

# Continuous and simultaneous determination of anions and cations in rainwater by ion chromatography

Qun Xu, Wen Zhang, Chun Xu and Litong Jin\*

Department of Chemistry, East China Normal University, Shanghai, 200062, China.  
E-mail: [hsuchun@tonghua.com.cn](mailto:hsuchun@tonghua.com.cn); Fax: +86 021 62451876

Received 1st February 2000, Accepted 10th April 2000

Published on the Web 22nd May 2000

A simple and sensitive method was investigated for the continuous and simultaneous determination of inorganic anions ( $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{F}^-$ ) and cations ( $\text{Na}^+$ ,  $\text{NH}_4^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ) in rainwater over a period of 18 h. A solution of  $5 \times 10^{-3} \text{ mol L}^{-1}$  DL-malic acid–5% methanol–water was used as the eluent. Good simultaneous separation of anions and cations based on an ion-exclusion mechanism and a cation-exchange mechanism was achieved within 30 min with conductimetric detection. The method was successfully applied to rainwater detection, and proved to be a very useful method for real-time rainwater analysis.

## Introduction

With the development of industry, more and more waste gases such as  $\text{SO}_2$  and  $\text{NO}_x$  are emitted into the air. Acid rain, mainly caused by  $\text{SO}_2$  and  $\text{NO}_x$ , is now a very harmful environmental problem. The major cations in rainwater are  $\text{H}^+$ ,  $\text{Na}^+$ ,  $\text{NH}_4^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  and the major anions are  $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$  and  $\text{HCO}_3^-$ ; other ions such as  $\text{F}^-$ ,  $\text{CH}_3\text{COO}^-$ ,  $\text{HCOO}^-$  and  $\text{NO}_2^-$  are also sometimes present in rainwater. The continuous and simultaneous determination of these ions in rainwater could intuitively provide long-term information on rainfall for elucidating the major reasons for acid rain formation.

There are many methods for determining these ions, such as spectrophotometry,<sup>1,2</sup> ion-selective electrode analysis,<sup>3,4</sup> atomic absorption spectrometry,<sup>5</sup> atomic emission spectrometry,<sup>6,7</sup> oscillographic titration,<sup>8,9</sup> capillary electrophoresis,<sup>10,11</sup> flow injection analysis<sup>12</sup> and chemiluminescence analysis.<sup>13</sup> However, most of these methods cannot determine anions and cations simultaneously. As an effective analytical method, ion chromatography (IC) can provide a convenient way to separate anions and cations. There are several basic ion-exchange separation methods for the simultaneous determination of anions and cations by IC, such as the use of chelating agents as eluents,<sup>14,15</sup> on bifunctional ion-exchange resin,<sup>16</sup> on mixed-bed columns<sup>17–19</sup> and on suitably connected anion- and cation-exchange columns.<sup>20–23</sup> However, they could only achieve the simultaneous determination of these anions and cations to a certain extent, and their processes are complicated. Tanaka *et al.*<sup>24–27</sup> separated common anions and cations simultaneously using tartaric acid solution as eluent by single-column ion-exclusion chromatography–cation-exchange chromatography based on ion-exclusion and cation-exchange mechanisms, that is, the separation of anions was by ion exclusion and that of cations was by cation exchange.

In this work, a method of monitoring rainwater was developed for continuously and simultaneously determining anions and cations during a period of rainfall over 18 h. The separation and detection were achieved within 30 min by single-column ion-exclusion chromatography–cation-exchange chromatography (IEC-CEC) with conductimetric detection. DL-Malic acid–methanol–water was used as the eluent for the first time in this method. Replicate samples were collected and quality control procedures<sup>28</sup> were employed. The ranges of linear relationships were over two orders of magnitude of concentration and the correlation coefficients were all  $>0.99$ .

The detection limits of these ions calculated using  $3\sigma$  (where  $\sigma$  represents the standard deviation of a blank solution) were all lower than  $5.12 \times 10^{-6} \text{ mol L}^{-1}$ . The relative standard deviations of chromatographic peak height ( $\mu\text{S cm}^{-1}$ ) of anions and cations were  $<3.0\%$ . The recoveries of common anions and cations by this method were in the range 93–105%. The results indicate that the proposed method is a successful and useful method with satisfactory speed and sensitivity for real-time rainwater analysis during a period of rainfall.

## Experimental

### Chemicals and solutions

All reagents were of analytical-reagent grade and dissolved in de-ionized, distilled water ( $0.5 \mu\text{S cm}^{-1}$ ) for the preparation of standard solutions and eluents. Stock standard solutions of anions and cations were prepared by dissolving appropriate amounts of potassium chloride, calcium chloride, sodium fluoride, magnesium sulfate, ammonium nitrate (all from the Fourth Reagent Factory, Shanghai, China) at a concentration of  $1.0 \times 10^{-2} \text{ mol L}^{-1}$ , sodium phosphate, ammonium bromide, potassium iodide, sodium formate, sodium acetate, lithium chloride, strontium chloride, barium chloride (all from the First Reagent Factory, Shanghai, China) and rubidium nitrate and caesium nitrate (both from Merck, Darmstadt, Germany) at a concentration of  $1.0 \times 10^{-4} \text{ mol L}^{-1}$ . Malonic acid, tartaric acid and DL-malic acid (Nanxiang Reagent Co., Shanghai, China) were used components of the eluent, and the concentrations of their stock standard solutions were all  $0.5 \text{ mol L}^{-1}$ . All reagents were diluted as necessary. As one of the components of the eluent, absolute methanol (from the Fourth Reagent Factory) was required.

### Instrumentation

All experiments were performed on a Shimadzu (Tokyo, Japan) IC system including an LC-10AS eluent delivery pump, a CDD-6A conductimetric detector and a SIL-6B injector equipped with a  $25 \mu\text{L}$  sample loop. The recorder was a Dahua (Shanghai, China)  $x-t$  recorder. A Tosoh (Tokyo, Japan) TSK gel OA-PAK-A weakly acidic cation-exchange resin column with polyacrylate copolymer (particle size  $5 \mu\text{m}$ ,  $300 \times 7.8 \text{ mm}$  id) was used for the simultaneous separation of anions and cations.

A Twin B-212 pH meter (Horiba, Kyoto, Japan) was used for measuring the pH values of samples. A QC-50 ultrasonic degasser (Binengxin, Shanghai, China) was used for de-gassing the eluent.

### Chromatographic conditions

The eluent, composed of  $5.0 \times 10^{-3}$  mol L<sup>-1</sup> DL-malic acid–5% methanol–water, should be de-gassed for 20 min before being pumped through the column. The gain of the conductimetric detector was 1  $\mu$ S cm<sup>-1</sup>, the range was 1, the response was STD (response time 1 s) and the polarity was positive. The eluent flow rate was 1.2 mL min<sup>-1</sup> (column pressure 38 kg cm<sup>-2</sup>). The baseline drift of the chromatograms was minimized by keeping the column temperature at 25 °C. The instrument was equilibrated for about 30 min prior to use. Before each injection, the 'zero' button of the conductimetric detector should be pushed to make a baseline correction. The injection volumes of the standard and sample solutions were all 25  $\mu$ L. A blank solution (de-ionized, distilled water) test should be performed before detection.

### Rainwater analysis

Rainwater samples were collected at East China Normal University (ECNU), which is in Putuo district, Shanghai, China, using polyethylene bottles with wide polyethylene funnels. The sampling vessels were washed with detergent, soaked with acid and then rinsed thoroughly with de-ionized, distilled water and oven-dried at 40 °C. The installations were placed on the ground at a height of about 1.2 m. From the beginning of rainfall, rainwater was sampled once per hour. The sampling time was 5–10 min and the sample volume was 10–20 mL. The sample water was poured in a 50 mL polyethylene bottle that had been washed with detergent, acid soaked and then rinsed thoroughly with de-ionized, distilled water, and finally oven-dried at 40 °C. Two replicate samples were collected throughout. After collection, the pH value of each sample was measured and then the sample was filtered with a 0.45  $\mu$ m nylon-66 membrane filter (Bandao, Shanghai, China) (soaked in de-ionized, distilled water for 24 h) prior to direct analysis. Subsequently, all the samples were analysed according to the chromatographic conditions specified.

## Results and discussion

### Selection of eluting agent

In single-column IEC-CEC, a solution of weak acid–methanol–water is suitable as the eluent for separating anions and cations simultaneously.<sup>24</sup> This is because when water is used as eluent, it is possible to separate anions alone by ion exclusion; the separation of cations is impossible since they are fixed on the resin. However, when a strong acid (such as sulfuric acid) is used as eluent, it is possible to separate the cations alone by cation exchange; the separation of anions is impossible because all of them are incompletely ion excluded from the resin. Only when weak acids are used as eluent is it possible to separate anions and cations simultaneously by ion exclusion and cation exchange, respectively. In this experiment, three weak acids, namely malonic acid ( $pK_{a1} = 2.86$ ), DL-malic acid ( $pK_{a1} = 3.40$ ) and tartaric acid ( $pK_{a1} = 3.22$ ), were tested as eluting agents to separate the anions ( $Cl^-$ ,  $NO_3^-$ ,  $SO_4^{2-}$ ,  $F^-$ ,  $CH_3COO^-$ ,  $HCOO^-$  and  $NO_2^-$ ) and cations ( $Na^+$ ,  $NH_4^+$ ,  $K^+$ ,  $Mg^{2+}$  and  $Ca^{2+}$ ). Good simultaneous separations of these ions were achieved except for  $HCO_3^-$  in its molecular state ( $H_2CO_3$ ,  $pK_{a1} = 6.38$ ) in an acidic eluent.<sup>24</sup> There were  $F^-$  ions present

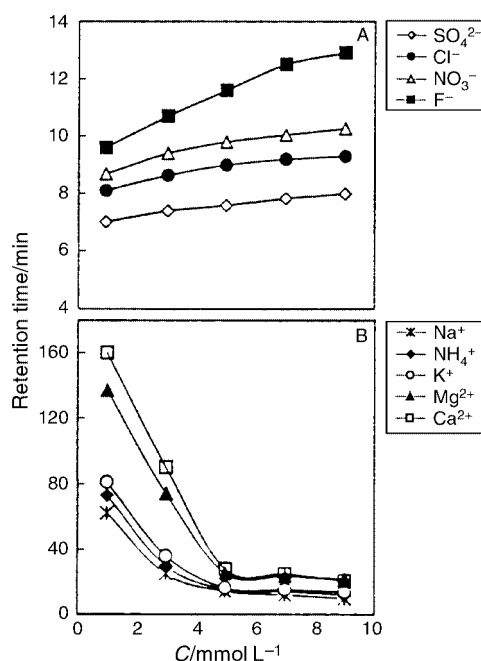
in the rainwater in Shanghai (about  $1.0 \times 10^{-5}$  mol L<sup>-1</sup>),<sup>29</sup> which could only be qualified using DL-malic acid as eluent under the chromatographic conditions mentioned above. In addition, the background conductivity was 610  $\mu$ S cm<sup>-1</sup> for malonic acid, 559  $\mu$ S cm<sup>-1</sup> for DL-malic acid and 582  $\mu$ S cm<sup>-1</sup> for tartaric acid under the same chromatographic conditions. It was obvious that the background conductivity of DL-malic acid was the lowest, so it was chosen as the eluting agent.

### Effect of DL-malic acid concentration

In order to optimize the simultaneous separation and detection of these cations and anions, the effects of DL-malic acid concentration in the eluent on the retention time ( $t_R$ ) of the anions and cations and the eluent background conductivity were investigated. In the separation of anions, the  $t_R$  values of anions increased with increasing concentration of DL-malic acid in the eluent [as shown in Fig. 1(A)]. In the separation of cations, the  $t_R$  values of cations decreased drastically with increasing concentration of DL-malic acid in the eluent [as shown in Fig. 1(B)]. The eluent background conductivity increased with increasing DL-malic acid concentration in the eluent. An increase in the eluent background conductivity could cause a decrease in the sensitivity of conductivity detection. The optimum concentration of DL-malic acid was  $5.0 \times 10^{-3}$  mol L<sup>-1</sup>.

### Effect of methanol concentration

Methanol<sup>24–26</sup> and 18-crown-6<sup>27</sup> were added to the eluent to improve the peak resolution of cations in IEC-CEC. Methanol<sup>30</sup> could also improve the peak resolution of anions in IC. The effect of methanol concentration in the eluent was investigated. As shown in Fig. 2, the  $t_R$  values of the anions were almost unchanged and those of the cations increased gradually for monovalent cations and decreased gradually for divalent cations. Considering these results, the optimum concentration of methanol in the eluent was *ca.* 4–7%.



**Fig. 1** Effect of DL-malic acid concentration in the eluent on retention time ( $t_R$ ) of (A) anions and (B) cations. Column, Tosoh TSK gel OA-PAK-A; column temperature, 25 °C; eluent, DL-malic acid–5.0% methanol–water; eluent flow rate, 1.2 mL min<sup>-1</sup>; injection volume, 25  $\mu$ L; sample, mixture of  $1.0 \times 10^{-4}$  mol L<sup>-1</sup> KCl,  $CaCl_2$ , NaF and  $NH_4NO_3$ ;  $1.6 \times 10^{-4}$  mol L<sup>-1</sup>  $MgSO_4$ .

## Effect of eluent flow rate

Increasing the eluent flow rate could shorten the separation time; *e.g.*, it took about 28 min to achieve the separation of these ions at a flow rate of 1.2 mL min<sup>-1</sup> and about 43 min at 0.8 mL min<sup>-1</sup>. However, if the flow rate was too fast, the baseline was unstable and the background conductivity was too high (as shown in Fig. 3), which could cause a decrease in the sensitivity of the method. The optimum flow rate was 1.2 mL min<sup>-1</sup>.

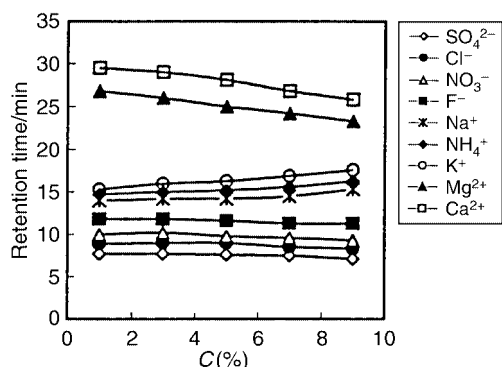
## Retention behavior of common anions and cations

Table 1 gives the retention times ( $t_R$ ) of common anions and cations obtained using  $5.0 \times 10^{-3}$  mol L<sup>-1</sup> DL-malic acid–5% methanol–water as the eluent at a flow rate of 1.2 mL min<sup>-1</sup>.

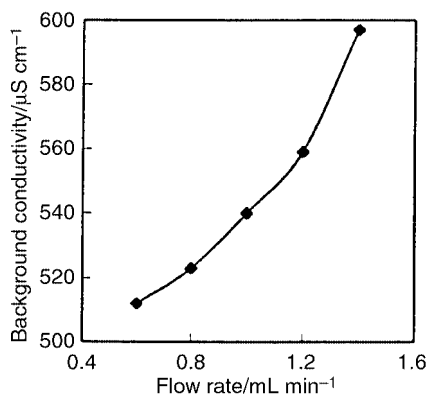
For the retention of monovalent weak acid anions such as NO<sub>2</sub><sup>-</sup>, F<sup>-</sup>, HCOO<sup>-</sup> and CH<sub>3</sub>COO<sup>-</sup>,  $t_R$  depended on their  $pK_1$

values (NO<sub>2</sub><sup>-</sup> < F<sup>-</sup> < HCOO<sup>-</sup> < CH<sub>3</sub>COO<sup>-</sup>). For the retention of mono- and divalent strong acid anions such as SO<sub>4</sub><sup>2-</sup>, S<sub>2</sub>O<sub>3</sub><sup>2-</sup> and Cl<sup>-</sup>, the  $t_R$  depended on their charge (Cl<sup>-</sup> < SO<sub>4</sub><sup>2-</sup> = S<sub>2</sub>O<sub>3</sub><sup>2-</sup>) rather than their  $pK_1$  values (complete dissociation). The  $t_R$  of NO<sub>3</sub><sup>-</sup> depended on the hydrophobic adsorption of NO<sub>3</sub><sup>-</sup> by the polyacrylate resin rather than the differences in the charge and the  $pK_1$  values, so the  $t_R$  of NO<sub>3</sub><sup>-</sup> was larger than that of PO<sub>4</sub><sup>3-</sup>, which is a weak acid anion ( $pK_1$  = 2.1).<sup>25</sup> For the retention of monovalent strong acid halide anions such as Cl<sup>-</sup>, Br<sup>-</sup> and I<sup>-</sup>, which were ionized completely, the effect of hydrophobic adsorption by the polymeric resin based on the difference in their ionic radii (Cl<sup>-</sup> < Br<sup>-</sup> < I<sup>-</sup>) might be predominant in their separation.<sup>24</sup>

For the retention of cations, their  $t_R$  was strongly related to their cation-exchange affinity (their ionic radii and charge). The elution order of mono- and divalent cations was almost identical with those in conventional cation-exchange chromatography with an acidic eluent.



**Fig. 2** Effect of methanol concentration in the eluent on retention times ( $t_R$ ). Eluent,  $5.0 \times 10^{-3}$  mol L<sup>-1</sup> DL-malic acid–methanol–water; other chromatographic conditions as in Fig. 1.



**Fig. 3** Effect of flow rate on background conductivity of eluent. Eluent,  $5.0 \times 10^{-3}$  mol L<sup>-1</sup> DL-malic acid–5% methanol–water; other chromatographic conditions as in Fig. 1.

**Table 1** Retention time ( $t_R$ ) of common anions and cations on elution with  $5.0 \times 10^{-3}$  mol L<sup>-1</sup> DL-malic acid–5% methanol–water

Anion	$t_R$ /min	Cation	$t_R$ /min
SO <sub>4</sub> <sup>2-</sup>	7.6	Li <sup>+</sup>	13.7
S <sub>2</sub> O <sub>3</sub> <sup>2-</sup>	7.6	Na <sup>+</sup>	14.2
Cl <sup>-</sup>	9.0	NH <sub>4</sub> <sup>+</sup>	15.2
PO <sub>4</sub> <sup>3-</sup>	9.2	K <sup>+</sup>	16.3
Br <sup>-</sup>	9.4	Rb <sup>+</sup>	17.0
NO <sub>3</sub> <sup>-</sup>	9.8	Cs <sup>+</sup>	18.0
I <sup>-</sup>	10.5	Mg <sup>2+</sup>	25.0
NO <sub>2</sub> <sup>-</sup>	11.0	Ca <sup>2+</sup>	28.1
F <sup>-</sup>	11.6	Sr <sup>2+</sup>	30.5
HCOO <sup>-</sup>	13.2	Ba <sup>2+</sup>	45.5
CH <sub>3</sub> COO <sup>-</sup>	13.5		

## Interferences

Some weak acid anions such as NO<sub>2</sub><sup>-</sup>, CH<sub>3</sub>COO<sup>-</sup> and HCOO<sup>-</sup> are sometimes present in rainwater; the retention time of NO<sub>2</sub><sup>-</sup> was close to that of F<sup>-</sup> and those of CH<sub>3</sub>COO<sup>-</sup> and HCOO<sup>-</sup> were close to that of Na<sup>+</sup>. The experimental results indicated that a 20-fold excess of NO<sub>2</sub><sup>-</sup> eluting before F<sup>-</sup> did not interfere in the determination of F<sup>-</sup> and an eightfold excess of CH<sub>3</sub>COO<sup>-</sup> and HCOO<sup>-</sup> eluting before Na<sup>+</sup> did not interfere in the determination of Na<sup>+</sup>.

## Linearity and detection limits

To determine the linearity for SO<sub>4</sub><sup>2-</sup>, Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, NO<sub>2</sub><sup>-</sup>, F<sup>-</sup>, CH<sub>3</sub>COO<sup>-</sup>, HCOO<sup>-</sup>, Na<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup> and Ca<sup>2+</sup> by this IC method with conductivity detection, a series of standard solutions of these anions ranging from  $1.0 \times 10^{-6}$  to  $1.0 \times 10^{-3}$  mol L<sup>-1</sup> were tested. The ranges of linear relationships observed between conductivity and concentration were over two orders of magnitude and the correlation coefficients were > 0.99. The detection limits of these ions were calculated using  $3\sigma$  ( $n = 11$ ). The analytical data for the anions and cations are summarized in Table 2.

## Reproducibility and recovery

The reproducibility was estimated by making replicate injections ( $n = 5$ ) of a mixture of rainwater sample and a standard solution containing SO<sub>4</sub><sup>2-</sup>, Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, F<sup>-</sup>, Na<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup> and Ca<sup>2+</sup> ions. The relative standard deviations of chromatographic peak height ( $\mu$ S cm<sup>-1</sup>) of anions and cations were < 3.0%.

The recoveries with this method were tested by the analysis of a spiked rainwater sample and replicate injections ( $n = 5$ ). The results are given in Table 3 and the chromatograms are shown in Fig. 4. They demonstrate that the proposed IC method is suitable for the simultaneous determination of common inorganic anions and cations.

## Application to the continuous and simultaneous determination of anions and cations in rainwater

The proposed IC method was applied to the continuous and simultaneous determination of common anions and cations in rainwater during rainfall over a period of 18 h. CH<sub>3</sub>COO<sup>-</sup>, HCOO<sup>-</sup> and NO<sub>2</sub><sup>-</sup> ions were not found. All of the ion balances of the ions detected in the rainwater were nearly 1.0. The results

**Table 2** Linearity and detection limits of the anions and cations in IC with conductimetric detection<sup>a</sup>

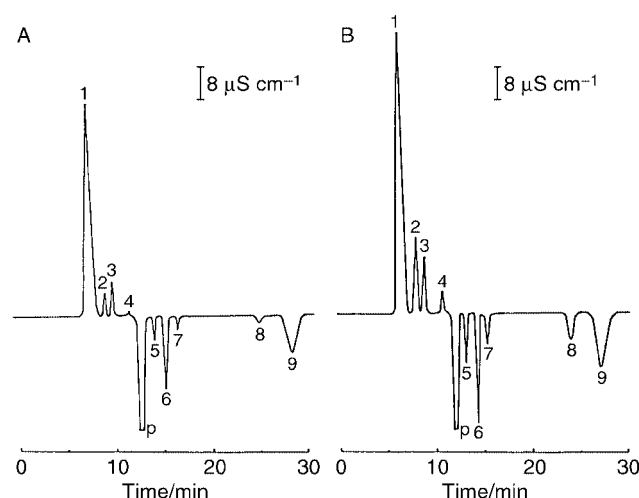
Anion	Regression equation <sup>b</sup> : $y = ax + b$	Correlation coefficient ( $r^2$ )	Linear range/mol L <sup>-1</sup>	Detection limit <sup>c</sup> / 10 <sup>-6</sup> mol L <sup>-1</sup>
SO <sub>4</sub> <sup>2-</sup>	$y = 414.7x + 0.1600$	0.9993	$5.0 \times 10^{-6}$ – $1.0 \times 10^{-3}$	1.64
Cl <sup>-</sup>	$y = 195.7x + 0.1984$	0.9992	$5.0 \times 10^{-6}$ – $1.0 \times 10^{-3}$	3.28
NO <sub>3</sub> <sup>-</sup>	$y = 243.0x + 0.7200$	0.9965	$5.0 \times 10^{-6}$ – $1.0 \times 10^{-3}$	0.50
NO <sub>2</sub> <sup>-</sup>	$y = 173.2x + 0.1875$	0.9941	$5.0 \times 10^{-6}$ – $1.0 \times 10^{-3}$	3.77
F <sup>-</sup>	$y = 161.1x + 0.2240$	0.9981	$5.0 \times 10^{-6}$ – $1.0 \times 10^{-3}$	3.82
HCOO <sup>-</sup>	$y = 149.6x + 0.1203$	0.9965	$2.0 \times 10^{-5}$ – $1.0 \times 10^{-3}$	4.81
CH <sub>3</sub> COO <sup>-</sup>	$y = 140.5x + 0.1165$	0.9965	$3.0 \times 10^{-5}$ – $1.0 \times 10^{-3}$	5.12
Na <sup>+</sup>	$y = 248.8x + 0.7420$	0.9937	$5.0 \times 10^{-6}$ – $1.0 \times 10^{-3}$	0.40
NH <sub>4</sub> <sup>+</sup>	$y = 207.3x + 0.6304$	0.9993	$5.0 \times 10^{-6}$ – $1.0 \times 10^{-3}$	1.01
K <sup>+</sup>	$y = 182.5x + 0.2880$	0.9958	$8.0 \times 10^{-6}$ – $1.0 \times 10^{-3}$	3.02
Mg <sup>2+</sup>	$y = 133.4x + 0.1680$	0.9938	$1.0 \times 10^{-5}$ – $1.0 \times 10^{-3}$	5.03
Ca <sup>2+</sup>	$y = 189.4x + 0.2560$	0.9930	$1.0 \times 10^{-5}$ – $1.0 \times 10^{-3}$	3.08

<sup>a</sup> Chromatographic conditions as in Fig. 4. <sup>b</sup>  $y$  and  $x$  represent the peak height ( $\mu\text{S cm}^{-1}$ ) and the concentration of the ions ( $10^{-3}$  mol L<sup>-1</sup>), respectively.

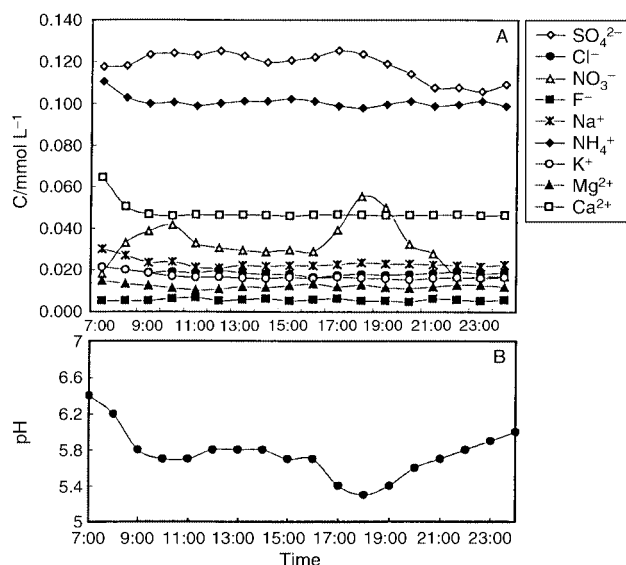
<sup>c</sup> Calculated using  $3\sigma$  ( $\sigma$  represents the standard deviation of a blank solution,  $n = 11$ ).

**Table 3** Results of recovery test on ions in rainwater by IC (mean values of five determinations)

	Sample ions								
	SO <sub>4</sub> <sup>2-</sup>	Cl <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>	F <sup>-</sup>	Na <sup>+</sup>	NH <sub>4</sub> <sup>+</sup>	K <sup>+</sup>	Mg <sup>2+</sup>	Ca <sup>2+</sup>
Added/10 <sup>-6</sup> mol L <sup>-1</sup>	40.0	75.0	25.0	25.0	25.0	25.0	25.0	40.0	25.0
Detected/10 <sup>-6</sup> mol L <sup>-1</sup>	38.4	72.6	26.3	23.3	26.4	24.2	25.5	42.1	23.5
Recovery (%)	96	97	104	93	104	96	102	105	94



**Fig. 4** Chromatograms of (A) rainwater sample and (B) rainwater sample A + standard solution (mixture of  $2.5 \times 10^{-5}$  mol L<sup>-1</sup> KCl, CaCl<sub>2</sub>, NaF and NH<sub>4</sub>NO<sub>3</sub>;  $4.0 \times 10^{-5}$  mol L<sup>-1</sup> MgSO<sub>4</sub>). Peaks: 1 = SO<sub>4</sub><sup>2-</sup>; 2 = Cl<sup>-</sup>; 3 = NO<sub>3</sub><sup>-</sup>; 4 = F<sup>-</sup>; 5 = Na<sup>+</sup>; 6 = NH<sub>4</sub><sup>+</sup>; 7 = K<sup>+</sup>; 8 = Mg<sup>2+</sup>; 9 = Ca<sup>2+</sup>; p = eluent dip. Column, Tosoh TSK gel OA-PAK-A (particle size 5  $\mu\text{m}$ ,  $300 \times 7.8$  mm id); eluent,  $5.0 \times 10^{-3}$  mol L<sup>-1</sup> DL-malic acid–5.0% methanol–water; injection volume, 25  $\mu\text{L}$ ; flow rate, 1.2 mL min<sup>-1</sup>; column temperature, 25 °C.



**Fig. 5** Results of the detection of major anions and cations in first rainfall. The samples were collected once per hour at ECNU in Putuo district, Shanghai, from the beginning of rainfall at 6:00 to 24:00 on November 24th, 1999. Eluent,  $5.0 \times 10^{-3}$  mol L<sup>-1</sup> malonic acid–water. Other chromatographic conditions as in Fig. 4.

are shown in Fig. 5. As can be seen, there was some correlation between the pH value [as shown in Fig. 5 (B)] and the NO<sub>3</sub><sup>-</sup> concentration in rainwater [as shown in Fig. 5 (A)]. With increase in NO<sub>3</sub><sup>-</sup> concentration, the pH value of rainwater decreased, and *vice versa*. Comparing with the results for a rainwater sample detected by the IC method and other methods, the data were consistent (Table 4). This suggests that the proposed IC method was reliable and sensitive for the continuous determination of the anions and cations in real water samples.

## Conclusions

This study has shown that single column ion-exclusion–cation-exchange chromatography with conductimetric detection using DL-malic acid–methanol–water as the eluent is a rapid, simple, efficient and highly sensitive method for the continuous and simultaneous detection of anions and cations in rainwater during a period of rainfall. It could quickly provide important information about acid rain and contribute to the study on the reasons for acid rain formation. Future work will be focused on the continuous and simultaneous determination of ions includ-

**Table 4** Results of determination of major anions and cations ( $\times 10^5$  mol L<sup>-1</sup>) in rainwater samples<sup>a</sup> by single-column ion-exclusion–cation-exchange chromatography

Method	Ion								
	SO <sub>4</sub> <sup>2-</sup>	Cl <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>	F <sup>-</sup>	Na <sup>+</sup>	NH <sub>4</sub> <sup>+</sup>	K <sup>+</sup>	Mg <sup>2+</sup>	Ca <sup>2+</sup>
IC	10.68	0.857	1.924	0.009	0.920	1.681	0.123	0.161	2.452
UV <sup>b</sup>	10.69	0.850	1.931	—	—	—	—	—	—
AAS <sup>c</sup>	—	—	—	—	0.925	—	0.124	0.157	2.480
ISE <sup>d</sup>	—	—	—	0.009	—	1.688	—	—	—

<sup>a</sup> The rainwater sample was collected at ECNU in Putuo district, Shanghai, on March. 15th, 2000. Chromatographic conditions as in Fig. 4. <sup>b</sup> Determined by UV spectrophotometry. <sup>c</sup> Determined by atomic absorption spectrometry (AAS). <sup>d</sup> Determined by ion-selective electrode (ISE) analysis.

ing organic anions and cations in organism and industry analysis, etc.

## Acknowledgements

The authors were grateful to Professor Kazuhiko Tanaka (National Industrial Research Institute of Nagoya, Aichi, Japan) and Professor Hiroki Haraguchi and Dr. Akihito Itoh (Department of Applied Chemistry, School of Engineering, Nagoya University, Nagoya, Japan) for their enthusiastic help.

## References

- J. C. Martinez and J. V. M. Garcia, *Analyst*, 1998, **123**, 429.
- Z. M. Xu, *Chin. J. Anal. Chem.*, 1995, **23**, 1472.
- X. M. Lin and K. Umezawa, *Anal. Sci.*, 1998, **14**, 99.
- S. Matysik and F. M. Matysik, *Electroanalysis*, 1998, **10**, 181.
- A. N. Araujo and R. C. C. Costa, *Anal. Chim. Acta*, 1998, **358**, 111.
- T. Umemura and R. Kitaguchi, *Anal. Chem.*, 1998, **70**, 936.
- X. Y. Zhang and K. Satoh, *Anal. Sci.*, 1997, **13**, 890.
- Y. R. Wong, H. Z. Zhu and H. Gao, *Chin. J. Anal. Chem.*, 1994, **22**, 972.
- B. Fan, *Chin. J. Anal. Chem.*, 1993, **21**, 554.
- B. Saad and F. W. Pok, *Food Chem.*, 1998, **61**, 249.
- A. Padarauskas and V. Olsauskaite, *J. Chromatogr. A*, 1998, **800**, 369.
- L. M. B. C. Alvares-Ribeiro and A. A. S. C. Machado, *Analyst*, 1998, **123**, 653.
- D. B. Li, *Chin. J. Environ. Chem.*, 1993, **14**, 460.
- K. Ohta and K. Tanaka, *Anal. Chim. Acta*, 1998, **373**, 189.
- K. Ohta, K. Tanaka and J. S. Fritz, *J. Chromatogr. A*, 1996, **731**, 179.
- W. Hu and H. Haraguchi, *Anal. Chem.*, 1994, **66**, 765.
- D. J. Pietrzyk, S. M. Senne and D. M. Brown, *J. Chromatogr.*, 1991, **546**, 101.
- M. Y. Ding, Y. Suzuki and H. Koizumi, *Analyst*, 1995, **20**, 1773.
- M. Y. Ding, Y. Suzuki and H. Koizumi, *Chromatographia*, 1995, **40**, 539.
- M. Y. Ding, Y. Suzuki and H. Koizumi, *Bunseki Kagaku*, 1994, **34**, 117.
- M. Y. Ding, Y. Suzuki and H. Koizumi, *Bunseki Kagaku*, 1993, **42**, 343.
- U. K. Tones and J. G. Tarter, *Analyst*, 1988, **113**, 183.
- M. Y. Ding, Y. Suzuki and H. Koizumi, *Anal. Sci.*, 1995, **11**, 239.
- K. Tanaka, K. Ohta, J. S. Fritz, S. Matsushita and A. Miyanaga, *J. Chromatogr. A*, 1994, **671**, 239.
- K. Tanaka and J. S. Fritz, *Am. Environ. Lab.*, 1995, **3**, 30.
- K. Tanaka, K. Ohta, P. R. Haddad, J. S. Fritz, K. P. Lee, K. Hasebe, A. Ieuji and A. Miyanaga, *J. Chromatogr. A*, 1999, **850**, 311.
- S. M. Kwon, K. P. Lee, K. Tanaka and K. Ohta, *J. Chromatogr. A*, 1999, **850**, 79.
- J. S. Cui, Q. Y. Wang and H. P. Han, *Monitoring Methods of Atmosphere Pollution*, Chemical Industry Press, Beijing, 2nd edn., 1997.
- Chinese Environmental Science Institute, *Corpus of Acid Rain*, Chinese Environmental Science Press, Beijing, 1989.
- F. Qu and S. F. Mou, *Microchem. J.*, 1999, **63**, 317.