

Development of an Automated Diffusion Scrubber-Conductometry System for Measuring Atmospheric Ammonia

Bokyoung Lee,^{†,*} Chong Keun Lee, and Dong Soo Lee*

Department of Chemistry, Yonsei University, Seoul 120-749, Korea. *E-mail: dslee@yonsei.ac.kr

[†]University College, Yonsei University, Seoul 120-749, Korea. *E-mail: bklee@yonsei.ac.kr

Received February 8, 2011, Accepted April 14, 2011

A semi-continuous and automated method for quantifying atmospheric ammonia at the parts per billion level has been developed. The instrument consists of a high efficiency diffusion scrubber, an electrolytic on-line anion exchange device, and a conductivity detector. Water soluble gases in sampled air diffuse through the porous membrane and are absorbed in an absorbing solution. Interferences are eliminated by using an anion exchange devices. The electrical conductivity of the solution is measured without chromatographic separation. The collection efficiency was over 99%. Over the 0-200 ppbv concentration range, the calibration was linear with $r^2 = 0.99$. The lower limit of detection was 0.09 ppbv. A parallel analysis of Seoul air over several days using this method and a diffusion scrubber coupled to an ion chromatography system showed acceptable agreement, $r^2 = 0.940$ ($n = 686$). This method can be applied for ambient air monitoring of ammonia.

Key Words : Ammonia, Diffusion scrubber, On-line measurement, Conductivity, Non-linear response

Introduction

Ammonia acts as a neutralizer of acidic gases and plays important roles in aerosol formation and in the nitrogen cycle. The principle natural sources of ammonia are the metabolisms of living things and the degradation of animal manure. It also is emitted during agricultural activities¹ and recently motor vehicle equipped with a catalytic converter emerging an important source of ammonia.^{2,3} Ammonia is known to be acting as a catalyst for the oxidation of the acidic gases, SO₂ and NO_x, and consequently stimulates their deposition.⁴⁻⁶ Ammonia is a base but it converts to acids after deposition into soil and causes soil acidification. An Excess of ammonia also causes eutrophication of the soil and surface water. And it brings about atmospheric visibility reductions through the formation of ammonium aerosols.⁴

Owing to the importance of atmospheric ammonia, the development of simple and reliable analytical methods has been a priority since the 1950s. The conventional methods for sampling ammonia are the use of an impinger or a filter-pack. For using impinge, dilute solutions of strong acid, 0.05 M H₂SO₄ for example, is used for the absorbing solution.⁷ In filter-pack method, ammonia is collected on a filter membrane, which is coated with suitable acids.⁸ Instead of the filter, porous metal disk coated with citric acid was recently used to collect indoor ammonia.⁹ These are simple methods that provide quantitative sampling, so they have been used as the representative official methods.^{9,10}

However, they require long sampling times due to low concentration rates, and they are not easily automated. Most importantly, they need a prefilter to remove particulate matters from the sampled air, which causes various sampling artifacts. Positive errors are not avoidable due to the volatilized ammonia from the ammonium salts collected on

the prefilters.⁴ Negative errors are also possible by the sorption of gaseous ammonia by the filter matrix and/or the acidic particulate matters collected on the prefilters. These sampling artifacts are more significant at high sampling rate in warm wether. The absence of the prefilters results in at least partial collection of the aerosol ammonium and cause positive errors.

Diffusion-based methods such as the diffusion denuder¹¹⁻¹⁴ and the diffusion scrubber^{4,15,16} are used for the separate sampling of gaseous and particulate species in the atmosphere. Using a diffusion denuder, water soluble gases are absorbed into the thin film of the absorbent, typically water or an aqueous solution, which flows over the surface of chemically-treated glass. A diffusion scrubber has a porous membrane between the sampled air and the absorbent solution, and the water soluble gases are dissolved through the membrane into the absorbent. These methods provide improved concentration rates and lower limits of detection (LOD) by using a small volume of absorbent and a large flow rate for the sampled air. Our previous article showed that atmospheric gaseous ammonia and low molecular aliphatic amines can be automatically analyzed using a high efficiency planar type diffusion scrubber coupled to an ion chromatography (HEDS-IC) system.¹⁷ Ion chromatographic analysis provides selectivity but requires longer analysis time for the separation.

Direct detection of the ammonia without separation has the advantage of a short analysis time and provides real time or semi-real time monitoring results. Of these, conductometry is the simpler and faster method, as it does not require any derivatization reactions. However, direct detection requires the elimination of interfering, water soluble gases such as SO₂, CO₂, and NO_x before the conductivity measurement.

Friedl used a diluted sulfuric acid as an absorbing solution

and determined the ammonia concentration by measuring the conductivity decrease due to the neutralization of the sulfuric acid by absorbed ammonia.¹⁸ Carlson collected Kjeldahl digests into a solution, and ammonia was selectively evaporated from the absorbing solution through the addition of sodium hydroxide.¹⁹ The evaporated gaseous ammonia was re-collected through a porous silicon membrane tube into deionized water inside the porous membrane tube. Conductivity was also measured. Wyers *et al.* developed a method for ammonia measurement using annular denuder sampling with online analysis (AMANDA).²⁰ In AMANDA, water soluble atmospheric gases are collected using an annular denuder, and the absorbing solution is mixed with a 0.50 M sodium hydroxide solution in order to selectively evaporate the basic gases, typically ammonia.^{5,20,21} The ammonia gas migrates through a porous PTFE membrane and absorbs into deionized water. Conductivity is measured in order to determine the concentration of ammonia. Slania *et al.* developed a monitoring system for aerosolized ammonia by combining AMANDA with an aerosol collector.²²

This involves the ammonia in an absorbing solution being selectively re-converted into a gas phase, migrating through a porous membrane, then being re-dissolved into an aqueous solution. The interferences of acidic gases such as SO₂, CO₂, HNO₂ and HNO₃ were eliminated from the sample gas in the phase transition process. However, time consuming calibration process is needed due to the decrease in collection efficiency, which is approximately 30% under normal conditions. In addition, the nonlinear response of conductivity was important at a sub-ppb level of ammonia. Carlson and Pasquini used quadratic calibration curves, but these are not applicable to concentrations of ammonia below 10⁻⁵ M.^{19,23} Wyers *et al.* added 60 ppb ammonium salt to the sodium hydroxide solution in order to solve the non-linear response problem.²⁰

In this study, HEDS coupled with an electrolytic anion exchanging device was used to selectively collect gaseous-phase ammonia from the atmosphere. The function of the electrolytic anion exchanger was the continuous removal of the anionic species produced from the dissolved acidic gases. Water soluble gases that exist in comparable levels to that of ammonia become potential interferences for the conductometric detection. All of the water soluble atmospheric gases except for ammonia and amines exist in the form of anions and can be absorbed into the solution. The concentrations of amines are below 1/1000th that of the ammonia.¹⁷ Therefore, only the anionic species must be removed, whereas the cationic interference need not be. As this device avoids the re-volatilization of ammonia from the absorbing solution with a strong base, the sampling device can be simplified, and collection efficiency loss is not a concern. The non-linear response problem has been addressed by adding small amounts of sodium salts to the absorbing reagents. The method was applied to air monitoring over the city of Seoul, and a comparison analysis was performed to assess the method.

Theoretical Review of the Non-linear Response of the Conductivity. One of the most important problems in the conductometric detection of ammonia is a non-linear response at low ppbv levels. The total conductivity of the solution is the sum of the concentrations of the dissolved ions multiplied by their limiting molar conductances.

$$\Lambda_{tot.} = \sum C_i \lambda_i, \quad (1)$$

where Λ_{tot} is total conductivity, λ_i is a limiting molar conductance of ion i , and C_i is the molar concentration of ion i .

When ammonia is dissolved into deionized water, NH₄⁺, H⁺ and OH⁻ are the ionic species in the solution. The total conductivity is thus given by,

$$\Lambda = C_{NH_4^+} \lambda_{NH_4^+} + C_{H^+} \lambda_{H^+} + C_{OH^-} \lambda_{OH^-}. \quad (2)$$

For the electrical neutrality of the aqueous solution,

$$[H^+] + [NH_4^+] = [OH^-]. \quad (3)$$

So, self dissociation constant of water, $K_w = [H^+][OH^-] + [NH_4^+]$.

The molar concentrations of H⁺ and OH⁻ can be described as functions of the ammonium concentration by solving equation (4). Total conductivity in equation (2) is given as a function of the ammonium concentration as follows.

$$\Lambda = \left(\lambda_{NH_4^+} - \frac{\lambda_{H^+}}{2} + \frac{\lambda_{OH^-}}{2} \right) + \frac{(\lambda_{H^+} + \lambda_{OH^-})}{2} \sqrt{[NH_4^+]^2 + 4K_w} \quad (5)$$

The second term in equation (5) represents the deviation from the linear response. This suggests that a non-linear

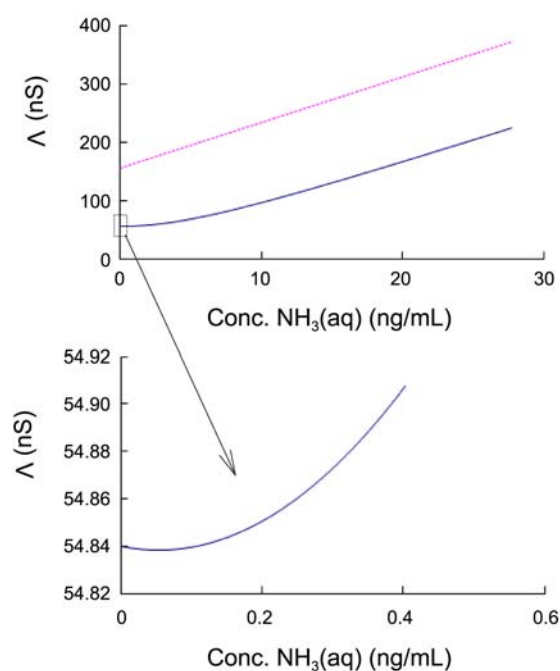


Figure 1. Theoretically calculated conductivity of aqueous solutions of ammonia. The solid line represents for pure water as a solvent and the dashed line represents for 2×10^{-7} M Na₂SO₄ solution as an absorbing solution.

response is more significant when the total conductivity is very low. When the ammonium concentration is very high, $[\text{NH}_4^+] \gg 4K_{10}$, non-linear response is not a significant problem. The calculated conductivity derived by equation (5) is shown in Figures 1(a) and (b). As found in Figure 1 (b), the conductivity is lower than that of pure water when the ammonium concentration is less than 0.1 ng/mL.

The nonlinear response principally originated from the suppression of protons due to the production of hydroxide by the hydrolysis reaction of ammonia. As the cation concentration increases, the second term of equation (5) becomes less significant; consequently, the nonlinear response is not an important problem. In order to show this, the calculated conductivity of a 2×10^{-7} M Na_2SO_4 solution as a function of the ammonium concentration is presented as a dotted line in Figure 1. The calculation details and nonlinear response of the suppressed-type ion chromatography will be presented elsewhere.

Experiments

HEDS. The high efficiency diffusion scrubber (HEDS) was fabricated using a modification of Frenzel's design.²⁴ The HEDS consisted of a porous PTFE membrane (70 μm thickness, 0.2 μm pore size, 160 mm \times 25 mm, Osmonics, USA), two Teflon spacers, and a stainless steel support located between two acrylic plates (15 mm thickness, 200 mm \times 40 mm). The volume of the air channel (1 mm thickness \times 175 mm length \times 15 mm wide) was larger than that of the liquid channel (0.5 mm thickness \times 165 mm length \times 15 mm wide). The stainless steel mesh supported the membrane against the hydraulic pressure of swelling. The construction details were described in our previous article.¹⁷

Ammonia Analyzer. The ammonia analyzer consisted of an air pump, an HEDS, a liquid pump, an anion exchange device, and a conductivity detector. The schematic diagram of an ammonia analyzer is presented in Figure 2. An eluent pump and a conductivity detector (Dionex model 4000i) were used for delivery of the absorbing solution and dissolved ammonia detection, respectively. An ion suppressor (CSRS-ultra, Cation Self Regeneration Suppressor, Dionex) was used for the exchange of anions, and a programmable timer (Chronrol, Model CD-03) was used to control the air pump, liquid pump, and sampling duration. The air samples were drawn through polyethylene tubing (Nalgene) using an air pump (Model VP-0125, Medo, Korea). A Visi-float flow meter (Model VFA-3-SGV, Dwyer) was used to control the air flow rate.

Standard Gas Generation. Ammonia standard gases were generated using the process of Dasgupta *et al.*²⁵ A porous PTFE membrane tubing (length: 9 cm, diameter: 2 mm, mean pore size: 3.5 μm , surface porosity: 70%, W. L. Gore and Associates, Elkton, MD) was immersed into a mixed solution of ammonium nitrate (2.0×10^{-4} M) and sodium hydroxide (1.0×10^{-3} M) in an airtight container. Ammonia was diffused through the PTFE membrane into the carrier gas which flowed inside the tube at a rate of 0.6

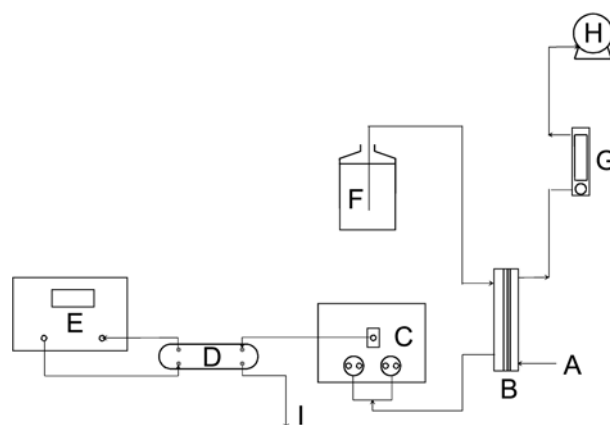


Figure 2. Schematics of the ammonia analyzer. A: Air inlet; B: High efficiency diffusion scrubber; C: IC pump; D: Suppressor; E: Conductivity detector; F: Absorbing solution; G: Flow controller; H: Air pump; I: To waste

$\text{L}\cdot\text{min}^{-1}$. The generated ammonia gas (approximately 200 ppbv) was diluted in a mixing chamber with zero gas. The diluted gas was fed into the HEDS at a flow rate of 0.5 $\text{L}\cdot\text{min}^{-1}$, and the concentration of ammonia in the effluent from the HEDS was determined using an ion chromatograph with standard solutions. Zero gas was prepared through a trap column which was filled with acid-treated silica gel, normal silica gel, activated carbon, and soda lime in a series. Acidified silica gel was made from 200 g silica gel (20 mesh) with 10 mL 6 N sulfuric acid, dried for one night in an oven at 70 $^{\circ}\text{C}$. The temperature of the solution reservoir was maintained at 0.0 ± 0.1 $^{\circ}\text{C}$. In order to avoid condensation of the water vapor in the flow passes through the mixing chamber and sampling lines, the temperature of the gas generation system was maintained at a temperature lower than that of the ambient air.

Automated Ammonia Monitoring System (HEDS-Conductometry). Air samples were drawn with an air pump through an air channel of the HEDS at a flow rate of 0.5 $\text{L}\cdot\text{min}^{-1}$ in the opposite direction as that of the absorbing solution. Absorbing solution flowed through the liquid channel of the HEDS according to gravity. 2.0×10^{-7} M sodium sulfate aqueous solution was used for the absorbing solution in order to overcome the non-linear response of conductivity. The sampled liquid was fed into an anion exchanger (CSRS-ultra, Dionex) at a flow rate of 0.5 $\text{L}\cdot\text{min}^{-1}$ using an IC pump. The electrical current of the CSRS-ultra for the continuous electrolysis of water to produce hydroxide was maintained at 50 mA. In the CSRS-ultra, the anionic interferences such as sulfate, nitrite, carbonate and nitrate were exchanged with the hydroxide ions. The effluent from a suppressor was fed into the conductivity detector. Air flow was stopped for 15 minutes every three hours in order to measure the background conductivity. This method was successfully applied to the monitoring of atmospheric ammonia and indoor ammonia for several times.

For the comparison purpose, simultaneous analysis was performed with HEDS coupled ion chromatography. The

Table 1. Analytical conditions for HEDS-IC system

Pump	Alltech 325 HPLC Pump
Detector	Alltech 350 Conductivity Detector
Analytical column	Dionex CS-12
Suppressor	Dionex Cation Self-Regenerating Suppressor (CSRS-ultra)
Suppressor current	100 mA
Absorbing solution flow rate	0.5 mL/min
Eluent	20 mM MSA
Eluent flow rate	1.0 mL/min
Sample loop volume	250 μ L
Sampling air flow rate	0.5 L/min
Analysis interval	10 min

sampling duration of HEDS-IC was ten minutes. The flow rate of the effluent was 500 μ L \cdot min⁻¹, and the volume of the sample loop was 250 μ L. Therefore, the concentrations for the last 30 seconds in every ten minutes were determined. Ion chromatographic system used in this study consists of Model 325 HPLC pump (Alltech), a CS-12 column (Dionex), a cation self-regenerating suppressor, and a Model 350 conductivity detector. 20 mM methansulfonyl acid is used for the eluent at a flow rate of 1.0 mL \cdot min⁻¹. The sample injection volume was 250 μ L, which is significantly larger than the normal condition. Large sample volume has the advantage of the improvement in the detectability. A comparison experiment was conducted to analyze atmospheric ammonia over Seoul from June 8 through 13, 2001.

Results & Discussion

Collection Efficiency. Collection efficiency, derived by the following equation, was determined using two HEDSs connected in serial, both of which used standard gases.¹⁵

$$f_{\text{exp}}(\%) = \left(1 - \frac{C_2}{C_1}\right) \times 100(\%),$$

where C_1 and C_2 represent the concentrations of ammonium from the effluent from the first and the second HEDS, respectively.

The theoretical collection efficiency for the planner type diffusion scrubber as a function of axial position, in which only one side is a perfect sink, can be calculated with the Gormley-Kennedy equation,^{12,26}

$$1 - f_{\text{calc}} = 0.91^{-6.77\alpha DL/Q}$$

Here, D is the diffusion coefficient of gas, L is the length of the tube, and Q is the volumetric air flow rate. The parameter α is given by $\alpha = 2b/a$, where a and b are the short and long dimensions of the active cross-section of the scrubber, respectively. The diffusion coefficient used for ammonia is 0.23 cm²/s.¹⁵

The collection efficiencies, both those calculated (dotted line) and those experimentally obtained (solid line), for various air flow rates from 0.2 to 1.8 L \cdot min⁻¹ are presented in Figure 3. The standard gas concentration was 50 ppbv,

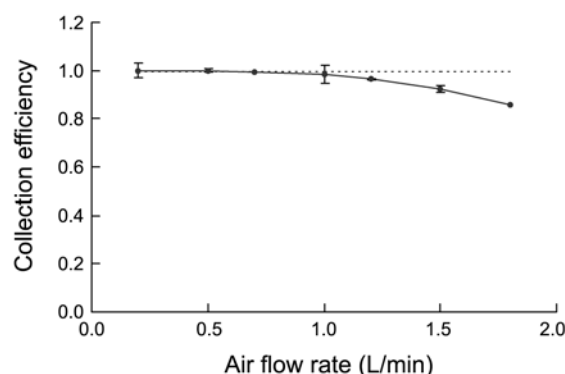


Figure 3. Collection efficiency of HEDS as a function of air flow rate. The error bar means a standard deviations of three measurements.

and the error bar is the standard deviation for three measurements. Experimentally obtained collection efficiencies were lower than the theoretical collection efficiencies, but were still greater than 98% for air flow rates up to 1.0 L \cdot min⁻¹. The deviation from the theoretical performance was more significant with increases in the flow rate. Since the collection efficiency for the absorbing surface calculated with the Gormley-Kennedy equation is for a perfect sink, the experimentally obtained collection efficiency was expected to be lower than that of the theoretical efficiency. The porosity of the PTFE membrane, typically below 1.0, is one of the reasons for the discrepancy. Since the diffusion of the liquid phase is the limiting process in the absorption process of ammonia, the absorption occurred in the boundary, the thin layer of the absorbing solution. At higher flow rates of sample gas, the solution in the boundary layer was saturated with ammonia. As the flow rate of sample gas increased, the practical collection efficiency decreased.

Response Time and Memory Effects. Fast response and a minimum memory effect are important for the real-time analysis of atmospheric gases. After the detector showed stable background conductivity with a zero gas, the gas sampling line was switched to a standard gas of 25 ppbv, and the time needed for obtaining a stable signal was measured. After the detector signal was stabilized with a standard gas, the air pump was stopped and the time at which the detector signal reached background conductivity was measured. Figure 4 shows a typical result. At zero minutes, the gas flow switched from zero air to a 25 ppbv standard gas, and at ten minutes the air pump was stopped. The signal reached 90% of the total within three minutes after the standard gas condition was initiated and stabilized within five to six minutes. One minute after the standard gas flow was stopped, the conductivity started to decrease and reached background conductivity \pm 5% within ten minutes. When the gas flowed in the same direction as the liquid flow, the response time and the memory effect were increased by approximately three times. The gas was eliminated near the exit of the air flow in the opposite direction as that of the gas and liquid flows, while the gas was eliminated near the inlet of the air in the same direction as that of the two flows. This

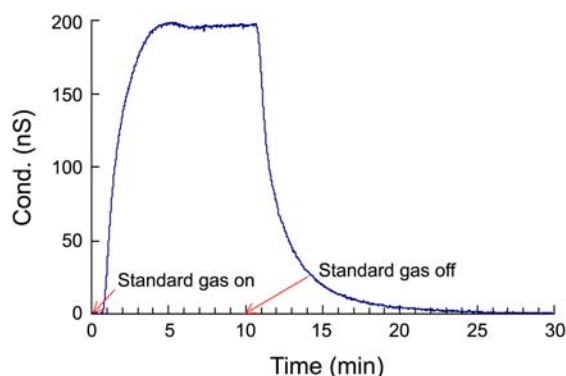


Figure 4. Response time and memory effect. $t = 0$: standard gas on, $t = 10$ min: standard gas stop.

may explain why the memory effect for the counter flows of the air and liquid was less significant.

For fast response and a minimum memory effect, the total volume of liquid path from scrubber to detector has to be minimized. A small volume of liquid in the channel of the HEDS is a good stratagem for fast response. The increase in the liquid flow rate is expected to decrease the memory effect but also decreases the concentration rate and detectability. If the liquid pump (C in figure 2) can be positioned in front of the scrubber, the volume of the sample path and the response time will be shortened. However, this arrangement pressurized the liquid in the HEDS, and the membrane swelled under the hydraulic stress, frequently resulting in liquid leakage. The liquid pump-HEDS-anion exchanger arrangement with a membrane which has better resistance to the pressure leads to a faster response and a reduced memory effect. Thus, we are now experimenting with various membrane materials.

Reproducibility and LOD. For the calculation of reproducibility, a standard gas of 35 ppbv was sampled and analyzed with this system 20 times. The relative standard deviation (σ) was 1.43%. The lower limit of detection (LOD) was determined by 3σ of a repeated analysis of a standard gas whose concentration was near the LOD. The concentration of the standard gas used was 0.96 ppbv, and the standard deviation of 12 sets of measurements was 0.029 ppbv; therefore, the LOD of the method was 0.086 ppbv.

By increasing the gas flow rate and decreasing the liquid flow rate, the LOD can be lowered. However, increasing the air flow rate causes a loss in collection efficiency. Reducing the liquid flow results in a slower response and a more serious memory effect. Furthermore, the lowest concentration of atmospheric ammonia is significantly higher than the LOD. Therefore, there is no need to improve the detectability of the system for atmospheric ammonia monitoring.

Calibration Curves and Linear Dynamic Range. Calibration curves were produced at various background conductivities using deionized water and various concentrations of sodium sulfate solution as absorbing solutions. When 2.0×10^{-7} M and 5.0×10^{-8} M sodium sulfate solutions were used as absorbing solutions, the background conductivities were approximately 100 nS and 25 nS above that of the water,

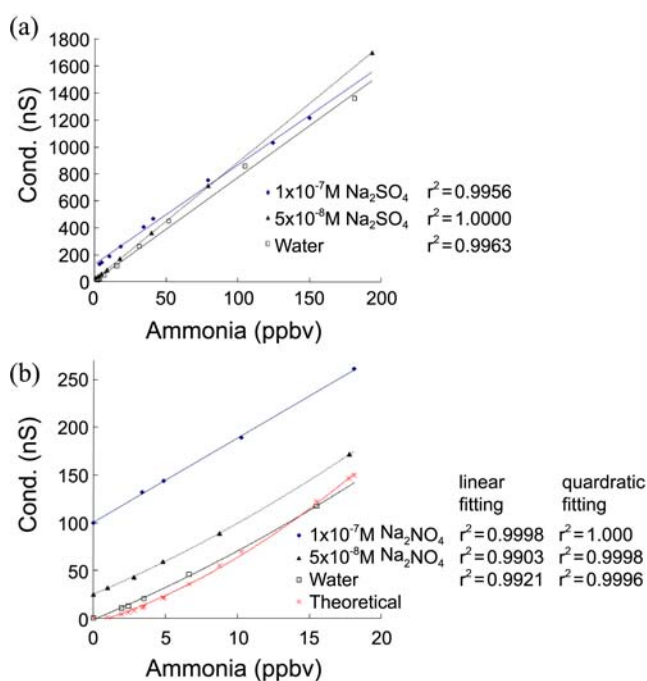


Figure 5. Calibration curves at various background conductivities by using sodium sulfate solutions as absorbing solutions. (a) for the concentration range from 0 to 200 ppbv (b) for the concentration range from 0 to 20 ppbv.

respectively. The calibration curves are shown in Figures 5(a) and (b). The concentration ranges from 0 to 20 ppbv were enlarged in Figure 5(b) in order to show the non-linear response of the conductivity in the lower concentration range. The theoretically calculated conductivity for pure water is also presented in Figure 5(b). As shown in Figure 5(a), the correlation coefficients (r^2) for the deionized water, 5.0×10^{-8} M Na_2SO_4 and 1.0×10^{-7} M Na_2SO_4 cases were 0.9963, 1.0000, and 0.9956, respectively. In all cases, the linear dynamic ranges covered up to 200 ppbv ammonia. The atmospheric concentrations of ammonia were less than 100 ppbv in most cases except near large ammonia point sources like livestock confinement buildings.

However, calibrations curves for the low concentrations, less than 20 ppbv, showed nonlinear responses; the correlation coefficients (r^2) were 0.9921, 0.9903, and 0.9998 for deionized water and for the 5.0×10^{-8} M Na_2SO_4 and for 2.0×10^{-7} M Na_2SO_4 absorbing solutions, respectively. This suggests that the background conductivity must be over 100 nS greater than that of deionized water for linear calibration. When using deionized water and 5.0×10^{-8} M Na_2SO_4 absorbing solutions, the use of quadratic equations ($r^2 = 0.9969$ and $r^2 = 0.9998$ for deionized water and 5.0×10^{-8} M Na_2SO_4 , respectively) may possibly provide better calculation results. The calibration curve for deionized water deviated from the theoretical one. This could be the result of incomplete elimination of anionic impurities in the ion suppressor or trace levels of cationic impurities. Atmospheric ammonia peaked at 50 ppbv in most cases, and approximately 25% of our monitoring data points were below 20 ppbv. Therefore, 1.0×10^{-7} M Na_2SO_4 is recommended for

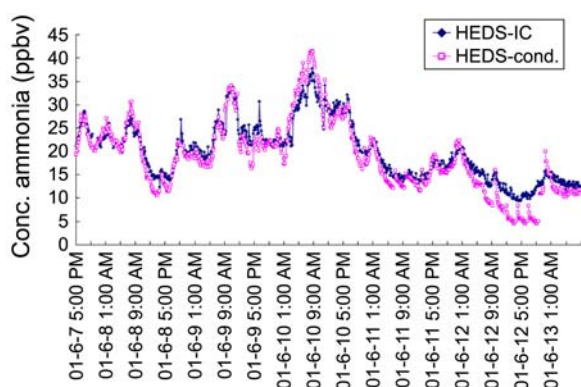


Figure 6. Temporal variation of ammonia in the ambient air at Seoul by using a HEDS-conductivity system (—□—) and HEDS-IC system (—◆—).

use as the absorbing solution in order to avoid a nonlinear response.

Ambient Air Monitoring and a Comparative Analysis.

The HEDS-conductometry method was applied to the continuous monitoring of atmospheric ammonia at a science building on the Yonsei University campus for six days. The University is located northwest of Seoul, 100 meters from a 12-lane road. Seoul is a metropolitan city with a population of 10.5 million and 2.4 million vehicles. In order to evaluate the method, a HEDS-IC system was used for simultaneous analysis. Our previous study showed that atmospheric ammonia and low molecular weight amines were able to be quantitatively sampled and analyzed by the HEDS-IC system.¹² The results from the two independent methods are well correlated ($r^2 = 0.9409$, $n = 686$) however the values from HEDS-conductivity were slightly higher than those from HEDS-IC system. The most likely impurities are amines like methyl amine, dimethyl amine and trimethyl amine; however, the atmospheric levels are less than 0.1% of that of ammonia.²⁰

Temporal variations in ammonia concentration are presented in Figure 6. Atmospheric ammonia ranged from 4.5 ppbv to 41.6 ppbv with an average of 18.9 ppbv, comparable to the reported value of 28 ppbv measured in 1995.²² This is slightly lower than those in urban areas of China and India and slightly higher than those of urban areas in Japan.²⁸ As shown in Figure 6, ammonia concentrations have a bimodal distribution; the first peak appears around 7 AM and the second peak appears around 6 PM. One possible explanation is the rush-hour traffic at those times. Ammonia emissions from catalytic converter-equipped vehicles have been shown to be dramatically higher than those of precatalyst vehicles.^{2,3} The sampling site was located near a crowded road in a downtown area of Seoul. Most of the passenger cars in Korea have been equipped with catalytic converters since the late 1980s, so the ammonia from heavy traffic could be the principle reason for the peaks. However, ammonia con-

centrations are closely related to the concentrations of SO_2 and NO_x and to the relative humidity. Therefore, long-term, comprehensive monitoring is necessary to develop an understanding of ammonia chemistry in the atmosphere.

Acknowledgments. This work was funded by the Korea Research Foundation (ROI-2008-000-20355-0).

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