Determination of Low Molecular Weight Monocarboxylic Acid Gases in the Atmosphere by Parallel Plate Diffusion Scrubber-Ion Chromatography

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Abstract

A method has been developed for the determination of the concentration of low molecular weight monocarboxylic acid gases in the atmosphere. The method involves quantitative collection of analyte gases using a parallel plate diffusion scrubber and subsequent ion analysis by ion chromatography. Among the gases are formic acid, acetic acid, propionic acid, *n*-butyric acid, and *n*-valeric acid. Method detection limits are on the order of sub to low parts-per-trillion by volume. The method has been successfully applied to ambient air analysis.

Introduction

Low molecular weight organic acids are important atmospheric gases due to their contribution to the acidity of precipitation, fog, and dew. These organic acids have been found to be the major contributors to precipitation acidity in remote areas (1). Among them, iso-valeric acid (i-VA) and n-valeric acid are odorous at low parts-per-trillion (ppt) levels and are of increasing concern to public and regulatory organizations (2). These acids are also known to cause damage to materials, including shells, stonework, and lead (pewter and bronze) (1). Formic acid (FA) and acetic acid (AA) have been reported to be the dominant species. The reported research results indicate that the concentrations of FA and AA are in the low to sub-ppbv in background areas (3,4) and elevated ppbv levels in urban areas (5–7). Although these acids are important, their origin is not yet exactly clear (8). Measurement results are not sufficient to understand the chemistry of these acids, especially for compounds with more than four carbons.

Atmospheric organic acids are known to be directly released by both biogenic and anthropogenic sources. The major source of atmospheric formic and AAs are emissions from vegetation through direct or indirect pathways. Gas phase hydrocarbons and their degradation products, which are principally generated via photochemical oxidation, are major precursors of these organic acids. Soils and biomass burning are the other direct sources. Direct emission from fuel combustion and industry is a minor source on the global scale but can be important in urban areas. Motor vehicle exhaust may also be a locally significant source. Once released from various sources, these organic acids have low reactivity in the atmosphere because they are terminal products of photo-oxidation. Low molecular weight organic acids are water-soluble. Consequently, dry and wet deposition are their principal sinks (9,10). Plants uptake these compounds at the branch level as a function of the atmospheric mixing ratio, and this provides another removing mechanism of these acids.

Atmospheric concentration data with temporal and spatial resolution is needed to understand the atmospheric chemistry of these organic acids. However, measurement data for these acids are still limited because there are analytical difficulties with their sampling and analysis. KOH-impregnated filters have been used to collect air samples, and organic acids have been analyzed with chromatographic techniques, both gas chromatography (GC) and ion chromatography (IC) (11,12). A gas diffusion denuder has been used for the collection of gas phase organic acids (8,14). GC methods provide good detectability, but a derivatization process is required for separation. The derivatization processes are time-consuming and concerns about contamination are not clearly eradicated. Because organic acids can be directly analyzed without any pretreatment, IC-based methods have an advantage in analyzing these acids. Filter-based methods have the advantages of being embodied in simple and compact devices; however, they require time-consuming filter pretreatment and extraction processes. On-line monitoring is possible with a diffusion based collector coupled to IC. A high-efficiency, parallel plate diffusion scrubber (PPDS) coupled with IC has been used for the on-line analysis of water-soluble basic gases in the atmosphere, such as ammonia and amines, by our research group (14). The PPDS-IC system also has been successfully applied to semi-real-time monitoring of gaseous aldehydes in the atmosphere (15). In this research, low molecular weight, mono-

carboxylic acids in the atmosphere are analyzed using a PPDS-IC system. The analytical details and the characteristics of the organic acids in Seoul's atmosphere are presented.

Experiments

Reagents and standards

High purity potassium hydroxide solution was prepared with an EG40 eluent generator (Dionex, Sunnyvale, CA) and was used as the eluent in ion chromatographic analysis. A mixed standard solution of FA, AA, propionic acid (PA), butyric acid (BA), iso-butyric acid (i-BA), valeric acid (VA), and i-VA was prepared by dissolving ACS reagent grade FA (98%, Fluka, Buchs, Switzerland), AA (99.99+%, Sigma Aldrich, Palo Alto, CA), PA (99.5+%, Sigma Aldrich), BA, (99+%, Sigma Aldrich), isobutyric acid (99+%, Sigma Aldrich), VA 35 (99+%, Sigma Aldrich), and isovaleric acid (99+%, Sigma Aldrich), respectively. Working standard solutions of low concentration were prepared by serial dilution of the stock solution with deionized water. The deionized water was produced from a Milli-Q water purification system (Millipore, Billerica, MA). All other reagents used were of analytical reagent grade or equivalent.

High efficiency PPDS

The PPDS employed in this study is modeled after Frenzel (16). It was designed not only for quantitative collection and fast response time, but also with regard to ease of construction and use. PPDS consist of two acrylic support plates, a PTFE membrane inserted between an air and a liquid channel. Approximately 2.5 cm below each end of the acrylic plates, two holes were drilled, respectively. The air inlet and outlet connections were made with 3 mm-i.d. and 4 mm-o.d. PTFE tube with gripper fittings and threaded male nuts. The liquid inlet and outlet connections were made with 0.5 mm-i.d. PEEK tube. Two rectangular spacers were placed at the internal face of acrylic plates to make the air and liquid channels, respectively. The inside dimensions of both these channels were 15 mm wide and 160 mm long, but the thickness of the air and liquid channels were 1 and 0.2 mm, respectively. A stainless steel screen (40 × 200 × 0.1 mm) was inserted between the air channel and PTFE membrane to prevent deformation of the membrane by swelling. A PTFE membrane (F02UP00010, 70 µm thickness, 0.22 µm average pore size, 80% surface porosity, Osmonics, Minnetonka, MN) has an effective air-liquid contact surface of ca. 145 mm × 15 mm. The hold-up volume for air was ca. 2500 µL, and for scrubbing liquid of water was ca. 400 µL. The materials and configuration are depicted in the previous articles (14,15).

Standard gas generation

The mixture of organic acid gases was generated following Dasgupta and Dong's method (17). The mixed standard gases of FA, AA, PA, BA, and VA were generated by the permeation of vapor into high-purity N_2 flowing through a microporous PTFE tube (2-mm o.d., 3.5 µm pore size, 70% surface porosity, 90-cm long, W.L. Gore & Associates, Elkton, MD)

immersed in a generation solution. The generation solution, consisting of FA, AA, PA, BA, and BA, was placed in a thermostat controlled water bath at 20 ± 0.5ºC and was adjusted to an acidic level with a purified sulfuric acid of 10 mM. The generated gas was immediately diluted with dilution gas in a quartz manifold. The dilution gas was made from acid-free zero air by passing through a column containing silica gel, activated carbon and soda-lime in order. The condition for standard gas generation in this study is summarized in Table I.

The concentration of the generated gas was determined by a PPDS-IC system developed in this study under a 0.5 L/min gas sampling rate, 3.0 L/min dilution gas flow rate, and a 60 µL/min scrubbing liquid flow rate. Reproducibility of the generated standard gases was evaluated by seven measurements under identical conditions. The coefficient of variation of the generated gas was less than 10–14% at a concentration level of 2.7–4.3 ppbv. Low concentration standard gases were prepared by further diluting with zero gas.

IC analysis

The analysis of the scrubbing liquid of the PPDS system was automatically carried out with ion chromatography (DX-500, Dionex). Separation was performed in a Dionex Ionpac AS11 analytical column (250 mm length × 4 mm i.d.) with a Dionex Ionpac AG11 guard column (50 mm length × 4 mm i.d.) using a KOH-water gradient elution at a flow rate of 1.5 mL/min. The water–KOH mobile phase gradient began with an initial KOH concentration of 0.1 mM held for 8 min, then the KOH concentration was increased to 1 mM over 12 min, increased to 4 mM over 10 min, increased to 25 mM over 10 min, held for 10 min, and then decreased to the initial value of 0.10 mmol/L over 1 min. The 25 mM KOH was eluted for 10 min in order to eliminate chemical species from the atmosphere with long retention times. The gradient system was run with a Dionex Model ATC-3 column (9 × 24 mm, Anion Trap Column) and CR-ATC (Continuously Regenerated-Anion Trap Column) column in front of the injection valve to minimize the baseline shift caused by carbonate and other contaminants in the eluent. The background conductivity ranges from 150 to 250 nS/cm. Column temperature was maintained at 35 ± 0.5ºC. System control and chromatogram recording were carried out using Dionex Chromeleon 6.60 software.

Table I. Operation Parameters for the Generation of Mixed Standard Gases	
Reagent concentration and generation conditions	
HCOOH	25 mg/L
CH_3COOH	30 mg/L
CH_3CH_2COOH	39 mg/L
$CH_3CH_2CH_2COOH$	45 mg/L
$CH_3CH_2CH_2CH_2COOH$	53 mg/L
H_2SO_4	10mM
Carrier gas flow rate	0.5 L/min
Dilution gas flow rate	3 L/min
Temperature	20 ± 0.5

An automated measurement using the PPDS-IC system

The configuration for the automated PPDS-IC system is illustrated in Figure 1. Ambient air, calibration gas, or diluting gas can alternately be introduced at the bottom of the PPDS using a manual switching valve. An air sample was drawn into the PPDS at a flow rate of 0.5 L/min with a diaphragm air pump. The gas flow rate was controlled using a needle-valve flow meter (Cole-Palmer, Vernon Hills, IL) located between PPDS and the air pump. Deionized water as a scrubbing liquid was continuously aspirated through the liquid channel with a countercurrent to the air flow into the sample loop (volume 500 µL) of the IC system with a peristaltic pump (Miniplus4, Gilson, Middleton, WI) at a flow rate of 60 µL/min. The injection valve was programmed automatically to inject 500 µL of absorbing solution at the desired time interval, typically 60 mins, by a time controller (Model XT Chrontron, USA).

Results and Discussion

IC optimization

The separation of seven major organic acids (FA, AA, PA, BA, i-BA, VA, and i-VA) and major inorganic acids such as Cl^-, NO_2^-, NO_3^-, and SO_4^{2-} requires a gradient elution. Contaminants in the eluent may bring a baseline drift during the gradient elution. In anion analysis systems, anionic contaminants in the eluent cannot be removed in the suppressor and can cause a baseline increase, while cationic impurities can be substituted by H^+ going through the ASRS and did not contribute to baseline drift. The most probable problematic anionic impurities come from dissolved CO_2. The KOH solution absorbs atmospheric CO_2 during storage in a reservoir, but use of a freshly generated eluent may minimize CO_2 absorption. An on-line eluent generation system of EG 40 (Dionex) was adapted for this purpose. In order to minimize baseline shift during gradient operation, an IonPac ATC-3 column was set up prior to the EG 40 system. The ATC-3 Anion Trap Column contains a high-capacity, low-efficiency, anion-exchange resin in the hydroxide form, and exchanges anionic contaminants to hydroxides, which did not contribute any baseline conductivity. CR-ATC

was installed between EG 40 and the injection valve to continuously remove contaminants in the eluent and provide a very low baseline drift during the gradient operations.

AS10 and AS11 separation columns were examined for the simultaneous separation of major organic acids and inorganic acids. The previously mentioned seven organic acids and four inorganic acids were separated within 50 min with an AS10 column under a proper gradient operation condition. Formate and butyrate peaks were partially overlapped but can be quantified independently in this condition. However, because the AS10 column is a high-capacity column, it requires a strong solvent as an eluent. High concentration may as well be avoided for developing a long-term monitoring method because the lifetime of the EG 40 cartridge and the suppressor depends on the concentration of the eluent. Simultaneous analysis of organic acid and inorganic acid can be possible within 40 min with an AS11 column under gradient elution. In this condition, the separation of i-BA and FA was not complete and i-VA peak was overlapped with that of Cl^-. However, the atmospheric concentrations of i-BA and i-VA were found to be below 1/30 of those of FA and HCl, respectively (11). In addition, all interested analytes can be separated with an AS11 column by gradient elution with lower concentrations of eluent due to the low capacity of the column. Therefore, the AS11 column is well-adapted for the monitoring system of PPDS-IC.

Collection efficiency

The collection efficiencies for FA, AA, PA, BA, and VA at various gas flow rates have been determined by using two PPDSs connected in series (18). The standard gas passed through the two PPDSs in series, and then the order of the PPDSs was changed in order to determine the average performance of the two PPDSs. The absorbing solution from the outlet of the first PPDS was connected to the liquid inlet of the second PPDS, and the effluent from the second PPDS was introduced to the injection valve of the IC system. The effects of gas flow-rate, gas concentration, and the coexisting strong acid gases were investigated. The collection efficiencies at various gas flow rates are illustrated in Figure 2. The concentrations of FA, AA, PA, BA, and VA were 4.0, 4.3, 2.7, 2.7, and 3.7 ppbv, respectively.

The dashed lines show the empirical collection efficiencies (f_{emp}), determined using the following equation:

$$f_{emp} (\%) = (1 - C_2 / C_1) \times 100.$$

where C_1 and C_2 denote the concentrations of the individual organic acid collected by the first and the second PPDS, respectively.

The solid lines show the theoretical collection efficiencies (f_{theor}), calculated from the following equation (19):

$$f_{theor} (\%) = (1 - 0.896e^{-1.22\alpha DL / Q}) \times 100.$$

Here, D is the diffusion coefficient of the gas, L is the length of the scrubber, and Q is the volumetric flow rate. The parameter α is given by:
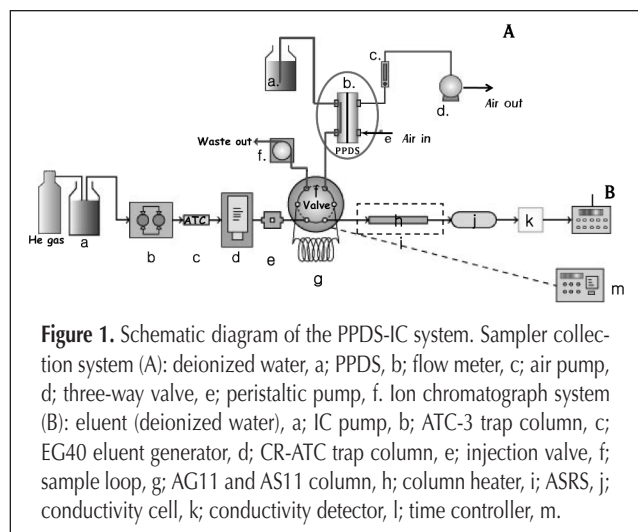
$$\alpha = 2b / a.$$

Figure 1. Schematic diagram of the PPDS-IC system. Sampler collection system (A): deionized water, a; PPDS, b; flow meter, c; air pump, d; three-way valve, e; peristaltic pump, f. Ion chromatograph system (B): eluent (deionized water), a; IC pump, b; ATC-3 trap column, c; EG40 eluent generator, d; CR-ATC trap column, e; injection valve, f; sample loop, g; AG11 and AS11 column, h; column heater, i; ASRS, j; conductivity cell, k; conductivity detector, l; time controller, m.

where a and b are the short and long dimensions of the active cross-section of the scrubber, respectively. Diffusion coefficients for FA and AA used in this calculation are 0.152 and 0.123 cm^2/s, respectively (CRC handbook). Diffusion coefficients for PA, BA, and VA are 0.114, 0.107, and 0.099 cm^2/s, respectively, as computed according to Graham's law. In this equation, the collection efficiencies of PPDS are given as a function of axial position, in which only one side is a perfect sink.

The experimental collection efficiencies are generally lower than the theoretical efficiencies. The discrepancy between f_{ideal} and f_{emp} becomes larger with increasing gas flow rate (Figure 2). This deviation may be explained by the fact that the membrane porosity is not considered in the theoretical calculations. Membrane thickness and tortuosity may be another cause for the deviation of the empirical collection efficiency from the ideal fit. Quantitative collection (> 95%) for the five
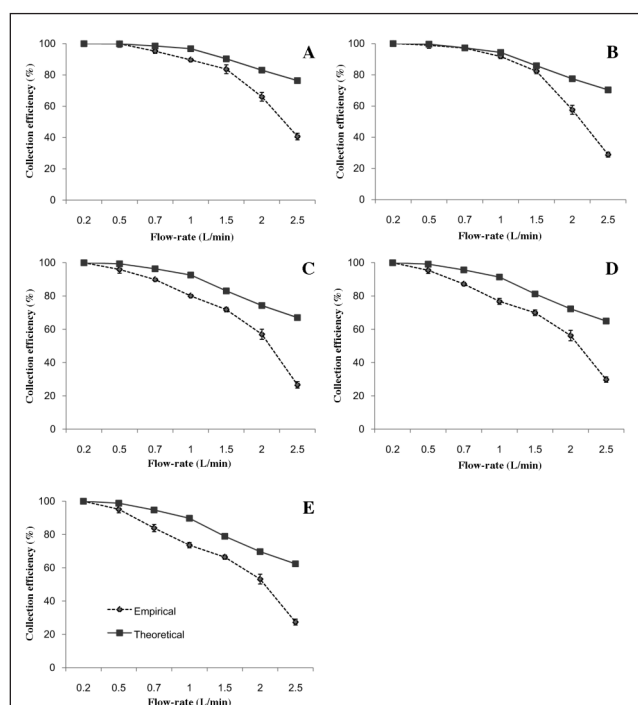

Figure 2. Effect of gas flow rates on the PPDS-IC system collection efficiencies for FA (A), AA (B), PA (C), BA (D), and VA (E) at a liquid flow rate of 3.0 L/min. The error bar means one standard deviation.
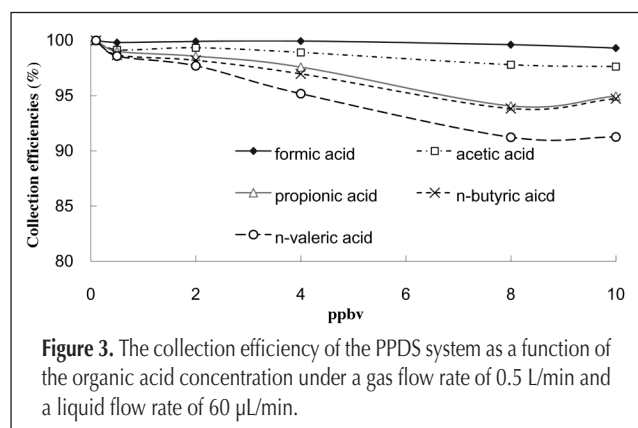

Figure 3. The collection efficiency of the PPDS system as a function of the organic acid concentration under a gas flow rate of 0.5 L/min and a liquid flow rate of 60 μL/min.

organic gases was achieved at flow rate up to 0.5 L/min. Quantitative collection (> 95%) was achieved for FA, AA, and PA at a flow rate of 0.7 L/min; however, the collection efficiencies of BA and VA fell to 87.2 ± 1.0 and 93.9 ± 2.2, respectively. The collection efficiencies of AA fell to 92% and 82% at flow rates of 1.0 and 2.0 L/min, respectively. The reduction became more intensified for VA, which fell to 74% and 66% at flow rates of 1.0 and 2.0 L/min, respectively. The collection efficiencies decreased with increasing molar mass at the same flow rate, reflecting the reduction trends in water solubility and diffusion coefficient.

Although the collection efficiency over 95% supports quantitative sampling and analysis of the developed method, this cannot affirm the accuracy. The accuracy can be evaluated by an analysis of standard reference materials or by a concurrent analysis with a proven method. However, due to the difficulties for obtaining standard reference materials and finding a proven semi-continuous method for atmospheric organic acids, further study for method validation still remains.

Because organic acids are weak acids, absorption by water is not an irreversible process. The absorption equilibrium is influenced by the pH of the absorbing solution. There are lots of coexisting acidic gases in the atmosphere, such as the organic acids SO_2, HCl, and HNO_3. As a result of the coexisting acidic gases, the absorbing solution becomes acidic and the solubility of the organic acids decreases, which consequently leads to a reduction in the collection efficiency. In order to estimate the effect of the pH of the absorbing solution, collection efficiencies were measured at not only various concentrations of the organic gases but also at various concentrations of H_2SO_4 solution as an absorbing solution. First, while changing the concentrations of organic acid, collection efficiencies were measured with five sets of mixed standard gases at a gas flow rate of 0.5 L/min and a liquid flow rate of 60 μL/min. The results are summarized in Figure 3. The concentrations were varied from 0.1 to 10 ppbv with the same concentrations of the all tested organic acids. The collection efficiencies for FA, AA, PA, BA, and VA were ~100% at 0.1 ppbv and over 95% for the concentrations up to 4 ppbv. The collection efficiencies for 8 ppbv BA and VA fell to 94% and 91%, respectively. For AA and FA, collection efficiencies did not show any significant decrease for concentrations up to 25 ppbv. However, because the concentrations of atmospheric organic acids ranges from sub ppbv to low ppbv, there is no concern about signal suppression from the coexistence of organic acids. The trends given in

Table II. The Signal Suppression of Organic Acids Under Various Concentrations of H_2SO_4 as Absorbing Solutions.

H_2SO_4 (mg/L)	FA	AA	PA	n-Butyric acid	i-VA	n-Valeric acid
1.0	21	27	12	15	13	14
0.50	12	26	14	13	14	11
0.25	11	11	11	10	10	11
0.10	10	10	11	9	8	13

Figure 3 can be explained, except FA and AA, by the limit in solubility. Solubility can restrict the linear response of the higher molecular weight acids at higher concentrations of co-existing organic acids.

On the other hand, atmospheric strong acids were expected to affect the collection efficiencies of the organic acids. Our previous research showed that SO_2 is the most predominant inorganic acid gas in the atmosphere at Seoul, followed by HNO_2, HCl, and HNO_3. During the sampling with PPDS, large parts of the sulfite are oxidized to sulfate by the coexisting oxidants such as ozone and peroxides in the atmosphere, while the oxidation process in condenser-type diffusion denuder is significantly slower (20). In this research, collection efficiencies with various concentrations of sulfuric acid solution as absorbing solution were measured under ordinary experimental conditions. The results are summarized in Table II. The organic acid peaks using a 0.10 mg/L H_2SO_4 solution as an absorbing solution decreased by 8–13% compared to those using deionized water as the absorbing solution. In the presence of high concentrations of H_2SO_4 [i.e., 1.0 mg/L (ca. SO_2 42ppbv at 0.5 L air flow-rate and 60 µL liquid flow rate under oxidantrich atmosphere)], the organic acid peak areas were suppressed by 12–27%. The concentration is one order higher than the average SO_2 concentration of Seoul, the most industrialized city of South Korea. This suggests that the atmospheric SO_2 does not affect the collection efficiencies of the organic acids in normal conditions. However, because the atmospheric SO_2 varies dramatically with time, the possibility of a significant decrease in the collection efficiency, especially for AA and FA, still remains for an extremely polluted condition.

Reproducibility and limits of detection

The reproducibility of the PPDS-IC system was evaluated by repeated measurements of mixed standard gases under ordinary conditions of a 0.50 L/min gas flow rate and 60 µL/min liquid flow-rate. The results are summarized in Table III. The coefficient of variance was 1.8~7.6% at a concentration range of 12~20 ppbv (n = 7). At a low concentration of 3.4~7.1 pptv, the coefficient of variance of each organic acid was in the range of 7.8~23 % (n = 7). These results reflect a combination of uncertainties in standard gas generation, sampling by PPDS, and analysis by IC. Five point calibrations for FA, AA, PA, BA, and VA gases were described by linear equations with correlation coefficients (R^2) of > 0.99 (Figure 4). In order to determine the limit of detection (LOD), zero gas was analyzed with a PPDS-IC system. During the zero gas analysis, no blank peaks of organic acids were detected. An average (A) and standard deviation (σ) were calculated from five zero air blank analyses. Limits of detection, derived by A + 3σ, were 0.77 pptv, 0.51 pptv, 0.59 pptv, 0.59 pptv, and 1.50 pptv for FA, AA, PA, BA, and VA, respectively. Because the LOD depends on the gas and liquid flow rate, it can be improved at higher gas flow rates with lower liquid rates.

Ambient air measurements

The PPDS-IC system was applied to the analysis of atmospheric organic gases from August 30 2006 to April 2007 in Seoul. During the study period, automatic measurement was carried out every hour for 11–28 days in each season for the four seasons. A typical chromatogram for Seoul air is presented in Figure 5. FA and AA are the predominant organic acids in Seoul air, while PA, n-butyric acid, and n-valeric acid are normally determined at an order of lower than those of the two predominant acids. Nitrous acid, sulfuric acid, nitric acid, and hydrochloric acids were the dominant inorganic acids in

Table III. The Reproducibility of the PPDS-IC System Calculated Seven Repeated Measurements Under Ordinary Conditions of a 0.50 L/min Gas Flow Rate and 60 µL/min Liquid Flow Rate

	FA	AA	PA	n-Butyric acid	n-Valeric acid
For lower concentration					
Average	3.4	4.8	3.4	4.3	7.1
SD	0.53	0.60	0.26	0.84	1.7
RSD(%)	13	12	7.8	18	23
For higher concentration					
Average	20.0	13.0	12.0	15.0	15.0
SD	1.0	1.0	0.2	0.7	1.1
RSD(%)	5.7	5.7	1.8	5.2	7.6
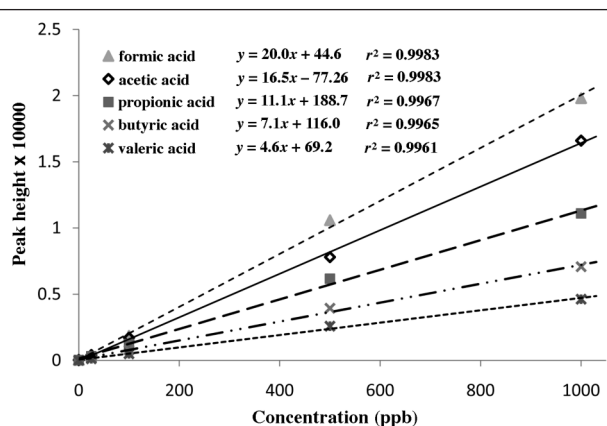
Figure 4. Calibration curves for the five low molecular weight carboxylic acids.

formic acid $y = 20.0x + 44.6$ $r^2 = 0.9983$
acetic acid $y = 16.5x - 77.26$ $r^2 = 0.9983$
propionic acid $y = 11.1x + 188.7$ $r^2 = 0.9967$
butyric acid $y = 7.1x + 116.0$ $r^2 = 0.9965$
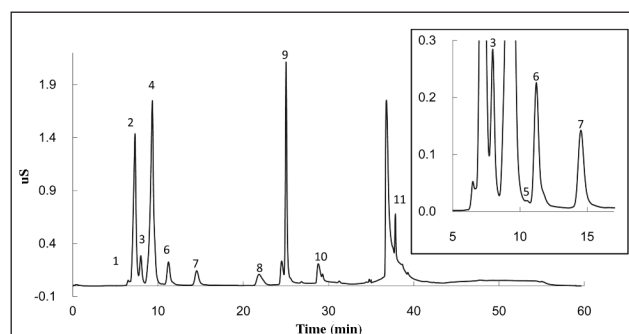valeric acid $y = 4.6x + 69.2$ $r^2 = 0.9961$

Figure 5. A typical chromatogram of the ambient air sample collected by the PPDS-IC system. A 500-mL injection volume, 0.5 L/min gas sampling rate, and 60 mL/min liquid flow rate. Peaks: fluoride, 1; acetate, 2; propionate, 3; formate, 4; iso-butyrate, 5; butyrate, 6; n-valerate, 7; chloride, 8; nitrite, 9; nitrate, 10; sulfate, 11.
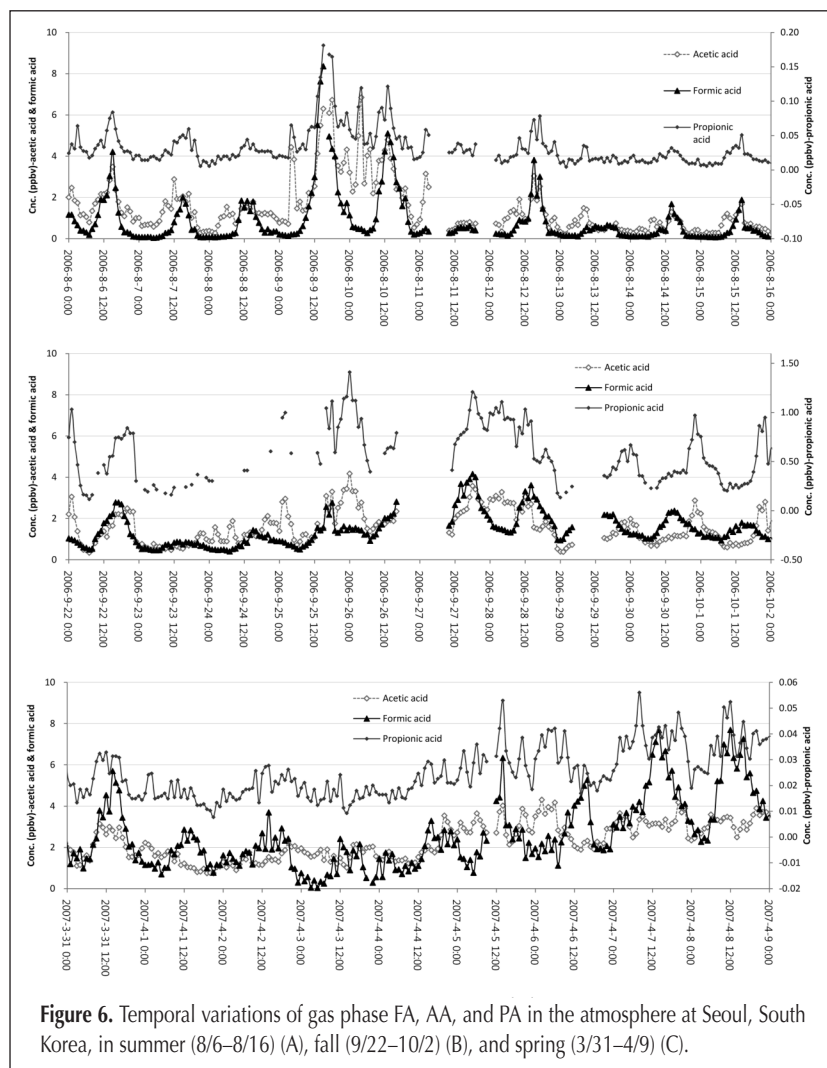
Figure 6. Temporal variations of gas phase FA, AA, and PA in the atmosphere at Seoul, South Korea, in summer (8/6–8/16) (A), fall (9/22–10/2) (B), and spring (3/31–4/9) (C).

nounced diurnal variation is most likely related to mixed layer dynamics, in addition to daytime biogenic and photochemical source inputs and gaseous dry deposition at nighttime. The time variations of the three dominant organic acids were very similar, suggesting a common sources and removal mechanism of these acids. For example, the removal of these acids from the nighttime boundary layer may be aided by the uptake of their vapors into dew. During the study period, the concentrations of atmospheric CO and O_3 determined the meteorological parameters including precipitation, solar radiation intensity, and relative humidity. The concentrations of three major organic acids were very closely correlated temporal variations in CO, O_3, RH, and solar radiation. This suggests that these continuous measurement data will likely help source apportionment and understanding of the atmospheric chemistry of the atmospheric organic acids. These results will be presented elsewhere.

Conclusion

An automated, semi-continuous method for measuring low molecular weight gas phase organic acids in the atmosphere was developed with a PPDS coupled IC system. The PPDS-IC system was adequate for the simultaneous measurement of gaseous low molecular weight organic acids and the major inorganic acids simultaneously with a good precision. The detection limits of this method were less than 3.3 pptv for a 30 L air sampling volume. The developed method was employed in urban air measurement over a year and very similar temporal trends were found between FA, AA, and PA.

Seoul air. The concentrations of organic acids were normally higher than those of HCl and HNO_3, but lower than those of the major inorganic acids such as SO_2 and HNO_2. The concentrations of atmospheric organic acids were even higher than those of major inorganic acids, SO_2 and HNO_2, during the daytime in the hot summer season. Grosjean (21,22) had reported that daytime peak concentrations of FA and AA in southern California urban air were in the range of 8–10 ppb, 5 higher than the average concentrations of the major inorganic acids, HNO_3 and HCl, during the summer.

Figure 6 shows time variations of FA, AA, and PA. The concentrations were lowest prior to sunrise, increased steadily thereafter, peaked 1–3 hours after midday, and began to decline by late afternoon, again reaching very low levels in the early morning hours. Diurnal variations were clear in the hot summer season but were not very clear during rainy or cold periods. The concentration peaked at 1–3 PM, implying a photochemical production of these acids in the atmosphere. The minimum concentration was found just before the dawn, concurrent with the lowest ambient temperature and maximum humidity. This means that the gas-particle partition equilibrium may involve the determination of gaseous organic acids in the atmosphere. Talbo et al. (23) explained that this pro-

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