

Determination of Nitrogen Dioxide in the Atmosphere by Microflow-Injection Absorptiometry with a Portable-Type Flow System after Batchwise Absorption Collection

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Abstract

Nitrogen dioxide (NO_2) in the atmosphere could be determined by developing a simple collection procedure with a small volume of an absorbing solution and a measuring method using a microflow injection system with a small sample size. The absorption efficiency of NO_2 in the atmosphere was improved by using a triethanolamine aqueous solution (TEA, 1~2 g/l) as the absorbing solution: absorption efficiency was more than 95 percent. The absorbed NO_2 , which was converted to NO_3^- and NO_2^- , was determined by measuring the concentrations of NO_3^- and NO_2^- in the absorbing solution. A microflow injection analysis (μFIA) with a portable-type FIA system (P/ μFIA) was used as a detection system. The limits of detection (LODs) of NO_2^- and NO_3^- were 10^{-8} M and 2×10^{-8} M, respectively. The azo compound, which was quantitatively produced by diazotizing sulfanilamide with nitrite and coupling the diazonium ion with 1-naphthylethylenediamine in an acidic medium, was used for the determination of NO_2^- . The determination of NO_3^- was carried out in a similar manner to that of NO_2^- after reducing NO_3^- to NO_2^- with a copperized cadmium (Cd/Cu) mini column (0.5 mm i.d. x 5 cm). The molar ratio of NO_2^- to NO_3^- was ascertained to be 1:1 in the absorbing solution. The NO_2 concentration more than 10 ppb (v/v) in the atmosphere could be determined by the proposed method.

Keywords: microflow injection system, atmosphere, nitrogen dioxide, Cd/Cu mini column, ambient air and indoor air.

1. Introduction

Nitrogen oxides (NO_x) in the atmosphere increases with an increase in exhaust gas of automobiles, power plants and emission gas from oil combustion systems. In these days, the determination of NO_x and other oxide ions of nitrogen in atmospheric and aquatic environment is very important to protect our health and the growth of plants. The residence time of NO_x in the atmosphere seems to be about 8h[1], and it is oxidized to be nitric acid and/or other oxides. The fallout quantity of nitrate on the earth approaches that of sulphate in recent years[2]. Also, NO_2 , as well as SO_2 , gives serious influence to human respiratory organs.

Sampling methods for NO_2 in air are classified into two groups: one is the method based on the introduction of sample gas into an absorption solution at a regular speed (an active sampling method), and the other is based on the transportation of NO_2 by diffusion (a passive sampling method). In the active sampling method, gaseous NO_2 is trapped in an aqueous medium by bubbling air samples through the absorbing solution. Most of standard methods adopted as an official

method are essentially composed of the active sampling method coupled with such detection methods as Saltzman method[3], chemiluminescence method[4], sodium arsenite method[5], and triethanolamine guaiacol/ sodium metabisulfite (TGS) method[6]. The measurement of NO_2^- and/or NO_3^- in absorbing solutions can be done in short time, whereas a long interval time is required for absorbing and concentrating NO_2 in the absorbing solutions. Further, apparatuses used are expensive, big, and heavy; therefore, such apparatuses cannot be used outdoor. When it is necessary to measure the environmental concentration of NO_2 in a wide area, the passive sampling method is used. In the method described above, NO_2 is usually collected by diffusion on absorbent-impregnated screens in badges or capsules. The apparatuses in passive sampling methods are simple, small and less expensive. Several kinds of the passive sampling methods have been used so far: a nitration plate with firebrick[7], a soaked glass beads[8], and a silica gel[9][10] soaked in a triethanolamine (TEA) solution, an alkali filter paper[11], and a TEA filter paper method[12][13]. Recently, the methods with Teflon membrane filter[14], capillary[15] and kieselguhr

(C-22) [16], which are coated with TEA, have been developed.

In both the active and passive sampling methods, average values of NO_2 within 10 min[17]-24 h (the active sampling methods) and 8 h-60 days (the passive sampling method) is used as an exposed amount. Therefore, the development of the NO_2 analytical method on site during a short time is required.

In this work, a new sampling method with a small volume of absorbing solution was developed, followed by measuring the concentrations of NO_2^- and NO_3^- in the absorbing solutions by a portable-type microflow injection system (P/ μ FIA) with a small sample size. By shaking a small volume of the absorbing solution and an atmospheric sample in a separatory funnel, NO_2 can be easily absorbed in the absorbing solution; the NO_2 quantity in the atmosphere can be determined by measuring the concentration of NO_2^- and/or NO_3^- in the absorbing solution. The absorption maximum of an azo compound, which is formed by the diazotization-coupling reactions with sulfanilamide and 1-naphthylethylenediamine, is 538nm; the wavelength was used for the determination of nitrite ion by a microflow-injection method. By the proposed method, the NO_2 concentrations in indoor and outdoor air were determined easily and rapidly.

2. Experimental

2.1. Apparatus

A flow diagram of a portable-type microflow injection system (P/ μ FIA) used in this work is shown in Fig. 1. The measurement of absorbances was performed by a visible absorptiometry. The detector was incorporated in the system, and was composed of a diode sensor, a flow cell, an interference filter of 530 nm and a light emitting diode (LED; $\lambda_{\text{max}} = 525 \text{ nm}$) as a light source. The light path of the flow cell was 10 mm (0.8 mm i.d., capacity: 5.0 μl). Peaks were recorded with a chart strip recorder or a notebook computer. A carrier solution (CS) and a reagent solution (RS) were propelled with a double plunger micro pump (Asahi Techneion), in which one stroke of the plunger can propel 2.5 μl of solutions. In the proposed method, each flow rate of the carrier and the reagent solution was fixed to 50 $\mu\text{l}/\text{min}$. A six-way valve with a sample loop (20 μl) was used to inject sample solutions into the carrier stream, which flowed downstream and merged with a reagent stream, and flowed into a 75 cm of 0.25 mm i. d. reaction tubing. The PTFE tubing of an inner diameter of 0.25 mm was used as a reaction tubing and a connecting tubing. All of the system components of P/ μ FIA, except for the recording apparatus, were packed in a small box (16 cm width x 16 cm height x 32 cm depth), and worked with a 12 V battery. The

P/ μ FIA system was equipped with a controller for the adjustment of a flow rate, temperature of the reaction compartment and a dynamic range of the detector. The weight of the system was 7.5 kg. Therefore, the system can be moved easily everywhere, and can be used even outdoors.

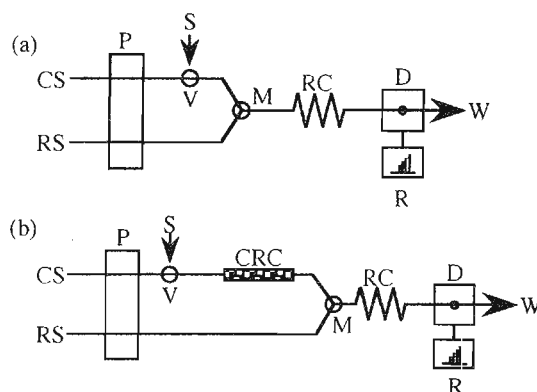


Fig.1. Flow diagrams for nitrite and nitrate determination. (a) Nitrite determination; (b) Nitrate determination.

CS : (a) H_2O or triethanolamine (TEA) (1 g or 2 g/l),
(b) 10^{-3} M EDTA + NaOH (pH=8.1 ~ 8.4);

RS : sulfanilamide (20 g/l) + N-(1-naphthyl)ethylene-diamine (NED) (0.5 g/l) + conc. HCl(25 ml/l);

P : pump (each flow rate , 50 $\mu\text{l}/\text{min}$);

S : sample injection; V : six way injection valve (25 μl);

CRC : cadmium reduction column (0.5 mm i.d. x 10 cm);

RC : reaction coil (0.25 mm i.d. x 75cm); D : detector (LED 525 nm, interference filter 538 nm);

M : mixing joint; R : recorder; W : waste.

2.2. Reagents

All chemicals used in this work were of analytical reagent grade, and purified water with a MilliQ Labo (Millipore) was used for preparing solutions.

Triethanolamine (TEA) absorbing solution (0.1 % and 0.2 % w/v): The stock solution was prepared by dissolving 20 g of triethanolamine in 1 l of water. Then 5 ml or 10 ml of the stock solution were diluted with purified water to 100 ml to give a 0.1% and a 0.2% solution, respectively.

Reagent solution: A reagent solution was prepared to give a 100 ml solution containing 2 g sulfanilamide, 0.05 g N-(1-naphthyl) ethylenediamine and 2.5 ml of concentrated hydrochloric acid.

Carrier solution: Purified water or the TEA absorbing solution (0.2 % w/v) was used in the system (a) of Fig.1. Ethylenediaminetetraacetic acid (EDTA) disodium salt (Wako Co.) solution was used as a carrier in the system (b) of Fig.2. The stock solution was prepared by adding 2.92 g of EDTA disodium salt to 100 ml purified water to give a 0.1 M solution. Then, 3 ml of the stock EDTA solution and 297 ml of purified water were mixed and the pH was adjusted to 8.1 ~ 8.4 by adding a small volume of 0.1 M sodium hydroxide

solution.

Standard nitrite solution: The stock solution was prepared by dissolving 0.345 g of sodium nitrite dried at 110°C for 3 h in 100 ml of water to give a 5.0×10^{-2} M solution. This solution was diluted accurately using the purified water or the TEA solution to give working solutions of nitrite.

Standard nitrate solution: The stock solution was prepared by dissolving 0.425 g of sodium nitrate dried at 110°C for 3 h in 100 ml of water to give a 5.0×10^{-2} M solution. This solution was diluted accurately using the purified water or the TEA solution to give working solutions of nitrate.

2.3. Preparation of reducing mini column packed with copperized cadmium

A copperized cadmium column was prepared as follows: powdered cadmium (Wako Pure Chem., 60-80 mesh) was copperized according to the procedure of the Japanese Industrial Standard (JIS K-0101-1991), and the copperized cadmium obtained was packed in a silica tubing (0.53 mm i.d. x 10 cm).

2.4. Procedure for the collection of NO₂ from air and the measurement of NO₂⁻ and NO₃⁻

Air samples were pumped through separatory funnels (260 ml) for 2 min in order to sufficiently exchange air in the separatory funnels for the sample. Then, 2ml of an absorption solution was added into each separatory funnel, and the separatory funnels were shaken vigorously for 4 min. After standing for 1 min, nitrate and/or nitrite ion in the absorbing solutions were measured by the proposed μ FIA.

3. Results and Discussion

3.1. Preparation of calibration graph by μ FIA

The concentrations of nitrate and nitrite ions in absorbing solutions, which absorbed NO₂ in the atmosphere, were determined by the P/ μ FIA system, when the molar ratio of nitrate ion to nitrite ion in the absorbing solution was determined. When only the nitrite ion in the absorbing solutions was determined, the same solution as the absorbing solution was used as the carrier in the P/ μ FIA system.

Nitrite has often been determined spectrophotometrically on the basis of a diazotization-coupling reaction with sulfanilamide and N-(1-naphthyl)-ethylenediamine; the azo compound thus produced was measured at about 540 nm. Such a color development reaction was investigated by using the P/ μ FIA system at 525 nm of LED, the wavelength being a little shorter than the maximum absorption wavelength of the azo compound. Typical flow

signals for trace amounts of NO₂⁻ are shown in Fig. 2 (a). The sensitivity obtained by the proposed method was enough for the determination of nitrite ion in the atmospheric samples, as well as in river and seawater samples. The limit of detection (LOD) of NO₂⁻ corresponding to the signal to noise ratio of 3 was about 10^{-8} M NO₂⁻. Nitrate was determined by using the same reagent solution as in nitrite and 10^{-3} M EDTA (pH 8.1 ~ 8.4) as a carrier. Nitrate was reduced to NO₂⁻ with a copperized cadmium (Cd/Cu) column installed in the carrier stream just after the sample injection valve. The typical flow signals for trace amounts of NO₃⁻ are shown in Fig. 2 (b). A reducing mini column of Cd/Cu developed for this purpose was used. LOD of NO₃⁻ was about 2×10^{-8} M.

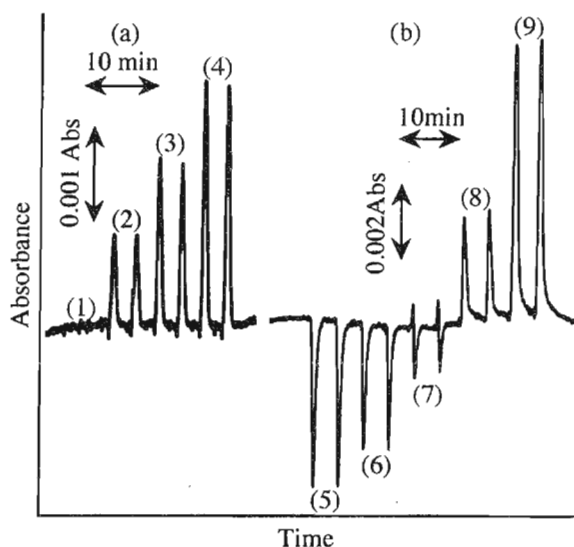
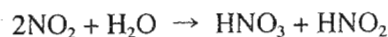


Fig.2. Flow signals for nitrite (a) and nitrate (b) by μ FIA
(a) CS : H₂O;
Sample ([NO₂⁻]/10⁻⁸ M):(1) 0, (2) 2.0, (3) 4.0, (4) 6.0;
(b) CS : 10⁻³ M EDTA + NaOH (pH=8.1~8.4);
Sample ([NO₃⁻]/10⁻⁷ M):(5) 0, (6) 1.0, (7) 2.0, (8) 4.0,
(9) 6.0.

3.2. Determination of nitrogen dioxide in the atmosphere

Nitrogen dioxide in the atmosphere can be determined by using the proposed μ FIA, when it can be concentrated in the absorbing solution by 100-200 folds as a volume ratio from the atmosphere which contains NO₂ corresponding to more than about one tenth of the WHO Guideline of an ambient environmental quality standard (0.08 ~ 0.21 ppm as NO₂). As is shown in the following equation, NO₂ in the atmosphere can be converted into nitric and nitrous acid when it dissolves in water:



3.3. Absorption efficiency of NO₂ with various kinds of absorbing solutions

Several absorbing solutions, such as the aqueous solutions of triethanolamine (TEA), sodium hydrogen carbonate and sodium hydroxide, have been used so far in the active sampling methods for the spectrophotometric determination of NO_2 in the atmosphere. In this work, first, pure water was examined as the absorbing solution. The absorption efficiency was determined by repeating the absorption procedure several times using the same air sample with each 2 ml portion of the absorbing solution. The results obtained were shown in Table 1: only 54% of NO_2 in the atmosphere was

Table 1. Absorption efficiency of NO_2 from air using various kinds of absorbing solutions

Absorbing solutions	Absorption efficiency ^{a)} (%)	NO_2 content ^{a)} (ppm)
(1) Pure water	54	0.053
(2) 10^{-1} M NaOH	30	0.053
(3) 10^{-3} M EDTA (pH = 10)	56	0.053
(4) TEA (g/l)		
0	52	0.030
0.5	80	0.030
1.0	95	0.030
2.0	>98	0.030

a) Air sample: ambient air in a room. The NO_2 contents were obtained by totaling each content of absorbed NO_2 in each absorbing solution obtained by repeating several times the absorbing procedures. The contents of NO_2 in the air samples used in this experiments were not necessarily identical, because the experiments were carried out on different days.

absorbed with pure water. For improving the absorption efficiency, other absorbing solutions were also studied. The absorption of NO_2 from air has been carried out with an alkaline solution of 0.1 M NaOH[18]-[20]. Secondly, 0.1M NaOH was studied as the absorbing solution. The absorption efficiency was less than pure water, and was only 30%. The absorption efficiency was almost the same as that indicated by Yamate[21], who reported that the absorption efficiency of 0.1M NaOH for NO_2 was 35% in the standard measuring method proclaimed by the US Environmental Protection Agency (EPA)[22]. The next candidate was 10^{-3} M EDTA (pH 8.2), which was used as a carrier for nitrate determination. The absorption efficiency was 56%, being better than the pure water and the 0.1 M NaOH solution. The last one was a TEA solution. The good affinity of TEA for NO_2 has been reported by Levaggi et al.[7]. Later, TEA has been used for quantitative collection of NO_2 from air. The absorption efficiency of TEA has been said to

be about 95~98%. The concentrations of TEA were examined by varying from 0.5 to 2.0 g/l. By using the TEA solution of 2.0 g/l, the absorption efficiency of more than 98% could be achieved as shown in Table 1. In further experiments, 2.0 g/l TEA solution was used as the absorbing solution, for the determination of NO_2^- , and 1.0 g/l TEA solution was used when NO_2^- and NO_3^- were determined simultaneously, because 2.0 g/l TEA can damage the reducing efficiency of copperized cadmium.

3.4. Shaking time for the collection of NO_2 with TEA solution

The effect of shaking time on the absorption efficiency of NO_2 was examined: the result obtained for NO_2^- in the absorbing solution is shown in Fig. 3. When 2g/l TEA solution was used as the absorbing solution, the absorption efficiency became almost

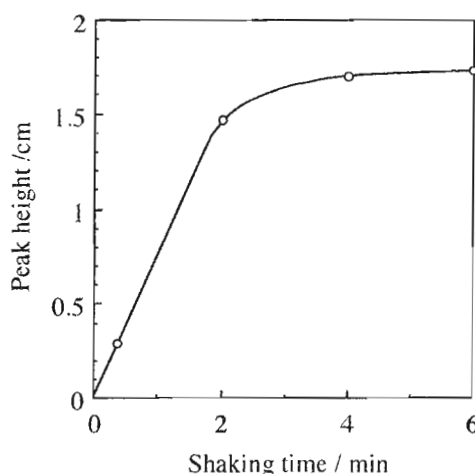


Fig. 3. Effect of shaking time on the absorption efficiency of NO_2

Air sample: sampled in a room at the same time, 260 ml; Absorbing solution: 2 g/l TEA, 2 ml. Peak height was obtained for NO_2^- in the absorbing solutions.

constant by shaking for more than 4 min, whereas 20 min was needed when pure water was used as the absorbing solution.

3.5. Reproducibility for the collection of NO_2 with TEA solution

The reproducibility of the proposed collection method was examined by measuring the NO_2^- concentration in a 1 g/l and a 2 g/l TEA absorbing solution by using the practical air samples at concentration levels of 10^{-8} M of NO_2 , which were sampled in our laboratory. The results are shown in Table 2. The standard deviations were in the ranges of 0.6~3.9% and 3~13%, with 2 g/l TEA, and 1 g/l TEA, respectively. From these results, 2 g/l TEA is recommended. However, higher concentration of TEA could damage the copperized cadmium

Table 2. Determination of NO₂ in practical air samples

No. ^{*1}	Peak height ^{*2} (cm)	SD	RSD ^{*3} (%)	[NO ₂ ⁻] 10 ⁻⁸ M	NO ₂ ^{*4} (ppm)
1	1.11 ± 0.06	0.03	3.1	3.7	0.013
2	1.24 ± 0.09	0.05	3.9	4.5	0.015
3	1.22 ± 0.06	0.03	2.8	4.3	0.015
4	1.31 ± 0.01	0.01	0.6	4.8	0.016
5	1.19 ± 0.06	0.03	2.4	4.1	0.014
6	1.97 ± 0.29	0.25	12.5	9.5	0.032
7	1.77 ± 0.17	0.10	5.7	8.4	0.028
8	1.85 ± 0.22	0.11	6.2	8.9	0.030
9	1.61 ± 0.09	0.05	3.0	7.7	0.026

Air sample: 260 ml; absorbing solution (1g/l or 2 g/l TEA, 2 ml); concentration ratio was 130.

*¹ Samples 1-5 were sampled at a time, and shaken with 2 ml of 2 g/l TEA. Samples 6-9 were sampled at a time on different day and shaken with 2 ml of 1 g/l TEA.

*² Each absorbing solution was measured seven times by μFIA, and the mean values of peak height with the largest deviation were shown.

*³ Relative standard deviation of seven measurements.

*⁴ NO₂ contents in air (ppm), which were calculated on the assumption that NO₂⁻ and NO₃⁻ are the same concentration in the absorbing solutions.

column. Therefore, 1 g/l TEA was used only when NO₂⁻ and NO₃⁻ is measured simultaneously.

The stability of NO₂⁻ and NO₃⁻ absorbed in the TEA absorbing solution was tested. In the TEA absorbing solution, NO₂⁻ and NO₃⁻ were very stable at room temperature for a long time, and their concentrations were not changed at least for 3 days. The LODs for NO₂⁻ and NO₃⁻ in the proposed μFIA were 1 × 10⁻⁸ M and 2 × 10⁻⁸ M, respectively, and the overall LODs for NO₂ in the atmosphere was 0.002 ppm as NO₂⁻ and 0.004 ppm as NO₃⁻, when NO₂ in 260 ml air was collected in 2 ml of TEA solution. The sensitivity was enough for measuring more than one tenth of the NO₂ value in the atmosphere regulated by WHO and others.

3.6. Nitrogen oxide species existing in the TEA absorbing solution

Levaggi et al.[7] reported that NO₂ absorbed in TEA absorbing solution changed to nitrite and nitrate ester or salts with TEA. Okita et al.[23] reported that the collection of NO₂ into TEA solutions was not done through the reaction of HNO₂ and HNO₃ with TEA as reported by Levaggi

et al.[7], and was carried out by direct absorption into the TEA solution. In the present investigation, NO₂ was easily absorbed in TEA solution in a short time, and the concentrations of NO₂⁻ and NO₃⁻ in the solution were almost identical as is shown in Table 3. Therefore, we consider the reaction in the alkaline solution of TEA is carried out by a simple disproportionation/ acid-base reaction as follows:

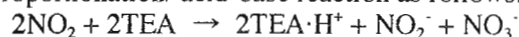


Table 3. Determination of the molar ratio of nitrate and nitrite ions in absorbing solution

Peak height (cm)	RSD (%)	[NO ₂ ⁻]+[NO ₃ ⁻] 10 ⁻⁷ M	[NO ₂ ⁻] 10 ⁻⁷ M	NO ₂ ^{*1} (ppm)	[NO ₃ ⁻] [NO ₂ ⁻] ^{*2}
(a) 5.43 ± 0.08	1.3		5.08	0.18	1.19
2.53 ± 0.03	1.0	11.1		0.20	
(b) 5.61 ± 0.04	0.6		5.26	0.19	1.19
2.66 ± 0.04	1.2	11.5		0.21	
(c) 5.59 ± 0.09	1.6		5.24	0.19	1.23
2.73 ± 0.12	4.0	11.7		0.21	
(d) 4.22 ± 0.12	2.5		3.95	0.14	1.33
1.93 ± 0.08	3.5	9.2		0.17	
(e) 4.69 ± 0.14	2.7		4.39	0.16	1.13
1.96 ± 0.03	1.0	9.3		0.17	

Air samples used were sampled in a room, and 260 ml of the sample was shaken with 2 ml TEA absorbing solution.

*¹ Contents of NO₂ in air samples calculated by using NO₂⁻ or NO₃⁻ concentration.

*² Molar ratio of the concentration of NO₃⁻ to NO₂⁻ in the absorbing solutions.

As a result, either NO₂⁻ or NO₃⁻ in the TEA absorbing solution is enough to be measured for the determination of NO₂ in the atmosphere. As the results obtained in this work, the nitrite determination in the absorbing solution with 2 g/l TEA is recommended with respect of high sensitivity, simple flow system and good absorption efficiency.

3.7. Determination of NO₂ in indoor air and outdoor air

The concentrations of NO₂ in indoor air become higher than in outdoor air because fossil fuel is used for heating in winter. Indoor air pollution is very harmful since most humans spend 80% of their time in enclosed indoor space, and inhale about 1 × 10⁴ l of air per day to live[24]. It is found that the NO₂ concentration increased to (0.32 ~ 0.38) ppm when a gas stove was burned for 2 h, as is shown in Table 4.

The concentrations of NO₂ in ambient air were also shown in Table 4. The NO₂ concentrations were about 0.1 ppm, which corresponds to the lowest values of WHO Guideline.

Table 4. Determination of NO₂ in rooms

No. *1	Peak height (cm)	RSD (%)	[NO ₂ ⁻] 10 ⁻⁷ M	NO ₂ *2 (ppm)
(1)	10.73±0.13	0.9	10.10	0.32
(2)	10.82±0.23	1.5	10.15	0.38
(3)	11.33±0.23	1.5	10.64	0.38
(4)	10.40±0.27	1.4	9.77	0.36
(5)	2.71±0.11	2.0	1.31	0.044
(6)	2.83±0.11	1.6	1.36	0.046
(7)	3.41±0.13	2.4	1.64	0.055
(8)	3.04±0.16	3.0	1.47	0.050
(9)	2.81±0.23	6.0	1.36	0.046
(10)	2.62±0.13	3.0	1.26	0.042
(11)	3.23±0.13	2.9	2.00	0.12
(12)	2.28±0.08	2.5	1.70	0.10

*1 Samples (1)-(4): a gas stove was burned in a room of 24 m² for 2 h.

Samples (5)-(10): a gas stove was not used.

Samples (11)-(12): ambient air sampled outdoors, where car traffic was relatively heavy.

*2 The concentrations of NO₂ in air samples, which were calculated by using the concentrations of NO₂⁻ in the absorbing solutions on the assumption that NO₂⁻ was present at the same concentration of NO₃⁻.

4. Conclusion

In this work, a rapid and simple sampling method with a small volume of TEA solution as an absorbing solution was developed; by coupling the proposed sampling method with a μFIA method the concentrations of NO₂ in the atmosphere could be determined using P/μFIA system with a small sample size. Thus, the concentration of NO₂ could be measured on site for a short time by the proposed method. The overall LOD for measuring atmospheric NO₂ was 0.002 ppm, which corresponds to less than one tenth of WHO (0.08 ~ 0.21 ppm).

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