## Measurement of Aerosol Acidity (H<sup>+</sup>) in Ambient Air

### Hak-Sung Lee

Dept. of Environmental Science, Seowon University, Chongju, 360-742, Chung-Buk (Manuscript received 12 June 1994)

#### Abstract

To collect and evaluate an aerosol acidity (H<sup>\*</sup>) in ambient air, the cyclone/annular denuder/filter pack sampling system (ADS) was used. Aerosol acidity was collected in Chicago using the ADS for 81 12-hr samples divided in spring/summer/fall 1990 and winter 1991. This study illustrated that the ADS was suitable for measuring aerosol acidity. The 10<sup>-5</sup>N HClO<sub>4</sub> extraction solution for pH determination provided more reliable scale than 10<sup>-4</sup>N HClO<sub>4</sub>. NH<sub>3</sub> should be removed prior to particle collection to accurately measure H<sup>\*</sup> concentration on the filter. There was seasonal variation in aerosol acidity concentrations. Aerosols were more acidic in the summer. High correlations between SO<sub>4</sub><sup>2-</sup> and NH<sub>4</sub><sup>+</sup>, and between SO<sub>4</sub><sup>2-</sup> and H<sup>\*</sup> were observed during the entire sampling period.

Key Words: Aerosol acidity (H<sup>+</sup>), annular denuder system (ADS).

### 1. INTRODUCTION

Acidic air pollutants, especially fine particles or aerosols, have been associated with adverse health effects, mainly respiratory diseases. Large particles (>5  $\mu$ m) often deposit in the upper airways of the lungs, whereas smaller particles are capable of penetrating deep into the lung to alveoli. The fine particles also affect the visibility reduction. The term "Aerosol acidity" refers to a gaseous suspension of either solid or liquid particles that yield hydrogen ions (H<sup>+</sup>) (Lipfert et al., 1989). It has been reported that respiratory responses to acid exposure are associated with H<sup>+</sup> rather than with sulfate, sulfite, nitrate and nitrite anions. Chemical reactivity in the airways and the acid particle size determine the specific region of the respiratory tract to which hydrogen ions can be delivered (Spengler et al., 1990). Strong acids found in the atmosphere include HCl (gas), HNO<sub>3</sub> (gas), H<sub>2</sub>SO<sub>4</sub> (aerosol), and NH<sub>4</sub>HSO<sub>4</sub> (aerosol). Weak acids include dissolved SO<sub>2</sub> (H<sub>2</sub>SO<sub>3</sub>); nitrous acid (HNO<sub>2</sub>); formic, acetic, and pyruvic acids (mostly gas phase); and ammonium sulfate [(NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>]. These secondary pollutants are formed through heterogeneous (gas-particle) or homogeneous (gas or aqueous) phase oxidation of SO<sub>x</sub> and NO<sub>x</sub>. A wide varity of acidic gases and particles that exist in the ambient environment has either been directly or indirectly linked to the phenomenon of acid rain formation. A significant fraction of these acid precipitation precursors(SO<sub>X</sub> and NO<sub>X</sub>) are due to emissions from fossil fuel combustion used for energy generation.

In Korea, Aerosol acidity (H<sup>†</sup>) has been measured from the rain ("Acid Rain"), which it already was neutralized. Hence, it may not good indicator for evaluating health effects. To accurately evaluate adverse health effects, it is necessary to measure the aerosol acidity from

dried ambient air that people are breathing. It can be done by the annular denuder system (ADS). Hydrogen ion (H<sup>+</sup>) using the ADS has successfully been measured (Koutrakis et al., 1988; Spengler et al., 1990; Wilson et al., 1991). The ADS selectively removes acidic gases of interest before the respirable particles (RP)  $(d_{50}<2.5 \mu m)$  are deposited. Ambient air is drawn in laminar flow through a Teflon-coated aluminum cyclone to remove coarse particles  $(d_{50}>2.5 \mu m)$ . The air then contacts the annular denuder walls which have been etched and coated with appropriate chemicals to absorb pre-selected gases. The RP in the air stream is then collected on the filter. The chemical species measured are HNO3, HNO2, SO2 and NH<sub>3</sub> in the gas phase and H<sup>+</sup>, SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup> and NH<sub>4</sub> in the particulate phase.

Atmospheric sulfates are mostly associated with submicron particles (Koutrakis and Mueller, 1989). Hydrogen and sulfate ions have been reported to show similar size distribution (mostly between 0.18 and 0.6  $\mu$ m), which suggests that H<sup>+</sup> may be primarily associated with  $SO_4^{2-}$  (Koutrakis *et al.*, 1989). For convenience, aerosol acidity is often expressed in (mass) units of  $H_2SO_4$ .

The purpose of this study was to collect and evaluate an aerosol acidity in dried ambient air. This paper also shows the effects of using 10<sup>-5</sup>N HClO<sub>4</sub> extraction solution and NH<sub>3</sub> removal for H<sup>+</sup> determination. The author hopes that this paper will give good information for the study of acid aerosol.

### 2. MATERIAL AND METHODS

### 2.1 SAMPLE COLLECTION

A total of 81 ambient air samples (20 in each

season) were collected in over a 12 month period from 2 April 1990 to 17 March 1991. The rooftop monitoring site (University of Illinois School of Public Health building, 20m above ground level) was located in an inner-city neighborhood about 3 km west of the Chicago Loop. There were no major point sources, and no large buildings to disrupt wind flow patterns. The sampling periods were equally divided into day/night intervals(12-hour sample), and were collected on an everythird-day of the week equally.

The day period was 8:00 to 20:00 and the night period was from 20:00 to 8:00.

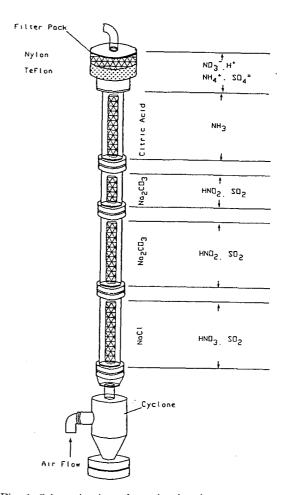


Fig. 1. Schematic view of annular denuder system.

The ADS (Figure 1) consisted of (1) a Teflon-coated aluminum cyclone ( $d_{50}$ <2.5  $\mu$ m, University Research Glassware); followed by (2) 4 annular denuders (University Research Glassware); (3) a filter pack which has Teflon (47 mm diameter with 1µm pore size, Gelman Science) and Nylasorb (47 mm diameter with 0.8 µm pore size, Gelman Science) membrane a flow controller (4) (University Research Glassware) with timer, pump and rotameter; and (5) a housing box (University Research Glassware) to protect the annular denuder and filter pack. The extracts from the denuders and filters were analyzed by ion  $QIC^{TM}$ (Dionex Ionchrom chromatography Analyzer). Details of the preparation and analysis procedures are available elsewhere (Lee et al., 1993).

### 2.2 HYDROGEN ION (H<sup>+</sup>) MEASUREMENT

To determine quantitatively the strong-acid  $(H_2SO_4)$  acidity of fine particle (<2.5  $\mu$ m) dried-aerosol as hydrogen ion (H') by pH, the Teflon filter (Gelman Science), chosen because this filter has a low background of acid and sulfate concentrations, was used. Preparation and extraction of the Teflon filter must be performed in a clean ammonia-free glove box (i.e., a flexible glove cabinet, VWR Scientific) to protect the filter from NH<sub>3</sub>, which may cause the neutralization of acid aerosol collected on the filter. The glove box has a citric acid-coated filter paper (Whatman No. 5), which is placed on the bottom of it, to remove NH<sub>3</sub> in the glove box. The Teflon filter was extracted with 6 ml of 10<sup>-4</sup>N perchloric acid (HClO<sub>4</sub>) solution and 100 μl of ethanol to wet the filter. It is necessary to use HClO<sub>4</sub> because it inhibits CO2 from dissolving into the solution

and keeps the organic compounds in solution from dissociating. Both these activities, if allowed to take place, can cause the ionic strength of solution to change. Filters were extracted in 125 ml screw-cap polyethylene vials with the filters placed face-downwards and completely covered by extraction solution. Filter bottle was put in an ultrasonic bath (Fisher Scientific) for about 20 minutes to extract sample solution from the filter. Samples should be analyzed as soon after collection as possible. It is imperative that the solutions and procedures be prepared extraction performed on the day of pH analysis, and keep samples in a clean refrigerator at 5 °C until extracted and analyzed. Two 1 ml aliquots of extract solution were transferred to 4 ml sampling cups for pH analysis. The residual 4 ml was stored in a refrigerator until anion and cation analyses (SO<sub>4</sub><sup>2-</sup>, NH<sub>4</sub><sup>+</sup>, NO<sub>3</sub><sup>-</sup>, and NO<sub>2</sub><sup>-</sup>) using ion chromatography. 20 µl of 0.04M KCl, which increases the strength, was added to each 4 ml cup to use for pH measurement. Using 1N H<sub>2</sub>SO<sub>4</sub>, hydrogen ion standards were prepared over four seasons. These standard solutions were prepared by adding each amount of 1N H<sub>2</sub>SO<sub>4</sub> in extraction solution (10<sup>-4</sup>N HClO<sub>4</sub> 0.04M KCl and ethanol). The range of H calibration was in 0-440 nmole H/m<sup>3</sup> for this sampling condition (12-hr at 10 l/min) which corresponds to  $0.0-21.6 \mu g$  of  $H_2SO_4/m^3$ . The pH determination was made using a Beckman Model 3500 with a micro-electrode (Fisher Scientific). The pH of standards and filter extracts was tested using two 4 ml cups. The first 4 ml cup was to rinse the micro-electrode, and the second 4 ml cup was to determine the pH. Two 4 ml cups of filter blank extract were used between each sample measurement; the first was used for rinsing the

Table 1. Summary of results.

			Concentrat	Concentration (µg/m³)	
Species	Time <sup>a</sup>	Mean	SD <sup>b</sup>	Range	N°
H <sup>+d</sup>	Day	6.88	9.3	0.00-49.3	41
	Night	8.54	13.7	0.00-78.0	40
	All	7.70	11.6	0.00-78.0	81
SO <sub>4</sub> <sup>2-</sup>	Day	5.38 (56.0)*	3.99	0.26-15.8	41
	Night	5.73 (59.7)	7.27	0.79-34.8	40
	All	5.55 (57.8)	5.81	0.26-34.8	81
NH₄ <sup>⁺</sup>	Day	2.78 (154.4)	2.23	0.17-10.3	40
	Night	2.70 (150.0)	2.37	0.38-12.6	38
	All	2.74 (152.2)	2.29	0.17-12.6	78
NH <sub>3</sub>	Day	1.51	1.48	0.15-5.60	41
	Night	1.76	1.86	0.11-8.20	40
	All	1.63	1.67	0.11-8.20	81

a Day=8AM-8PM, Night=8PM-8AM.

electrode, and the second was used to measure the pH as a control. The H<sup>+</sup> concentration of each sample filter extract was subtracted from the filter blank to determine the actual ambient H<sup>+</sup> concentration as follows:

$$[H^{\dagger}] = 10^{-pHS} - 10^{-pHB}$$

where pHS and pHB are the pH of the sample filter extract and the filter blank extract, respectively.

### 3. RESULTS AND DISCUSSION

### 3.1 RESULTS

Table 1 shows the mean, standard deviation, range and the number of samples for  $H^+$ ,  $SO_4^{2^-}$ ,  $NH_4^+$  and  $NH_3$ . Mean concentrations were: 7.70 nmole/m³ for  $H^+$ , 5.55  $\mu g/m^3$  for  $SO_4^{2^-}$ , 2.74  $\mu$  g/m³ for  $NH_4^+$  and 1.63  $\mu$ g/m³ for  $NH_3$ . Table 2 shows  $H^+$ ,  $SO_4^{2^-}$ ,  $NH_4^+$  and  $NH_3$  concentrations by daytime (8AM–8PM) and nighttime

(8PM-8AM) within each season. In the case of the hydrogen ion (H<sup>+</sup>) concentration, a negative value (the filter extract was alkaline than the filter blank) was assigned a zero (8 cases in the spring, 1 case in the summer, 9 cases in the fall and 3 cases in the winter). The mean H<sup>+</sup> concentration was the highest in the summer but the lowest in the fall. Table 3 shows correlation matrix of NH<sub>4</sub><sup>+</sup>, H<sup>+</sup> and SO<sub>4</sub><sup>2-</sup> by season. High correlations between SO<sub>4</sub><sup>2-</sup> and NH<sub>4</sub><sup>+</sup>, and between SO<sub>4</sub><sup>2-</sup> and H<sup>+</sup> were observed during the entire sampling period. A high correlation was suspected to reflect increased atmospheric reactivity or association of species in the atmosphere (or at the source).

# 3.2 COMPARISON OF 10<sup>-4</sup>N HCIO<sub>4</sub> AND 10<sup>-5</sup>N HCIO<sub>4</sub> SOLUTION FOR H<sup>+</sup> MEASUREMENT

Because of the strong acidity of the 10<sup>-4</sup>N HClO<sub>4</sub> extraction solution (pH value=4.00), there

b Standard deviation.

c Number of samples.

d Unit is nmole/m³; cases where the filter extract was more alkaline than the filter blank are reported as zero.

e Unit of ( ) is nmole/m<sup>3</sup>.

Table 2. H',  $SO_4^{\,2^{\circ}}$ ,  $NH_4$ ' and  $NH_3$  concentrations by day and night within each season.

		Concentration (µg/m³)					
Species	Time	Mean	SD	Range	N		
H <sup>†a</sup>	Spring	7.02	11.5	0.00-49.3	20		
	Day	10.20	15.7	0.00-49.3	10		
	Night	3.82	3.7	0.00-11.1	10		
	Summer	13.80	17.0	0.00-78.0	20		
	Day	8.24	5.8	2.96-18.7	10		
	Night	19.30	22.5	0.00-78.0	10		
	Fall	2.18	3.0	0.00 70.0	20		
	Day	1.73	3.2	0.00	10		
	Night	2.63	2.9	0.00 7.7	10		
	Winter	7.80	7.9	0.00-31.0	21		
	Day	7.29	6.7	0.00-24.6	11		
	Night	8.37	9.4	0.00-24.0	10		
2-							
SO <sub>4</sub> <sup>2-</sup>	Spring	6.15	4.06	1.07-14.5	20		
	Day	7.21	4.41	2.84-14.5	10		
	Night	5.09	3.59	1.07-12.9	10		
	Summer	8.84	9.23	0.26 - 34.8	20		
	Day	4.93	3.94	0.26- 9.9	10		
	Night	12.80	11.40	2.36-34.8	10		
	Fall	3.21	2.92	0.59-10.6	20		
	Day	4.54	3.60	0.59 - 10.6	10		
	Night	1.88	1.07	0.79- 4.5	10		
	Winter	4.09	3.36	1.34-15.8	$\frac{1}{21}$		
	Day	4.90	3.99	1.83-15.8	11		
	Night	3.19	2.39	1.34- 7.7	10		
NH₄⁺	Spring	2.57	1.64	0.38- 5.77	17		
	Day	2.67	1.77	0.66- 5.77	9		
	Night	2.45	1.59	0.38- 4.82	8		
	Summer	2.95	3.06	0.17-12.60	20		
	Day	1.65	1.25	0.17-12.00			
	Night	4.25	3.81	0.17- 3.33	10		
	Fall	2.23	2.02		10		
		2.23 2.96	2.59	0.20- 8.15	20		
	Day			0.20- 8.15	10		
	Night	1.50	0.90	0.61 - 3.06	10		
	Winter	3.17	2.16	0.64-10.30	21		
	Day	3.73	2.70	1.03-10.30	11		
	Night	2.56	1.19	0.64-4.96	10		
$1H_3$	Spring	1.66	1.49	0.39-6.80	20		
	Day	1.25	0.65	0.52-2.87	10		
	Night	2.07	1.97	0.39-6.80	10		
	Summer	3.06	1.73	1.16-8.20	20		
	Day	2.67	1.28	1.38-5.60	10		
	Night	3.44	2.09	1.16-8.20	10		
	Fall	1.60	1.55	0.24-5.60	20		
	Day	2.05	1.96	0.24-5.60	10		
	Night	1.15	0.89	0.24-2.68	10		
	Winter	0.29	0.24	0.11-1.06	21		
	Day	0.23	0.24	0.11 1.00	11		
	Night	0.36	0.34	0.11-1.06	10		

a Unit is nmole/m<sup>3</sup>.

Table 3. Correlation matrix of  $SO_4^{\ 2}$ ,  $NH_4^+$  and  $H^+$  by season.

Species	SO <sub>4</sub> <sup>2-</sup>	NH <sub>4</sub> <sup>+</sup>	H⁺
SO <sub>4</sub> <sup>2-</sup>		0.88 <sup>a</sup>	0.75
		0.92 <sup>b</sup>	0.97
		$0.99^{c}$	0.76
		0.98 <sup>d</sup>	0.83
ł		0.93 <sup>e</sup>	0.30
		0.76 <sup>f</sup>	0.96
		0.93 <sup>g</sup>	0.77
		0.73 <sup>h</sup>	0.87
NH4 <sup>†</sup>			0.44
			0.90
			0.72
			0.90
			0.12
			0.71
			0.61
			0.51

a Spring day.

b Spring night. c Summer day.

d Summer night.

e Fall day.

f Fall night.

g Winter day. h Winder night.

is the possibility that small changes in pH due to atmospheric particle H<sup>+</sup> will not be detected. Consequently, I considered decreasing the acidity of the extraction solution to increase the sensitivity of the procedure. An experiment was performed to investigate the effect of using

10<sup>-5</sup>N HClO<sub>4</sub> extraction solution (pH=5.00) which may provide more sensitivity. Another ADS having two denuders and using the lower acidity extraction solution (10<sup>-5</sup>N HClO<sub>4</sub>) was performed simultaneously for a series of 9 ambient 12-hour samples. The first denuder was coated with 10 ml of 1 %(w/v) Na<sub>2</sub>CO<sub>3</sub>, 1 %(w/v) glycerol in a 1:1 methanol/water solution to collect HNO3, HNO2 and SO2. The second denuder was coated with 10 ml of 2 % (w/v) citric acid in methanol to collect NH<sub>3</sub>. The Teflon filter was extracted with 10<sup>-5</sup>N HClO<sub>4</sub> solution. The calibration for H measurement was performed using 10<sup>-5</sup>N HClO<sub>4</sub> extraction. Sulfate was also measured to be sure that the collection characteristics of the two-denuder system was the same as that of the four denuder system, which used the 10<sup>-4</sup>N extraction solution.

As shown in Table 4, the  $H^+$  and  $SO_4^{2-}$  concentrations are similar for two extraction solutions. However, pH differences between the blank and sampled Teflon filters using  $10^{-5}N$  HClO<sub>4</sub> solution are always larger and

Table 4. Comparison of H<sup>+</sup> concentration between 10<sup>-4</sup>N HClO<sub>4</sub> and 10<sup>-5</sup>N HClO<sub>4</sub> extraction solutions.

No.	10 <sup>-4</sup> N HClO <sub>4</sub> Solution					10 <sup>-5</sup> N HClO₄ Solution				
	pHS <sup>a</sup>	pHB <sup>b</sup>	Diff <sup>c</sup>	$H^{*d}$	SO <sub>4</sub> <sup>2-e</sup>	pHS <sup>a</sup>	pHB <sup>b</sup>	Diff <sup>c</sup>	H⁺d	SO <sub>4</sub> <sup>2-e</sup>
1	4.09	4.11	0.02	5.0	2.26	5.02	5.09	0.07	4.7	2.02
2	4.06	4.10	0.04	9.0	4.28	4.93	5.08	0.15	6.6	4.36
3	4.10	4.11	0.01	3.3	2.08	5.36	5.08	-0.28	$0.0^{\rm f}$	2.12
4	4.09	4.10	0.01	3.4	4.57	4.94	5.10	0.16	6.7	4.34
5	4.04	4.10	0.06	13.1	2.55	4.67	5.08	0.41	15.9	2.38
6	4.09	4.10	0.01	3.3	7.49	5.04	5.12	0.08	4.8	7.61
7	4.12	4.09	-0.03	$0.0^{\rm f}$	1.34	5.34	5.06	-0.28	$0.0^{f}$	1.38
8	3.97	4.11	0.14	31.0	7.72	4.38	5.04	0.66	34.6	8.24
9	4.09	4.10	0.01	3.2	3.21	5.39	5.04	-0.35	$0.0^{f}$	3.35

a pH value of Teflon filter sampled.

b pH value of blank filter.

c pH value difference between blank and sampled filters.

d Unit is nmole/m<sup>3</sup>.

e Unit is  $\mu g/m^3$ .

f Negative value was assigned a rero.

consequently more reliable than when using  $10^{-4}N$  HClO<sub>4</sub> solution. The sensitivity of pH meter (Beckman, Model 3500) is  $\pm 0.01$  pH (Four cases in "Diff" column with the  $10^{-4}N$  HClO<sub>4</sub> solution were within this range). This result suggests that  $10^{-5}N$  HClO<sub>4</sub> solution provides a more reliable scale for pH determination. By paired t-tests, H $^{+}$  and SO<sub>4</sub> $^{2-}$  concentrations measured by two solutions are not statistically different(p=0.82 and p=0.69, respectively).

# 3.3 NH<sub>3</sub> EFFECT ON THE DETERMINATION OF H<sup>+</sup> CONCENTRATION

The EPA manual (1989) maintains that NH<sub>3</sub> should be removed by the citric acid coated denuder prior to particle collection to prevent neutralization of particulate sulfate. Otherwise, it would be impossible to accurately measure pH of acid aerosol on the filter. However, no formal data were given to support this recommendation. Some investigators still consider NH3 removal unnecessary, and the neutralization of sulfuric acid by ammonia may apply to atmospheric acid aerosols (Koutrakis and Mueller, 1989). The increased neutralization of acid particles in urban area may not be caused by NH3 (Lipfert, et al., 1989). An experiment was performed to examine H concentration effect between NH<sub>3</sub> removal and NH<sub>3</sub> non-removal for NH<sub>3</sub> concentrations which actually occur in ambient air. Another ADS for NH<sub>3</sub> non-removal having two denuders was used simultaneously for a series of 8 ambient 12-hour samples. Two denuders were coated with 10 ml of 1 % (w/v) glycerol Na<sub>2</sub>CO<sub>3</sub> 1% (w/v)in methanol/water solution to collect HNO3, HNO2 As and SO<sub>2</sub>. shown in Table 5. Η,

concentrations with  $NH_3$  removal are always higher than those without  $NH_3$  removal. This result suggests that  $NH_3$  should indeed be removed prior to particle collection to accurately measure  $H^{+}$  concentration on the filter.

Table 5. Comparison of H' concentration between NH<sub>3</sub> removal and NH<sub>3</sub> non-removal.

No	o. pH <sup>a</sup>	pHWO <sup>b</sup>	рНВ <sup>с</sup>	H⁺d	H <sup>*</sup> WO <sup>e</sup>	$NH_3$
1	4.07	4.14	4.09	5.39	-6.98 <sup>f</sup>	0.24
2	4.12	4.23	4.09	-3:79 <sup>f</sup>	-19.90 <sup>f</sup>	0.16
3	4.06	4.10	4.09	7.35	$-0.30^{f}$	1.06
4	4.08	4.19	4.09	3.29	-14.50 <sup>f</sup>	0.25
5	4.13	4.34	4.08	-7.62 <sup>f</sup>	-34.30 <sup>f</sup>	0.52
6	4.07	4.09	4.10	7.10	3.24	0.40
7	4.08	4.09	4.09	3.34	1.47	0.86
8	4.06	4.08	4.10	8.82	5.05	0.24

- a pH value of Teflon filter sampled with NH<sub>3</sub> removal.
- b pH value of Teflon filter sampled without NH<sub>3</sub> removal.
- c pH value of blank filter.
- d H' concentration (nmole/m³) with NH<sub>3</sub> removal.
- e H' concentration (nmole/m³) without NH<sub>3</sub> removal.
- f Negative value represents that pH value of blank filter is lower than that of Teflon filter sampled.

### 3.4 EVALUATION OF H<sup>+</sup> CONCENTRATION

Many pollutants show a strong diurnal pattern. Vertical mixing, which is typically more vigorous during daytime than at night, coupled with photochemical production of secondary aerosol, could lead to significant changes in the composition and concentration of samples measured at ground level. For example, the rise in sulfate concentration during the morning and the decrease sulfate concentration during the night correspond to the vertical mixing pattern. Generally, acid aerosol concentrations are higher during the day than at night, but distinct diurnal patterns are not always evident. Diurnal variations of aerosol

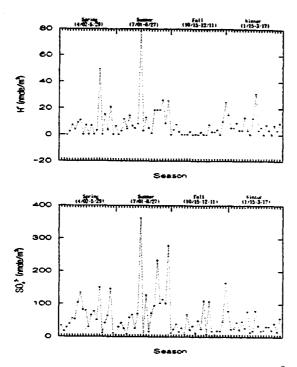


Fig. 2. Variation in daily H<sup>+</sup> and SO<sub>4</sub><sup>2-</sup> concentrations.

acidity and sulfate were observed (Wilson et al., 1991). H<sub>2</sub>SO<sub>4</sub> concentrations were higher during the summer, but periods of elevated concentrations also could occur in the winter (Spengler et al., 1990). From this study, seasonal variations of aerosol acidity and sulfate have been observed (Fig. 2). As expected, when the mean  $SO_4^{2-}$  concentration was the highest in the summer, the mean H<sup>+</sup> concentration was the highest (Table 2). It was higher in the spring daytime than in the nighttime, but the reverse was true in summer. However, there was no day/night variation in the fall and winter. Although the mean  $SO_4^{2-}$  concentrations were similar in the fall and winter, the mean H concentration was higher in the winter (7.80 nmole/m<sup>3</sup>) than in the fall (2.18 nmole/m<sup>3</sup>). This may be explained by the fact that the mean NH<sub>3</sub> concentration, which can neutralize H<sup>+</sup>, was lower in the winter  $(0.29~\mu g/m^3)$  than in the fall  $(1.60~\mu g/m^3)$ . However, Spengler *et al.* (1989) in four U.S. cities (Steubenville, OH, Portage, WI, Kingston, TN and St. Louis, MO) observed that H $^{+}$  concentrations in the winter months were substantially lower than in late spring and the summer months.

From Table 3, there were high correlations between H<sup>+</sup> and SO<sub>4</sub><sup>2-</sup> observed during the entire sampling period except for fall days. For the daytime sampling in the fall, 7 cases of the filter extract among the total 10 case samples were negative values (reported as zero), which the filter extract sampled was more alkaline than the blank filter. This may be the reason why the correlations between SO<sub>4</sub><sup>2</sup>and H<sup>+</sup>, and between NH<sub>4</sub><sup>+</sup> and H<sup>+</sup> were so low. Higher relationships were observed in the nighttime than in the daytime during the entire sampling period. High correlation between NH<sub>4</sub> and SO<sub>4</sub><sup>2-</sup> was also observed. These results show that NH<sub>4</sub>, H and SO<sub>4</sub><sup>2</sup> are composited in ambient air.

### 4. CONCLUSIONS

This study illustrated that the cyclone /annular denuder/filter pack sampling system was suitable for measuring aerosol acidity (H<sup>+</sup>). It was found that 10<sup>-5</sup>N HClO<sub>4</sub> extraction determination solution for the of H' concentration was more reliable than 10<sup>-4</sup>N HClO<sub>4</sub>. NH<sub>3</sub>, which is collected by citric acid denuder, should be removed prior to particle collection to accurately measure  $\mathbf{H}^{\dagger}$ concentration on the filter. There was seasonal variation in aerosol acidity concentrations. The highest H concentration was observed in the  $SO_4^{2}$ summer. Although the mean

concentrations were similar in the fall and winter, the mean H<sup>+</sup> concentration was higher in the winter than in the fall. It may be due to lower NH<sub>3</sub> concentration in the winter than in the fall. High correlations between SO<sub>4</sub><sup>2-</sup> and NH<sub>4</sub><sup>+</sup>, and between SO<sub>4</sub><sup>2-</sup> and H<sup>+</sup> were observed during the entire sampling period.

### **ACKNOWLEDGEMENTS**

I would like to thank Drs. R.A. Wadden and P.A. Scheff, who are the professors of the University of Illinois School of Public Health, for giving the opportunity to participate in this project. This project was supported by EPA Grant R-814715-01-0 from the Office of Exploratory Research and NIOSH award 2T150H07104 (Industrial Hygiene) University of Illinois School of Public Health.

### REFERENCES

- EPA, 1989, Determination of reactive acidic and basic gases and particulate matter in indoor air, U.S. EPA Compendium Chapter IP-9, Atmospheric Research and Exposure Assessment Laboratory, Research Trangle Park, NC.
- Lee, H.S., R.A. Wadden and P.A. Scheff, 1993, Measurement and evaluation of acid air pollutants in Chicago using an annular denuder system, Atmos. Environ., 27A(4),

543-553.

- Lipfert, F.W., S.C. Morris and R.E. Wyzga, 1989, Acid aerosols: The next criteria air pollutant?, Environ. Sci. Technol., 23(11), 1316-1322.
- Koutrakis, P. and P.K. Mueller, 1989, Atmospheric acidity: Chemical and physical factors, Presentation at the 82nd Annual Meeting of AWMA, Anaheim, CA. June 89–71.4.
- Koutrakis, P., J.M. Wolfson and J.D. Spengler, 1988, An improved method for measuring aerosol strong acidity: Results from a nine-month study in St Louis, Missouri and Kingston, Tennessee, Atmos. Environ., 22(1), 157-162.
- Koutrakis, P., J.M. Wolfson, J.D. Spengler, B. Stern and C.A. Franklin, 1989, Equilibrium size of atmospheric aerosol sulfates as a function of the relative humidity, J. Geophy. Res., 94(D5), 6442-6448.
- Spengler, J.D., G.J. Keeler, P. Koutrakis, P.B. Ryan, M. Raizenne and C.A. Franklin, 1989, Exposures to acidic aerosols, Environ. Health Perspect., 79, 43-51.
- Spengler, J.D., M. Brauer and P. Koutrakis, 1990, Acid air and health, Environ. Sci. Technol., 24(7), 946-956.
- Wilson, W.E., P. Koutrakis and J.D. Spengler, 1991, Diurnal variations of aerosol acidity, sulfate, and ammonia in the atmosphere, Presentation at the 84th Annual Meeting of AWMA, Vancouver, British Columbia, June, 91–89.9.

## 대기중의 산성도(H<sup>+</sup>) 측정

### 이학성

서원대학교 환경과학과 (1994년 6월 12일 접수)

대기중의 산성도(H')를 측정하기 위하여 디누더 시스템(Annular Denuder System)을 이용하였다. 산성도 측정은 1990년 4월 부터 1991년 3월 까지 미국 시카고에서 81개 샘플을 12시간 동안 낮과 밤을 구분하여 측정하였다. 본 연구를 통하여 대기중의 산성도 측정은 디누더시스템을 이용하면 보다 정확한 결과를 얻을 수 있음을 알 수 있었다. 여과지에 포집된 산성도(H')를 추출해 낼때 사용하는 HClO4용액은  $10^{-5}$ N의 농도를 사용하는 것이  $10^{-4}$ N의 농도보다더 정확한 결과를 얻을 수 있다. 보다 정확한 산성도를 측정하기 위해서는 에어로졸이 여과지에 포집되기 전에 가스 상태의  $NH_3$ 가 먼저 제거되어야 한다. 산성도는 계절에 따라 변하였고 여름에 가장 높은 농도를 나타냈다.  $SO_4^{2^-}$ 와  $NH_4$ , 그리고  $SO_4^{2^-}$ 와  $H^+$ 의 상관관계는 높은 것으로 나타났다.