

## Research Article

# The Comparisons of Real-time Ammonia Adsorption Measurement in Varying Inlet Tubes and the Different Ammonia Measurement Methods in the Atmosphere

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**ABSTRACT** Ammonia ( $\text{NH}_3$ ) is an important, albeit sticky, precursor for producing secondary inorganic aerosols (SIA), especially in the form of ammonium nitrate ( $\text{NH}_4\text{NO}_3$ ) and ammonium sulfate ( $(\text{NH}_4)_2\text{SO}_4$ ). To reduce SIAs, many researchers have attempted to measure the concentration of ambient  $\text{NH}_3$  using real-time or passive methods. However,  $\text{NH}_3$  is a highly sticky gas and is therefore difficult to measure using real-time methods without incurring losses during measurement. In this study, four different tubing materials, semi seamless tubes, perfluoroalkoxy (PFA), polytetrafluoroethylene (PTFE), and polyvinylidene fluoride (PVDF), were used to ascertain the adsorption of  $\text{NH}_3$  in inlets using real-time instruments. Without heating sample tubes and at 0% relative humidity (RH), this study shows that PTFE had the least adsorption (i.e., 0% at 1 and 2 m of sample tube), and semi-seamless tubes had the highest adsorption (i.e., 27.5% at 1 m of sample tube). To calculate the adsorption of  $\text{NH}_3$  under ambient conditions, at various inlet lengths, the RH of  $\text{NH}_3$  was varied from 20% to 80%, which showed that shorter inlets and higher RH lower  $\text{NH}_3$  adsorption at inlets (i.e.,  $1.74 \text{ ppb m}^{-1}$  at 80% RH and  $7.48 \text{ ppb m}^{-1}$  at 20% RH). Additionally, inlet heating was effective in reducing the adsorption of  $\text{NH}_3$  as the RH decreased. Applying the inlet system (i.e., 2 m of PTFE tube with heating) showed excellent correlation (slope: 0.995 and coefficient: 0.992) between two different real-time measurements while measuring ambient air.

**KEY WORDS** Ammonia, Inlet adsorption, Polytetrafluoroethylene, Protocol, Ammonia measurement

## 1. INTRODUCTION

Ammonia ( $\text{NH}_3$ ) is a gaseous substance with very high adsorption properties (Bobrutski *et al.*, 2010). It is emitted into the atmosphere via various activities such as excreta management, agriculture, and substances such as mobile pollutants (Paulot *et al.*, 2014).  $\text{NH}_3$  emissions in South Korea have gradually increased from 292 Gg in 2014 to 301 Gg in 2016 (Park *et al.*, 2019). When  $\text{NH}_3$  reacts with nitric acid ( $\text{HNO}_3$ ), sulfuric acid ( $\text{H}_2\text{SO}_4$ ), or hydrochloric acid (HCl),



which are all gaseous substances, they transform into ammonium nitrate ( $\text{NH}_4\text{NO}_3$ ), ammonium sulfate ( $(\text{NH}_4)_2\text{SO}_4$ ), or ammonium chloride ( $\text{NH}_4\text{Cl}$ ), respectively. These are important components for producing secondary inorganic aerosols (SIAs) (Park *et al.*, 2019; Hsieh and Chen, 2010; Sharma *et al.*, 2009). Such reactions result in reduced visibility and adverse effects on the human body (Kang *et al.*, 2020). Among the particulate matter currently found in South Korea, SIAs account for more than 50% of secondary particulate matter (Kim *et al.*, 2020; Park *et al.*, 2018), whereas  $\text{NH}_4\text{NO}_3$  and  $(\text{NH}_4)_2\text{SO}_4$  account for 35–62% of all secondary particulate matter (Jordan *et al.*, 2020).

Since  $\text{NH}_3$  was identified as a major component of SIA formation, studies on the distribution of  $\text{NH}_3$  in the atmosphere have been conducted worldwide. In the United States of America,  $\text{NH}_3$  concentrations in various regions of the country have been measured since 2007 using passive samplers that capture  $\text{NH}_3$  over a long time through the Ammonia Monitoring Network (AMoN) project of the National Atmospheric Deposition Program (NADP) (Zhou *et al.*, 2015). China has also studied the concentration of  $\text{NH}_3$  in its atmosphere using passive samplers (Pan *et al.*, 2018). Although the passive sampler method has the advantage of being capable of simultaneously measuring  $\text{NH}_3$  concentrations at various locations, it has the disadvantage of being unable to identify changes in concentration over time. Research on changes in  $\text{NH}_3$  concentration over time, using real-time  $\text{NH}_3$  measurement equipment, is being actively conducted (Zhou *et al.*, 2019). This real-time measurement is disadvantageous as it makes it difficult to accurately measure  $\text{NH}_3$  concentrations due to underestimation resulting from a loss in the inflow tube, attributed to a high  $\text{NH}_3$  adsorption force (Yi *et al.*, 2021; Bobruzki *et al.*, 2010). The real-time measurement of black carbon also has disadvantages at low concentration in some cases (Lee, 2019). Research is being actively conducted on these real-time measurements to resolve the underestimation (Pollak *et al.*, 2019; Ellis *et al.*, 2010). However, there is a lack of research on the degree of  $\text{NH}_3$  adsorption onto the inflow tube and the resultant reduced  $\text{NH}_3$  concentration when measuring atmospheric  $\text{NH}_3$  levels.

Therefore, this study aimed to investigate the degree to which  $\text{NH}_3$  is adsorbed onto inlet tubes using real-time  $\text{NH}_3$  analysis equipment. Additionally, the degree to which  $\text{NH}_3$  is adsorbed onto the tube was studied according to moisture, tube length, and heating status

after tubes made of different materials were selected, with the ultimate objective of identifying a material that is most suitable for use in actual measurements. Furthermore, the “most suitable” experimental tube identified here is defined as an inlet tube for real-time analysis equipment, to compare the actual atmospheric  $\text{NH}_3$  concentrations and the  $\text{NH}_3$  concentrations measured at one-week intervals using  $\text{NH}_3$  adsorption and collection methods.

## 2. EXPERIMENT

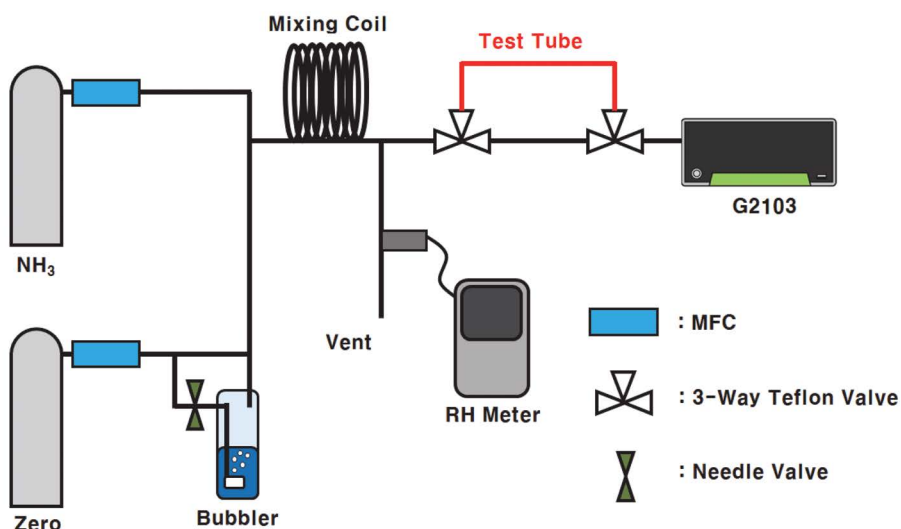
### 2.1 Measurement Site

In this study, a comparison of the properties of  $\text{NH}_3$  adsorption according to moisture, inlet tube length, inlet tube material, and heating status was carried out at the Natural Science College on the Global Campus at the Hankuk University of Foreign Studies, Cheoin-gu, Yongin-si, Gyeonggi-do, South Korea (37.34°N, 127.27°E). To further identify the differences in  $\text{NH}_3$  concentrations between real-time analysis equipment and the method of analyzing  $\text{NH}_3$  after long-term data collection, atmospheric  $\text{NH}_3$  concentrations were measured from May 19, 2020, to July 12, 2020, and from December 4, 2020, to January 3, 2021, at the Honam Air and Environment Research Institute located in Gwangju, South Korea (35.23°N, 126.85°E). The Honam Air and Environment Research Institute is located northwest of the Gwangju Metropolitan City, with agricultural land near the measuring station and residential complexes concentrated to the south side of the measuring station.

### 2.2 Method for Measuring $\text{NH}_3$ Adsorption Depending on Moisture and Inlet Sampling Conditions

Real-time  $\text{NH}_3$  measurements, according to humidity and heating of inlet tubes, were analyzed at intervals of 1 s using the G2103 (Picarro, California, USA), based on the principle of cavity ring-down spectroscopy (CRDS). Standard  $\text{NH}_3$  gas at a concentration of 1.001 ppm (Rigas, Daejeon, Korea) and purified zero air (Union Gas, Gyeonggi-do, Korea) were diluted to 100 ppb using a mass flow controller (MKP, Gyeonggi-do, Korea) to measure atmospheric  $\text{NH}_3$  concentrations. Moreover, by installing an additional needle valve and a bubbler in the tube that connects to zero air, the moisture content in the sample can be adjusted, as zero air can contain mois-





**Fig. 1.** Schematic diagram of  $\text{NH}_3$  adsorption test. The bubbler flow and composition of the test tube (red line) were changed after each measurement.

ture. All background tubes through which the gases were diluted and passed through were made of PTFE, with an outer diameter of 6.35 mm and valves divided from the background tube to the sample tube (made of Teflon) to minimize  $\text{NH}_3$  adsorption. To measure the amount of moisture produced through the bubbler, HYGROLOG NT (Rotronic AG, Switzerland), a temperature and moisture meter, were additionally installed in a discharge tube without entering the equipment (see Fig. 1).

The various tube materials used to investigate the degree of  $\text{NH}_3$  adsorption, according to the material of the inlet tube, were semi-seamless tubes (SUS316L) made out of perfluoroalkoxy (PFA), polytetrafluoroethylene (PTFE), and polyvinylidene fluoride (PVDF) (see Table 1) with an outer diameter of 6.35 mm to minimize the difference due to the tube diameter. Furthermore, a tube made of PTFE (outer diameter: 6.35 mm) was divided into 1, 2, 3, and 4 m lengths to study the degree of  $\text{NH}_3$  adsorption according to tube length. The relative humidity (i.e., 20, 40, 60, and 80%) of the injected sample was altered to determine the effect of moisture on adsorption (see Table 2). In all experiments conducted in this study, a waiting time of 60 min was spent both before and after the experiment for each tube to stabilize the background tube at a specific injection concentration, temperature, and humidity. Moreover, to keep the experimental tubes as clean as possible, they were cleaned from inside using  $\text{N}_2$  (Air Korea) for 2 h both before and after use.

**Table 1.** Materials used during  $\text{NH}_3$  adsorption test.

| Tube material           | Manufacturer | Outer diameter (mm) | Inner diameter (mm) |
|-------------------------|--------------|---------------------|---------------------|
| Semi seamless tube      | Hohwon       | 6.35                | 4                   |
| Perfluoro alkoxy        | iXAK         | 6.35                | 4                   |
| Polytetrafluoroethylene | iXAK         | 6.35                | 4.4                 |
| Polyvinylidene fluoride | Masterflex   | 6.35                | 2.6                 |

To investigate the adsorptive properties of  $\text{NH}_3$ , the area of adsorption was reduced until  $\text{NH}_3$  concentrations were reduced after changing  $\text{NH}_3$  concentrations using the experimental tube, which then returned to its original concentration before the induced change. These data were then used to calculate the ratio of lost  $\text{NH}_3$ , as shown in Fig. 2 (Vaithinen *et al.*, 2014).

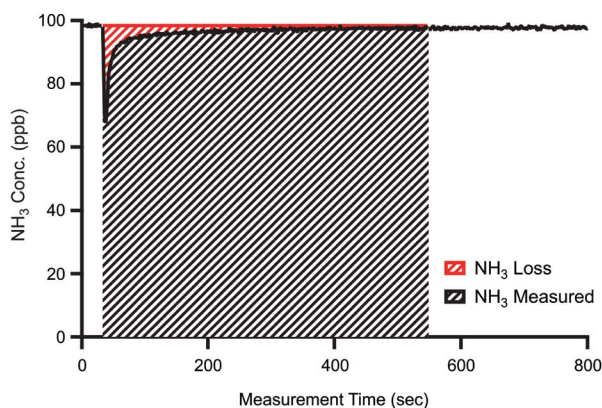
### 2.3 Measurement of Atmospheric $\text{NH}_3$ Using Real-time and Non-real-time Measurement Methods

For the measurement of atmospheric  $\text{NH}_3$  concentrations, real-time analysis was carried out using the EAA-30r-EP (Los Gatos Research, California, USA) from May 2020 to July 2020 and from December 2020 to January 2021; used alongside G2103 in December 2020, the samples from this equipment were collected using annular denuders (URG Corporation, USA) and passive



**Table 2.** Measurement conditions of each test.

| Test type     | Tube material           | Length (m) | Heating | RH (%)         |
|---------------|-------------------------|------------|---------|----------------|
| Material      | Semi seamless tube      | 1          | No      | 0              |
|               | Perfluoro alkoxy        | 1, 2       | No      | 0              |
|               | Polytetrafluoroethylene | 1, 2       | No      | 0              |
|               | Polyvinylidene fluoride | 1, 2       | No      | 0              |
| Length and RH | Polytetrafluoroethylene | 1, 2, 3, 4 | No      | 20, 40, 60, 80 |
| Heating       | Polytetrafluoroethylene | 2          | Yes, No | 20, 40, 60, 80 |



**Fig. 2.** Real-time measurement of  $\text{NH}_3$  loss used to calculate adsorption ratio. The red area indicates the loss of  $\text{NH}_3$ , and black indicates the measured concentrations of  $\text{NH}_3$ .

samplers (Radiello, Pavia, Italy) every week during the study period (see Fig. 3). Before measurement, the EAA-30r-EP equipment designed to measure real-time  $\text{NH}_3$  and the G2103 measurements from December 2020 to January 2021 were calibrated by diluting 1 ppm of standard gas. Because of the characteristics of EAA-30r-EP, it can be calibrated using only one concentration; it was calibrated by injecting 38.23 ppb, followed by sequential injections of 29.36, 19.66, 9.85, and 0 ppb after calibration to ensure the reliability of the measured values at low concentrations, as shown in Fig. 4 (slope: 1.03, intercept: -0.8). Unlike EAA-30r-EP, G2103 can be calibrated using various concentrations; G2103 was calibrated using 38.23, 29.36, 19.66, 9.85, and 0 ppb injections into the EAA-30r-EP, followed by 29.36, 9.85, and 0 ppb re-injections after calibration, to ensure reliability even at low concentrations (slope: 0.99, intercept: 0.41).

The passive sampler collected samples every week, using 10 mL of ultrapure water (DI water) for elution, after which the  $\text{NH}_4^+$  concentration was measured using

Dionex Aquion (Thermo Fisher Scientific, USA) equipment. Dionex Aquion utilizes ion chromatography through a 20 mM mobile phase of  $\text{CH}_3\text{SO}_3\text{H}$ , a CS12A column, and a guard column of CG12A. The concentration of atmospheric  $\text{NH}_3$  was calculated using Eq. 1.

$$D_{\text{NH}_3}(T, P) = D_{0.1} \times \left(\frac{P_0}{P}\right) \times \left(\frac{T}{T_0}\right)^{1.81} \quad (1)$$

where  $D_{\text{NH}_3}$  is the diffusivity of  $\text{NH}_3$  in the atmosphere, calculated using the  $D_{0.1} = 0.1978 \text{ cm}^2 \text{ s}^{-1}$  when the temperature ( $T$ ) and pressure ( $P$ ) at the time of measurement are  $0^\circ\text{C}$  and 1 atm, respectively (Massman *et al.*, 1998). The adsorption flow rate ( $Q_{\text{NH}_3}$ ) in the passive sampler was calculated using Eq. 2.

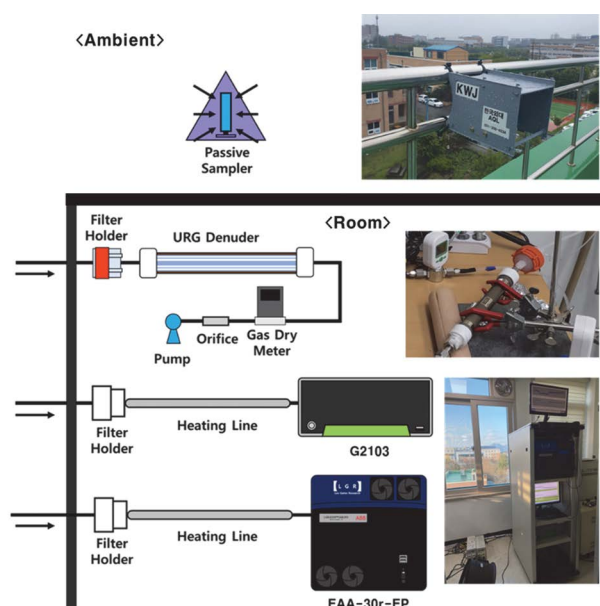
$$Q_{\text{NH}_3} = D_{\text{NH}_3}(T, P) \times \frac{A}{\Delta X} \quad (2)$$

where  $A$  is the cross-sectional adsorption area available to the passive sample, and  $\Delta X$  is the diffusion distance of the sampler. According to a previous study (Puchalski *et al.*, 2011),  $A/\Delta X$  values of the  $\text{NH}_3$  passive sampler of Radiello used in this study were reported to be 14.2 cm.  $Q_{\text{NH}_3}$  was used to calculate the concentration of atmospheric  $\text{NH}_3$  ( $C_{\text{NH}_3, \text{passive}}$ ), and the mass of  $\text{NH}_3$  ( $m_{\text{NH}_3}$ ) calculated by ion chromatography (IC) using Eq. 3 is as follows:

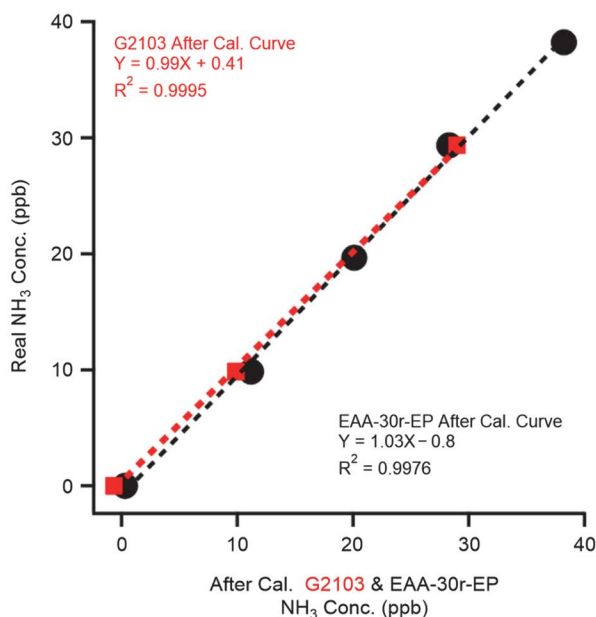
$$C_{\text{NH}_3, \text{passive}} = \frac{10^6 \times m_{\text{NH}_3}}{t \times Q_{\text{NH}_3}} \quad (3)$$

Samples were collected every alternate week using an annual denuder and phosphorous acid; a capture material, such as a passive sampler was dissolved in methanol to coat the denuder. They were extracted using 10 mL of ultrapure liquid and analyzed using the same method as that of a passive sampler, and the concentration of  $\text{NH}_4^+$  in the atmosphere ( $C_{\text{NH}_3, \text{denuder}}$ ) was calculated using Eq. 4:





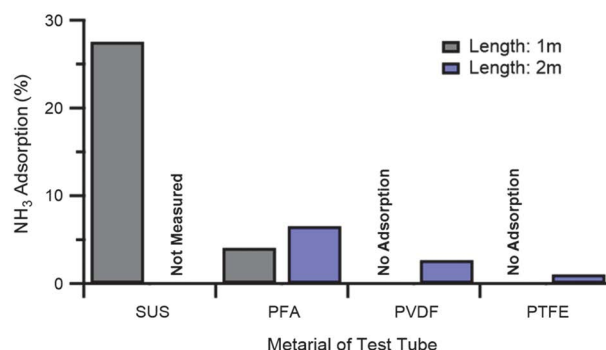
**Fig. 3.** The schematic diagram for measuring ambient  $\text{NH}_3$  concentration.



**Fig. 4.** Post-calibration curve of real-time  $\text{NH}_3$  measuring instruments.

$$C_{\text{NH}_3, \text{denuder}} = \frac{0.945 \times c_{\text{NH}_4} \times V_{\text{ext}}}{V_{\text{act. air}}} \quad (4)$$

where 0.945 is the ratio of the weights of  $\text{NH}_3$  and  $\text{NH}_4^+$ ,  $c_{\text{NH}_4^+}$  is the concentration of  $\text{NH}_4^+$  measured by ion chromatography (in  $\mu\text{g m}^{-3}$ ),  $V_{\text{ext}}$  is the amount of ultrapure



**Fig. 5.** Adsorption ratio of  $\text{NH}_3$  on different test tube materials.

liquid used for the denuder extraction (in L), and  $V_{\text{act. air}}$  is the amount of sample collected from the atmosphere (L).

### 3. RESULTS

#### 3.1 $\text{NH}_3$ Adsorption Depending on Moisture and Inlet Conditions

Upon comparing the degree of adsorption according to the different tube materials, the concentration of  $\text{NH}_3$  absorbed by SUS was the highest (27.53%) when a 1 m tube was used without moisture, followed by PFA at approximately 4.08% (see Fig. 5); PVDF and PTFE did not show  $\text{NH}_3$  adsorption. In the 2 m experimental tube, the SUS tube was excluded because it showed the highest adsorption; the adsorption onto other materials was in the descending order of PFA (approximately 6.56%), PVDF (approximately 2.67%), and PTFE (approximately 1.03%). Based on these results, the PTFE tube was found to have the lowest degree of  $\text{NH}_3$  adsorption; thus, further experiments in this study on humidity, length, and inlet tube heating using a PTFE tube need to be conducted.

The concentration of  $\text{NH}_3$ , according to the humidity divided by the length of the PTFE tube, was stabilized at 100 ppb for a similar time. The adsorption ratio of all the tubes measured was very low, that is, 1%. The differences in concentration reduction were due to the moisture influencing the  $\text{NH}_3$  concentration, which momentarily dropped immediately after  $\text{NH}_3$  was injected (see Fig. 6). It was judged that regardless of the length, the degree of instantaneous adsorption of  $\text{NH}_3$  decreased with increasing moisture. It was found that moisture reduces the adsorption of  $\text{NH}_3$  at an appropriate humidity level



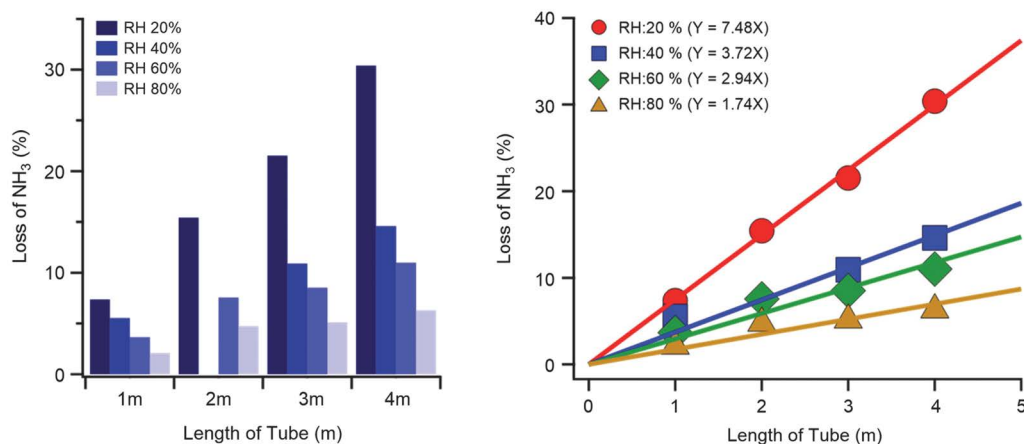


Fig. 6. The maximum loss of NH<sub>3</sub> at different lengths and RHs of each test tube.

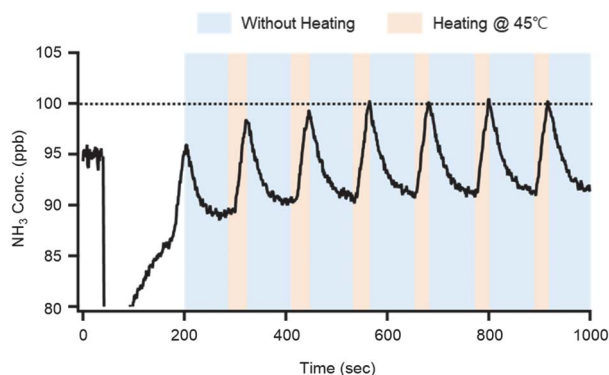


Fig. 7. Timeline of NH<sub>3</sub> adsorption by a heating test tube.

(Vaithinen *et al.*, 2018). It was confirmed that NH<sub>3</sub> adsorption at high moisture could be measured more accurately through real-time measurements of the general air quality. However, as the length of the tube increased, the degree of NH<sub>3</sub> adsorption increased. The decrease in NH<sub>3</sub> concentration according to the length was found to be 1.74% m<sup>-1</sup> at 80% moisture, 2.94% m<sup>-1</sup> at 60% moisture, 3.72% m<sup>-1</sup> at 40% moisture, and 7.48% m<sup>-1</sup> at 20% moisture. Thus, it was concluded that the length of the inlet tube affected the real-time NH<sub>3</sub> concentration measurements, especially in areas with low moisture.

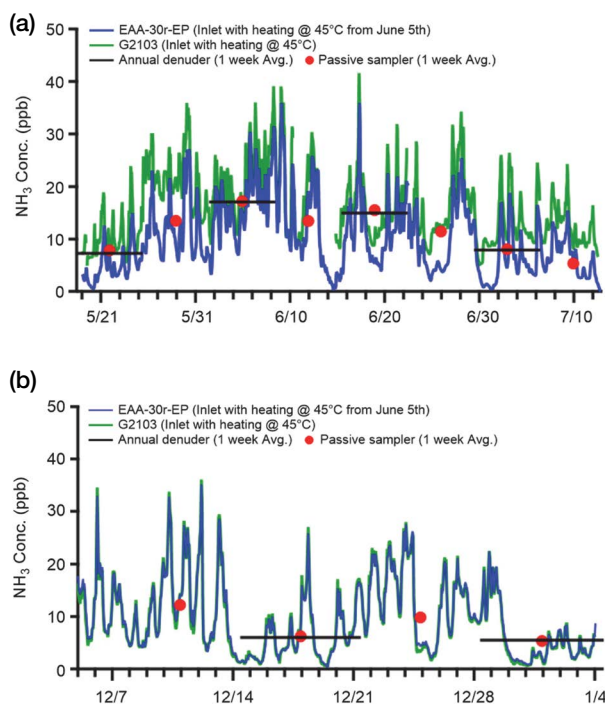
Fig. 7 shows the change in the concentration measured when the heating was repeatedly turned off and on in the experimental tube to investigate whether there is a difference in NH<sub>3</sub> adsorption and if the inlet tube is heated or not. Neuman (1999) reported that the adsorption of HNO<sub>3</sub> in the sampling tube, which is similar to the chemical properties of NH<sub>3</sub> (sticky molecules), was not

observed when the tube temperature was higher than 30°C. In this test, 45°C was chosen because the box and cavity temperatures of G2103 are usually 45°C. When 100 ppb NH<sub>3</sub> was injected into the experimental tube, it was measured to be 90.96 ppb without heating. However, it rapidly increased to 100.31 ppb during heating. Thus, the concentration of NH<sub>3</sub> adsorbed to the experimental tube increased as the degree of adsorption in the tube was reduced by heating compared to that without heating.

### 3.2 Measurement of Atmospheric NH<sub>3</sub> Using Real-time and Non-real-time Measurement Methods

Real-time NH<sub>3</sub>, measured using EAA-30r-EP and G2103 from May 19, 2020, to July 12, 2020, at the Honam Air and Environment Research Institute, was prepared by manufacturing a PVDF tube, conventionally announcing it to have the lowest adsorption of NH<sub>3</sub> (Vaithinen *et al.*, 2018). The length of the inlet tube was 2 m, and the tube was heated to 45°C. At that time, EAA-30r-EP and G2103 were calibrated using different calibration devices and gases. Before June 5, measurements were performed with the heater of the inlet tube of EAA-30r-EP turned off to confirm the difference in ammonia concentration measured when the inlet tube was not heated and when it was heated. For EAA-30r-EP and G2103, NH<sub>3</sub> measurements were performed between December 5, 2020, and January 3, 2021, and these were manufactured using PTFE inlet tubes, that is, those measured to have the lowest degree of adsorption in section “3.1 NH<sub>3</sub> adsorptions depending on moisture and inlet

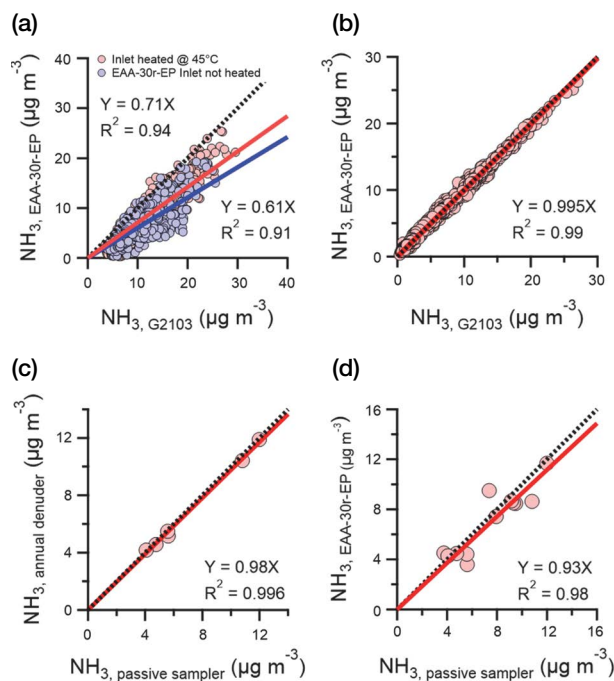




**Fig. 8.** Timeline of  $\text{NH}_3$  measurement of ambient in Gwang-ju from (a) May 2020 to July 2020. The EAA-30r-EP inlet was not heated from May 5 to June 5, and the two instruments were calibrated separately. (b) Measurement between December 2020 and January 2021 after completing calibration by the same system.

tube conditions” Furthermore, measurements were performed after simultaneous calibration using the same calibration device and calibration gas.

From May 19, 2020, to July 12, 2020, the average concentration of  $\text{NH}_3$  measured using the EAA-30r-EP real-time measuring equipment was 10.09 ppb ( $\pm 6.74$  ppb) and that by using the G2103 equipment was 16.11 ppb ( $\pm 6.82$  ppb). The passive sampler measured data every week during the same period. The average value was 10.74 ppb ( $\pm 3.84$  ppb); the annual denuder averaged 11.41 ppb ( $\pm 4.06$  ppb). The average concentration of  $\text{NH}_3$ , measured from December 5, 2020, to January 3, 2021, was 9.54 ppb ( $\pm 6.98$  ppb) for the EAA-30r-EP, 9.46 ppb ( $\pm 7.16$  ppb) for the G2103, 8.4 ppb ( $\pm 2.95$  ppb) for the passive sampler, and 5.74 ppb ( $\pm 0.29$  ppb) for annual denuder (see Fig. 8). The standard deviation of the passive sampler and annual denuder was lower than that of real-time analysis equipment because the concentrations calculated from the sample collected for one week cannot be reflected in the change in  $\text{NH}_3$  concentration, which changes in real-time within a certain



**Fig. 9.** Comparison of various types of  $\text{NH}_3$  measurement. (a) Comparison of real-time  $\text{NH}_3$  measurement by heating or not heating the inlet (May 2020–July 2020). (b) Comparison of two types of real-time  $\text{NH}_3$  measuring instruments (December 2020–January 2021). (c) Comparison of annual denuder with a passive sampler (May 2020–July 2020 and December 2020–January 2021), and (d) Comparison of real-time measurements with the passive sampler (June 2020–July 2020 and December 2020–January 2021).

range. For the annual denuder, samples were collected every alternate week. Hence, the concentration was lower than that measured by the passive sampler every week and other real-time measurement equipment.

Fig. 9 shows the correlation between the analysis methods both in real-time and non-real-time during the same period. To minimize the change in concentration due to temperature differences over time, the results of real-time  $\text{NH}_3$  concentration were averaged to 1 h data and then converted from ppb into  $\mu\text{g m}^{-3}$  using atmospheric temperature and pressure measurements by the Honam Air and Environment Research Institute. Fig. 9 a is based on comparisons between the two types of real-time measuring equipment used between May and July 2020; the EAA-30r-EP, without heating the inlet tube, was approximately 39% lower than G2103 with a heated inlet tube. When EAA-30r-EP is heated, it measures approximately 29% lower than G2103; a 10% reduction



in the difference was observed based on whether the inlet tube was heated or not, indicating that heating the inlet tube during the real-time measurement is necessary. Moreover, based on comparisons of  $\text{NH}_3$  concentrations measured in real-time using different calibration devices and gases, the coefficient of determination was found to be 0.94, indicating dispersed correlation when inlet tubes were used under similar conditions. To investigate whether the dispersed correlation resulted from using other equipment for measurements between December 2020 and January 2021, the aforementioned real-time measurement devices were calibrated using the same calibration device and gas (Fig. 9, b). EAA-30r-EP was found to be 0.5% lower than that of G2103, and the coefficient of determination was 0.99, that is, a very high correlation. It has been confirmed that the calibration method and the heating of the inlet tube are very important for real-time  $\text{NH}_3$  measurements. Fig. 9, c shows that the annual denuder collecting data biweekly for one week was 2% higher than the passive sampler collecting  $\text{NH}_3$  during the same period. The coefficient of determination was calculated to be 0.996, showing a very high correlation between the two non-real-time  $\text{NH}_3$  measurements. Based on the comparisons and analysis of the  $\text{NH}_3$  concentration measured by the passive sampler collected every week during the measurement period and real-time equipment with a heated inlet tube (June 5, 2020, to July 12, 2020, and December 5, 2020, to January 3, 2021) (see Fig. 9, d), the concentration of  $\text{NH}_3$  measured using real-time equipment and non-real-time measurement methods was correlated at 0.98, with a difference of 7%.

## 4. CONCLUSIONS

This study evaluated  $\text{NH}_3$  adsorption in inlet tubes used in real-time  $\text{NH}_3$  measurements according to the material, length, humidity, and heating of the inlet tube. Furthermore, atmospheric  $\text{NH}_3$  was measured using the inlet tube with the lowest adsorption. It was compared and analyzed with the concentration measured in the passive sampler and annual denuder, non-real-time measurement methods. The materials used to make tubes for the inlet tube experiment were SUS316L, PFA, PTFE, and PVDF; the injection concentration of  $\text{NH}_3$  was stabilized at 100 ppb. The absorption rate of  $\text{NH}_3$  in the PTFE tube was measured to be the lowest (i.e., 1.03%) at

2 m when using the PTFE tube. Based on these results, the  $\text{NH}_3$  adsorption, according to length and moisture, measured using the PTFE tube was the lowest, the relative humidity increased from 20% to 80%, and the degree of instantaneous adsorption decreased from 7.48 ppb  $\text{m}^{-1}$  to 1.74 ppb  $\text{m}^{-1}$ ; indicating that the moisture reduces  $\text{NH}_3$  adsorption to the inlet tube. Furthermore, the degree of adsorption to the tube was reduced when the experimental tube was heated. It was proven to be more effective at low humidity.

From May 2020 to July 2020 and December 2021 to January 2021, atmospheric  $\text{NH}_3$  was measured using real-time techniques and non-real-time measurement methods at the Honam Air and Environment Research Institute. The results indicated that the average concentrations of  $\text{NH}_3$  measured with real-time equipment EAA-30r-EP were 10.09 ppb and 9.54 ppb for both study periods, respectively. The concentrations measured with G2103 were 16.11 ppb and 9.46 ppb, respectively. The average concentration from the passive sampler, a non-real-time measuring instrument, was 10.74 ppb and 8.4 ppb, respectively. When comparing the two methods, the real-time methods, EAA-30r-EP, and G2103 showed a concentration difference of 0.5%. The non-real-time measurement method using the annual denuder passive sampler, showed a difference of 2%.

Moreover, the  $\text{NH}_3$  concentration was approximately 10% lower when the inlet tube of the real-time equipment was not heated. It was also confirmed that there is a difference in concentration according to the calibration device and gas. Overall, real-time  $\text{NH}_3$  measurement can minimize the lack of  $\text{NH}_3$  measurement using an inlet tube made of PTFE, a material that can be heated. It is important to provide uniformity to the calibration method, and the calibration gas used when measuring the  $\text{NH}_3$  concentration in real-time at various places or times.

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## DISCLAIMER

All the results in this study were obtained by setting the parameters for the passive sampler and denuder, according to the referenced literature.

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