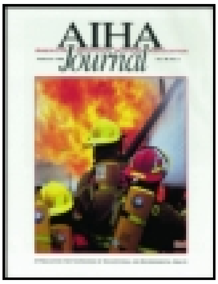

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A solid sorbent personal sampling method for the simultaneous collection of nitrogen dioxide and nitric oxide in air

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A sampling method is described for the collection of air samples containing both nitrogen dioxide (NO_2) and nitric oxide (NO) in the range of 0.5 to 5 ppm NO_2 and 9 to 50 ppm NO. These two gases are trapped on a solid sorbent sampling tube which employs the collection of the NO_2 on a triethanol-amine (TEA)-impregnated molecular sieve surface; the oxidation of NO to NO_2 by a solid oxidizer; and the collection of the converted NO on another section of TEA sorbent. The trapped NO/NO_2 on each TEA section is desorbed and the concentrations are determined spectrophotometrically. At all concentrations tested, the collection efficiency for NO_2 averaged approximately 96%. The collection efficiencies for NO were as follows: at 9 ppm, 97%; at 11 ppm, 106%; at 24 ppm, 84%; and at 50 ppm, 67%.

A solid sorbent personal sampling method for the simultaneous collection of nitrogen dioxide and nitric oxide in air

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introduction

Various chemical methods for the determination of nitrogen dioxide (NO_2) in air have been utilized.[1–4] Most have used impingers or other types of bubbling devices containing Griess-Saltzman reagent[1] or some modified form of this reagent. A new method for measuring work environment levels of NO_2 was recently developed[3,4] in which the NO_2 is absorbed in triethanolamine (TEA) solution or on a TEA-impregnated molecular sieve surface. The development of the following field method for sampling NO_2 and NO is based, in part, on the adsorption of NO_2 on a TEA-impregnated molecular sieve sorbent.

Most analytical procedures for nitric oxide (NO) involve oxidizing it to NO_2 and determining the concentration of NO_2. The NO_2 portion in the sample must therefore be determined or removed before the NO concentration could be reported. The Intersociety Committee tentative method for nitric oxide,[5] recommended that the air sample containing a mixture of NO_2 and NO be first passed through a section of solid sorbent containing TEA. This removes the NO_2. The remaining NO in the sample then passes through a humidifying section; followed by a chromium trioxide oxidizing section where the NO is converted to NO_2; and finally, it enters a bubbler containing Greiss-Saltzman reagent. The use of the liquid containing bubbler for collection of the NO_2 is not ideal for personal sampling as these devices are inconvenient and subject to leakage during and after sampling.

This paper describes a solid sorbent sampling tube for NO_2 and NO which combines the recent work on sampling for nitrogen dioxide[3,4] with the Intersociety Committee tentative method for NO.[5] This method was developed to allow sampling in the concentration range of the proposed National Institute for Occupational Safety and Health recommended standard for

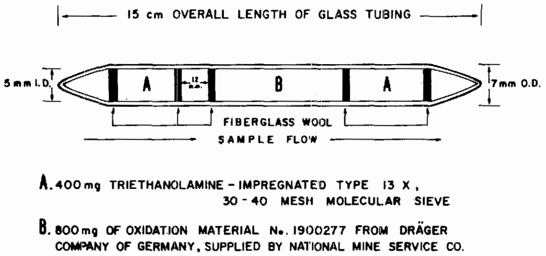

Figure 1—Nitrogen dioxide and nitric oxide sampling tube design.

NO_2 and NO in a work environment. These recommended standards are a ceiling of 1 ppm for NO_2 and 25 ppm as a time-weighted average concentration for NO. This method was therefore developed to sample NO_2 over the range of 0.5 to 5 ppm and NO over the range of 9 to 50 ppm in a 15 minute sampling period.

This work was performed in the laboratories of the Personal and Environmental Measurements Section of the Engineering Branch, Division of Physical Sciences and Engineering, National Institute for Occupational Safety and Health.

experimental apparatus

Spectrophotometer, Beckman Model 25 or any comparable instrument. Chemiluminescent NO-NO_2 Gas Analyzer, Thermo Electron Corporation (TECO) Model 14.

Sipin *personal sampler pumps*, Model SP-1.

Solid sorbent sampling tube, a 5-mm I.D., 7-mm O.D. pyrex glass tube containing two 400 mg sections of TEA-impregnated molecular sieve and one 800 mg section of oxidizer (Figure 1).

Generation System—Nitrogen dioxide concentrations over the range of 0.5 ppm to 5.5 ppm were dynamically generated using a 30 cm NO_2 permeation tube (Metronic Associates, Inc.) in a gas dilution system (Figure 2). The NO_2 permeation tube was kept at a constant temperature in a water jacketed condenser using a water bath (Forma Scientific Masterline 2095). The tube was weighed daily and a daily permeation rate was determined and used in calculating NO_2 concentrations. The purified dilution air was humidified by

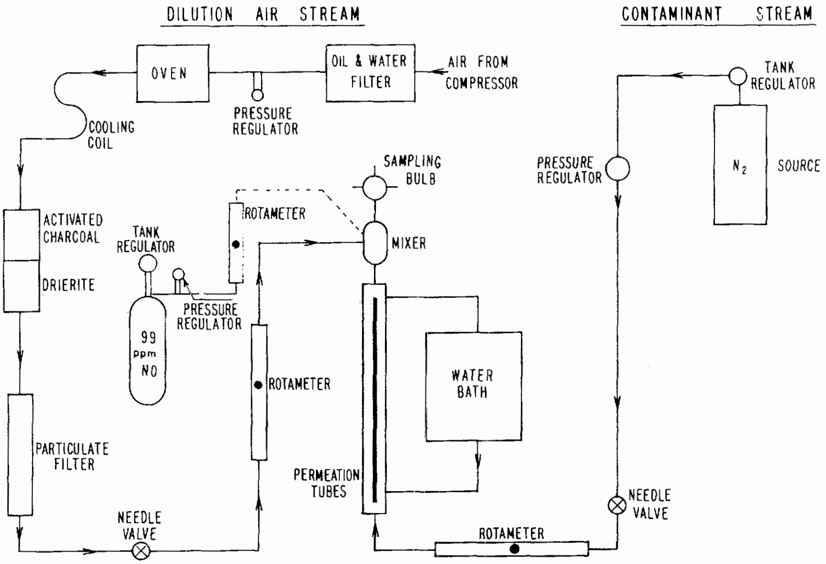

Figure 2—Permeation tube generation system.

bubbling it through distilled water for an approximate 50% RH as monitored by a hydrometer (Hygrodynamics, Model 15-3001). A mixture of 99 ppm NO in nitrogen was metered from a cylinder (Matheson Gas Products). The NO was added as part of the gas dilution system for NO_2 to obtain mixtures of NO and NO_2.

reagents

Oxidizer, No. 1900277 oxidation material from the Drager Company of West Germany (supplied by National Mine Service).

Other reagents—The reagents and preparation of standard curve are the same as described by Blacker.[4] The list is repeated here for the convenience of the reader.

Solid sorbent—Add 25 g of triethanolamine (Fisher Scientific T-407) to a 250-ml beaker; add 4 g of ethylene glycol (MC/B Manufacturing Chemists EX 0564), 50-ml acetone (Fisher Scientific A-19) and sufficient distilled water to bring volume up to 100-ml. To the mixture add about 50 cc of type 13 X, 30-40 mesh molecular sieve (MC/B Manufacturing Chemists MX 1583-1). Stir and let stand in a covered beaker for about 30 minutes. Decant the excess liquid, and transfer the molecular sieve to a porcelain pan which is then placed under a heating lamp until most of the moisture has evaporated. Complete the drying in an oven at 110°C for 1 hour. The sorbent should be free flowing. Store in a closed glass container.

Liquid absorber—Dissolve 15.0 gm of triethanolamine in approximately 500 ml of distilled water, and 0.5 ml of n-butanol, and dilute to 1 liter.

Hydrogen peroxide—Dilute 0.2 ml of 30% hydrogen peroxide to 250 ml with distilled water.

Sulfanilamide—Dissolve 10 g of sulfanilamide in 400 ml distilled water. Add 25 ml of concentrated phosphoric acid, mix well, and dilute to 500 ml.

NEDA—Dissolve 0.5 g of N-(1-napthyl) ethylenediamine dihydrochloride in 500 ml of distilled water.

Standard solution—Dissolve 0.1500 gm of reagent grade sodium nitrate in distilled water and dilute to 1 liter. This solution contains 100 μg of NO_2 (ion) per milliliter.

analytical procedure

The analytical procedure followed is basically that found in the paper on collecting NO_2 on a TEA impregnated sorbent.[4] The only modification to this procedure is the use of 20 ml of absorbing solution instead of 50 ml when sampling low concentrations of NO_2. A reproduction of the analytical procedure is included for the reader's convenience.

preparation of standard curve

Dilute 2 ml of stock standard (100 μg of NO_2 (ion) per milliliter) to 100 ml with absorbing solution to prepare a solution containing 2 μg of NO_2 (ion) per milliliter. To a series of 25 ml glass-stoppered graduated cylinders add 0, 1, 3, 5 and 7 ml of standard (2 μg of NO_2 (ion) per milliliter). Add absorbing solution to bring the volume in each cylinder up to 10 ml. Add 1 ml of hydrogen peroxide solution, 10 ml of sulfanilamide solution, and 1.41 ml of NEDA solution, with thorough mixing after the addition of each reagent. Allow 10 minutes for complete color development, and measure absorbance at 540 nm, using the treated blank to zero the spectrophotometer. Prepare the standard curve by plotting absorbance versus concentration.

analysis of sorbent tube

With a tweezer remove and discard the glass wool plug and transfer the TEA sorbent to a 50 ml glass-stoppered graduate. Label the graduate as to location of TEA sorbent in respect to the oxidizer section. Add 50 ml of the liquid absorbing solution and shake vigorously for about 30 seconds. For concentrations below 5 ppm NO_2 or NO, add only 20 ml of the absorbing solution instead of 50 ml to increase the sensitivity. The other section of TEA sorbent in the tube is treated in the same manner. Allow a few minutes for the solids to settle and then transfer 10-ml to a 25-ml glass-stoppered graduate. Prepare a blank from unexposed molecular sieve obtained from a sorbent tube. Develop the color in the same manner as described for the preparation of the standard curve and determine the amount of NO_2 (ion) in the aliquot from the standard curve. Intensely colored solutions can be diluted with water to

TABLE I
Collection Efficiency of TEA Sorbent

Generated NO_2 (ppm)	Total % NO_2 Recovery	Wt of Each Sorbent Section (mg)	% of Total NO_2 Recovered on 1st Section	% of Total NO_2 Recovered on 2nd Section
6	100	200	77	23
6	101	300	89	11
3	108	400	97	3

obtain an absorbance readable on the spectrophotometer.

testing and results

Preliminary studies were conducted to determine the collection efficiency of the TEA sorbent. In these tests, tubes were constructed containing 2 equal sections of TEA sorbent separated by a glass wool plug. The individual section masses varied between 200 mg to 400 mg. Air, containing approximately 3 or 6 ppm NO_2, was passed through the two-section tube at various sampling rates of up to 150 cc/min. The total sample volume ranged between 9.0 to 33.4 liters. The collection efficiency for all tubes tested was found to be approximately 100%, with the amount of NO_2 collected on the first section varying with the section mass. The results are presented in Table I. Tests with two 200 mg TEA sections in series sampling 6 ppm NO_2 indicated approximately 77% of the NO_2 was collected on the first TEA section. Tests with two 300 mg TEA sections sampling 6 ppm NO_2 resulted in 89% collected on the first section and tests with two 400 mg TEA sections sampling 3 ppm NO_2 resulted in about 97% of the NO_2 collected on the first section. A later experiment in which the TECO NO-NO_x analyzer was used to monitor NO_2 breakthrough, tubes contructed with one 400 mg section of TEA sorbent indicated negligible breakthrough after 2 hours sampling 25 ppm at NO_2 at 50 cc/min. Therefore, 400 mg TEA sorbent was chosen as the final TEA section weight.

The initial oxidizer used to convert the NO to NO_2 was prepared according to the Intersociety Committee tentative method for NO.[5] In this method a 15-mm I.D. glass tube is filled with 10 ml of chromium trioxide oxidizer pellets between two glass wool plugs. Before the oxidizer section, a humidity regulator is required to provide steady 40 to 70 percent relative humidity. The above humidifier and oxidizer arrangement was scaled down to tubes containing 100 to 1150 mg oxidizer and 100 to 500 mg humidifier before a 300 mg section of TEA sorbent.

The initial sampling was done at flow rates of approximately 150 cc/min. These tubes produced a recovery of less than 7% of the 25 ppm NO generated. However, only about a 37% recovery for NO was achieved using 1 gram of oxidizer and a 25 cc/min sampling rate. The highest recovery, 60%, resulted from a U-tube containing 20 grams of oxidizer sampling 5 ppm NO at a rate of 79 cc/min.

In an attempt to obtain higher conversion efficiencies, the Drager oxidizer was substituted for the oxidizer prepared via the Intersociety Method directions.[5] In accordance with Drager's recommendation, no humidifier was included in the tubes. Initially, 300 mg of oxidizer and 300 mg of TEA sorbent were packed in a glass tube. Air, containing approximately 5 ppm NO, was passed through each tube at rates in the range of 50-75 cc/min. The total sample volume ranged from 1.5 liters to 19 liters. These tubes gave approximately 100% recovery of the NO as NO_2. One liter samples of 25 ppm NO, taken under the same sampling conditions, resulted in approximately 62% recovery. The amount of oxidizer was increased and the sampling rates were maintained at 50 cc/min. Tubes containing 800 mg oxidizer and 400 mg TEA sorbent and a sample volume of 1 liter produced an average recovery of 84% of the 25 ppm NO generated. Because of size limitations, the final constructed tubes contained one 800 mg section of oxidizer.

The final TEA-impregnated solid sorbent sampling tube for NO_2 and NO gases in the ambient work environment consists of four sections (Figure 1), as follows: TEA-sorbent, gap of 12-mm, oxidizer and TEA-sorbent. The

TABLE II
Results of Recovery for NO_2, NO Samples

Generated Samples				Recovered Sample	
Calculated (ppm)		TECO (ppm)		NO_2 (ppm)	NO (ppm)
NO_2	NO	NO_2	NO		
0.80	8.6	0.8	9.4	0.81	7.52
0.80	8.6	0.8	9.4	0.91	9.21
0.80	8.6	0.8	9.4	0.86	8.84
0.80	8.6	0.8	9.4	0.79	8.69
0.80	8.6	0.8	9.2	0.91	8.51
0.80	8.6	0.8	9.2	0.79	8.24
0.80	8.6	0.8	9.2	0.79	8.79
0.80	8.6	0.8	9.2	0.79	7.33

tube can be made in the following manner: using a gas-oxygen torch, heat a section of 5-mm I.D., 7-mm O.D. Pyrex glass tubing and pull apart to form a tube approximately 15 cm long with a taper 2 cm long. Seal one end of the tube in the flame. Allow to cool, then insert a small piece of glass wool through the open end of the tube; push to the sealed end of the tube with a thin wooden stick and pack gently. Weigh 400 mg of TEA sorbent and pour into the tube. Gently tap the tube on a table top several times to insure uniform packing. Insert another small piece of glass wool to keep the TEA sorbent in place. For the next section in the tube, pour 800 mg of oxidizer into the tube. Again tap the tube and insert a piece of glass wool, packing lightly. A gap of 12-mm is maintained between the oxidizing section and the second section of TEA sorbent by the insertion of another glass wool plug above the oxidizing section. Weigh 400 mg of TEA sorbent and pour into the tube. Carefully tap the tube and gently pack the plug so as not to eliminate the existing gap. The open end of the tube can now be sealed with the torch.

sampling procedure

The two ends of the sorbent tube are broken off to provide an opening approximately one-half the internal diameter of the tube. If personal sampling is to be done, mount the tube close to the worker's breathing zone. The tube should be placed in a vertical position to avoid channeling. The sorbent tube end without the air gap between the oxidizer section and TEA sorbent section is attached via a length of small diameter Tygon tubing to a small, battery-powered pump. Samples are taken at an approximate flow rate of 50 cc/min for 20 minutes.

To test the final design of the solid sorbent tube, various concentrations of NO and NO_2 were generated simultaneously. Low levels of NO_2 and NO were monitored with a TECO NO-NO_2 monitor. The results of these experiments are reported in Table II.

The calculated values for NO_2 were the same as that monitored by the TECO and the calculated values for NO were within 10% of that monitored by the TECO. Using the mean for recovered NO_2, 0.83 ppm, and for recovered NO, 8.39 ppm, the percent recovery was 90% or greater whether using the calculated value or TECO reading for either the NO_2 or NO concentrations.

An examination of the validity of this recommended sampling and analytical procedure included analysis of four sets of samples taken at an approximate flow rate of 50 cc/min for 20 minutes and at 50% relative humidity. Recovery percentages were determined for mixtures of NO_2 and NO in approximate concentrations of 0.8 ppm NO_2 and 8.6 ppm NO; 1.2 ppm NO_2 and 11 ppm NO; 2.5 ppm NO_2 and 24 ppm NO; and at 5.5 ppm NO_2 and 50 ppm NO. The proposed standard for NO_2 is 1 ppm as a ceiling value; and for NO, is 25 ppm as a time-weighted average. The data is presented in Table III. The values are the average of four samples. Although the NO_2 and NO are reported separately, they were generated and sampled simultaneously.

The experiments were designed for a 15 to 20 minute sampling period. A minimum sample volume of 0.75 liter must be taken to measure 0.5 ppm NO_2. Sample volumes should not exceed 1.5 liter if concentrations of 50 ppm or greater NO are expected. The average recovery for NO_2 was greater than 96% with a coefficient of variation of 7.2%. The average recoveries for NO were as follows: at 8.6 ppm, 97.4%; at 11.0 ppm, 106%; at 24.0 ppm, 84%, and at 50 ppm, 67%. The total coefficient of variation for NO was 5.5%. Analysis of the data for NO indicates the oxidizer is less efficient at higher concentrations of NO. The chemistry of the NO to NO_2 conversion has not been quantified. The data does show that the procedure for both NO_2 and NO sampling has an acceptable degree of precision for industrial hygiene work.

TABLE III
Results of Recovery for NO_2, NO Samples*

	NO_2			NO	
Generated (ppm)	Recovered (ppm)	% Recovery	Generated (ppm)	Recovered (ppm)	% Recovery
0.8	0.84	105	8.6	8.5	99
0.8	0.82	103	8.6	8.5	96
1.2	1.13	95	12.0	12.5	104
1.2	1.13	95	11.0	12.0	109
2.6	2.5	95	24.0	19.9	83
2.5	2.3	90	24.0	20.4	85
5.6	5.6	100	50.0	31.7	63.
5.5	5.5	101	50.0	35.1	70.

*Each value represents the average of four samples.

To evaluate the stability of a sample while collected on the TEA sorbent, duplicate samples of 0.6 ppm NO_2 and 8.5 ppm NO were collected. One sample from each test was analyzed immediately and the other was capped and stored at room temperature for 10 days prior to analysis.

Results of parallel samples of 0.6 ppm varied by 0.07 ppm or less. Results for the TEA section for collecting the converted NO varied by approximately 0.3 ppm or less. The results are shown in Table IV.

It is believed that the stability of the collected samples is adequate for the delay before analysis which is sometimes encountered when sampling in the field.

summary

A method for determining nitrogen dioxide and nitric oxide in an occupational environment has been presented. A single solid sorbent tube can be used to sample for 15 to 20 minutes and collect nitrogen dioxide and nitric oxide. The nitrogen dioxide is collected on the front section of triethanolamine-impregnated molecular sieve. The nitric oxide is converted to nitrogen dioxide and then passes into another triethanolamine-impregnated molecular sieve section where it is collected as NO_2. The triethanolamine sections are separately desorbed and analyzed by a spectrophotometer. Personal monitoring can be easily accomplished with a portable pump and this solid sorbent sampling tube.

TABLE IV
Effect of Storage on Nitrogen Dioxide Concentration in Solid Sorbent Samples

		Analysis of Duplicate Samples	
Generated (ppm)		Immediate (ppm)	After 10 days (ppm)
0.6	NO_2	0.6	0.7
8.5	NO	8.6	8.5
0.6	NO_2	0.7	0.7
8.5	NO	8.5	8.3

acknowldegements

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