Journal of Chromatography, 370 (1986) 121–129
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

CHROM. 18 986

ION CHROMATOGRAPHIC DETERMINATION OF NITROGEN DIOXIDE IN THE ATMOSPHERE BY USING A TRIETHANOLAMINE-COATED CARTRIDGE

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(First received June 18th, 1986; revised manuscript received July 29th, 1986)

SUMMARY

Nitrogen dioxide in air was sampled by the use of Sep-Pak C_{18} cartridge impregnated with triethanolamine. The trapped nitrogen dioxide was determined as nitrite and nitrate ions by ion chromatography. In the active sampling mode, air could be sampled at 0.8–1.2 l/min through the cartridge. Nitrogen dioxide in an air sample was determined with a 2.7% relative standard deviation at a concentration of 84 ppb with an 87–94% recovery. In the passive sampling mode, the average NO_2 concentration was determined as nitrite with a 2.2–9.8% relative standard deviation at atmospheric levels for 7–42 days.

INTRODUCTION

Nitrogen dioxide (NO_2) is one of various air pollutants that is photochemically reactive in the atmosphere. A number of automatic analytical instruments have been developed to monitor continuously the NO_2 concentration in the atmosphere or at emission sources. Atmospheric NO_2 is usually monitored by a chemiluminescence method[1] or the Saltzman method[2] at air monitoring network stations. These instrumental analyses may be inconvenient for personal monitoring or field work not covered by the monitoring stations. The instruments are expensive and should be operated in an air-conditioned room or automobile unit equipped with a stable power supply.

On the other hand, simple and convenient methods have been developed for sampling simultaneously a number of NO_2 samples at various locations difficult to cover by monitoring networks. In the active sampling mode, gaseous NO_2 is usually trapped by bubbling an air sample through an absorbing solution. The collection efficiency is poor, however, and sample preparation involving clean-up and concentration may be tedious and troublesome. Passive sampling, in which NO_2 is collected by diffusion on triethanolamine (TEA)-impregnated screens in badges or capsules exposed to air, may be simple and convenient for long-term monitoring of atmo-

0021-9673/86/$03.50

spheric NO_2[3–11]. Nitrogen dioxide is trapped on the materials through the formation of adducts with TEA[12]. The conventional methods are unusable, however, for monitoring for more than 1 week because the amount of TEA impregnated is limited. The methods encounter problems such as tedious sample preparation and effects of contamination during the analysis.

Recently, convenient cartridges such as Sep-Pak C_{18} (SP) and Sep-Pak Florisil have been used to sample traces of aliphatic aldehydes[13], aliphatic amines[14,15] and alkanethiols[16] in air samples with considerable savings of time and labour. However, no such cartridges have been used to sample NO_2 in air. Recent, ion chromatography (IC) has proved useful for the determination of traces of inorganic substances in air samples with high sensitivity. A number of reports have been published concerning the application of IC to the analysis of acid rain and airborne particulates[17–21].

The purpose of this study was to develop convenient methods for the determination of NO_2 in air samples at locations such as parks, recreation areas, roadside sites, parking lots and construction sites, which are difficult to cover by monitoring networks. In this paper, an SP cartridge impregnated with TEA is described for sampling NO_2 in ambient air by both active sampling and passive sampling. The NO_2 trapped on the cartridge is removed by passing a buffer solution through it and determined by IC. Passive sampling has been used for monitoring atmospheric NO_2 for more than 70 days without any effects due to temperature or humidity. The proposed method provides a simple and easy determination in the field of traces of NO_2 in air.

EXPERIMENTAL

Reagents and materials

All the chemicals were of special grade from Wako (Osaka, Japan) and Tokyo Kasei (Tokyo, Japan). A Sep-Pak C_{18} (SP) cartridge was obtained from Waters Assoc. (Milford, MA, U.S.A.). Standard nitrogen dioxide (NO_2), nitrogen oxide (NO) and sulphur dioxide (SO_2) at levels of 97, 47.5 and 184.4 ppm in nitrogen cylinders were purchased from Seitetsu Kagaku (Osaka, Japan).

Apparatus

A Dionex (Sunnyvale, CA, U.S.A.) 2010i ion chromatograph equipped with a loop injector with a 50-μl sample volume was employed. The analytical column and the ion suppresser were a Dionex AS-4A ion-exchange column and a Dionex P/N 035691 anion fibre suppresser, respectively. The mobile phase was 2 m*M* sodium carbonate (Na_2CO_3)–0.75 m*M* sodium hydrogen carbonate ($NaHCO_3$) solution at a flow-rate of 1.7 ml/min. The ion-suppressing solution was 25 m*M* sulphuric acid at flow-rate of 1.7 ml/min. A Kimoto (Osaka, Japan) NO-A chemiluminescence nitrogen oxides analyser and a Yanagimoto (Kyoto, Japan) APF-510 SO_2 analyser were used to monitor the concentrations of NO_2 and SO_2, respectively, in the test samples.

Preparation of the sampling cartridge

An SP cartridge was washed with 5 ml of methanol and with 10 ml of deionized water. A 3–4-ml volume of 2% (v/v) TEA in methanol was forced through the cartridge and the empty part of the cartridge was wiped with filter-paper. The cartridge was dried for 1 h under reduced pressure in a stream of nitrogen and then by passing pure nitrogen at 100 ml/min for 30 min. The cartridge was closed with glass plugs, sealed in a vial and stored in a cool place in the dark until used.

Preparation of test samples (NO_2, NO and SO_2) and sampling test

Fig. 1 shows the system for the preparation and both active and passive sampling of test samples. The calibration gases and other test samples were dynamically produced at 1–3 l/min by diluting the cylinder gases to 20–400 ppb* levels with purified air in the distributor. In the active sampling test, a 35–74-l volume of the NO_2 sample was sampled at 0.8–1.2 l/min through the coated cartridge.

Active sampling

A 100–500-l volume of air sample was sampled at 0.8–1.2 l/min with a coated cartridge after filtration with a Sumitomo (Osaka, Japan) FP-045 Fluoropore filter and a Sartorius (Götingen, F.R.G.) SM 11904 (0.8 μm) polyamide filter.

Passive sampling

A coated cartridge was attached to a holder as shown in Fig. 2 and placed at a sampling site for 7–42 days.

Analytical procedure

The cartridge was wetted with 0.3 ml of methanol and the adsorbed substances were eluted with a 4 m*M* Na_2CO_3–1.5 m*M* $NaHCO_3$ solution. In active sampling, the elution was performed in the direction opposite to that of the sampling flow. An

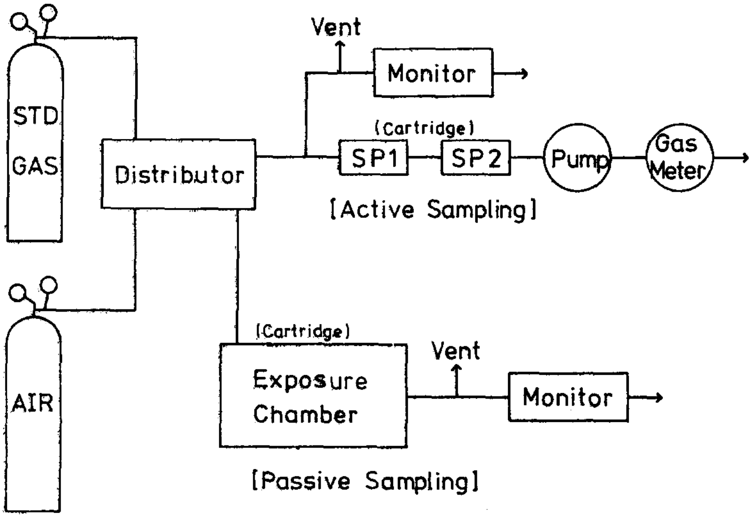

Fig. 1. Preparation and sampling of test gases. The exposure chamber was a 5-l brown-glass bottle. In the passive sampling mode, 30 SP cartridges were placed in the chamber in the calibration test.

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* Throughout the article the American billion (10^9) is meant.

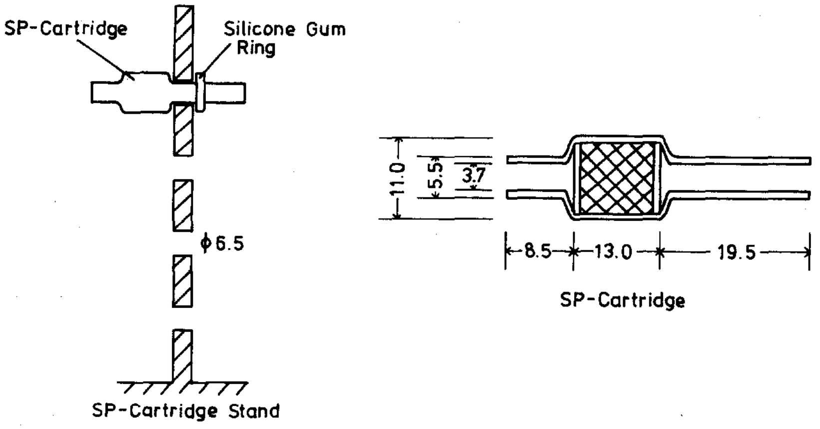

Fig. 2. Passive sampling with the use of an SP cartridge.

initial 5-ml volume of the eluate was collected. The sample solution was filtered through a Millipore (Bedford, MA, U.S.A.) HAWP (0.45 μm) filter and 50 μl of the sample were analysed by IC. The anionic substances were identified by retention time and quantified by peak area. A blank test was carried out with a coated SP cartridge in a similar manner.

Calculation

Active sampling. The concentration of NO_2 was calculated from the total amounts of nitrite and nitrate ions determined by IC.

Passive sampling. A calibration graph was prepared by plotting amount of nitrite ion detected by IC against the time-weighted average (TWA) concentration, defined as the product of NO_2 concentration (ppb) and exposure period (days). The concentration of NO_2 was calculated from the amount of nitrite ion detected by IC by using the calibration graph.

RESULTS AND DISCUSSION

The SP cartridge showed a high permeability of air through it. The cartridge used was packed with 0.4 g of porous packing with a large surface area (300 m^2/g). It was allowed to retain 8–10 mg of TEA, which is far more than the amounts used in conventional devices.

A recovery test was carried out with anionic species, including chloride and sulphate in addition to nitrite and nitrate, placed on a coated SP cartridge. Volumes of 10 μl of aqueous solutions containing 2.5–12.5 μg of the anions were injected on to the cartridge by using a microsyringe and 3 l of nitrogen were passed through the cartridge at 1 l/min. The anionic substances were eluted in the same direction as that of the nitrogen flow. The anions were eluted in the first 5 ml of eluate and no anions were detected in the later eluate, except chloride (observed at 0–3% levels in the second 5 ml of eluate). Table I indicates that 96–99% of the anions were recovered with a 0.4–5.1% relative standard deviation.

TABLE I

RECOVERY OF ANIONS PLACED ON AN SP CARTRIDGE

Anion	*Amount added (μg)*	*Amount found ± S.D.* (μg)*	*R.S.D.** (%)*	*Recovery (%)*
Cl^-	2.5	2.45 ± 0.125	5.1	98.1
NO_2^-	12.5	12.0 ± 0.128	1.1	96.3
NO_3^-	10.0	9.64 ± 0.142	1.5	96.4
SO_4^{2-}	12.5	12.3 ± 0.047	0.4	98.6

* Average of four runs ± standard deviation.

** Relative standard deviation.

Active sampling

The sampling conditions and analytical accuracy were investigated by passing 14–74 l of the test samples at 0.8–1.2 l/min through a Fluoropore filter, a polyamide filter and two coated SP cartridges in series. The concentration of NO_2 in the test samples was 84 ppb. The NO_2 in the samples passed through the filters without any adsorption and was completely trapped on the first cartridge; no NO_2 was detected on the second cartridge. The NO_2 trapped on the cartridge was detected as NO_2^- and NO_3^- by IC. Table II reports the determination of NO_2 in the standard samples. Nitrogen dioxide was determined with a 2.7% relative standard deviation at the 84 ppb level. The concentration obtained from the total of NO_2^- and NO_3^- corresponded to 87–94% of that determined by the NO_2 analyser. The conversion factor of NO_2 to NO_2^- was 0.81–0.85, which is similar to those (0.5–1.0) reported previously by a number of workers[3,12,22].

The Fluoropore filter was used to remove particulate materials more than 0.45 μm in diameter. The polyamide filter effectively excluded nitric acid vapour and trapped part of the SO_2 before the coated SP cartridges. Volatile chlorides seemed to pass substantially through the filters and to be trapped on the cartridges.

Nitrogen dioxide-free samples containing 20–200 ppb of NO or 37–184 ppb of SO_2 were used to investigate the effects of the co-existing substances on the determination. A 14–73-l volume of test gas was passed through the coated cartridge. No NO was trapped and detected on the cartridge, whereas SO_2 was completely trapped on the first cartridge at the above concentration levels and quantitatively detected by IC as sulphite and sulphate ions. These ions and other co-existing ions were separated from NO_2^- and NO_3^- by IC. Fig. 3 shows typical ion chromatograms from a blank sample and from ambient air. The co-existing substances in the atmosphere did not interfere with the determination of atmospheric NO_2. The detection limit of NO_2 in the active sampling mode was 0.4 ppb for a 100-l air sample.

A number of air samples were sampled and analysed both by the proposed method and with the NO_2 analyser. Fig. 4 shows plots of the NO_2 concentration determined by the proposed method against those obtained with the NO_2 analyser. Good agreement was obtained, the average ratio of the former to the latter values being 1.03.

These features suggest that the proposed method in the active sampling mode

TABLE II

DETERMINATION OF NITROGEN DIOXIDE IN THE ACTIVE SAMPLING MODE

Run No.	*Sample volume* (l)*	*Concentration of NO_2 detected (ppb)***			*Total/84 × 100 (%)*	*NO_2^-/NO_2*
		NO_2^-	*NO_3^-*	*Total*		
1	35	71.6	7.4	79.0	94	0.85
2	36	70.7	7.0	77.7	93	0.84
3	72	67.7	5.7	73.4	87	0.81
4	74	71.0	5.8	76.8	91	0.85
Average ± S.D.***				76.7 ± 2.07		0.83 ± 0.016
R.S.D.§ (%)				2.7		1.9

* The concentration of NO_2 in sample used was 84 ppb.

** The concentration was that of NO_2 to which the corresponding ions were converted under the standard conditions (at 25°C and 760 mmHg).

*** Average of four runs ± standard deviation.

§ Relative standard deviation.

is useful for the determination and/or monitoring of NO_2 in the atmospheric environment.

Passive sampling

Conventional passive devices are limited to use for the long-term monitoring

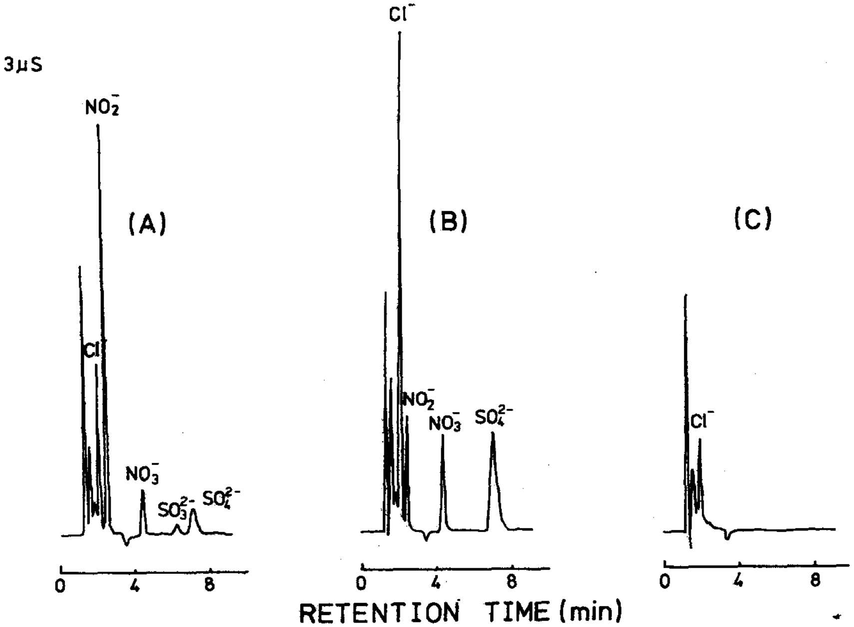

Fig. 3. Typical ion chromatograms for air samples. (A) Active sampling, sample volume 164 l, NO_2^- 71 ng, NO_3^- 16 ng, SO_3^{2-} 8 ng, SO_4^{2-} 15 ng; (B) passive sampling, sampling period 3 weeks, NO_2^- 18 ng, NO_3^- 24 ng, SO_4^{2-} 56 ng; (C) blank.

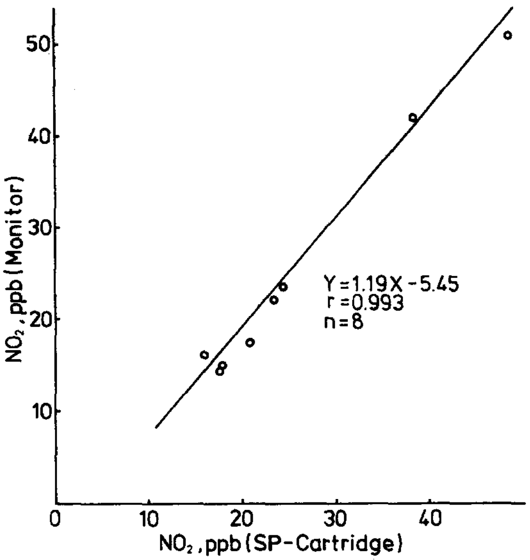

Fig. 4. Nitrogen dioxide concentrations determined by the active sampling mode *vs.* those obtained with the NO_2 analyser. Sampling volume, 120–300 l; sampling date, August 21st and 22nd and September 4th and 5th, 1985; sampling site, Environmental Pollution Control Centre, Osaka, Japan; temperature, 29.8–34.0°C (1-h average); relative humidity, 50–69% (1-h average).

of NO_2 in indoor or ambient air. The allowable exposure period may be less than 1 week. Also, the sampling devices, which depend on physical principles of mass transport across a diffusion layer or permeation through a membrane as the rate-limiting step, are susceptible to effects of temperature and humidity. One of the purposes of this study was to develop a passive sampling mode usable for long-term monitoring of NO_2 in indoor and/or ambient air.

The IC determination of NO_2 in the active sampling mode may be subject to effects of nitrate compounds on particulare matter trapped in the cartridge in the passive sampling mode. Fortunately, the conversion ratio of NO_2 to NO_2^- was constant (0.83 ± 0.016) in trapping with TEA, as shown in Table II. Hence the calibration graph could be constructed by plotting the amount of NO_2^- detected by IC against TWA concentration. In the calibration, coated cartridges were exposed to streams of standard gases at various concentration levels at 20 ± 1°C for 6 days. The practical sampling rate of NO_2, obtained from the slope of the calibration graph, was 2.55 ng/pbb · day in the SP cartridge. The linearity range of the calibration was 100–2000 ppb · day, which was ten times greater than those of conventional methods[3–11]. The detection limit of NO_2 was 50 ppb · day. Nitrite ion could be determined with a 2.2–9.8% relative standrd deviation in the calibration range. The cartridge can be used for monitoring NO_2 at atmospheric levels for more than 70 days. Virtually no effects of temperature and humidity on the determination of NO_2 were observed. This may be due to the high air permeability, the large surface area and the large amount of TEA retained in the SP cartridge.

A number of air samples were sampled for 7–42 days in the passive sampling mode. Fig. 3 shows a typical chromatogram obtained from a coated cartridge after

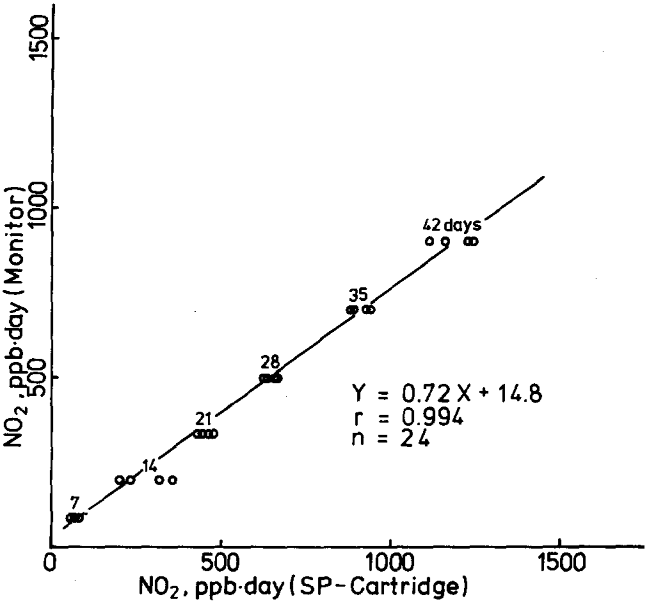

Fig. 5. TWA concentrations of NO_2 determined by the proposed method *vs.* those obtained by a monitoring instrument (Saltzman method). Sampling period, August 9th–September 20th, 1985; sampling site, Environmental Pollution Control Centre, Osaka, Japan; temperature, 22.9–30.7°C (1-day average); relative humidity, 52–81% (1-day average); wind velocity, 1.4–4.0 m/s (1-day average).

a passive sampling. The relative amounts of Cl^-, NO_3^- and SO_4^{2-} to NO_2^- were much higher than those in the active mode. This may be due to the introduction of particulate matter or an aerosol containing the ion species. Fig. 5 shows the relationship between TWA concentrations of NO_2 determined by the proposed method and those obtained by the monitoring instrument. Good linearity was obtained between the two variables, although the former tended to be slightly higher.

CONCLUSIONS

The features described above suggest that the use of the coated SP cartridge is simple and convenient for the determination of NO_2 in indoor and ambient air in both the active and passive sampling modes. The proposed method may have advantages over conventional methods in terms of rapidity and simplicity, high analytical sensitivity and low background effects. The passive sampling mode may be especially suitable for long-term monitoring of NO_2 in ambient air.

ACKNOWLEDGEMENTS

The authors cordially thank H. Yoshikawa, Chief, Surveillance Section, Environmental Pollution Control Centre, and his co-workers for their assistance in preparing the standard samples and in operating the NO_2 monitoring instrument.

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