

Development of Continuous Monitoring System of Acidic Pollutants for The Studies of Their Diffusion in The Atmosphere

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대기오염의 확산 연구를 위한 산성 오염물질의 연속 측정법의 개발

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ABSTRACT. An ion-exchange/conductometric method is applied for the determination of total acidity in simulated atmospheric samples. Non-H⁺ cations and strong acid anions are enriched by the preconcentrator columns in series and eluted through the corresponding parallel suppressor units. The conductivities from each channel correspond to the concentrations of the resulting ionized species in equivalents per unit volume. The difference is the measure of acidity due to strong acids. With 5-min sampling at a flow rate of 0.3 mL/min, the detection limits for NH₄⁺ and SO₄²⁻ are 0.3 and 0.1 μ equiv/L, respectively. The acidity for samples composed of various ions can be determined without significant error, usually less than 5%. The proposed method discriminates against the artifact from the CO₂ dissolution. Principles of acidity measurements are also presented.

Key Words : Ion-exchange/conductometric method, atmospheric samples.

INTRODUCTION

Acidic aerosols and gases, mainly resulting from SO₂ and NO_x emissions in modern civilization process, have long been a major concern on human health, and other ecological problems such as plant damage, visibility, and corrosion of materials¹⁻³. To assess these

problems, air samples can be extracted into the liquid phase⁴⁻⁶ and analyzed for strong acid anions (e.g., SO₄²⁻) to estimate acidity^{7,8}. However, the actual acid concentration can be lower as a result of the neutralization reactions between initial acidic pollutants and relatively abundant NH₃ gas in ambient air⁹. In addition, other cations such as Na⁺, K⁺, and Ca²⁺

which would appear as neutralizing agents may also result in a biased error.

The acid concentration in rainwater can be obtained by measuring the conductivity of a sample solution before and after the cation exchange column¹⁰. The difference corresponds to the contribution of the non- H^+ cations. Although this work provides a good theoretical background, trace concentrations of acidic pollutants, frequently encountered in the ambient air, would not be readily detected.

In this paper, tandem cation and anion conductometric detection systems equipped with two preconcentrator columns are described to measure the total acidity. With the proposed enrichment and elution technique, strong acidity in the simulated liquid effluent can be determined. Moreover, a CO_2 problem in anion measurements is also eliminated.

EXPERIMENTAL

Reagent and Material

The aqueous stock solutions (100 mM) of Na_2CO_3 , $NaHCO_3$, $(NH_4)_2SO_4$, NH_4HSO_4 , and NH_4Cl were used to prepare more dilute solution. Double deionized nanopure water and reagent grade chemicals were used.

Cation and anion preconcentrator columns (2.5 × 50mm) were prepared by packing surface-sulfonated chloromethylated poly(styrenedivinylbenzene) (Bio-Beads S-X1, 200 mesh) and weakly basic anion exchange (Bio-Rad AG4-X4, 100-200 mesh). The $R^+ - OH^-$ and $R^+ - A^-$ columns (4 × 95mm) were prepared with analytical grade anion exchange resin (Bio-Rex 5, 100-200 mesh, Cl^- form, all from Bio-Rad Lab., Richmond, Calif). A Nafion hollow-fiber suppressor using a perfluorosulfonic acid membrane (Perma-pure Products, Toms River, NJ), was prepared as follows: A Nafion fiber of 80cm was cut, soaked in ethanol for about 10 min, a 10 lb nylon filament was inserted, and the assembly was coiled around a 15 gauge stainless steel tube with closely spaced turns. To increase the

extent of hydration and maintain the helical form, the above unit was boiled in deionized water for about two hours and the supporting rod was then removed. The filament filled helix (FFH) device was enclosed in a Teflon tubing jacket (45 × 350mm) with inlet/outlet tees. This jacket was about half filled with the cation exchange resin. The function of this device has been described elsewhere^{11,12}.

Apparatus

A block diagram of the continuous analysis system for the measurement of the total cations and anions is shown in *Figure 1*. All channels are pumped by a multichannel peristaltic pump (Gilson Minipuls 2, Middleton, WI). The valves V1 - V3 are electro-pneumatically driven 6-port polytetrafluoroethylene (PTFE) rotary loop injectors under timer control. The on-loop cation preconcentrator column (CPC) and the anion preconcentrator column (APC) are mounted on V2 and V3, respectively.

All measurements were performed with two identical conductivity detectors (Model 1212, Wescan Instruments, Inc., Santa Clara, CA) connected to a chart recorder. The conductivity signals were also input to a digital data processing unit (Dionex Advanced Computer Interface, Model II, Dionex Corporation, Sunnyvale, CA) installed in a 386 PC computer.

Procedure

In the "load" mode (shown in *Figure 1*), the cations in the sample solution are first preconcentrated into CPC and the remaining anions into APC. After a suitable period of sampling, all the valves are switched to the "elution" mode. Each loop is placed in-line and the carrier streams flow through the corresponding loop. In the cation analysis system (top channel), the HCl eluent as a plug of 100 μL elutes the trapped cations and is itself neutralized to H_2O by the $R^+ - OH^-$ form suppressor. Subsequently, the solute ions pass through the linearizing column to yield the final species to be detected. In the anion analysis sys-

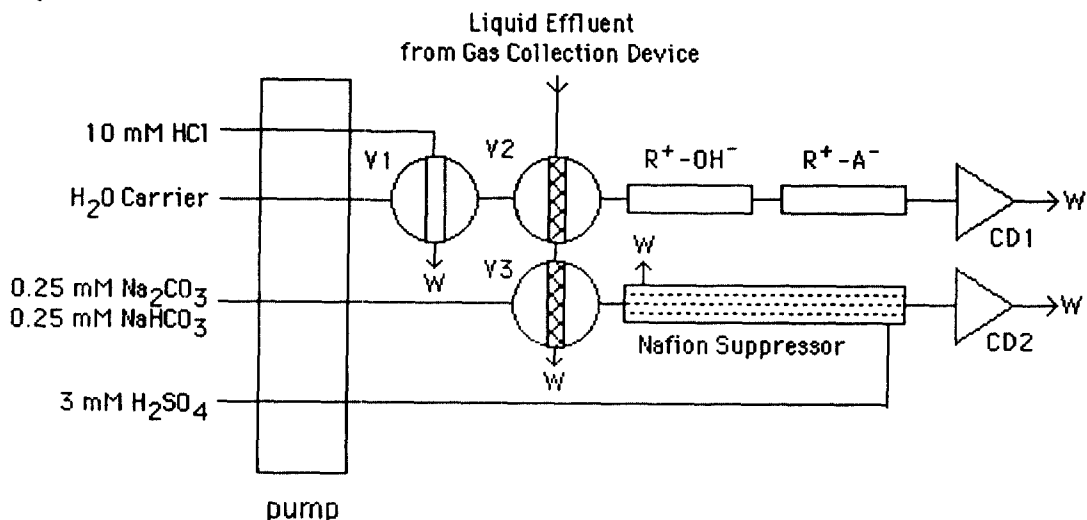


Figure 1. Schematic diagram of the ion-exchange/conductometric method for acidity measurements.

tem (bottom channel) involving a hollow-fiber suppressor, the eluent continuously passes through the interior of the Nafion fiber, while a H₂SO₄ regenerant solution passes over the exterior in a countercurrent direction. The background conductivity is contributed by the H₂CO₃ in the effluent. When the trapped anions are eluted, the resulting species are in the acid form such as H₂SO₄ and HNO₃.

PRINCIPLES

The principle described below is based on a simple ion exchange/conductometric approach. The ionic species, extracted from air samples into aqueous solution (acceptor) by a suitable collection device, are respectively preconcentrated by a cation-exchange and an anion-exchange preconcentrators in series. The trapped ions are eluted and the total non-H⁺ cation equivalents and the total (strong acid) anion equivalents are measured. The strong acid H⁺ equivalents are determined by the difference. In principle, the conductivities due to all ions in fully ionized form in dilute solution are in direct proportion to their

concentrations.

For the determination of non-H⁺ cations, the preconcentrated cations (mostly NH₄⁺) are eluted by an injected plug of HCl and the HCl is suppressed to H₂O by the R⁺-OH⁻ column. The resulting species (e.g., NH₄OH or NaOH) further pass through a linearizing column (R⁺-A⁻ form, A⁻ = Cl⁻ or C₂O₄²⁻) to convert NH₄OH into fully ionized NH₄⁺ and A⁻. This second column is necessary because of the weak base nature of NH₄OH and consequent nonlinear calibration behavior. The measured conductance, G₁, due to the non-H⁺ cations is given by

$$G_1 = K (\sum (A_{Mi} C_{Mi}) + A_A C_A) \quad (1)$$

where K is the calibration constant, A_{Mi} and A_A are the equivalent conductances of a cation i and A⁻, and C_{Mi} and C_A are the corresponding concentrations. Note that C_A is the total concentration of A⁻. Since the neutralization reaction of acidic aerosols is almost exclusively due to the ammonia gas in ambient air and thus forms ammonium salts, the term A_M can be represented by the equivalent conductance of NH₄⁺

(73.4) or by a weighted average value of 72 (the equivalent conductance value of Na^+ , K^+ , and Ca^{2+} are 50.2, 73.5, and 59.5, respectively) without significant error. Since C_A is the same as $\sum C_{Mi}$, the equation 1 is reduced to

$$G_1 = K A_\alpha \sum C_{Mi} \quad (2)$$

where the value of A_α is the sum of the limiting equivalent conductances of NH_4^+ (or weighted average value) and A^- .

Unlike the cation analysis, the pre-concentrated anions are eluted by the continuous flow of a $\text{Na}_2\text{CO}_3/\text{NaHCO}_3$ carrier stream and the eluent is suppressed to H_2CO_3 , while the anions result in the form of strong acids. The measured conductance, G_2 , due to the strong acid anions is given by

$$G_2 = K^1 (A_H C_H + \sum (A_{Xi} C_{Xi})) \quad (3)$$

where K^1 is the calibration constant, A_H and A_{Xi} are the limiting equivalent conductances of H^+ ion and an anion i , and C_H and C_{Xi} are the corresponding concentrations. The equivalent conductances of most probable anions (80.0, 71.4, and 76.4 for $1/2 \text{SO}_4^{2-}$, NO_3^- , and Cl^-) are much smaller than that of H^+ (349.9). The equivalent conductance of SO_4^{2-} can be applied for the value of A_X in most cases. Accordingly, the above equation 3 yields

$$G_2 = K^1 A_\beta \sum C_{Xi} \quad (4)$$

where A_β is the sum of the limiting equivalent conductances of H^+ and SO_4^{2-} (or weighted average value of 78).

Combining equation 2 and 4, the total strong acidity can be obtained by

$$[\text{H}^+] = G_2 / (K^1 A_\beta) - G_1 / (K A_\alpha) \quad (5)$$

The acidity can be obtained without any standard

solutions if the instrumental parameters (cell constant) and experimental conditions (temperature, dispersion of sample plug, etc.) variables are accurately known.

Typically, the total concentrations of cations and anions can be calculated from the separate calibration plots and the total acidity can be obtained by the difference:

$$[\text{H}^+] = \sum C_{Xi} - \sum C_{Mi} \quad (6)$$

In all of the above, the concentrations are in μ equiv/L, the conductance in S/cm, and the limiting equivalent conductance is in $\text{Scm}^2\text{equiv}^{-1}$.

RESULTS AND DISCUSSION

Cation Analysis System

To test long-term reliability of the system, the valves 1 and 2 were alternated every 5 minutes between "load" and "elution" positions. The $\text{R}^+ - \text{Cl}^-$ form linearizer provided a good between-run precision over several hours. The typical relative standard deviation (RSD) value of the peak height was 1% or less. However, prolonged use of the Cl^- form linearizer showed continuous increase in the background conductivity because of continuous release of Cl^- , possibly by hydrolysis. Further, the net signal due to the analyte decreased. Sampling of 5 nequiv of $(\text{NH}_4)_2\text{SO}_4$ yielded a peak height of 1.5 $\mu\text{S/cm}$ above H_2O conductivity and thus yielded only 0.3 $\mu\text{S/cm}$ net signal when the background increased to 1.2 $\mu\text{S/cm}$ after 4 days use. Even though the use of Cl^- form linearizer does not limit the method, it appears that erroneous results without frequent calibration may be obtained at low levels.

Among the tested linearizer columns in HCO_3^- , $\text{C}_2\text{O}_4^{2-}$, $\text{B}(\text{OH})_4^-$, NO_3^- , NO_2^- , SO_4^{2-} , CH_3COO^- , I^- , CN^- , and F^- forms, most conjugated bases of weak acids except NO_2^- and F^- showed the same conductivity of water before and after passing through the properly prepared column. The background conduc-

tivity was stable for at least one week of continuous use with the reproducibility better than 2% RSD. Figure 2 shows the dependence of the conductivity on the preconcentration time with HCO_3^- , $\text{C}_2\text{O}_4^{2-}$, $\text{B}(\text{OH})_4^-$ ($\text{Na}_2\text{B}_4\text{O}_7$ regenerant), and CH_3COO^- form linearizers. An oxalate form was chosen for further studies because it provided better linear dynamic range and higher sensitivity.

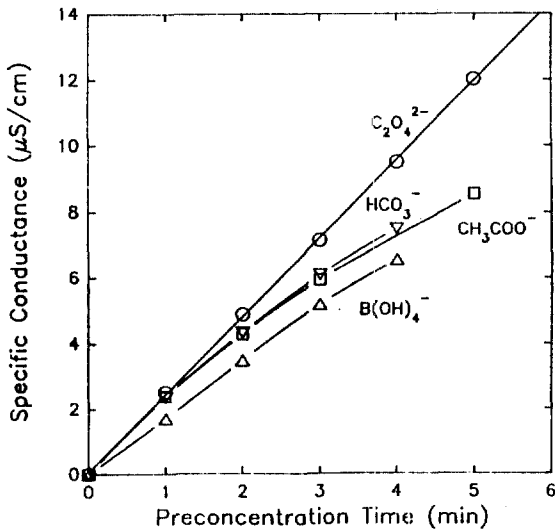


Figure 2. Response curves with various anionic-form linearizers. NH_4^+ conc, $10 \mu\text{M}$. Flow rate: sample, $0.5 \text{ mL}/\text{min}$, H_2O carrier, $1.1 \text{ mL}/\text{min}$; sample, $0.5 \text{ mL}/\text{min}$; HCl eluent, $0.5 \text{ mL}/\text{min}$.

Anion Analysis System

Due to the intrusion of atmospheric CO_2 into the aqueous solution at low acidity levels, it would be desirable to eliminate the CO_2 artifact. A CO_2 saturated water and $10 \mu\text{M}$ Na_2CO_3 samples were collected into the APC and eluted by an 1 mM NaOH eluent. The resulting responses were not negligible, yielding responses equivalent to 0.4 and $0.6 \mu\text{M}$ SO_4^{2-} . When the eluent contains more than 0.5 mM carbonate, the conductivity signal due to carbonate in the sample was not observed. The eluent of 0.25 mM each in Na_2CO_3

and NaHCO_3 was chosen for further studies.

When a column suppressor is used instead of the proposed hollow-fiber suppressor, the CO_2 problem would be aggravated. If the carbonate-containing aqueous carrier or a plug of eluent (e.g., NaOH , or $\text{Na}_2\text{CO}_3/\text{NaHCO}_3$) passes through the APC, significant amount of carbonate is retained and a spurious conductivity signal results. Note that due to the limited total ion-exchange capacity, the continuous flow of $\text{HCO}_3^-/\text{CO}_3^{2-}$ of eluent through the suppressor column is not desirable. With the hollow-fiber suppressor that allows continuous regeneration, such inherent problem due to CO_2 can be easily avoided.

Calibration Data

Different concentrations of $(\text{NH}_4)_2\text{SO}_4$ and

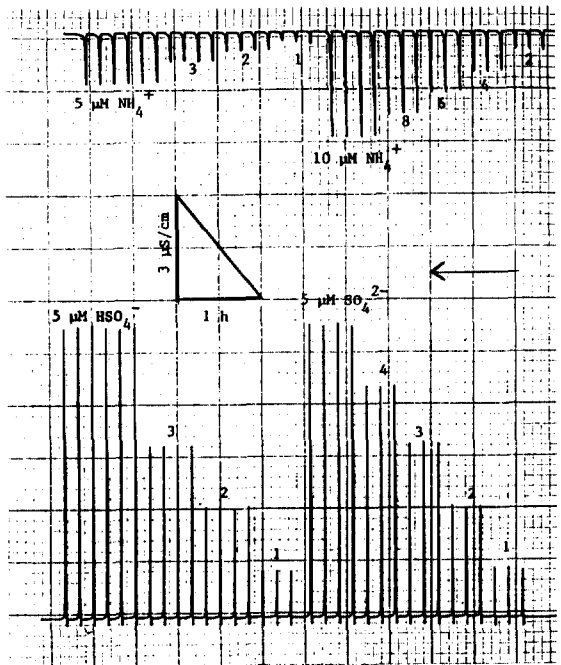


Figure 3. Typical system outputs for the simultaneous determination of cations (top trace) and anions (bottom trace). Flow rate: sample, $0.30 \text{ mL}/\text{min}$; H_2O carrier, $0.68 \text{ mL}/\text{min}$; $\text{Na}_2\text{CO}_3/\text{NaHCO}_3$ carrier, $0.68 \text{ mL}/\text{min}$; regenerant, $1.85 \text{ mL}/\text{min}$.

NH_4HSO_4 standard solutions were sampled for 5 minutes to obtain calibration data (Figure 3). The responses for SO_4^{2-} and HSO_4^- are the same as expected because the final species after the preconcentration/suppression step are the same. Water dips are observed in anion measurement and the resulting conductivities due to anions are much higher than those for cation.

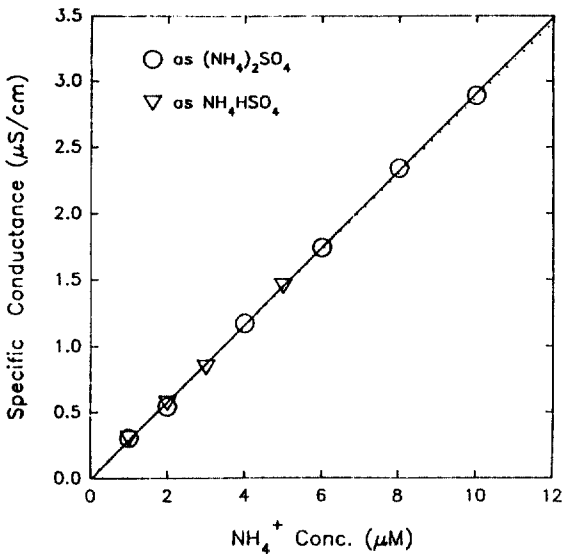


Figure 4. Calibration curves for the determination non- H^+ cations with the NH_4^+ standards. The data were taken from Figure 3.

The calibration curves based on the peak height for NH_4^+ and SO_4^{2-} determination are shown in Figure 4 and 5 and the corresponding responses can be expressed as:

$$G_1 = -8.6 \times 10^{-3} + 0.29 [\text{NH}_4^+], r^2 = 0.9998 \quad (7)$$

$$G_2 = -2.9 \times 10^{-2} + 0.88 [\text{SO}_4^{2-}], r^2 = 0.9997 \quad (8)$$

where the measured conductances are in the unit of S/cm and the concentrations are in $\mu\text{equiv}/\text{L}$. These

data indicate excellent linearity and Y-intercepts statistically indistinguishable from zero. The detection limits, defined as 3 times the noise level of the blank divided by the calibration slope, are 0.3 and $0.1 \mu\text{equiv}/\text{L}$ for NH_4^+ and SO_4^{2-} , respectively. For the data shown in Figure 5, the RSD values were 1.2% or less in all cases. Since $[\text{NH}_4^+]$ and $[\text{SO}_4^{2-}]$ represent the concentrations of the total cations and the total anions, the acidity in terms of $\mu\text{equiv}/\text{L}$ is given by

$$[\text{H}^+] = 1.14 (G_2 - 3.0 G_1) + 3.3 \times 10^{-3} \quad (9)$$

The contribution due to NH_4^+ effectively compensated the equivalent amount of SO_4^{2-} when an $1 \mu\text{M}$ H_2SO_4 was added to 1, 2, and $3 \mu\text{M}$ $(\text{NH}_4)_2\text{SO}_4$ solutions. The calculated H^+ concentration values agree with the predicted value ($2 \mu\text{equiv}/\text{L}$) within 2.5%. The calibration data with the pure H_2SO_4 standard solutions yielded the same calibration slope as in equation 8, while no responses in the cation analysis channel were observed.

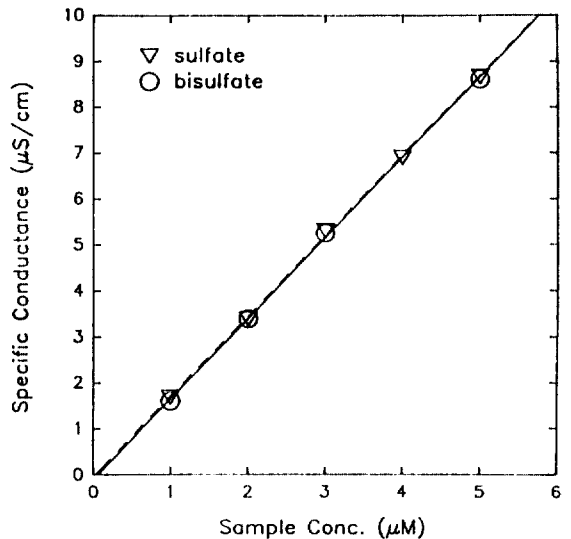


Figure 5. Calibration curves for the determination of strong acid anions with SO_4^{2-} standards. The data were taken from Figure 3.

Various Sample Mixtures

To test the existence of any significant change in the total response due to cations other than NH_4^+ ion, Na^+ ions of 0.5 and 1.0 $\mu\text{equiv/L}$ were added to the 6.0 $\mu\text{equiv/L}$ NH_4^+ solution. Based on the calibration data with the NH_4^+ standards, the cation concentrations determined for the above two samples (6.52 ± 0.06 and 7.08 ± 0.4 $\mu\text{equiv/L}$, respectively, $n=5$ in each case) agree well with the resulting total cation equivalents of 6.5 and 7.0 $\mu\text{equiv/L}$. This indicates that when NH_4^+ ion is the dominant cation in real samples, the contribution of other ions such as Na^+ to the total response can be considered to be essentially the same as NH_4^+ ion itself without significant error.

When sample mixtures (SO_4^{2-} , NO_3^- , and Cl^- as ammonium salts) were preconcentrated in the APC, all trapped anions are readily eluted without noticeable separation and yielding a single peak. The resulting peak heights and peak areas due to various sample

mixtures (Table 1) agree within 5% of the prediction based on a calibrant comprising of sulfate only. This can be explained by the fact that the limiting equivalent conductance of H^+ ion is much larger than those anions of interest and the H^+ ion is the common ion as the counterparts of all anions at the time of detection. Either the peak height or the peak area can be satisfactorily applied for the determination of sample mixtures.

CONCLUSIONS

A continuous ion-exchange/conductometric method has been shown to be a simple, reliable, and effective tool for detecting and measuring the low-level acidity. It is demonstrated that the total non- H^+ cations and the total strong anions are enriched into the two separate preconcentrators and each contribution in total amount can be determined by the conductivity. Although ionic species in the sample are not identified due to the fact that all trapped ions are eluted as a

Table 1. Results of Anion Mixtures with Different Quantitation Protocols¹.

Sample	Conc. (μM)	Manual Peak Height ² (nS)	Dionex AI-450	
			Peak Height ³ (nS)	Peak Area ⁴
SO_4^{2-}	3	204 ± 0.71	217 ± 1.3	956 ± 62
NO_3^-	6	196 ± 1.3	212 ± 1.3	940 ± 29
HSO_4^-	3	197 ± 0.82	210 ± 0.67	912 ± 19
$\text{SO}_4^{2-} + \text{NO}_3^-$	2+2	198 ± 0.50	212 ± 1.6	978 ± 59
$\text{SO}_4^{2-} + \text{HSO}_4^-$	2+1	204 ± 0.17	217 ± 2.5	964 ± 30
$\text{SO}_4^{2-} + \text{HSO}_4^- + \text{NO}_3^-$	1+1+2	194 ± 2.2	207 ± 0.78	933 ± 24
$\text{SO}_4^{2-} + \text{NO}_3^- + \text{Cl}^-$	1+2+2	210 ± 2.5	224 ± 2.9	951 ± 16
		200 ± 5.7	214 ± 5.6	948 ± 22

¹Experimental conditions were the same as in Figure 3 except the $\text{Na}_2\text{CO}_3/\text{NaHCO}_3$ flow rate (0.45 mL/min).

²Data were extracted from chart paper (blank signal due to H_2O , which yielded negative peak, was not accounted).

³Since the water dip (negative peak comes just before the analyte signal and the software adjusts baseline by connecting the highest negative peak point and the point at the end of the analyte signal, slightly higher numbers than the data in column 2 are obtained.

⁴Data in arbitrary units.

single component, the method allows to obtain the total acidity without significant error. Usually, the calibration plots for the cations and the anions can be prepared with NH_4^+ and SO_4^{2-} standards. Inevitably encountering problem due to $\text{CO}_2(\text{g})$ dissolution has been eliminated by the use of the carbonate-containing eluent.

Since the whole process is continual and does not require frequent maintenance, the analysis system in combination with a suitable collection device is very suitable for deployment in polluted areas to monitor the change in acid level in the ambient air. The constant flow rate of the liquid effluent from the collection device with constant flow rate and manipulation of the data in an appropriate manner are only necessary. Tedious and often difficult enrichment processes in the collection device can be omitted since the system includes the preconcentration units. The technique should also be applicable for the determination of the acidity in samples of rainfall of other natural freshwater.

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