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ION CHROMATOGRAPHIC DETERMINATION OF NITROGEN DIOXIDE AND SULPHUR DIOXIDE IN THE ATMOSPHERE USING TRIETHANOLAMINE–POTASSIUM HYDROXIDE-COATED CARTRIDGES

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SUMMARY

Nitrogen dioxide (NO_2) and sulphur dioxide (SO_2) in air were sampled by the use of a Sep-Pak C_{18} cartridge impregnated with triethanolamine–potassium hydroxide. The trapped NO_2 and SO_2 were eluted with a 8 m*M* sodium carbonate–3 m*M* sodium hydrogencarbonate solution and simultaneously determined by ion chromatography. In the active sampling mode, NO_2 was determined with 5.2% relative standard deviation at 95 ppb and SO_2 was determined with 2.4–5.3% relative standard deviation at 54–184 ppb. The recoveries were 85–98% for NO_2 and 91–105% for SO_2. In the passive sampling mode, the average concentrations of NO_2 and SO_2 were determined with 2.4–6.8 and 2.8–7.9% relative standard deviation, respectively, at atmospheric levels for 6–24 days.

INTRODUCTION

Nitrogen dioxide and sulphur dioxide are major air pollutants arising mainly from combustion processes. A number of manual or instrumental methods have been developed to determine the levels of NO_2[1–5] and SO_2[5–11] in the atmosphere, including spectrophotometry, chemiluminescence, conductimetry and ultraviolet fluorescence. However, few reports have been published concerning the simultaneous determination of atmospheric NO_2 and SO_2. Ion chromatography (IC) is useful for the simultaneous determination of such inorganic substances in air samples with high sensitivity[12–14].

We have previously described a convenient method of determining NO_2 in air by IC[14] in which a triethanolamine-coated cartridge is used for sampling purposes. However, it was difficult to determine NO_2 and SO_2 simultaneously in the passive sampling mode because of interference from particulates or aerosols containing SO_4^{2-}.

In this study, a Sep-Pak cartridge impregnated with triethanolamine (TEA)–potassium hydroxide was used to sample NO_2 and SO_2 in ambient air, both in an active sampling mode and in a passive sampling mode.

EXPERIMENTAL

Reagents and materials

The chemical reagents were of special grade from Wako (Osaka, Japan) and Tokyo Kasei (Tokyo, Japan). The triethanolamine (TEA)–potassium hydroxide solution was 2% (v/v) TEA in 0.02 g/ml potassium hydroxide in methanol. Standard gases, nitrogen dioxide (NO_2), nitrogen oxide (NO) and sulphur dioxide (SO_2), 97, 47.5 and 184.4 ppm in nitrogen, were obtained from Seitetsu Kagaku (Osaka, Japan). A Sep-Pak C_{18} cartridge was from Waters Associates (Milford, MA, U.S.A.).

Apparatus

A 2010i ion chromatograph (Dionex, Sunnyvale, CA, U.S.A.) equipped with a 50-μl loop injector was employed. The analytical column was a Dionex AS-4A ion-exchange column and the ion suppressor used was a Dionex P/N 035691 anion fibre suppresser. The mobile phase was 2 m*M* sodium carbonate–0.75 m*M* sodium hydrogencarbonate solution at a flow-rate of 1.7 ml/min. The ion-suppressing solution was 25 m*M* sulphuric acid at a flow-rate of 1.7 ml/min. A NO-A chemiluminescence nitrogen oxides analyser (Kimoto, Osaka, Japan) and an APF-510 sulphur dioxide analyser (Yanagimoto, Kyoto, Japan) were used to monitor the concentrations of NO_2 and SO_2 in the test gases. An AH-1P hygrometer (Ace, Tokyo, Japan) was used to monitor the relative humidity in the exposure chamber.

Preparation of the sampling cartridge

The Sep-Pak cartridge was washed with 5 ml of methanol and then with 10 ml of deionized water prior to use. A 3–4-ml volume of the triethanolamine–potassium hydroxide solution 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 nitrogen stream and then by passing pure nitrogen at 100 ml/min for 30 min. The passive sampling cartridge was prepared by cutting off one side of a coated cartridge as shown in Fig. 1.

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

Fig. 2 shows the preparation of test samples and both the active and passive sampling systems. The calibration gases and other test samples were dynamically produced at 2–3 l/min by diluting the cylinder gases to 40–200 ppb* in purified air in a distributor. Humid air was prepared by passing clean air over a wetted cloth to which water was continuously supplied. Different relative humidities for the samples were achieved by the use of humid air in the dilution process.

Sampling

In the active sampling, 100–300 l of air samples were sampled at 0.8–1.2 l/min through a coated cartridge after filtration with a FP-045 Fluoropore filter (Sumitomo, Osaka, Japan) to remove particulates.

In passive sampling, the coated cartridge was wrapped with a No. 5c cellulose

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

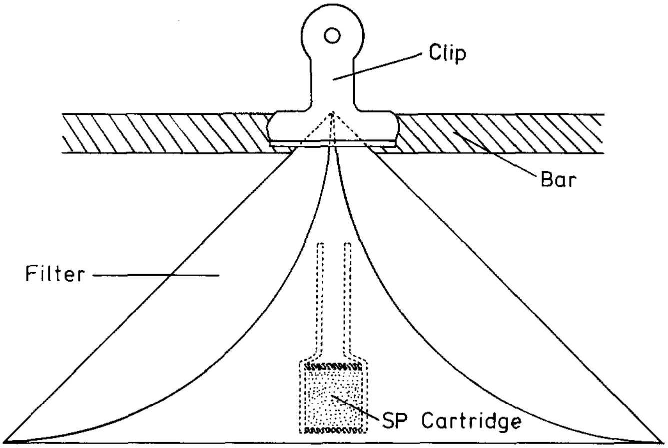

Fig. 1. Passive sampling by the use of a modified Sep-Pak (SP) cartridge.

filter (diameter 11 cm) (Toyo Roshi, Tokyo, Japan) as shown in Fig. 1 and placed at a sampling site for 6–24 days.

Analytical procedure

The cartridge was wetted with 0.3 ml of methanol. The adsorbed substances were then eluted with 8 m*M* sodium carbonate–3 m*M* sodium hydrogencarbonate solution. In the case of active sampling, the elution was performed in the direction contrary to that of the sampling flow. An initial 5-ml volume of the eluate was collected. The sample solution was filtered through an HAWP (0.45-μm) filter (Millipore, Bedford, MA, U.S.A.) and a 50-μl aliquot of the sample was analysed by IC. The anionic substances were identified by their retention times and quantified by peak area. The blank test was performed similarly with a coated Sep-Pak cartridge.

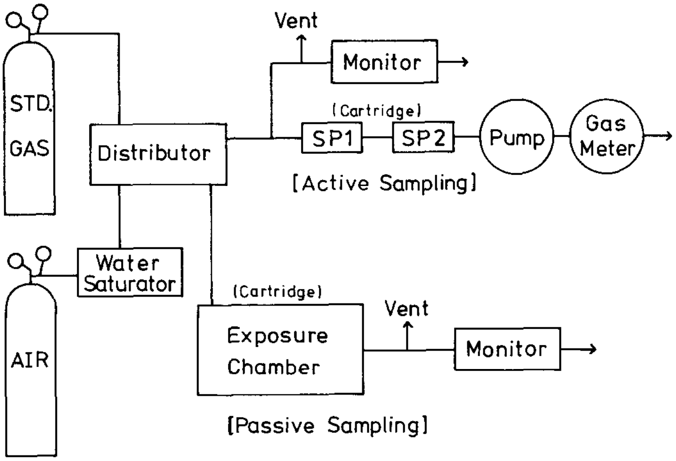

Fig. 2. Preparation and sampling of standard gases.

Calculation and calibration

The concentration of NO_2 was calculated from the total amounts of nitrite (NO_2^-) and nitrate (NO_3^-) ions, and that of SO_2 was calculated from the total amounts of sulphite (SO_3^{2-}) and sulphate (SO_4^{2-}) ions detected by IC.

In passive sampling, the calibration graph for NO_2 or SO_2 was prepared by plotting the amounts of (NO_2^- + NO_3^-) or (SO_3^{2-} + SO_4^{2-}) calculated against the time-weighted average (TWA) concentration, defined as the product of the concentration (ppb) of NO_2 or SO_2 and the exposure period (days).

RESULTS AND DISCUSSION

Active sampling

The sampling conditions and analytical accuracy were investigated by passing 36–74 l of the standard samples at 0.8–1.2 l/min through two triethanolamine–potassium hydroxide coated Sep-Pak cartridges in series. The concentrations of NO_2, NO and SO_2 in the standard samples were 95, 48 and 54–184 ppb, respectively. The NO_2 and SO_2 in the samples were trapped on the first cartridge only. No NO_2 or SO_2 was detected on the second cartridge. The NO_2 on the cartridge was detected as NO_2^- and NO_3^- by IC. No NO was trapped and detected on the cartridge. Table I gives the results of the determination of NO_2 and SO_2 in the standard samples. The concentration of NO_2 or SO_2, trapped in the cartridge, was defined as that of NO_2 or SO_2 under the standard conditions (at 25°C and 760 mmHg) calculated from the corresponding species detected. Nitrogen dioxide was determined with a 5.2% relative standard deviation (R.S.D.) at the 95 ppb level. The concentration obtained from the total amounts of NO_2^- and NO_3^- corresponded to 85–98% of that determined by the nitrogen oxides analyser. On the other hand, the SO_2 trapped on the cartridge was detected only as SO_3^{2-} by IC in the case of the standard sample. Sulphur dioxide was determined with a R.S.D. of 2.4–5.3% at the 54–184 ppb level. The concentration obtained by the proposed method corresponded to 91–105% of that determined by the sulphur dioxide analyser.

A number of field air samples were taken and analysed by the method proposed. Typical ion chromatograms are shown in Fig. 3. As the Fluoropore filter was used before the cartridge in active sampling, nitrate and sulphate particulates could not interfere with the determination of NO_2 and SO_2 as their vapours. The SO_2

TABLE I

DETERMINATION OF NITROGEN DIOXIDE AND SULPHUR DIOXIDE IN THE ACTIVE SAMPLING MODE

Std. gas	*Concn. of std. gas (ppb)*	*Sample volume (l)*	*Concn. of std. gas trapped in the cartridge, av. ± S.D.* (ppb)*	*R.S.D. (%)*	*Recovery** (%)*
NO_2	95	36–53	86.4 ± 4.51	5.2	85–98
SO_2	54	48–74	51.3 ± 1.25	2.4	92–98
SO_2	184	36–69	178.9 ± 9.51	5.3	91–105

* Average of four determinations ± standard deviation.

** From minimum to maximum recovery in four determinations.

trapped on the cartridge was detected as SO_3^{2-} and SO_4^{2-} by IC in the case of field samples. This may be due to oxidation of SO_3^{2-} to SO_4^{2-} in air containing various oxidizing species. Table II reports the concentrations of NO_2 and SO_2 determined by method proposed and those obtained by the monitoring instruments. The two sets of values were in good agreement, although the sulphur dioxide concentrations by the proposed method tended to be lower.

Passive sampling

Passive sampling depends on mass transport of the gas by diffusion or permeation[15]. The IC determination of NO_2 and SO_2 may be subject to effects of the corresponding nitrate and sulphate compounds on particulate matter trapped in the cartridge in the passive sampling mode[14]. To remove their effects, the cartridge was wrapped with filter-paper shown in Fig. 1.

The modified Sep-Pak cartridge or passive sampler was evaluated at relative humidities of 13, 37, 37–76 and 76%. The wrapped cartridges were exposed to a humid stream of standard gases at various concentration levels for 7 days at 25 ± 1°C. Fig. 4 shows the effect of the relative humidity on the sampling rate, adsorbed amount of NO_2 or SO_2 divided by the TWA concentration. The sampling rate of NO_2 somewhat increased with increasing relative humidity, but that of SO_2 was independent of the relative humidity in the range 37–76% within experimental error. The humidity of the air sample had little effect on the sampling rates of NO_2 and SO_2.

In the calibration, coated cartridges were exposed to streams of the standard gases at various concentrations at 25 ± 1°C for 6 days. The calibration graphs for NO_2 and SO_2 were prepared by plotting the amount of (NO_2^- + NO_3^-) or (SO_3^{2-} + SO_4^{2-}) against the TWA concentration. The linearity range was 50–500 ppb · day, and the regression lines, correlation coefficients and the number of samples for NO_2 and SO_2 were $Y = 0.018X + 0.056$ ($r = 0.994$, $n = 18$) and $Y = 0.034X + 0.273$ ($r = 0.992$, $n = 18$), respectively. The NO_2 and SO_2 were determined with R.S.D.s

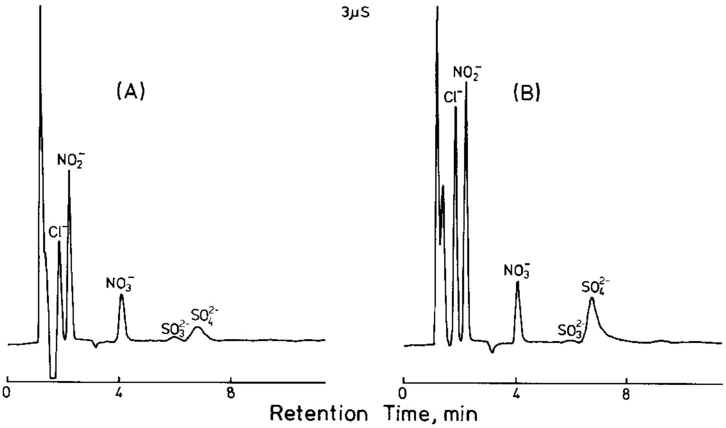

Fig. 3. Typical ion chromatograms for air samples. (A) Active sampling: sample volume 201 l; NO_2^- (118 ng), NO_3^- (72 ng), SO_3^{2-} (22 ng), SO_4^{2-} (47 ng). (B) Passive sampling: sampling period 24 days; NO_2^- (160 ng), NO_3^- (73 ng), SO_3^{2-} (4.7 ng), SO_4^{2-} (180 ng).

TABLE II

FIELD TESTS IN THE ACTIVE SAMPLING MODE*

Sample No.	*Sample volume (l)*	*Concn. of NO_2 trapped in the cartridge (ppb)*			*Monitored NO_2 concn.** (ppb)*	*Concn. of SO_2 trapped in the cartridge (ppb)*			*Monitored SO_2 concn.*** (ppb)*
		NO_2^-	*NO_3^-*	*Total*		*SO_3^{2-}*	*SO_4^{2-}*	*Total*	
1	135	24.9	5.2	30.1	32.3	2.5	5.8	8.3	12.0
2	133	25.5	5.8	31.3	37.5	4.2	2.6	6.8	12.5
3	126	50.7	13.6	64.3	64.3	5.5	6.5	12.0	14.0
4	191	53.5	17.5	71.0	61.8	8.1	9.3	17.4	18.6
5	201	31.2	14.2	45.4	39.7	3.4	6.0	9.4	9.9
6	150	35.7	10.1	45.8	42.0	5.0	4.9	9.9	12.3

* Sampling date: April 8–11th, 1986. Sampling site: Environmental Pollution Control Centre, Osaka, Japan. Temperature: 13.2–20.1°C (1-h average). Relative humidity: 22–94% (1-h average).

** Saltzman method.

*** Conductimetric method.

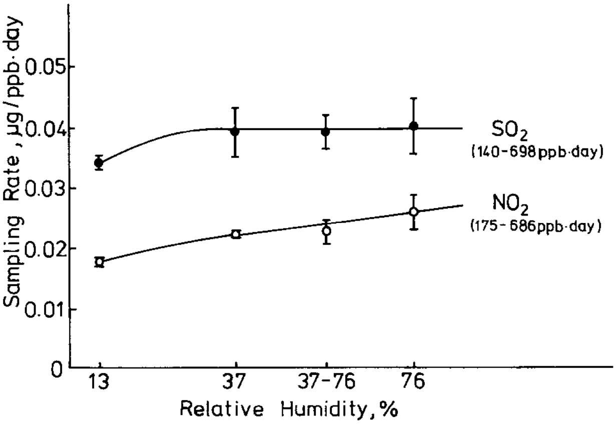

Fig. 4. Effects of humidity on the sampling rate in the passive sampling mode. The concentrations of NO_2 and SO_2 in the samples used were 55–113 and 46–168 ppb, respectively.

of 0.9–9.9 and 3.9–7.4%, respectively, in the calibration range. The practical sampling rates of NO_2 and SO_2, obtained from the slopes of the calibration graphs, were 0.018 and 0.034 μg/ppb · day, respectively, with the Sep-Pak cartridge.

A number of field air samples were sampled for 6–24 days in the passive sampling mode. Fig. 3 shows a typical ion chromatogram obtained from ambient air. The SO_2 was generally detected as SO_4^{2-}. This may be due to oxidation of SO_3^{2-} to SO_4^{2-} during the long-term sampling. Figs. 5 and 6 show the relationships between the TWA concentrations of NO_2 and SO_2 determined by the method proposed and

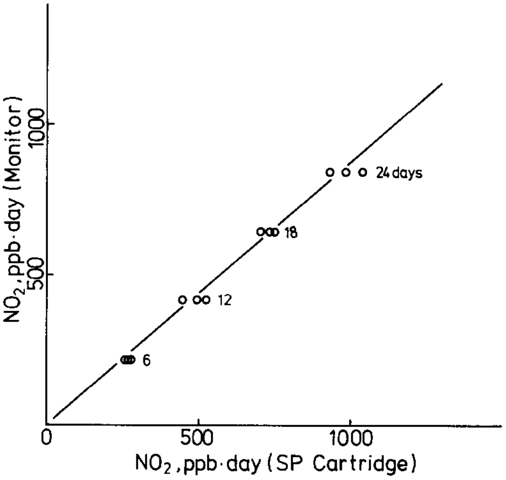

Fig. 5. Plot of the TWA concentrations of NO_2 determined by the proposed method *vs.* those obtained by a monitoring instrument (Saltzman method). Sampling period: May 17th–June 9th, 1986. Sampling site; Environmental Pollution Control Centre, Osaka, Japan. Temperature: 16.4–24.7°C (1-day average). Relative humidity: 48.0–84.6% (1-day average). Wind velocity: 1.5–3.6 m/s (1-day average). $Y = 0.87X + 8.3$; $r = 0.993$; $n = 12$.

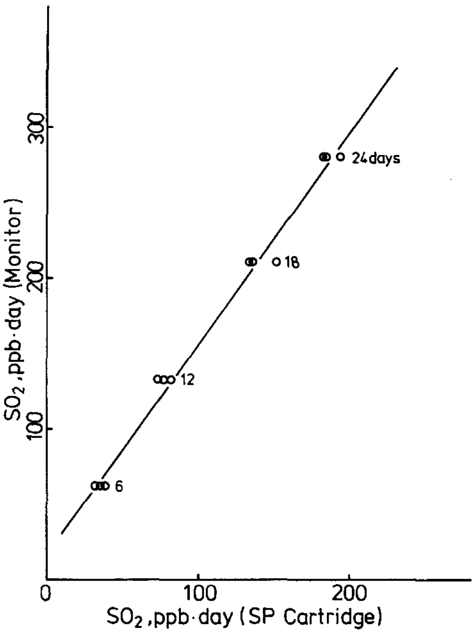

Fig. 6. Plot of the TWA concentrations of SO_2 determined by the proposed method *vs.* those obtained by the monitoring instrument (conductimetric method). For sampling conditions, see Fig. 5. $Y = 1.4X + 16.9$; $r = 0.994$; $n = 12$.

those obtained by the monitoring instruments, respectively. Good linearity was obtained between the two variables, although the former tended to be slightly higher in the case of NO_2 and slightly lower in the case of SO_2.

CONCLUSION

It is concluded that the use of the coated Sep-Pak cartridge is simple and convenient for the simultaneous determination of NO_2 and SO_2 in ambient air both in the active and the passive sampling mode.

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