AN AUTOMATIC MEASUREMENT OF GASEOUS NITRIC ACID IN THE URBAN ATMOSPHERE
BY COMBINATION OF A DIFFUSION SCRUBBER AND ION CHROMATOGRAPHY

KEISUKE TSUKAMOTO, SHIGERU TANAKA, YOSHIKAZU HASHIMOTO,
TAMOTSU INOMATA*, AND YUZURU HANAOKA*

Department of Applied Chemistry, Keio University, 3-14-1 Hiyoshi, Kohoku-ku,
Yokohama, 223 JAPAN
Yokogawa Electric Works, Ltd., 2-9-32, Naka-cho, Musashino-shi, Tokyo, 108
JAPAN

Abstract In this study, an automatic measurement of HNO_3 was investigated by using a diffusion scrubber and ion chromatography. The collection efficiency of HNO_3 standard gas of $36 \mu\text{g}/\text{m}^3$ was $93.1 \pm 3.3\%$ ($n=4$) by using 50 cm length of the diffusion scrubber at 1 l/min of air flow. The lower detection limit of HNO_3 by this method was $0.01 \mu\text{g}/\text{m}^3$ at sampling volume of 60 l. The concentration of HNO_3 in the urban atmosphere is a few $\mu\text{g}/\text{m}^3$. It is suitable for this method to measure HNO_3 at ambient level.

Key words gaseous nitric acid, diffusion scrubber, porous polytetrafluoroethylene (PTFE) tube, ion chromatography

INTRODUCTION

Recently, concentration of NO_x has gradually increased in the urban atmosphere while that of SO_2 has decreased due to its exhaust regulation in Japan¹⁾. A problem which gaseous nitric acid (HNO_3) increases with increasing NO_x concentration has occurred in the urban atmosphere. Because HNO_3 is secondarily produced by the photochemical reaction between NO_x and OH radical in the atmosphere. However, it does not advance to develop a monitoring system of HNO_3 concentration due to technical difficulties for HNO_3 measurement.

The diffusion denuder method has been used to separate gas and particle by a large difference of diffusion coefficients between gas and particle. Several types of diffusion denuder have been designed by many scientists^{2~5)} for collection of gases in the atmosphere. A diffusion scrubber has been developed by P.K. Dasgupta⁶⁾ in order to measure NH_3 in the atmosphere. The diffusion scrubber used in this work consists of dual tubes which are a porous PTFE tube inside and a glass tube outside. Deionized water as a scrubber solution is stored into a narrow annular gap between the porous PTFE tube and the glass tube. A porous PTFE tube has a special property that gas can pass through it and water can not. Gaseous HNO_3 in the air is collected into deionized water by crossing the wall of porous PTFE tube while particles such as nitrate salts pass through the porous PTFE tube. Because the diffusion coefficients of gas and particle are quite different. If the diffusion scrubber connects to an ion chromatograph and the deionized water stored is injected into the ion chromatograph, HNO_3 collected with deionized water can be determined by ion chromatography. Therefore, it is possible to measure automatically and continuously HNO_3 in the atmosphere by combination of the diffusion scrubber and the ion chromatograph.

EXPERIMENTAL

Experimental apparatus for measurement of HNO_3 collection efficiency by the diffusion scrubber is shown in Fig.1. As for generation of HNO_3 standard gas, a standard gas generator by diffusion tube (Gas Tech Corp., PD-1B) was used. HNO_3 standard gas at low concentration level was prepared by diluting with a purified air. The prepared HNO_3 standard gas was passed through two diffusion scrubbers in series. The diffusion scrubber consists of double

Fig.1 Experimental apparatus for measurement of HNO_3 collection efficiency

1. Diaphragm pump	5. Mix chamber
2. Silicagel	6. Polyamide filter
3. Molecular sieve	7. Diffusion Scrubber
4. Generator of HNO_3	8. Flow meter

annular tubes which are a porous PTFE tube (5 mm o.d., 4 mm i.d.) as the inner tube and a glass tube (9 mm o.d., 5.8 mm i.d.) as the outer tube. In this study, porous PTFE tubes with 50% and 70% of porosity were used as the inner tube of the diffusion scrubber.

HNO_3 collected with deionized water in the diffusion scrubber was analyzed by ion chromatography. Yokogawa Electric Works Model IC7000P was used as an ion chromatograph. ICS-A35 (Yokogawa) was used as an anion separation column, and 5 mM Na_2CO_3 /1 mM NaHCO_3 solution was used as eluent at a flow rate of 1 mL/min. Two kind of detectors were used in series for the determination of NO_3^- ion. One was a conductivity detector and the other was an UV absorption detector. The concentrations of HNO_3 collected by the first and the second diffusion scrubbers were measured by ion chromatography, and then the collection efficiency of HNO_3 was calculated.

RESULTS AND DISCUSSION

The relationship between the collection efficiency of HNO_3 by the diffusion scrubber and the air flow rate is shown in TABLE 1. 50 cm length of porous PTFE tube was used. At less than, the collection efficiency of HNO_3 was more than 90% at both of porous PTFE tubes with 50% and 70% of porosity. However, high air flow rate made the collection efficiency lower. It was suitable to operate at 1.0 L/min of air flow rate to get a good collection of HNO_3 by the diffusion scrubber.

TABLE 2 shows the relationship between the collection efficiency of HNO_3 and the length of porous PTFE tube. Air flow rate was set at 1.0 L/min, and the porous PTFE tube with 50% of porosity was used. As shown in Table 2, the collection efficiency of HNO_3 was more than 90% at 40 cm and 50 cm length of the porous PTFE tube, while the collection efficiency decreased at 30 cm length of porous PTFE tube. Therefore, it need more than 40 cm length of porous PTFE tube to get a good collection of HNO_3 .

TABLE 3 shows the collection efficiency of HNO_3 at low concentration level by the diffusion scrubber. The prepared HNO_3 standard gas was equal to the concentration in the urban atmosphere. As shown in TABLE 3, more than 90% of collection efficiency was obtained for HNO_3 at low concentration level. Therefore, it was possible to collect HNO_3 in the urban atmosphere by the diffusion scrubber.

Table 1 Collection efficiency of HNO_3 by diffusion scrubber using PPTFE tube

Collection efficiency		Air flow rate	
Air flow Rate	Concentration of HNO_3	Collection efficiency	
(l/min)	($\mu\text{g/m}^3$)	Measured value	theoretical value*
		(%)	(%)
Porosity of PPTFE tube: 50 %			
0.5	1420 ± 157 (n=4)	> 96.6	99.9
1.0	975 ± 126 (n=5)	> 94.7	98.0
1.5	528 ± 55 (n=5)	84.5 ± 2.5 (n=5)	93.0
2.0	501 ± 51 (n=5)	79.8 ± 2.1 (n=5)	87.0
Porosity of PPTFE tube: 70 %			
1.0	1120 ± 100 (n=4)	93.3 ± 0.8	98.0
2.0	656 ± 28 (n=4)	80.1 ± 1.4 (n=4)	87.0
3.0	678 ± 34 (n=4)	64.0 ± 1.5 (n=4)	76.0

Length of PPTFE tube: 50 cm

* calculated by Gormley-Kennedy equation

Table 2 Collection efficiency of HNO_3 by diffusion scrubber using PPTFE tube

Collection efficiency		Length of PPTFE tube	
Length of PPTFE tube	Concentration of HNO_3	Collection efficiency	
(cm)	($\mu\text{g/m}^3$)	Measured value	theoretical value*
		(%)	(%)
50	975 ± 126 (n=5)	> 94.7 (n=5)	98.0
40	978 ± 28 (n=5)	92.7 ± 1.1 (n=5)	95.7
30	1046 ± 23 (n=5)	83.5 ± 2.7 (n=5)	91.0

Air flow rate: 1.0 l/min , Porosity of PPTFE tube: 50 %

* calculated by Gormley-Kennedy equation

Table 3 Collection efficiency of HNO_3 at low concentration level by diffusion scrubber using PPTFE tube

Inner diameter of glass tube	Concentration of HNO_3	Collection efficiency
(mm)	($\mu\text{g/m}^3$)	(%)
5.8	36.0 ± 7.3 (n=4)	93.1 ± 3.3 (n=4)
7.0	50.6 ± 5.1 (n=4)	> 94.9

Air flow rate: 1.0 l/min ,

Porosity of PPTFE tube: 70 %, Length of PPTFE tube: 50 cm

The automatic measurement system for HNO_3 in the atmosphere which was developed in this study consists of the diffusion scrubber with porous PTFE tube and the ion chromatograph. After a sampling period, the sample solution which collected HNO_3 is automatically pumped into the ion chromatograph, and NO_3^- ion is trapped on the concentration column (SAM3-035, Yokogawa) inside the ion chromatograph. NO_3^- ion is separated from other anions and determined by the UV detector at 208 nm. This analytical procedure is automatically repeated at regular intervals by using a timer to measure automatically and continuously HNO_3 in the atmosphere.

Fig.2 shows diurnal variation of HNO_3 concentration in the atmosphere by using this automatic measurement system. The measurement was carried out on the roof at the building of Keio University, Hiyoshi, Yokohama, Japan from July 21 to 25, 1991. The instrument was operated on a 1-hour cycle. The concentration of HNO_3 in the atmosphere was $1 \sim 28 \mu\text{g}/\text{m}^3$ and this value was equal to 10% of NO_x concentration. As shown in Fig.2, the diurnal variation of HNO_3 concentration was observed, which increased during daytime and decreased from evening. This fact suggested that HNO_3 was produced by the photochemical oxidation of NO_x in the atmosphere.

FIG.2 DIURNAL VARIATION OF HNO_3 CONCENTRATION IN THE ATMOSPHERE,
AT YOKOHAMA, JAPAN, JULY 21-25, 1991

REFERENCE

1. Circumstances of Air Pollution in Japan, Annual Report. Environmental Protection Agency in Japan, 1990.
2. J. Forrest et al., *Atmos. Environ.*, **16**, 1473 (1982).
3. W.A. McClenny and P.C. Galley, *Anal. Chem.*, **54**, 365 (1982).
4. P. Koutrakis et al., *Environ. Sci. Technol.*, **22**, 1563 (1988).
5. D. Klockow et al., *Atmos. Environ.*, **23**, 1131 (1989).
6. P.K. Dasgupta, *Atmos. Environ.*, **18**, 1593 (1984).