Note

Analysis of nitrogen dioxide in ambient air by ion-exclusion chromatography with electrochemical detection

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Nitrogen dioxide (NO_2) is an important air pollutant and a precursor of acid rain. It is produced from nitrogen oxide (NO) in the atmosphere and plays a key role in the occurrence of smog[1]. With increasing global efforts to reduce emission of acid rain precursors such as sulfur dioxide (SO_2) and nitrogen oxides (NO_x), it is desirable to have a sensitive and convenient method for monitoring NO_2 present at ppb[a] concentrations in the ambient air.

Two common methods for NO_2 in ambient air are the chemiluminescence method[2] and the Saltzman method[3]. These and other instrumental methods such as laser absorption spectrometry[4] can measure NO_2 at ppb concentrations but are inconvenient for measurements at remote sites not covered by the air monitoring stations.

Trapping NO_2 in the air on a solid cartridge and determining the trapped NO_2 at a central laboratory is an economical and logistically sound alternative. In 1958, Jacobs and Hochheiser[5] described trapping NO_2 in 0.1 M sodium hydroxide solution and analyzing the resulting nitrite (NO_2^-) by diazotization–coupling reaction. Subsequent work involved trapping NO_2 on solid sampling devices followed by diazotization–coupling reaction[6,7], ion-exchange chromatography with conductivity detection[8–12], or reversed-phase high-performance liquid chromatography with UV detection[13].

Recently, we demonstrated that nitrite can be determined with an extremely high sensitivity and specificity using ion-exclusion chromatography with electrochemical detection[14]. It is the purpose of this paper to show that NO_2 in the ambient air at ppb or sub-ppb concentrations can be conveniently trapped and determined with a high sensitivity using ion-exclusion chromatography with electrochemical detection.

EXPERIMENTAL

Air sampling
Triethanolamine–sodium hydroxide-coated cartridge was prepared with a slight modification of the published procedure[11]. Maxi-Clean C_{18} cartridge (300-mg size,

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[a] Throughout this article the American billion (10^9) is meant.

Alltech, Deerfield, IL, U.S.A.) was washed by passing 3 ml methanol and 5 ml deionized water. Then 5 ml solution of 2% TEA (Baker, Phillipsburg, NJ, U.S.A.) and 1% sodium hydroxide in 50% aqueous methanol was passed through the cartridge. The cartridge was dried under infrared lamp for 2 h and both ends were sealed with Parafilm to protect from air until use.

LaMotte Model BD air sampling pump and Model LD adjustable flow meter (LaMotte, Chestertown, MD, U.S.A.) were used for sampling air. Outdoor sampling was facilitated by battery operation. Ambient air samples were collected at 1.0 l/min flow-rate for every 3 h about 1 ft. above ground in Wayland, MA, U.S.A. (a suburb about 15 miles west of Boston). Indoor air was sampled for 30 min at 1.0 l/min.

Apparatus

A Wescan Model 361 sulfite analyzer (Deerfield, IL, U.S.A.) was used for analysis of NO_2^-. It was equipped with an anion-exclusion Ion-Guard cartridge, anion-exclusion/HS column (sulfonated polystyrene–divinylbenzene; 100 × 4.6 mm I.D.), Rheodyne injector with a 50-μl sample loop, a Wescan Model 271 electrochemical detector with a platinum working electrode and a Ag/AgCl reference electrode, and a computing integrator (Spectra-Physics 4290, San Jose, CA, U.S.A.). The electrode surface was occasionally cleaned by manually setting the voltage at -1.0 V for several min and then at $+1.8$ V for another several min before reequilibrating the system at $+1.0$ V. The sulfite analyzer could also deliver a similar electrode cleaning pulse sequence, with a shorter duration, after each sample injection.

Analysis

Two aliquots of 4 ml 0.1 M sodium hydroxide solution were passed successively through the cartridge and the eluting solutions were injected directly into the chromatograph. A standard solution containing 0.1–0.5 ppm NO_2^- was injected next to the sample and the signal intensity was compared with the sample. The eluent was a 5 mM sulfuric acid solution degassed under vacuum. The flow-rate was 0.8 ml/min. The detector voltage was $+1.0$ V *vs.* Ag/AgCl reference electrode[14].

Calculation

A stoichiometric factor of 0.72 was used for conversion of NO_2 to NO_2^- (ref. 3). At the average ambient temperature of 25°C, 1 μg NO_2/m^3 corresponds to 0.532 ppb (v/v). Therefore, the NO_2 concentration in ppb derived from nitrite ion in the 4 ml eluting solution is given by:

$$NO_2 \text{ (ppb, v/v)} = \frac{\text{(peak height for sample)(ppm in standard} \times 4)(0.532)}{\text{(peak height for standard)(sampling time in min)}(10^{-3})(0.72)}$$

The contribution from the second 4 ml eluting solution was combined with the first 4 ml to yield the NO_2 concentration in the air.

RESULTS AND DISCUSSION

In 1970, Robinson and Robbins[15] considered the global atmospheric nitrogen cycle and estimated the ambient concentration of NO_2 on land to be 4 ppb. Schiff *et*

al.[4] observed a variation between 0.2 and 2.8 ppb during a 24-h period at a rural site. The U.S. Environmental Protection Agency (EPA) established the maximum allowable increase in ambient NO_2 concentration in Class I areas as 2.5 $\mu g/m^3$ (1.3 ppb)[16]. These figures suggest that an analytical method with a sub-ppb detection limit is needed to monitor the ambient NO_2 concentration. Commercially available chemiluminescence analyzers can detect sub-ppb levels of NO_2 in real time. Nevertheless, such *in situ* analyzers are expensive and not suitable for measurements at remote locations not covered by routine monitoring.

A logistically sound alternative is to collect air samples using an inexpensive sampling device and analyze the trapped NO_2 at a central laboratory. In this approach, the detection limit normally dictated by the sensitivity of the analytical method can be decreased by increasing the air sample volume. Conversely, a smaller volume of air will be required to achieve the same detection limit if a more sensitive analytical technique is used. For example, to achieve 1 ppb detection limit, 1200 l air sample is needed using diazotization–coupling method[6] and 250 l is needed by ion-exchange chromatography with conductivity detection[10].

It is well known that amperometric detection offers higher sensitivity than conductivity detection. A detection limit of about 1 ppb NO_2^- by ion-exchange chromatography with amperometric detection[17,18] has been reported. Under optimal conditions, we obtained a detection limit of 0.1 ppb NO_2^- in solution[14]. With such
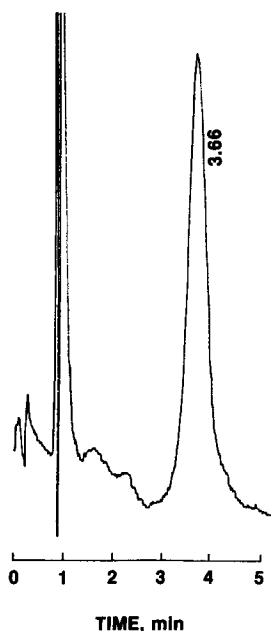

TIME, min

Fig. 1. Chromatogram of nitrite corresponding to 0.19 ppm in 4 ml 0.1 M sodium hydroxide eluting solution. Ambient air (180 l) was collected on a C_{18} cartridge treated with triethanolamine–sodium hydroxide and the cartridge was eluted with 4 ml eluting solution. Nitrite in the solution was determined using a Wescan Model 361 Sulfite Analyzer with an anion exclusion-HS column, a Pt working electrode set at +1.0 V *vs.* Ag/AgCl reference electrode. Eluent, 5 mM sulfuric acid; flow-rate, 0.8 ml/min. Injection volume, 50 μm. The maximum current for the nitrite peak at 3.66 min was 58 nA.
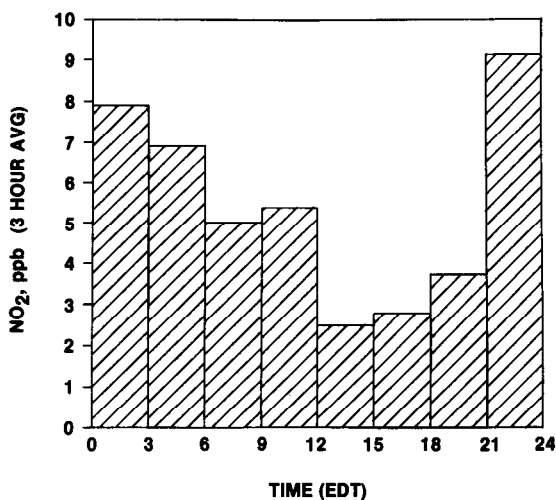
Fig. 2. Variation of 3 h average (AVG) NO$_2$ concentration in Wayland, MA, U.S.A. observed by ion-exclusion chromatography with electrochemical detection on July 23, 1989. EDT = Eastern Daylight Time.

a sensitivity, one can detect 1 ppb NO$_2$ in air with about 0.3 l sample, which represents a tremendous improvement in sensitivity over the previous methods[6–13].

In most cases, it is desirable to obtain an average NO$_2$ concentration over many hours. For example, EPA requires that State and Local Air Monitoring Stations (SLAMS) determine 24 h average when manual methods are used[19]. Fig. 1 shows a nitrite peak (0.19 ppm) at 3.66 min resulting from sampling 180 l ambient air in Wayland, MA, U.S.A., on a cartridge and eluting with 4 ml 0.1 M sodium hydroxide solution. Using the formula under *Calculation*, the NO$_2^-$ concentration was converted to 3.1 ppb NO$_2$ in the air. The Saltzman factor of 0.72 was used for the equivalence of NO$_2$ to NO$_2^-$ (ref. 3). Other reported values for the equivalence are 0.76 by Scaringelli *et al.*[20], 0.85 by Levaggi *et al.*[6], 0.63 by Blacker[7], 0.64 by Vinjamoori and Ling[8], and 0.83 by Nishikawa *et al.*[10]. NO$_2^-$ corresponding to 0.5 ppb NO$_2$ in air was observed in the second 4 ml eluting solution. Therefore, the total NO$_2$ concentration in the air was 3.6 ppb. No NO$_2^-$ was observed from a control cartridge.

NO$_2$ concentration of indoor air was measured similarly with 30 l air samples. 14.9 ppb NO$_2$ was observed near a gas burner in the basement. 3.7 ppb was observed in the living room. Others reported higher values in both living area and the kitchen with a gas stove[12,13].

Fig. 2 shows the variation of 3 h average ambient NO$_2$ concentration on July 23, 1989. The NO$_2$ concentration reached a maximum of 9.1 ppb around midnight and decreased gradually due to oxidation by ozone[4]. It increased slightly between 9 a.m. and noon possibly due to emission from the morning traffic. During the day, it decreased to a minimum of 2.5 ppb by photochemical reactions[4] and increased after sunset. A similar pattern was observed by Schiff *et al.*[4]. The daily minimum of 2.5 ppb is higher than about 0.2 ppb observed at Cold Creek, Canada, a clean rural site. The maximum of 9.1 ppb is well below the maximum permissible concentration of 0.05 ppm NO$_2$ (annual arithmetic mean).

These data suggest that the trapping of NO_2 on a solid cartridge followed by ion-exclusion chromatography with electrochemical detection may be a sensitive and convenient technique for measuring time-average NO_2 concentration at ppb levels in the ambient air. A 0.05 ppm nitrite peak is expected from 24 h sampling of air containing 0.1 ppb NO_2. The intensity of the 0.19 ppm NO_2^- peak in Fig. 1 suggests that this can be easily achieved. The high sensitivity suggests that a passive sampling device can be used to detect NO_2 at ppb concentrations with a short exposure. Mulik *et al.*[12] showed that 13 ppb NO_2 can be determined with a passive sampling device with 1 h exposure using ion-exchange chromatography and conductivity detection. The sensitivity of the passive sampling method can be significantly improved using the present method. The convenience of sampling and the sensitivity of the present method will be particularly useful for investigating the vertical concentration profile of the pollutant, which is critical for understanding the long range transport of this acid rain precursor[21].

REFERENCES

1 E. I. Shaheen, *Environmental Pollution: Awareness and Control*, Engineering Technology, Mahomet, IL, 1974, p. 46.
2 A. Fontijn, A. J. Sabadell and R. J. Ronco, *Anal. Chem.*, 42 (1970) 575.
3 B. E. Saltzman, *Anal. Chem.*, 26 (1954) 1949.
4 H. I. Schiff, G. W. Harris and G. I. Mackay, in R. W. Johnson and G. E. Gordon (Editors), *The Chemistry of Acid Rain* (*ACS Symposium Series*, No. 349), American Chemical Society, Washington, DC, 1987, p. 274.
5 M. B. Jacobs and S. Hochheiser, *Anal. Chem.*, 30 (1958) 426.
6 D. A. Levaggi, W. Siu and M. Feldstein, *J. Air Pollut. Control Assoc.*, 23 (1973) 30.
7 J. H. Blacker, *Am. Ind. Hyg. Assoc. J.*, 34 (1973) 390.
8 D. V. Vinjamoori and C.-S. Ling, *Anal. Chem.*, 53 (1981) 1689.
9 D. Brocco and R. Tappa, *J. Chromatogr.*, 367 (1986) 240.
10 Y. Nishikawa, K. Taguchi, Y. Tsujino and K. Kuwata, *J. Chromatogr.*, 370 (1986) 121.
11 Y. Nishikawa and K. Taguchi, *J. Chromatogr.*, 396 (1987) 251.
12 J. D. Mulik, R. G. Lewis, W. A. McClenny and D. D. Williams, *Anal. Chem.*, 61 (1989) 187.
13 F. Lipari, *Anal. Chem.*, 56 (1984) 1820.
14 H.-J. Kim and Y.-K. Kim, *Anal. Chem.*, 61 (1989) 1485.
15 E. Robinson and R. C. Robbins, *J. Air Pollut. Control Assoc.*, 20 (1970) 303.
16 EPA, Federal Register, 53 (1988) 40656.
17 V. Kordorouba and M. Pelletier, *Mitt. Geb. Lebensmittelunters. Hyg.*, 79 (1988) 90.
18 P. Pastore, I. Lavagnini, A. Boaretto and F. Magno, *J. Chromatogr.*, 475 (1989) 331.
19 EPA, *Code of Federal Regulations*, 40, Ch. 1, Pt. 58, Subpart B, Office of the Federal Register, National Archives and Records Administration, Washington, DC, 1988, p. 130.
20 F. P. Scaringelli, E. Rosenberg and K. A. Rehme, *Environ. Sci. Technol.*, 4 (1970) 924.
21 G. E. Gordon, in R. W. Johnson and G. E. Gordon (Editors), *The Chemistry of Acid Rain*, (*ACS Symposium Series*, No. 349), American Chemical Society, Washington, DC, 1987, p. 4.