NITROGEN DIOXIDE (Diffusive sampler) 6700

NO_2 MW: 46.01 CAS: 10102-44-0 RTECS: QW9805000

METHOD: 6700, Issue 2 **EVALUATION: FULL** **Issue 1: 15 February 1984**
Issue 2: 15 January 1998

OSHA : C 5 ppm
NIOSH: STEL 1 ppm/15 min
ACGIH: 3ppm; STEL 5 ppm
(1 ppm = 1.881 mg/m³ @ NTP)

PROPERTIES: yellowish-brown fuming liquid or reddish-brown gas; BP 21 °C; MP -9.3 °C; d 1.448 @ 20 °C; vap density (air=1) 1.59

SYNONYMS: nitrogen peroxide, dinitrogen tetroxide, Azote

SAMPLING

SAMPLER: DIFFUSIVE SAMPLER
(Palmes tube with three triethanolamine-treated screens) [1]

SAMPLING TIME **- MIN:** 15 min @ 5 ppm
- MAX: 8 h @ 10 ppm

SHIPMENT: routine

SAMPLE STABILITY: use sampler within 1 month after preparation; analyze within 1 month after sampling

BLANKS: 2 to 10 field blanks per set

ACCURACY

RANGE STUDIED: 1.2 to 80 ppm-h (0.13 to 8.5 µg NO_2 per sample) [2]

BIAS: − 6.8%

OVERALL PRECISION ($\hat{S}_{rT}$): 0.06 [3]

ACCURACY: ± 16.0%

MEASUREMENT

TECHNIQUE: VISIBLE ABSORPTION SPECTROPHOTOMETRY

ANALYTE: nitrite ion (NO_2^-)

REAGENT: aqueous solution of sulfanilamide, H_3PO_4, and N-1-naphthylethylenediamine dihydrochloride

WAVELENGTH: 540 nm

PATHLENGTH: 1 cm

CALIBRATION: solutions of $NaNO_2$ in reagent

RANGE: 0.13 to 8.5 µg NO_2 per sample [2]

ESTIMATED LOD: 0.01 µg NO_2 per sample

PRECISION ($\bar{S}_r$): 0.05 [2]

APPLICABILITY: The working range is 1.2 to 80 ppm-h [2]. The method is applicable for ceiling and short-term exposure measurements. In the development of this passive sampler, it was assumed that NO_2 was completely converted to nitrite ion [1]. Incomplete conversion of NO_2 to nitrite ion (Saltzman factor <1) will cause a negative bias [1]. Diffusive samplers have a lower collection efficiency at lower pressure (-7% @ 5500 m altitude) [4].

INTERFERENCES: In very dusty environments, particles may deposit on the inside surface of the sampler. Resuspension of the dust in analytical reagent can give a positive bias in the spectrophotometric reading.

OTHER METHODS: Short-term and long-term detector tubes, passive indicator tubes, and various other diffusive samplers and electrochemical instruments have been used to sample for NO_2. NMAM Method 6014 [5] also uses an active solid sorbent sampling method with similar color development .

REAGENTS:

1. Absorbing reagent. Combine 1 part reagent grade triethanolamine (TEA) with 7 parts analytical grade acetone.*
2. Sulfanilamide solution. Combine 2 g sulfanilamide and 5 mL conc. H_3PO_4, and dilute to 100 mL with distilled water.
3. N-1-naphthylethylenediamine dihydrochloride (NEDA) solution. Dissolve 70 mg NEDA in 50 mL distilled water.
4. Combined reagent. Combine 1 part sulfanilamide solution, 1 part water, and 0.1 part NEDA solution. Protect from light and refrigerate. Stable ~ 1 month .
5. Sodium nitrite stock solution, 0.05 *M*. Accurately weigh 0.345 g $NaNO_2$ (reagent grade). Dissolve in 100 mL deionized water. Protect from light and refrigerate. Stable 90 days.
6. Calibration stock solution. Dilute an aliquot of $NaNO_2$ stock solution with distilled water (e.g.,1:50 dilution yields1 nanomole NO_2^-/µL). Prepare fresh immediately before use.

*See SPECIAL PRECAUTIONS

EQUIPMENT:

1. Sampler: See APPENDIX (Potential sources of equipment given in reference [1]):
   a. Acrylic tubing, 3/8-inch (9.5-mm) ID.
   b. Stainless steel screen, 40x40 mesh/inch (16x16 mesh/cm).
   c. Polyethylene cap, unflanged, ½-inch (12.7-mm).
   d. Polyethylene cap, flanged, ½-inch (12.7-mm).
   e. Pen clips, 0.48-inch (12.2-mm).
   f. Electrical tape, plastic.
   g. Stopcock grease.
2. Spectrophotometer, 540 nm, with 1-cm cuvettes.
3. Volumetric flasks and pipets for preparation of standards.
4. Mixer, vibration or vortex (optional).
5. Forceps.

SPECIAL PRECAUTIONS: Acetone is a fire hazard.

SAMPLING:

1. Attach the sampler with flanged cap down. Start sampling by removing flanged cap. Estimate appropriate sampling time such that the amount of NO_2 collected is in the range 1.2 to 80 ppm-h (0.13 to 8.5 µg NO_2).
2. Terminate sampling by replacing flanged cap.

CALIBRATION AND QUALITY CONTROL:

3. Calibrate daily with at least six working standards over the range 0 to 40 nanomoles (0 to 1.84 µg) NO_2^- per 2.1 mL combined reagent.
   a. Prepare working standards from calibration stock solution immediately before use.
   b. Allow 10 min for color development.
   c. Transfer an aliquot of the working standard to a cuvette and analyze (steps 6 through 8).
4. Prepare a calibration graph (absorbance at 540 nm vs. NO_2^- mass in nanomoles.
   NOTE: The absorbance of 40 nanomoles NO_2^- is approximately 1 absorbance unit.
5. Check dimensions of the sampler. If cross-sectional area divided by length (A/L) of the sampler tube differs significantly from 0.10 cm, recalculate the diffusive collection rate (step 9).

MEASUREMENT:

6. Remove flanged cap from samplers. Add 2.1 mL combined reagent directly into samplers.

NOTE: If 2.1 mL is not sufficient to completely cover the exit slit of the spectrophotometer, a larger volume can be used provided the same volume is used for both standards and unknowns.

7. Recap the samplers and mix manually or with a mixer. Allow 10 min for the color to develop.
8. Transfer the solution to a cuvette and read the absorbance at 540 nm within 30 min from time reagent was added.
   NOTE: If sample reads beyond calibration graph, dilute sample with combined reagent or extend calibration range.

CALCULATIONS:

9. From calibration graph, read nanomoles nitrite ion (NO_2^-) collected by the sampler. Divide by 2.3 nanomoles/ppm-h (the diffusive collection rate [1]) and the sample exposure time, t (h), to obtain time-weighted average concentration, C (ppm NO_2), of NO_2:

$$C = \frac{\text{nanomoles } NO_2^-}{2.3\ t}$$

NOTE 1: If sampler dimensions are different from those specified in the APPENDIX, use 2.3•(actual A_f/L [cm]÷ 0.1 cm) nanomoles/ppm-h as the diffusive collection rate.

NOTE 2: The assumption is made that NO_2 is completely converted to NO_2^-, because of the small quantity collected [1].

EVALUATION OF METHOD:

This method is based on a method developed by E. D. Palmes *et al* at New York University [1]. Analytical precision and useful range were estimated from a laboratory evaluation conducted by NIOSH (1982) [2]. Overall precision ($\hat{S}_{rT}$ = 0.06) was estimated from side-by-side replicate samples collected in an underground salt mine [3]. In a laboratory study, this method gave results averaging 94 ± 4% (mean ± s_r) of a reference method over the range 1.3 to 79 ppm-h [2]. A field study found results for this method of 109 ± 9% (mean ± s_r) vs. a reference method in the range 12 to 19 ppm-h [3]. Sampling errors may exist in this method when the concentration is not constant in time and the sampling period is short [6, 7]. For example, the value of s_r associated with estimating the TWA of an isolated random 10-sec concentration pulse within a 15-min sampling period may be calculated [6] to equal 0.5. Secondly, reference [6] reports a specific set of real-time concentration data measured in an industrial environment. For these data, the error s_r in making 15-min TWA estimates is calculated to equal 0.12. Although these values are large, similar sampling errors due to time variations are expected to be better controlled for longer sampling periods as the variance of the sampling error varies inversely with the sampling period.

REFERENCES:

[1] Palmes ED, Gunnison AF, DeMattio J, Tomczyk C [1976]. Personal sampler for nitrogen dioxide. Am Ind Hyg Assoc J *37:*570-577.

[2] Woebkenberg ML [1982]. A comparison of three personal passive sampling methods for N_2O. Am Ind Hyg Assoc J *43:*553-561.

[3] Jones W, Palmes ED, Tomczyk C, Millson M [1979]. Field comparison of two methods for the determination of NO_2 concentration in air. Am Ind Hyg Assoc J *40:*437-438.

[4] Lindenboom R, Palmes ED [1983]. Effect of reduced atmospheric pressure on a diffusional sampler. Am Ind Hyg Assoc J *44:*105-108.

[5] NIOSH [1994]. Nitric oxide and nitrogen dioxide: Method 6014. In: Eller PM, Cassinelli ME, Eds. NIOSH Manual of Analytical Methods (NMAM), 4th ed. Cincinnati, OH: National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 94-113.

[6] Bartley DL, Doemeny LJ, Taylor DG [1983]. Diffusive monitoring of fluctuating concentrations. Am Ind Hyg Assoc J *44:*241-247.

[7] Hearl FJ, Manning MP [1980]. Transient response of diffusive dosimeters. Am Ind Hyg Assoc J *41:*778-783.

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APPENDIX: PREPARATION OF SAMPLER

1. Measure the average cross-sectional area of a length of 3/8 inch (9.5 mm) ID acrylic tubing.
   a. Cap one end of the tubing. Pour in a known volume, v (mL), of water to nearly fill the tubing (e.g., 100 mL water for a 180-cm (6-foot) length of tubing).
   b. Measure the height, h (cm), of the water column in the tubing.
   c. Determine the average cross-sectional area, A_t (cm^2), of the tubing.

$$A_t = \frac{v}{h}$$

2. Cut the tubing into lengths, L (ca. 7.1 cm), such that A_t / L = exactly 0.1 cm.
   NOTE: The collection rate is directly proportional to A_t / L. For A_t / L = 0.1 cm, the collection rate is 2.3 nanomoles/ppm-h [2].
3. Cut circular portions, 13/32 inch (10.3 mm) to 7/16 inch (11.1 mm) in diameter, from stainless steel screen using a 13/32 inch (10.3 mm) paper punch or other suitable means.
4. Clean the tubes, screens and caps with detergent solution in an ultrasonic bath. Rinse with distilled water. Air dry.
5. Dip the screens in absorbing reagent.
6. Using forceps, place the screens on absorbent paper. Press the screens momentarily with the forceps tips to blot. Allow the acetone to evaporate.
7. Stack three treated screens in the bottom of an unflanged cap. Insert the acrylic tube into the unflanged cap securing the screens (see the figures).
8. Slide the pen clip onto the acrylic tube touching the unflanged cap. Secure the pen clip and unflanged cap with a piece of electrical tape.
9. Apply a small amount of stopcock grease to the outside of the uncapped end of the acrylic tube and slide the flanged cap into place.

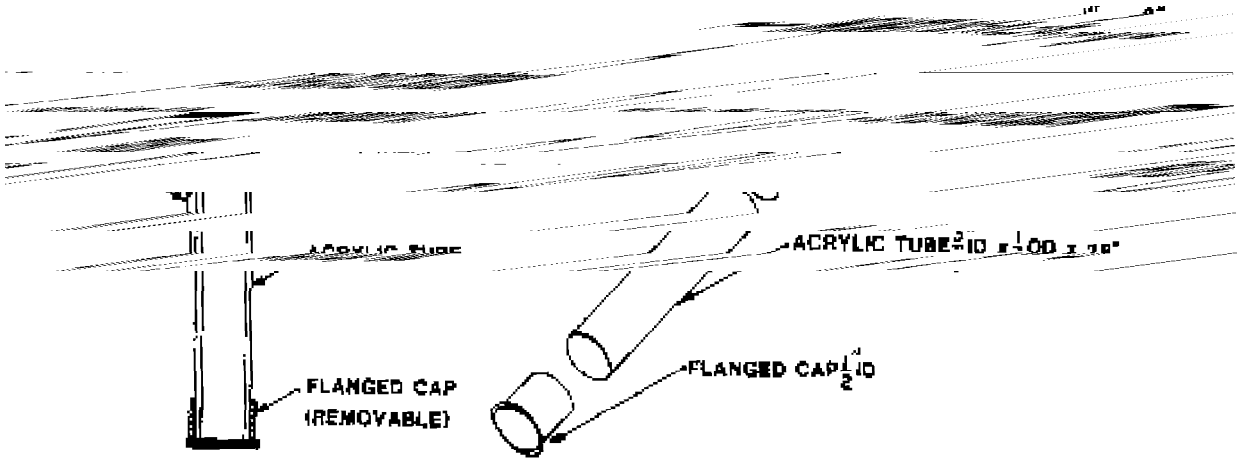

Figure 1. Assembled view (left) and exploded view (right) of sampler.