Evaluation of an Ammonia Passive Sampler Using Chamber System

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Abstract

The purpose of this study was to evaluate the efficiency of a passive sampler in measuring atmospheric ammonia concentrations using chamber system. The ability of the passive sampler to quantitatively determine atmospheric ammonia gas was almost identical to that of the reference method (indophenol method). There was no significant difference between concentrations measured by the two methods. The detection and quantification limits of the ammonia passive sampler were 16.9 ppb and 25.3 ppb, respectively, for a 24-h sampling period. The average coefficient of variation between replicated samplers was 6.7±4.2%. The concentrations measured by the two methods (passive sampler and indophenol method) were no significant difference with good a correlation (correlation coefficient=0.964).

Key words : Passive sampler, Ammonia, Chamber system, Odor

1. INTRODUCTION

Atmospheric ammonia reacts readily with acidic gases (such as NOx and SOx) has a relatively short atmospheric residence time and high adsorption activity on the surface of water. Ammonia also forms aerosols or precipitation containing ammonium and forms dry deposits on water and soil surfaces. Ammonia is a predominant species of nitrogen deposition, and its related deposits can lead to acidification of soil or water, eutrophication, and reduction in species diversity.

Agricultural activity, such as livestock raising, poultry production, and the use of livestock manure is the main source of atmospheric ammonia emissions. Other anthropogenic sources (e.g., waste or sewage disposal, industrial refrigerants, and vehicles) make a relatively small contribution to the total ammonia emission, but may have a significant negative effect on human working and living environments with respect to odor.

Because passive samplers can accurately and directly measure air pollutants, they have frequently been used to monitor and evaluate the spatial distribution of air pollutants (Stevenson *et al.*, 2001; Bernard *et al.*, 1999; Campbell *et al.*, 1994), and are well suited for indoor and personal monitoring (Vainiotalo *et al.*, 2001; Gillett *et al.*, 2000; Palmes *et al.*, 1976). Passive samplers do not require electricity and have no moving parts, such as the pumps and flowmeters associated with continuous analyzers. The cost of passive samplers is likely to be

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very low, especially in comparison with continuous analyzers. Furthermore, these samplers can be deployed almost anywhere to estimate the spatial distribution of air pollutants (UNEP/WHO, 1994).

Recently, a number of tools for measuring ambient ammonia concentrations, including diffusion scrubbers (Genfa et al., 1989), filter packs (Sickles et al., 1999), passive flux samplers (Sommer et al., 1996; Schjoerring, 1995), and tube-type passive samplers (Roadman et al., 2003; Thoni et al., 2003; Thijsse et al., 1998), have been studied and usually determined to be potentially suitable for the measurement of ammonia. Most of passive samplers for the measurement of ammonia in ambient air above-mentioned are a tube-type sampler with long diffusion length and narrow diffusion area. In addition, the tube-type passive sampler is required somewhat strong wind speed to ensure adequate diffusion of ammonia gas to the collection filter. With the redesigned sampler, the diffusion path and area can be larger than that of the tube-type sampler and two pre-filters of a semi-permeable membrane are mounted.

The aim of this study was to evaluate a redesigned badge-type passive sampler using a chamber system in the laboratory for measuring ambient air concentrations of ammonia.

2. MATERIALS AND METHOD

2.1 Passive sampler

A photograph of the passive sampler is shown in Fig. 1. The sampler consisted of a sampler end cap (55 × 55 × 18 mm), a sampler body (36-mm inside diameter (id)), and a diffusion screen (33-mm id) made of high-density polyethylene. The sampler body consisted of a filter retaining ring (28-mm id) and spacer ring (28-mm id) that maintained a diffusion distance of 10 mm, a semi-permeable membrane (Celgard-2500, micro porous polypropylene membrane, porosity: 55%, pore size: 0.209 μm × 0.054 μm, thickness: 25 μm, USA), and a coated collection filter (pure cellulose chromatography paper, absorption speed: 7.0 cm, thickness: 0.17
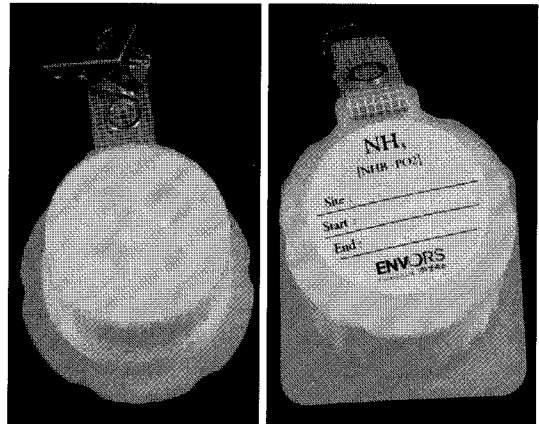

Fig. 1. Photograph of a passive sampler.

mm, 26 mm, Whatman, England). The filter retaining ring and spacer ring were made from polyethylene. The sampler body and end cap had an edge and screw thread for the downward-facing equipment of the passive sampler with a pole and wire. The semi-permeable membrane had 55% porosity, 0.209 × 0.054-μm pore size, and 25-μm thickness. The silicone flat ring (28-mm id) ensured an air-tight seal between the diffusion screen and the sampler body, and was mounted in the diffusion screen. The passive sampler was easy to handle because of the use of light (about 29 g) and safe components (Yim et al., 2005; Yim et al., 2004).

The coated collection filter was prepared individually by dropping 100 μL of absorbing solution (a mixture of 2% phosphoric acid and 2% glycerin) in the sampler body. The use of high viscosity glycerin as a constituent of the absorbing solution was necessary to maintain moisture on the surface of the coated collection filter (Koutrakis et al., 1993). After applying the absorbing solution, the passive sampler components were immediately assembled. Particular attention was given to handling samplers because they can be easily contaminated. All samplers were stored in sealed plastic bags in darkness at 4°C until used.

2.2 Chamber system

A schematic diagram of a chamber system for the
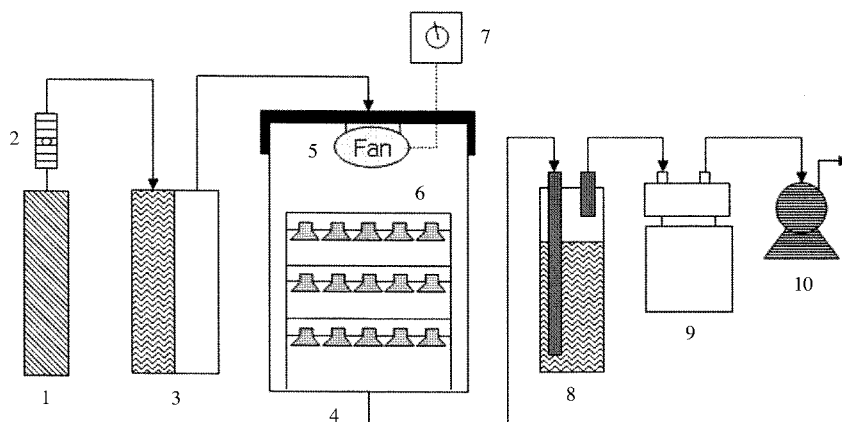
Fig. 2. Schematic diagram of a chamber system for the measurement of ammonia gas using a passive sampler: (1) air cylinder, (2) rotameter, (3) device for the generation of ammonia gas (4) exposure chamber (volume 20 L, diameter 380 mm, height 400 mm), (5) fan to mix gases, (6) passive samplers, (7) fan revolution controller, (8) device to collect ammonia gas using bubble absorbers, (9) dry gas meter, (10) pump.

measurement of ammonia gas using a passive sampler is shown in Fig. 2. The chamber system consisted of an air supply, devices for measuring gas volume and flow rate, an ammonia gas generation apparatus, an exposure chamber, a passive sampler, and an active sampler. A compressed air in cylinder did not require further cleaning or drying. The volume and flow rate of air introduced to and exhausted from the chamber were accurately measured and controlled using a rotameter (visi-float flowmeter, Dwyer, RMA-SSV, 2.5 L min^{-1}, USA) and a dry gas meter (Daesung, DSG-6L, Korea).

A Pyrex glass smog bubbler, an ammonia gas generator, was filled with ammonia solution (35% NH$_4$OH) and ammonia gas was produced by passing air through it. Air flow for the dilution of ammonia gas was accurately controlled by the flow meter and valves under constant conditions. An active sampling method (i.e., the indophenol method) (Lodge, 1998) and a detection tube (Gastec, 3 L, Japan) were used to measure the ammonia gas concentration in the inlet and outlet of the exposure chamber. The concentrations of ammonia gas were maintained at constant levels during the experiments by adjusting the flow of air.

The exposure chamber was an acrylic plastic cylinder with a length of 400 mm, an external diameter of 380 mm, and an internal volume of about 20 L. It consisted of a cylinder body, a flat outlet bottom, a removable inlet cover, a fan, and a rack for mounting the passive sampler. Generated ammonia gas was introduced through the cover inlet, and the fan was operated to evenly distribute the ammonia gas throughout the exposure chamber. The exposure chamber was maintained at room temperature, ranging from 20~30°C. All components for connecting devices in the chamber system were made of Teflon and stainless steel.

2.3 Reagents

All parts of the sampler were thoroughly cleaned with pure water (resistivity=18.3 MΩ cm, Millipore Milli-Q system) using an ultrasonic cleaner, and were dried overnight in a drying oven at 60°C. All reagents (reagent-grade) were purchased and used without further purification. Sodium hypochlorite and phenol solutions for the ammonia gas analysis were prepared by indophenol method. Standard solution of ammonia was prepared by dissolving ammonium sulfate dried at 130°C in pure water (Ministry of Environment, 2004). These solutions were prepared and used daily.

2.4 Analysis

After exposure, the coated collection filters were unloaded into glass bottles (10 mL) with PTFE-lined screw caps. Extraction was carried out with 2 mL of phenol solution and sodium hypochlorite solution for color development using a shaker (Jeio Tech, BS-21, Korea) with orbital shaking for 1 h. The agitation in the shaker was adjusted to produce a mild swirling of the extraction solution and a rotational frequency of 150 rpm.

The temperature of the solution in the extraction vials during color production was maintained above 20°C. The extracted and color developed solution (4 mL) was measured spectrophotometrically using a potable colorimeter (Unimeter, UM-1, Tsukubasoken, Japan). At least three blank samplers were prepared with the exposed samplers. Blanks were stored at room temperature during the test. The measured value of the blank samplers was subtracted from the exposed sample value to obtain the net concentration of ammonia gas.

The ammonia concentration measured by passive sampler can be calculated from the following equation (Gorecki and Namiesnik, 2002):

$$C = \frac{M}{SR \cdot t} \tag{1}$$

where SR is the sampling rate (mL min^{-1}), M is the mass of the ammonia gas transported by diffusion (mL), C is the concentration of ammonia gas (mL m^{-3}), and t is the sampling time (min). The sampling rates were experimentally investigated by exposing passive sampler and indophenol method at the same time. The ammonia concentration and sampling time for the exposure experiment were in the 0.02 to 0.18 ppm region and 24 hr, respectively. The sampling rate used for calculating ammonia concentration was 16.0 ± 2.0 mL min^{-1}.

3. RESULTS AND DISCUSSION

3.1 Stability of gas volume in chamber

The stability of the gas volume is an important factor in the measurement of a desired gas using the
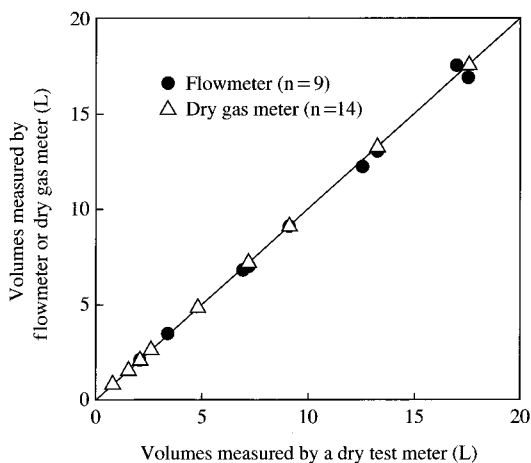

Fig. 3. Comparison of results obtained with volume measuring devices (rotameter and dry gas meter) and a dry test meter as standard meter.

chamber system because the active sampling method could be used as a reference method for estimating the sampling rate of a passive sampler. In this study, the dry gas meter and rotameter, which were installed to measure and control the gas going into and from the chamber, were evaluated using a dry test meter (Shinagawa, DC-1, Japan), even though they had acceptable accuracies in the range of ± 5%. Dry test meters are frequently used as transfer standards because their accuracy is better than ± 1% (Wight, 1994).

The results of the regression analysis of volume measuring devices (dry gas meter or rotameter and dry test meter) are shown in Fig. 3. There were no differences in air volume between the two instruments. The errors in air volume measurement of the rotameter and dry gas meter were 2.2 ± 1.2% and 4.7 ± 1.9%, respectively. Therefore, these devices were considered favorable for the evaluation of the passive sampler.

The variance in total flow at the inlet and outlet of the exposure chamber was estimated using the rotameter and dry gas meter, and this evaluation was repeated eight times. The air leaving the cylinder was constantly conducted into the chamber at 500 mL min^{-1} as a reference flow rate for 4 min. The flow rate measured at the inlet by the rotameter

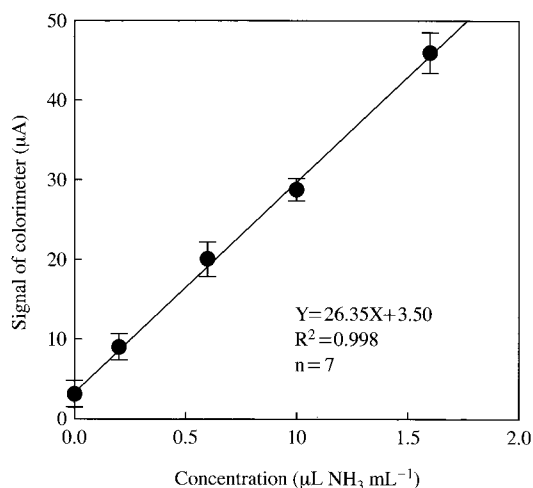**Table 1. Results obtained from relationship between standard solution and signal of colorimeter[a].**

Signal of colorimeter (μA)	Concentration of ammonia (μL NH$_3$ mL^{-1})				
	0	0.2	0.6	1.0	1.6
Mean	3.2	9.0	20.1	28.8	46.0
Min.	1.9	7.1	17.8	29.3	43.3
Max.	5.4	11.1	22.9	33.0	50.2
SD	1.6	1.7	2.1	1.4	2.6
n	7	7	7	6	7
% CV	50.0	18.4	10.6	4.4	5.6

[a]Min.=minimum value, Max.=maximum value, SD=standard deviation, n=number of sample, % CV=coefficient of variation

Fig. 4. Relationship between signal of colorimeter and concentration of ammonia solution for the standard curve.

was in the range of $505 \sim 517$ mL min^{-1} ($2,020 \sim 2,068$ mL total volume). At the outlet, the rate ranged from $492 \sim 504$ mL min^{-1} ($1,969 \sim 2,016$ mL total volume). The total volume of air at the outlet as determined by the dry gas meter also ranged from $1,916 \sim 1,984$ mL. The flow rate error at the inlet and outlet of the chamber system with respect to the reference flow rate was 2.2% (511 mL min^{-1}), 2.6% (498 mL min^{-1}), and 4.75% (487 mL min^{-1}), respectively. Because errors of less than 5% were obtained, the rotameter and dry gas meter were considered acceptable as air monitoring and measuring devices for providing a quick and easy way to check flow rates and to read air volumes.

3. 2 Evaluation of ammonia gas

The procedure given in the indophenol method was used to prepare the standard solutions for designing the standard curve, i.e., a plot of the absorbance of the obtained color against the corresponding concentration of ammonia solution (Wight, 1994). The standard curve for the determination of ammonia quantity in solution is shown in Fig. 4, and the statistical results are shown in Table 1. The colorimeter signal was linear over the range of prepared concentrations of ammonia solution (correlation coefficient=0.998, $p < 0.05$), and the statistically important intercept was small (intercept=3.67 ± 1.37). The coefficients of variation for low concentrations of ammonia solution were somewhat larger than those for high concentrations. The results of the analysis of variance (ANOVA) were

significantly correlated, with $p < 0.001$. The linear correlation between concentration of ammonia solution and absorbance almost satisfied with the 5% difference at 95% confidence intervals. The standard solution appeared to be appropriate for calculating the concentration of ammonia gas and for analyzing the samples.

Ammonia gas introduced into the exposure chamber was generated using air and an ammonia solution ranging in dilution rate from 1×10^4 to 8×10^4. The flow rate of air introduced to the apparatus for the generation of ammonia gas was kept constant at 500 mL min^{-1} throughout the experimental period. The concentration of ammonia gas in the exposure chamber was measured using two active sampling methods, i.e., the indophenol method and a detection tube, to evaluate the differences between methods. Only small differences were observed between the two methods (Fig. 5), so that these methods were considered suitable for the determination of ammonia gas concentration. The generated ammonia gas concentration ranged from $0.1 \sim 10$ ppm, was stable for 180 min, and then changed within 15% over time. The variation in ammonia gas concentration was dependent on the dilution rate and the volume of the ammonia solution.
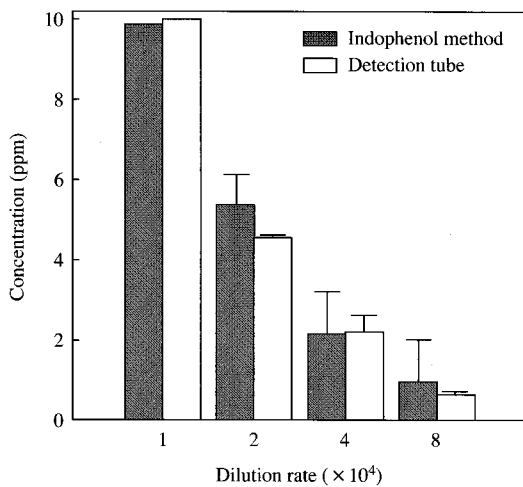
Fig. 5. Comparison of results of the ammonia gas concentration measured by active sampling methods (indophenol method and detection tube) with several dilution rate of ammonia solution. Sampling period is 1 hr.

3.3 Evaluation of passive sampler

Two kinds of filters, such as qualitative filter paper (alpha cotton cellulose, pore size: 1 µm, thickness: 0.21 mm, ADVANTEC, 5C, Japan) and pure cellulose chromatography paper were employed for the collection filter of passive sampler. These collection filters were ultrasonically cleaned to investigate the reduction of contaminant in the collection filter by cleaning. Collection filter was cleaned with pure water for 1 hr in the ultrasonic cleaner and was rinsed by three washing by pure water. The drying process for collection filter was carried out in oven at 60°C for 24 hr.

The evaluation of blank values is presented in Table 2. Contaminant level in the chromatography paper was lower than that in qualitative filter paper. After ultrasonic cleaning, ammonia level in blank passive sampler using chromatography paper was the lowest. Irrespective of the type of collection filter, ultrasonic cleaning was remarkably effective in order to reduce the contaminant level in the collection filter. Therefore, ultrasonically-cleaned chromatography paper was used throughout the course of this study.

Table 2. Evaluation of blank value for passive sampler[a].

| Sampler | Ammonia amount (µL NH$_3$) | | | |
| | Not cleaned | | Cleaned | |
	Filter paper (5C)	Chromatography paper (1Chr)	Filter paper (5C)	Chromatography paper (1Chr)
No. 1	1.53	0.78	0.89	0.23
No. 2	1.37	0.84	0.85	0.25
No. 3	1.41	0.63	0.92	0.18
No. 4	1.49	0.72	0.66	0.21
Mean	1.45	0.74	0.83	0.22
SD	0.07	0.09	0.11	0.03
% CV	4.9	12.1	13.8	12.8

[a]SD=standard deviation, % CV=coefficient of variation
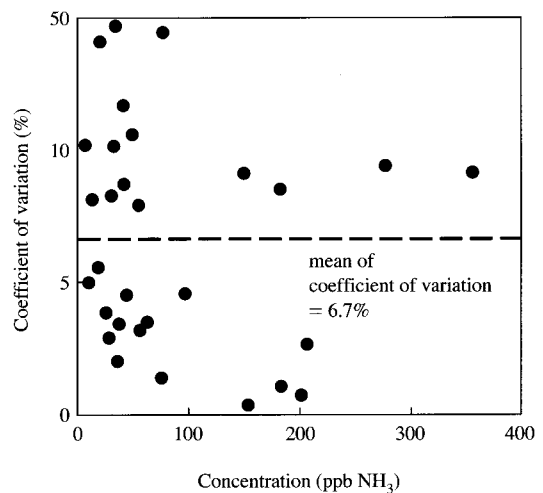

Fig. 6. Coefficient of variation on the mean concentration of passive samplers.

The limit of detection (LOD) and limit of quantification (LOQ) of samplers were 0.31 and 0.52 µL of ammonia, respectively: as defined by LOD (or LOQ)=$\bar{b}$+t$_{(n-1, 0.01)}$σ ($\bar{b}$ is the mean of field blank values, σ is the standard deviation of field blank values, and t$_{(n-1, 0.01)}$ is the 99 th percentile of the Student t distribution. 3 and 10 are generally used as values of t$_{(n-1, 0.01)}$ for calculating LOD and LOQ, respectively) (Gillett et $al.$, 2000; ACS, 1980).

The ammonia concentration with respect to a field blank for an exposure time of one day was calculated as 13.1±1.2 ppb. LOD and LOQ for one day
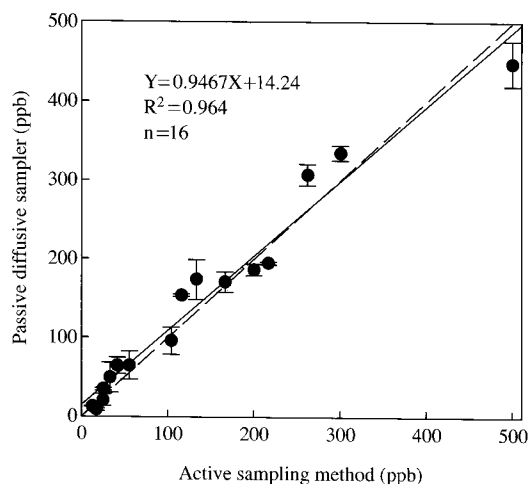
Fig. 7. Comparison of results of the ammonia gas con-
centration measured by passive samplers and
active sampling method (indophenol method).
Sampling period is 24 hr.

of application were 16.9 and 25.3 ppb, respectively.
The deployment period of the sampler should be
increased for lower ammonia gas concentrations.

To investigate reproducibility, we used replicate
samplers (30 pairs), deployed side by side under the
same experimental conditions (i.e., exposure time
and analytical procedure). The precision of ammo-
nia gas measurement was evaluated using the coef-
ficients of variation from replicate samplers. The
coefficients of variation at each mean concentration
are shown in Fig. 6. The mean coefficient of varia-
tion between replicates was $6.7 \pm 4.2\%$ and ranged
from $0.4 \sim 14.7\%$. The results were highly repro-
ducible, and therefore, the precision of the samplers
was considered acceptable.

The passive sampler and active sampling method
(indophenol method) (Ministry of Environment,
2004; Lodge, 1998) were performed simultaneously
at the same sampling sites and for the same expo-
sure time. The correlation between the two methods
was investigated using linear regression analysis
(Fig. 7). There was no significant difference between
the concentrations measured by the two methods,
and the relationship appeared to be 1 : 1 (dashed
line). The correlation coefficient and the slope were

0.964 and 0.9467, respectively, indicating that pas-
sive samplers appear to be suitable for measuring
atmospheric ammonia gas.

4. CONCLUSIONS

Passive sampler for measuring atmospheric ammo-
nia gas levels was evaluated in the laboratory. The
passive sampler was able to quantitatively measure
ammonia gas in ambient air as well as did the re-
ference method like indophenol method. LOD and
LOQ of the passive sampler were 16.9 ppb and 25.3
ppb, respectively, including the field blank (about
13.1 ppb), for a one-day sampling period. Average
coefficient of variation between replicates was 6.7
$\pm 4.2\%$. The concentrations measured by the two
methods (passive sampler and indophenol method)
were no significant difference, and the relationship
appeared to be 1 : 1. So that it was concluded that
the passive samplers is suitable for measuring atmo-
spheric ammonia gas.

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