.4% breakthrough occurred after 180 min. Quantitative recovery was obtained for samples containing 47 μg NO_2 which were stored for 12 days at ambient conditions.

REFERENCES:

- [1] Backup Data Report for Nitric Oxide, S321, prepared under NIOSH Contract No. 210-76-0123.
- [2] Backup Data Report for Nitrogen Dioxide, S320, prepared under NIOSH Contract No. 210-76-0123.
- [3] NIOSH Manual of Analytical Methods, 2nd ed., Vol. 4, Methods S320 and S321. U.S. Department of Health, Education, and Welfare. DHEW (NIOSH) Publication No. 78-175.
- [4] Willey, M.A., C.S. McCammon, and L.J. Doemeny, Am. Ind. Hyg. Assoc. J. **38**, 358 (1977).
- [5] NIOSH Manual of Analytical Methods, 2nd ed., Vol. 1, P&CAM 231, U.S. Department of Health, Education, and Welfare (NIOSH) Publ. 77-157-A (1977).
- [6] OSHA Analytical Methods Manual, 2nd ed., Part 2, Vol. 2, ID-182 and ID-190, U.S. Department of Labor, Salt Lake City, UT (1991).
- [7] Gold, A., Anal. Chem. **49**, 1443-1450 (1977).
- [8] NIOSH Research Report - Development and Validation of Methods for Sampling and Analysis of Workplace Toxic Substances, U.S. Department of Health and Human Services, Publ. (NIOSH) 80-133 (1980).

METHOD REVISED BY:

W. J. Woodfin and M. E. Cassinelli, NIOSH/DPSE; Method S321 validated under NIOSH Contract No. 210-76-0123.