

# A Combination of the Frozen Raindrop Collection Method and a High-performance Capillary Electrophoresis Technique for the Size-resolved Raindrops Study

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## Abstract

Although the importance of size-resolved raindrops study has been known, it has not been popularized up to the present. In the present study, an attempt was made to generalize the size-resolved raindrops study by a combination of the frozen raindrop collection method and a commercially available high-performance capillary electrophoresis (HPCE). Samplings were carried out at Kyoto, Japan in October 2002. The inorganic ions (chloride, nitrate, sulphate, calcium, ammonium, sodium, magnesium, potassium) in size-classified raindrop samples were successfully analyzed by HPCE with good repeatability. To assure the accuracy and precision of HPCE data, t-test was conducted with paired analytical data, which were experimentally constructed by analyzing standard solutions with HPCE and IC, respectively. T-test showed that there is no notable difference between the concentrations determined by the two analytical methods. Every ionic concentration in both cation and anion was found to be strong raindrop size dependence. Though there was slight increase of sodium and sulphate concentrations between 0.85 mm and 1.15 mm raindrop radius, it showed a strong decrease for every ionic component with increasing droplet radius. The combination of the frozen raindrop collection method and a commercially available HPCE can meet the need of size-resolved raindrops study.

**Key words** : Size-resolved raindrop, Capillary electrophoresis, Frozen raindrop collection

## 1. INTRODUCTION

Capillary electrophoresis, which has developed into an extremely powerful analytical technique, is now an established technique in various areas of analysis (Cole and Michael, 1991; Ong *et al.*, 1991). The term of "Capillary Electrophoresis (CE)" covers several modes of separation, all of which harness electrical forces in capillary tubes for analytical purposes. CE is used throughout chemistry,

pharmaceuticals, biotechnology and environment, with separations of both charged and uncharged species ranging in size from metal ions to proteins and polynucleotides. Especially, the use of CE is routine in many hospitals and clinics, particularly for analyzing serum proteins and disease markers. Types of molecules that can be separated by CE are proteins, peptides, amino acids, nucleic acids, inorganic ions, organic bases, organic acids, and whole cells. Advantages of CE are high separation efficiency, small sample amount required (10  $\mu$ L), fast separation, numerous modes to vary selectivity and wide applications, simple and automated instrumen-

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tation, low detection limit ( $10^{-5} \sim 10^{-8}$  molar), and reproducibility.

An effective process for the removal of ambient pollutants like particulate matters and gaseous materials from the atmosphere is washout by rainfall. Various processes such as Brownian diffusion, direct-interception, inertial impaction, thermophoresis, diffusio-phoresis, and electrical effects contribute to the collection of particles by raindrops. Although these processes are all coupled, one or more of them may dominate for various regimes of particle size, drop size, particle density, hydrodynamic temperature, and diffusion fields.

A large amount of studies including laboratorial experiment and model calculation have been carried out to determine the chemical composition of rain and the scavenging efficiency of particles by raindrops (Ma *et al.*, 2000; Chate and Kamra, 1997; Hallberg *et al.*, 1997; Baez *et al.*, 1995; Flossmann *et al.*, 1985; Battan and Reitan, 1957). The chemical processes in the atmosphere as the washout of particles and gases are not sufficiently described by the usual determination of chemical components in rain water, because the chemical content of raindrops is variable according to the mechanism such as condensation nuclei inside clouds, pollutant scavenging, collision, coalescence and break-up of falling raindrops, and evaporation (Ma *et al.*, 2001; Tenberken and Bächmann, 1996). Since the chemical content of raindrops depends on their size, the analysis of rain as bulk phase will lead to a loss of detailed information (Ma, 2001; Tenberken and Bächmann, 1996). Therefore, to get the detailed information on the chemical content of raindrops and the scavenging processes of atmospheric pollutants by rain event, the sampling and analysis of size-classified raindrops have to be performed.

However the sampling of raindrops as a function of their size is a prerequisite problem. Moreover, to determine the chemical content of size-resolved raindrops, one has to make possible to analyze the small amount of rain sample. Fortunately, recent frozen method (Ma, 2001; Tenberken and Bächmann, 1996) has provided new way by which chemical analysis of a single and classified-raindrops

can be carried out. It was successful in analyzing a single and classified-raindrops by means of the laboratory-built capillary zone electrophoresis system (Tenberken and Bächmann, 1996). However, since a commercially available CE was not certified for the analysis of size-resolved raindrop sample, this method cannot be popularized up to the present.

In the present study, an attempt was made to generalize the size-resolved raindrop study by a combination of the frozen method and a commercially available high-performance capillary electrophoresis (HPCE).

## 2. MATERIALS AND METHODS

### 2.1 Sampling of size-resolved raindrops

Sampling and handling systems of raindrops are displayed in Fig. 1. Sampling apparatus consists of a dewar vacuum flask filled with liquid nitrogen and four-stage stainless steel sieves (0.5, 1.0, 1.7, 2.3 mm mesh size) put on back-up stainless steel vessel. Samplings were performed on a five-story building of Kyoto University located in Kyoto, Japan during rain event in October 2002. Raindrop collector was exposed to the raining atmosphere for about 10 min. As described in the previous study (Ma, 2001; Ma *et al.*, 2001), fallen raindrops into the liquid nitrogen are frozen and they sink to lower

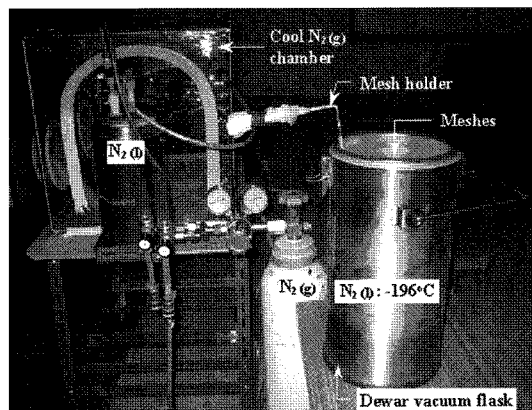


Fig. 1. Sampling and handling system for size-resolved raindrops.

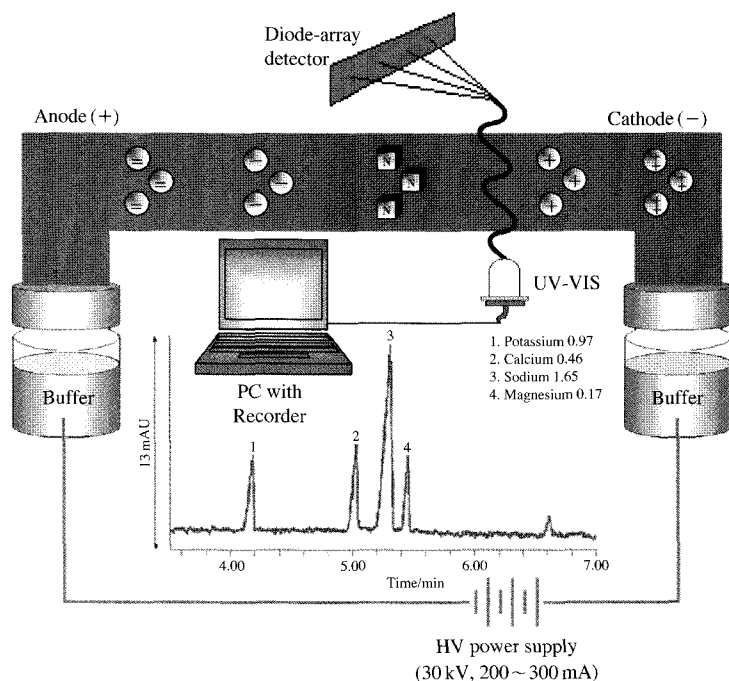


Fig. 2. A schematic representation of the arrangement of the main components of a HPCE instrument.

sieves owing to their higher density. Consequently, by using stainless steel sieves and vessel it is possible to collect five-step frozen raindrop samples according to drop size. Owing to the evaporation and contamination of collected raindrops prior to their analysis, one has to pay attention to their handling. For the handling of frozen raindrops without evaporation and contamination, we designed a clean air chamber system in this study. After sampling, the mesh holder was pulled out from the dewar vacuum flask and the frozen raindrops on each sieve were placed into the HPCE sample vials. Every handling process was performed in the clean air system filled with cool nitrogen gas.

## 2.2 HPCE analysis of size-classified raindrop sample

The frozen raindrops in vials were melted and analyzed by HPCE (Agilent technologies).

In HPCE, separation is performed in narrow-bore capillaries, typically of 25~75  $\mu\text{m}$  inner diameter. Fig. 2 illustrates the schematic diagram of HPCE

Table 1. Operation condition of HPCE.

	Cation	Anion
Buffer solution	4.0 mM formic acid, 4.0 mM copper (II) sulphate, 3.0 mM 18-crown-6	2.25 mM pyromellitic acid, 6.5 mM NaOH, 0.75 mM hexamethonium hydroxide, 1.6 mM triethanol-amine
Capillary	56 cm length, 50 $\mu\text{m}$ inner diameter	112.5 cm length, 50 $\mu\text{m}$ inner diameter
Injection pressure	50 mbar	50 mbar
Voltage	30.0 kV	-30.0 kV
Temp. of capillary	25°C	30°C
Detector	Diode-array detector	Diode-array detector
Detection wavelength	310 nm	350 nm
Band width	20 nm	20 nm

instrumentation. The ends of the capillary are placed in separate buffer reservoirs, each containing an electrode connected to a high-voltage power supply

capable of delivering up to 30 kV. The sample is injected onto the capillary by temporarily replacing one of the buffer reservoirs (normally at the anode) with a sample reservoir and applying either an electric potential or external pressure for a few seconds. After replacing the buffer reservoir, an electric potential is applied across the capillary and the separation is performed. Optical (UV-visible) detection of separated analytes can be achieved directly through the capillary wall near the opposite end (normally near the cathode). Operation condition of HPCE is listed in Table 1. The extended light-path in capillaries improves sensitivity and linearity to enables low level impurity analysis in a single run. The high injection pressure gives the flexibility to apply maximum voltages and use conductive mobile phases without out-gassing which causes column breakdown. Efficient capillary and sample temperature was controlled for accurate quantitative analysis. The diode-array detector was specially designed for on-capillary detection.

In order to quantitatively analyze the ionic components (potassium, magnesium, sodium, calcium, ammonium, nitrate, chloride, and sulphate) in size-resolved raindrop samples with HPCE method, 3-point external reference mixed standards were analyzed. Linear calibration formulas presented in Table 2 show that the correlation between the peak area (mAU) and concentration ( $\text{mg L}^{-1}$ ) was very good.

### 3. RESULTS AND DISCUSSION

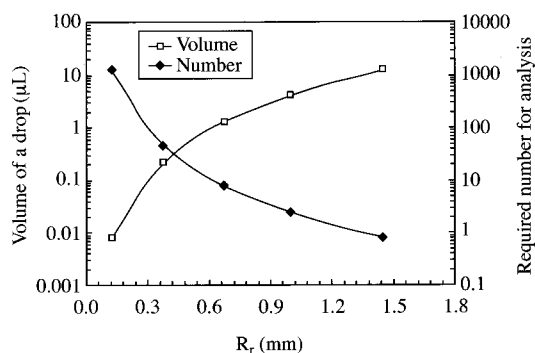
Fig. 3 displays the volume of a raindrop and the required drop number for HPCE analysis as a function of raindrop size. As mentioned earlier, the minimum amount of sample for HPCE analysis is 10  $\mu\text{L}$ . For this reason, to satisfy this minimum required sample volume, the collection duration time has to be adjusted depending on rain intensity.

#### 3.1 T-test for QA/QC

It is debatable point that the data obtained from HPCE analysis has credibility. Hence, to assure the

**Table 2. Linear calibration formula calculated by 3-point external reference mixed standards.**

	Mig. time (min)	Amount ( $\text{mg L}^{-1}$ )	Area (mAU)	$y=mx+b$
Ammonium	2.76	5	1.71E-02	m: 3.93E-03
		10	4.40E-02	b: 3.50E-04
		20	7.75E-02	R <sup>2</sup> : 0.984
Potassium	3.15	5	3.90E-03	m: 1.48E-03
		10	1.28E-02	b: -2.90E-03
		20	2.64E-02	R <sup>2</sup> : 0.995
Sodium	3.83	5	1.25E-02	m: 2.27E-03
		10	2.75E-02	b: 2.60E-03
		20	4.73E-02	R <sup>2</sup> : 0.988
Calcium	4.22	5	1.20E-02	m: 2.52E-03
		11	2.29E-02	b: -2.20E-03
		20	4.93E-02	R <sup>2</sup> : 0.986
Magnesium	4.51	5	1.76E-02	m: 4.34E-03
		10	4.29E-02	b: -2.65E-03
		20	8.34E-02	R <sup>2</sup> : 0.997
Chloride	6.21	5	7.60E-03	m: 1.63E-03
		10	1.77E-02	b: 2.00E-04
		20	3.25E-02	R <sup>2</sup> : 0.993
Sulphate	6.65	5	8.20E-03	m: 1.10E-03
		10	1.53E-02	b: 3.35E-03
		20	2.50E-02	R <sup>2</sup> : 0.990
Nitrate	6.84	5	9.30E-03	m: 1.47E-03
		10	1.47E-02	b: 1.15E-03
		20	3.10E-02	R <sup>2</sup> : 0.992



**Fig. 3. Volume of a raindrop vs. required drop number for HPCE analysis as a function of raindrop size.**

accuracy and precision of our data, the quality assurance and quality control (QA/QC) was conducted by analyzing a set of known standard samples and by doing interanalyzer crosscheck.

**Table 3. Paired data set designed by analyzing of the 10-step standard components by HPCE and IC.**

	Pair <sub>Ammonium</sub>		Pair <sub>Potassium</sub>		Pair <sub>Sodium</sub>		Pair <sub>Calcium</sub>		Pair <sub>Magnesium</sub>		Pair <sub>Chloride</sub>		Pair <sub>Sulfate</sub>		Pair <sub>Nitrate</sub>	
	X <sub>CEI</sub>	Y <sub>ICI</sub>	X <sub>CEI</sub>	Y <sub>ICI</sub>	X <sub>CEI</sub>	Y <sub>ICI</sub>	X <sub>CEI</sub>	Y <sub>ICI</sub>	X <sub>CEI</sub>	Y <sub>ICI</sub>	X <sub>CEI</sub>	Y <sub>ICI</sub>	X <sub>CEI</sub>	Y <sub>ICI</sub>	X <sub>CEI</sub>	Y <sub>ICI</sub>
X <sub>CE1</sub> , Y <sub>IC1</sub> (2) <sup>a</sup>	2.05	2.08	1.95	2.07	2.06	2.01	2.05	2.08	2.05	2.11	1.98	2.01	2.01	2.01	1.95	1.94
X <sub>CE2</sub> , Y <sub>IC2</sub> (4)	3.93	4.08	4.11	4.09	4.11	3.85	3.98	4.04	4.11	4.21	3.97	3.98	4.07	4.08	3.93	3.96
X <sub>CE3</sub> , Y <sub>IC3</sub> (6)	6.03	6.09	6.05	5.91	5.96	5.92	6.05	6.05	5.85	6.07	5.94	6.02	5.92	5.09	5.89	5.91
X <sub>CE4</sub> , Y <sub>IC4</sub> (8)	7.91	8.07	7.86	7.91	7.94	8.14	7.96	7.91	8.02	8.08	7.94	8.01	7.99	8.03	8.07	8.09
X <sub>CE5</sub> , Y <sub>IC5</sub> (10)	9.89	10.12	10.53	10.15	10.40	10.28	9.93	10.09	9.93	10.13	10.17	9.97	10.06	10.04	10.17	10.08
X <sub>CE6</sub> , Y <sub>IC6</sub> (12)	12.04	11.89	12.15	12.07	12.12	11.87	12.06	12.11	11.84	12.07	11.94	11.95	11.87	12.11	12.05	12.02
X <sub>CE7</sub> , Y <sub>IC7</sub> (14)	14.09	13.92	14.07	13.89	14.12	14.09	13.91	14.06	13.89	14.08	14.06	13.89	13.94	14.09	13.94	14.07
X <sub>CE8</sub> , Y <sub>IC8</sub> (16)	16.12	16.09	16.15	16.18	16.27	16.08	16.02	16.07	15.78	16.21	16.11	16.08	15.95	16.20	15.91	16.11
X <sub>CE9</sub> , Y <sub>IC9</sub> (18)	18.07	17.89	18.03	18.17	18.21	17.87	18.11	18.06	18.11	18.21	18.50	17.89	18.03	18.11	18.08	18.08
X <sub>CE10</sub> , Y <sub>IC10</sub> (20)	19.95	20.08	20.13	20.09	20.82	20.79	20.11	20.07	20.35	20.47	19.95	21.02	20.12	20.18	19.94	20.11
$\frac{n}{X}$	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10
S <sup>b</sup>	11.01	11.03	11.10	11.05	11.20	11.09	11.02	11.05	10.99	11.16	11.06	11.08	11.00	10.99	10.99	11.04
SM <sub>E</sub> <sup>c</sup>	6.08	6.02	6.09	6.09	6.23	6.20	6.08	6.07	6.09	6.13	6.14	6.22	6.07	6.20	6.07	6.12
S <sup>2d</sup>	1.92	1.90	1.93	1.93	1.97	1.96	1.92	1.92	1.93	1.94	1.94	1.97	1.92	1.96	1.92	1.93
S <sub>k</sub> <sup>e</sup>	36.94	36.23	37.10	37.11	38.81	38.39	36.96	36.81	37.11	37.54	37.68	38.64	36.79	38.45	36.80	37.39
K <sub>f</sub> <sup>f</sup>	0.002	0.011	-0.030	0.017	0.052	0.049	0.022	0.004	0.067	0.041	0.003	0.104	0.024	0.011	-0.020	-0.008
K <sub>r</sub> <sup>f</sup>	-1.25	-1.17	-1.19	-1.23	-1.14	-1.08	-1.19	-1.22	-1.13	-1.16	-1.24	-1.03	-1.17	-1.30	-1.19	-1.20

<sup>a</sup> Real value

<sup>b</sup> Standard deviation

<sup>c</sup> Standard error of the mean,  $SI/\sqrt{n}$

<sup>d</sup> Variance

<sup>e</sup> Skewness,  $\frac{n}{(n-1)(n-2)} \cdot \frac{\sum_{i=1}^n (X_i - \bar{X})^3}{S^3}$

<sup>f</sup> Kurtosis,  $\frac{n(n+1)}{(n-1)(n-2)(n-3)} \cdot \frac{\sum_{i=1}^n (X_i - \bar{X})^4}{S^4} - \frac{3(n-1)^2}{(n-2)(n-3)}$

**Table 4. T-test statistics for paired independent samples.**

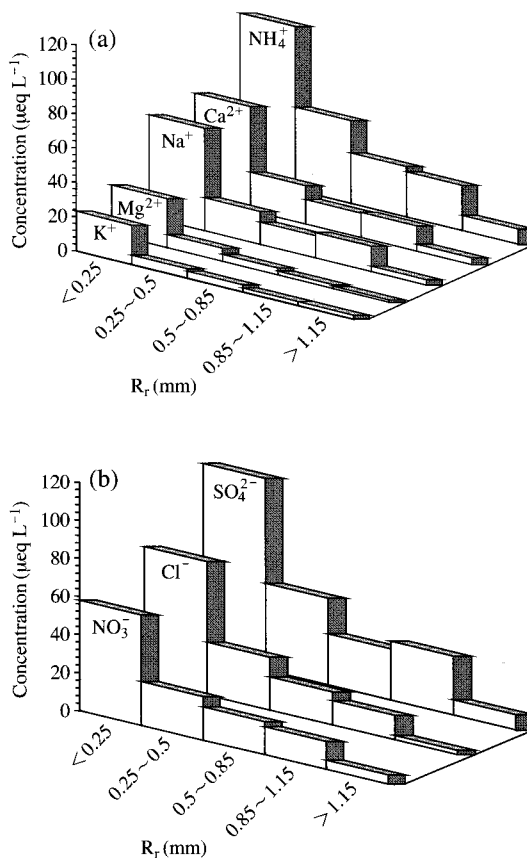
		95% Conf. Int. Dif. <sup>a</sup>		t value	df <sup>b</sup>	Sig. (p) <sup>c</sup> (2-tailed)
		Lower	Upper			
Pair <sub>Ammonium</sub>	$X_{CEi}-Y_{ICi}$	-0.130	0.084	-0.486	9	0.639
Pair <sub>Potassium</sub>	$X_{CEi}-Y_{ICi}$	-0.061	0.161	1.018	9	0.335
Pair <sub>Sodium</sub>	$X_{CEi}-Y_{ICi}$	-0.001	0.223	2.251	9	0.051
Pair <sub>Calcium</sub>	$X_{CEi}-Y_{ICi}$	-0.090	0.018	-1.509	9	0.166
Pair <sub>Magnesium</sub>	$X_{CEi}-Y_{ICi}$	-0.251	-0.091	-4.858	9	0.001
Pair <sub>Chloride</sub>	$X_{CEi}-Y_{ICi}$	-0.327	0.275	-0.195	9	0.849
Pair <sub>Sulphate</sub>	$X_{CEi}-Y_{ICi}$	-0.217	0.221	0.021	9	0.984
Pair <sub>Nitrate</sub>	$X_{CEi}-Y_{ICi}$	-0.110	0.022	-1.502	9	0.167

<sup>a</sup>95% confidence interval of the difference<sup>b</sup>Degrees of freedom<sup>c</sup>Significance (=p)

A t-test can be used to determine if the scores of two groups differ on a single variable. It is useful in analyzing scores of two groups on a particular variable or in analyzing scores of a single group on two variables. The data may either be paired or not paired. By paired, it means that there is a one-to-one correspondence between the values in the two samples. That is, if  $X_1, X_2, \dots, X_n$  and  $Y_1, Y_2, \dots, Y_n$  are the two samples, then  $X_i$  corresponds to  $Y_i$ .

In this study, a t-test was conducted to determine whether the means of two populations, which were designed by analyzing of the 10-step of standard major ionic components by HPCE and ion chromatography (IC) (Shimadzu LC-10A), are statistically different from each other. The null hypothesis for the t-test is that the means, which were determined by analyzing of mixed standard solutions by HPCE and IC, are homogeneous. The 95% confidence interval for the mean was set. If the 95% confidence interval of the mean difference includes zero, then the mean difference is not different from zero. Paired data set and basic statistical summary are presented in Table 3. The concentrations obtained by HPCE show a good agreement with those by IC. In Table 3, the skewness and kurtosis scores for the paired variables include zero indicating that scores meet the normality assumption with the exception of  $X_{CEi}$  of Pair<sub>Potassium</sub> and  $X_{CEi}-Y_{ICi}$  of Pair<sub>Nitrate</sub>.

Table 4 reports the t-test statistics for paired independent samples. The 95% confidence interval



**Fig. 4. Raindrop size-dependence of major ionic components. Rr means the half of mesh's pore size. (a) Major cation; (b) Major anion.**

for the mean difference found as including zero. This indicates that the null hypothesis cannot be rejected, that is, the means are homogenous. In this case the two means are not significantly different from each other. However in the case of Pair<sub>Magnesium</sub>, the 95% confidence interval ranges from  $-0.251$  to  $-0.091$ . It does not include zero, so the two means are significantly different from each other.

### 3.2 Raindrop size dependence of major ionic species

Fig. 4 shows the variation of concentrations of major ionic components as a function of raindrop size. As shown in figure, every ionic concentration in both cation and anion is found to be strong

raindrop size dependence. Though there is the slight increase of sodium and sulphate concentrations between 0.85 mm and 1.15 mm raindrop radius, it shows a strong decrease of every ionic component with increasing droplet radius. It is expected that the following several mechanisms are responsible for this raindrop size dependence of ionic concentration: the scavenging of particles by CCN mechanism, the uptake of gases inside the cloud, the scavenging of particles by impaction, collision, and coalescence below the clouds, the uptake of gases below the cloud as well as the collision and coalescence inside the cloud and raindrop evaporation below the cloud (Tenberken *et al.*, 1995). When raindrops fall from cloud base to ground, due to evaporation and below cloud scavenging of pollutants the solute concentration in raindrop will be increased. In addition, evaporation of falling raindrop mainly dominates the smallest drops. Hans and James (1998) reported that the scavenging efficiency of pollutants by falling raindrops decreases with increasing raindrop size with the range of 0.2 mm to 4 mm diameter. While on the other hand, Bächmann *et al.* (1993) reported that during a precipitation event the salt concentration across the raindrop spectrum evolves in time and often develops the maximum concentration in raindrops of 0.2 mm to 0.3 mm radius. By cloud model studies, Koop (1996) suggested that this maximum in small fraction raindrop is an indirect result of collisional breakup of large raindrops. However in the present study, a monomodal peak in the small raindrop range was not proved because the whole small raindrops (< 0.25 mm radius) were collected on back-up stage.

To interpret the raindrop size dependence of ionic concentration, two kinds of scavenging mechanism, namely, gas scavenging and aerosol scavenging mechanisms have to be distinguished. Schwarz (1984) made a model for reversible mass transport of HO<sub>2</sub> between the gas and aqueous phases of liquid water clouds and he reported the rate of gas absorption by the following equation.

$$f_i = \frac{p_i - c_i/H_i}{RT(2a/ShD_i + 4/V_i)} \quad (7)$$

where  $p_i$  is partial pressure,  $a$  is drop radius,  $c_i$  is concentration,  $Sh$  is Sherwood number,  $H_i$  is Henry constant,  $D_i$  is diffusion coefficient,  $R$  is gas constant,  $V_i$  is average velocity,  $T$  is temperature,  $i$  is accommodation coefficient.

Also Pilat and Prem (1976) reported the calculated particle collection efficiencies of single droplets including inertial impaction, Brownian diffusion, diffusiophoresis and thermophoresis. The particle collection efficiency of a single droplet  $E_c$  was given by

$$E_c = \frac{(Y_o + r_p)^2}{R_d^2} \quad (8)$$

where  $Y_o$  is the initial  $Y$  position (measured from the drop centerline) of the particle center trajectory that just grazes the droplet,  $r_p$  the particle radius, and  $R_d$  the droplet radius.

According to above two equations, the rate of gas absorption and particle collection efficiency increase with decreasing drop size.

#### 4. CONCLUSIONS

To fully understand the washout mechanism of air pollutants by rainfall, the size-resolved raindrops study should be performed. However, unfortunately, this method has not been generalized. In this study, an experimental verification for the popularization of this method was attempted by applying the frozen raindrop collector and a commercially available HPCE. T-test showed that the ionic concentrations obtained by HPCE have a good agreement with those by IC. The ionic components of size-resolved raindrops collected in urban area of Japan could be successfully determined by HPCE with good accuracy and precision. They showed the strong raindrop size dependence. In view of the results achieved in the present study, a combination of the frozen raindrop collection method and a commercially available HPCE can fairly accomplish the size-resolved raindrops study.

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