Microscale Absorption Procedure for Simple and Rapid Gas–Liquid Extraction and Its Application to the Determination of Nitrogen Dioxide in the Atmosphere Coupled with Microflow Injection Analysis

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A simple and miniaturized flow-through gas absorbing unit (GAU) using a small volume of an absorbing solution (0.5 mL) was developed and applied to the determination of nitrogen dioxide (NO_2) in the atmosphere. The measuring method was coupled with a microflow injection analysis system (μFIA) for a small sample size consumption. The absorption efficiency of NO_2 in the GAU was improved by packing hydrophobic poly(tetrafluoroethylene) (PTFE) particles in the unit, and by using a triethanolamine aqueous solution (TEA, 2 g/L) as an absorbing solution: absorption efficiency was increased up to more than 95%. The absorbed NO_2 was converted to NO_3^- and NO_2^-. The molar ratio was ascertained to be 1:1 by measuring the concentrations of NO_2^- and NO_3^- in the absorbing solution using μFIA. Nitrogen dioxide at concentrations above 10 ppb in the atmosphere could be determined by the proposed method.

Nitrogen dioxide (NO_2) is one of the most toxic oxides of nitrogen among the air pollutants. Many studies have been conducted to evaluate the health hazards of NO_2 in the atmosphere so far. Nitrogen dioxide has often been determined spectrophotometrically after being absorbed into aqueous solutions, which contain color-developing reagents such as Saltzman reagents.[1] In such a method, NO_2 concentrations obtained were averaged during 10–60 minutes. With recent developments whereby actual pollution concentration levels are required, such procedures are no longer useful. Nevertheless, there has never been developed a rapid and direct analysis method for on-the-spot determination of NO_2 in the atmosphere. In the present work, an active sampling method was developed and used to determine the concentration of NO_2 in the atmosphere by coupling it with a microflow injection method. Schepers et al. used a flow-through gas sensor just like a gas diffusion unit.[2] However, the absorption efficiency was less than 6%. Silva et al. used a bisegmented flow system by a single movement of the injection device with a film retaining an absorbing solution (10% v/v TEA, 100 μL) to absorb NO_2 in a gas phase: the absorption efficiency was 85% and the detection limit was ca. 25–250 ppb of NO_2 in the gas phase. However, a large volume (1–10 L) of a gas sample was necessary through the bisegmented flow system.[3,4] Simon et al. developed a chromatomembrane cell and applied it to gas–liquid and liquid–liquid extraction. The transfer of analytes from a gas phase to a liquid phase or from an aqueous phase to an organic phase was achieved in the cell containing a block specially made of biporous poly(tetrafluoroethylene) (PTFE) which is said to possess both macropores and micropores.[5–8]

In this work, we propose a simple and rapid flow-through gas absorbing unit (GAU), which consists of a small glass vessel (4 mL), PTFE particles (2 g) and an absorbing solution (0.5 mL). In the unit, commercially available PTFE particles were used instead of the biporous block specially made of PTFE, and applied to the determination of NO_2 in the atmosphere. The GAU developed in this work has the ability to trap analytes in a gas phase into an absorbing aqueous solution quantitatively. The analytes trapped in the absorbing solution were determined by a spectrophotometric method using the reaction of NO_2^- with a Saltzman reagent in a microflow system. In the system a carrier stream (CS: TEA solution) and a reagent stream (RS: Salzman reagent) were propelled at a flow rate of 50 μL/min each with a double-plunger micropump (Asahi Techneion), and a sample solution (20 μL) was injected into the CS. The two streams were merged; the azo dye was formed during flowing in a reaction tubing.

A microflow injection analysis system (μFIA) was applied to the determination of NO_2^- in the absorbing solution because it needed only a small sample size (20 μL). The visible absorption of the azo compound, which was produced by diazotizing sulfanilamide with nitrite and coupling the diazonium ion with *N*-(1-naphthyl)ethylenediamine in an acidic medium, was used for the determination of NO_2^-. The detector composed of a diode sensor, a flow cell (0.8 mm i.d. × 10 mm), an interference filter of 530 nm and a light emitting diode (LED; λ_{max} = 525 nm) as a light source was incorporated in the μFIA system. Peaks were recorded with a chart strip recorder. The PTFE tubing (0.25 mm i.d.), 75 cm long, was used as a reaction tube and a connecting tube. All chemicals used in this work were of analytical reagent grade. Purified water with a MilliQ Labo (Millipore) was used for preparing solutions.

In our previous work, an absorption/concentration of NO_2 in the air was successfully carried out by shaking the collected air with a TEA aqueous solution in a separatory funnel (260 mL),[9] the molar ratio of NO_2^- to NO_3^- in the TEA solution was found to be about 1:1, which was ascertained in a similar manner as in the present system. The shaking procedure, however, was very difficult to be automatized. In this work, a microscale absorption apparatus was developed as shown in Figure 1. In this unit, TEA solution (2 g/L) was first transferred into an absorbing vessel, then an air sample in the form of very small air-bubbles was introduced into the absorbing solution from the bottom of the unit through PTFE membrane filter and went up the absorbing solution. In this case, the absorption efficiency of NO_2 was ca. 35% or less, which was not sufficient enough, as shown in Table 1. To improve the contact of air sample with the absorbing solution, glass beads (300–400 μm) were packed in the GAU and examined; but it was very difficult to recover the absorbing solution when the absorbing solution was pumped out of the GAU toward μFIA system. This is because the TEA solution has a strong affinity to the hydrophilic surface of glass beads. As such, PTFE particles were packed and examined. The results obtained are shown in Table 1 and Figure 2. The use of PTFE particles represented a successful alternative for the extraction/concentration of the analyte from atmospheric air into the absorbing solution. Combined with the μFIA system, an automatization of the procedure was made possible. One or two

Table 1. Determination of NO_2 in practical air samples

No.[a]	PTFE /g	TEA soln. /mL	Concentration ratio	Peak height[b] /cm	SD	RSD[c] /%	$[NO_2^-]$ / 10^{-7}M	NO_2[d] /ppm
S 1	0	1	25	0.55 ± 0.05	0.05	4.2	0.33	0.060
S 2	0	1	25	0.76 ± 0.13	0.09	5.6	0.45	0.082
S 3	1	1	25	1.75 ± 0.13	0.13	4.1	1.05	0.192
S 4	1	1	25	1.61 ± 0.06	0.06	2.8	0.95	0.174
S 5	2	1	25	2.05 ± 0.05	0.06	2.3	1.21	0.221
S 6	2	1	25	1.01 ± 0.06	0.05	3.1	0.59	0.108
S 7	2	0.5	50	1.73 ± 0.01	0.04	1.9	1.02	0.093

[a] Samples (S1-S5), and (S6,S7) were sampled at a time, and NO_2 was absorbed in 1 mL or 0.5 mL of 2 g/L TEA. [b] Each absorbing solution was measured fourteen times (S7 was measured seven times), and the mean value s of peak height with the largest deviation were shown. [c] Relative standard deviation of fourteen or seven measurements. [d] NO_2 contents in air (ppm), which were calculated on the assumption that NO_2^- and NO_3^- were present at an identical concentration in the absorbing solutions.

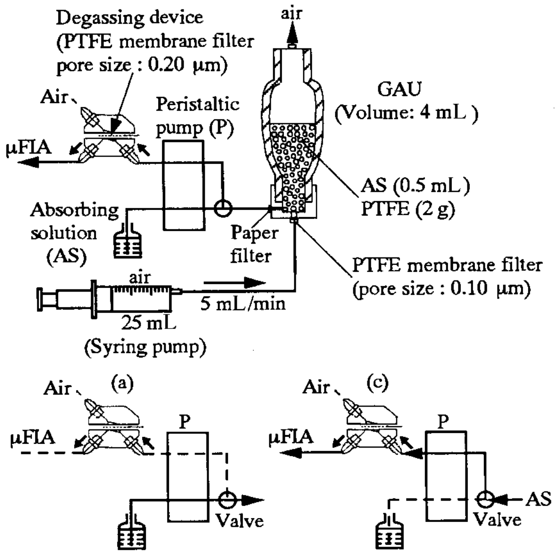

Figure 1. Apparatus for NO_2 absorption (solid lines shown in the valve are working). (a) The GAU is filled with the absorbing solution (0.5 mL, 2 g/L TEA); (b) the three-way valve is turned, and the gas sample is flowing through the unit (no Figure); (c) the three-way valve is turned, and the absorbing solution from the GAU is pumped toward the μFIA.

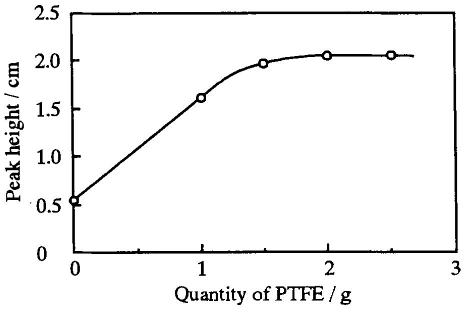

Figure 2. Effect of quantity of PTFE particles in the GAU on absorption efficiency. Absorbing solution: 1 mL; air sample: 25 mL of ambient air sampled in a laboratory room.

grams of PTFE particles (size, 400–700 μm, Daikin Co.) were packed in the GAU, in which the absorbing solution was filled. The effect of the volume of the absorbing solution was examined by varying the volume: 0.5 mL or 1.0 mL of 2 g/L TEA. The air sample (25 mL) was flowed through the GAU at the flow rate of 5 mL/min. After the injection of the air sample, the three-way valve was turned and the absorbing solution was pumped out of the GAU toward the μFIA system (Figure 1). Figure 2 shows the effect of PTFE quantity on the absorption efficiency of NO_2 from the air sample. More than 1.5 g of PTFE gave almost identical peak height: 2 g of PTFE was recommended, as can be seen from Table 1. When 0.5 mL of the TEA absorbing solution was used, the peak heights and contents of NO_2^- were doubled compared with the values in 1 mL of the absorbing solution. This indicates that the NO_2 in the air sample can be almost completely retained in the TEA solution and 50-fold concentration is possible.

In this work, it was demonstrated that the absorption efficiency of the GAU containing 0.5 mL of 2 g/L TEA absorbing solution and 2 g of PTFE was more than 95 %, which was ascertained by using the previous method.[9] The effect of PTFE particles in the GAU on the absorption efficiency was found to be excellent; when the PTFE particles were not used, the absorption was less than 40%. With such a system, it was possible to completely trap NO_2 from the air sample by using very small volumes (0.5 mL) of absorbing solution.

A simple and rapid method using the newly developed GAU containing a small volume of the TEA absorbing solution and PTFE particles was proposed. The concentrations of NO_2 in the atmosphere could be determined on the spot. By the proposed μFIA, the limit of detection (LOD) of NO_2^- was 10^{-8} M in the absorbing solution and therefore the LOD for measuring atmospheric NO_2 seem to be ca. 10 ppb by coupling μFIA with the proposed GAU.

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