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# Non-suppressed ion chromatography of inorganic anions, magnesium and calcium ions using a pyromellitate eluent and its application in evaluating environmental water quality

Kazutoku Ohta<sup>a,\*</sup>, Kazuhiko Tanaka<sup>a</sup>, James S. Fritz<sup>b</sup>

<sup>a</sup>National Industrial Research Institute of Nagoya, 1-1, Hirate-cho, Kita-ku, Nagoya-shi, Aichi 462, Japan

<sup>b</sup>Ames Laboratory and Chemistry Department, Iowa State University, Ames, IA 50011-3020, USA

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## Abstract

A simple, sensitive and convenient ion chromatographic (IC) method with UV photometric detection using pyromellitate (1,2,4,5-benzenetetracarboxylate)–methanol–water as the eluent on a silica-based anion-exchange column was established for the simultaneous determination of common inorganic anions including  $\text{HCO}_3^-$ ,  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  in environmental waters. The anions were detected indirectly, whilst  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  were detected directly because complexes having strong UV absorption were formed between pyromellitate and these cations. The proposed method was successfully applied to the simultaneous determination of the common anions,  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  in various river water samples.

**Keywords:** Water analysis; Inorganic anions; Anions; Cations; Magnesium; Calcium; Metal ions; Pyromellitate

## 1. Introduction

Ion chromatography (IC) with indirect UV photometric detection, developed by Small and Miller [1], is a useful and powerful technique for the simultaneous determination of both strongly acidic anions and weakly acidic anions with high sensitivity. In IC, a benzenepolycarboxylate having strong UV absorption, such as phthalate [1–3], trimellitate [2,4], trimesite [1–3], and pyromellitate (1,2,4,5-benzenetetracarboxylate) [2,3,5], is generally used as an eluent ion. Addi-

tionally, in order to determine simultaneously weakly acidic anions and strongly acidic anions with high sensitivity, the eluent is operated around neutrality.

However, when IC is applied to the determination of common inorganic anions and  $\text{HCO}_3^-$  in environmental waters, including river, lake and underground waters, both  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  in the waters often form UV-absorbing complexes with benzenepolycarboxylates and thus the complexes interfere in the determination of the anions and  $\text{HCO}_3^-$  [7,8].

In a previous paper [6], we reported IC with UV photometric detection for the simultaneous

\* Corresponding author.

determination of the common anions,  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  using pyromellitate as an eluent. When using a 0.2 mM pyromellitate eluent at pH 5.5, the common inorganic anions,  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  in environmental waters were successfully determined. However,  $\text{HCO}_3^-$  was not determined simultaneously owing to the low detection sensitivity and poor resolution among these ions.

The purpose of this study was to establish a simple, sensitive and convenient IC method with UV photometric detection for the simultaneous determination of the common inorganic anions,  $\text{HCO}_3^-$ ,  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  in environmental waters. When using a 0.15 mM pyromellitate–22.5% methanol–water eluent at pH 6.25, a high-resolution chromatogram of these ions was obtained in 20 min.

The proposed IC method was applied to the determination of the common anions,  $\text{HCO}_3^-$ ,  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  in various river waters. Additionally, conventional non-suppressed IC was used for the determination of monovalent cations ( $\text{Na}^+$ ,  $\text{NH}_4^+$  and  $\text{K}^+$ ) [9] to calculate the value of the ion balance. Since the values of the ion balance (total charge of cations/total charge of anions) [10] in the waters was almost 1.0, the proposed IC method is concluded to be useful for evaluating water equality.

## 2. Experimental

### 2.1. Ion chromatograph

The ion chromatograph consisted of a Tosoh (Tokyo, Japan) SC-8010 chromatographic data processor, a Tosoh CCPM eluent-delivery pump, a Tosoh SD-8012 on-line degasser, a Tosoh CO-8000 column oven, a Tosoh UV-8010 UV-Vis absorbance detector, a Tosoh CM-8000 conductimetric detector and a Rheodyne (Cotati, CA, USA) Model 7125 injector with a 20- $\mu\text{l}$  sample loop.

### 2.2. Analytical columns

A stainless steel analytical column (250  $\times$  4.6 mm I.D.) packed with a Tosoh TSKguardgel

QAE-SW (silica with anion-exchange capacity ca. 0.3 mequiv./g and particle size ca. 5  $\mu\text{m}$ ) was used for the simultaneous determination of common inorganic anions,  $\text{HCO}_3^-$ ,  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$ .

A Tosoh TSKgel IC-Cation column (50  $\times$  4.6 mm I.D.) packed with a lightly sulfonated styrene–divinylbenzene copolymer resin with cation-exchange capacity ca. 12  $\mu\text{equiv./ml}$  and particle size ca. 10  $\mu\text{m}$  was also used for the determination of monovalent cations.

### 2.3. Chemicals

All chemicals were of analytical-reagent or HPLC grade. Distilled, deionized water was used for the preparation of standard solutions and eluents.

The pH of the pyromellitate eluents was adjusted by using 1 M NaOH solution and measured with a Toa Denpa (Tokyo, Japan) IM-40S ion meter with a glass electrode.

The eluent used for the determination of monovalent cations was 2 mM nitric acid.

## 3. Result and discussion

### 3.1. Effect of pH of eluent

Since pyromellitic acid is a weak acid ( $\text{p}K_{a_1} = 1.92$ ,  $\text{p}K_{a_2} = 2.82$ ,  $\text{p}K_{a_3} = 4.49$  and  $\text{p}K_{a_4} = 5.64$ ), the eluent strength of pyromellitate is strongly dependent on the eluent pH. Thus, the retention volumes ( $V_R$ ) of common inorganic anions ( $\text{Cl}^-$ ,  $\text{NO}_2^-$ ,  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$ ) are influenced by the eluent pH. Additionally, the detection sensitivity of  $\text{HCO}_3^-$  is strongly influenced by the eluent pH because  $\text{H}_2\text{CO}_3$  is a weak acid ( $\text{p}K_{a_1} = 6.35$  and  $\text{p}K_{a_2} = 10.33$ ). Further, the  $V_R$  values of the  $\text{Mg}^{2+}$ – and  $\text{Ca}^{2+}$ –pyromellitate complexes formed are also expected to be influenced because the stability of the complexes depends on the pH.

Therefore, in order to determine simultaneously common inorganic anions,  $\text{HCO}_3^-$ ,  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$ , which are very important ionic species

in environmental waters, the pH of pyromellitate eluent was investigated in detail.

As shown in Fig. 1, with increasing eluent pH, the  $V_R$  values of the common inorganic anions decreased, whereas the  $V_R$  values of  $Mg^{2+}$  and  $Ca^{2+}$  increased. This might be because the stability of the complexes which formed between pyromellitate and these cations increased and thus the complexes were strongly retained on the column.

The  $V_R$  value of  $HCO_3^-$  increased slightly owing to the increase in the degree of the dissociation. Additionally, a reasonable detection sensitivity of  $HCO_3^-$  was obtained at  $pH \geq 6$ .

When considering the  $V_R$  values, the detection sensitivity and the chemical stability of the silica-based anion exchanger, a reasonable pH range of the eluent was concluded to be 6.0–6.5.

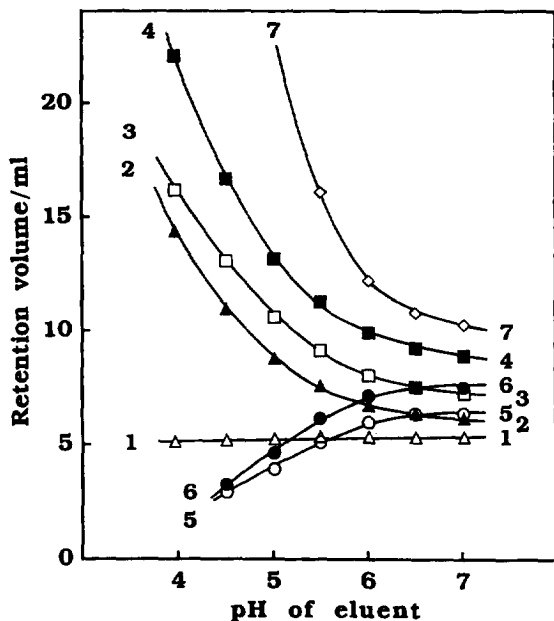


Fig. 1. Effect of pH of eluent on retention volume of the common inorganic anions,  $HCO_3^-$ ,  $Mg^{2+}$  and  $Ca^{2+}$ . Eluent, 0.2 mM pyromellitate; flow-rate, 1 ml/min; column, TSK-guardgel QAE-SW (250 × 4.6 mm I.D.); column temperature, 35°C; sample, mixture of 0.5 mM  $NaHCO_3$ , 0.1 mM  $MgSO_4$  and  $Ca(NO_3)_2$  and 0.2 mM  $NaCl$  and  $NaNO_2$ ; injection volume, 20  $\mu$ l. Lines: 1 =  $HCO_3^-$ ; 2 =  $Cl^-$ ; 3 =  $NO_2^-$ ; 4 =  $NO_3^-$ ; 5 =  $Mg^{2+}$ ; 6 =  $Ca^{2+}$ ; 7 =  $SO_4^{2-}$ .

### 3.2. Retention behavior of $Mg^{2+}$ and $Ca^{2+}$

In order to separate simultaneously the common inorganic anions,  $HCO_3^-$ ,  $Mg^{2+}$  and  $Ca^{2+}$ , the retention behavior of  $Mg^{2+}$ - and  $Ca^{2+}$ -pyromellitate complexes using pyromellitate eluents at pH 6.0 was compared with that of the common inorganic anions.

In conventional ion-exchange chromatography, it is well known that the relationships between the logarithm of the eluent ion concentration ( $\log [E^{x-}]$ ) and the logarithm of the capacity factor ( $\log k'$ ) of the solute ion is linear [11]:

$$\log k' = -(x/y) \log [E^{x-}] + C,$$

where  $x$  is the charge of the solute ion,  $y$  is the charge of the eluent ion and  $C$  is a constant.

As shown in Fig. 2, the relationships were linear for the common inorganic anions and  $HCO_3^-$ . The slope value for the divalent anion

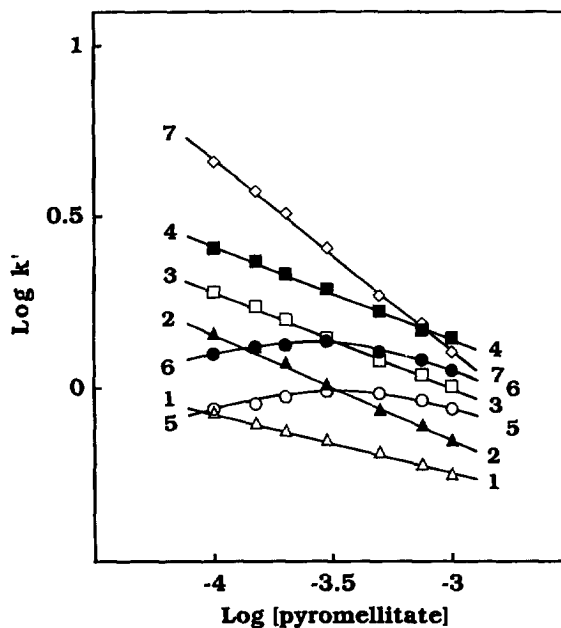


Fig. 2. Relationship between logarithm of capacity factor ( $k'$ ) and logarithm of concentration of pyromellitate eluent at pH 6.0. Eluent, pyromellitate at pH 6.0. Other chromatographic conditions as in Fig. 1. Lines: 1 =  $HCO_3^-$ ; 2 =  $Cl^-$ ; 3 =  $NO_2^-$ ; 4 =  $NO_3^-$ ; 5 =  $Mg^{2+}$ ; 6 =  $Ca^{2+}$ ; 7 =  $SO_4^{2-}$ .

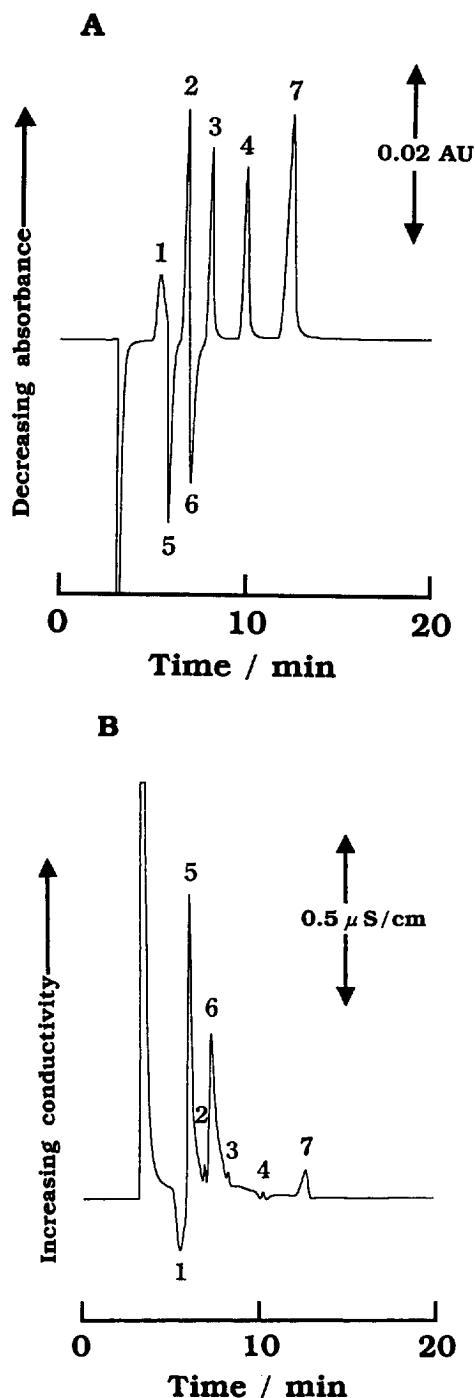


Fig. 3. Chromatograms of the common anions,  $\text{HCO}_3^-$ ,  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  using 0.2 mM pyromellitate at pH 6.0 as the eluent. Other chromatographic conditions as in Fig. 1. (A) UV photometric detection at 266 nm; (B) conductimetric detection. Peaks: 1 =  $\text{HCO}_3^-$ ; 2 =  $\text{Cl}^-$ ; 3 =  $\text{NO}_2^-$ ; 4 =  $\text{NO}_3^-$ ; 5 =  $\text{Mg}^{2+}$ ; 6 =  $\text{Ca}^{2+}$ ; 7 =  $\text{SO}_4^{2-}$ .

( $\text{SO}_4^{2-}$ ) was about twice those of monovalent anions. The slope value for  $\text{HCO}_3^-$  was smaller than those of monovalent anions owing to the low degree of dissociation at the pH used.

On the other hand, since the relationships were not linear for  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$ , the  $\text{Mg}^{2+}$ - and  $\text{Ca}^{2+}$ -pyromellitate complexes were assumed to be non-anionic species. In order to discuss the retention behavior of the complexes in detail, the chromatogram obtained by using UV photometric detection and that obtained by conductimetric detection were compared.

As shown in Fig. 3A, when using UV photometric detection, the common inorganic anions and  $\text{HCO}_3^-$  were detected indirectly (negative response), whereas  $\text{Mg}^{2+}$ - and  $\text{Ca}^{2+}$ -pyromellitate complexes were detected directly (positive response). This is because complexes having strong UV absorption were formed in the chromatographic process.

As shown in Fig. 3B, when using conductimetric detection,  $\text{HCO}_3^-$  with a low equivalent conductivity was detected indirectly (negative response), whereas the common inorganic anions and  $\text{Mg}^{2+}$ - and  $\text{Ca}^{2+}$ -pyromellitate complexes were detected directly (positive response). Additionally, the detection sensitivity of the complexes was higher than that of the common inorganic anions. The chromatogram obtained might indicate that the complexes were non-anionic species because the equivalent conductivity of the complexes was assumed to be smaller than that of eluent ion [ $(\text{pyromellitate})^{3-}/(\text{pyromellitate})^{4-}$ ].

From the above results, the complexes were concluded to be non-ionic species. A more detailed study of the retention mechanism will be the subject of future work.

### 3.3. Effect of methanol as organic modifier

As shown in Figs. 1 and 2, it was difficult to separate the common inorganic anions,  $\text{HCO}_3^-$ ,  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  simultaneously with high sensitivity by controlling the pH and concentration of the pyromellitate eluent.

Organic modifiers are well known to induce both the alteration of the ion-exchange selectivi-

ty and the acceleration of the formation of complexes between sample ions and eluent species [12]. Thus, in order to separate the common anions,  $\text{HCO}_3^-$ ,  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  completely, the effect of methanol, which is commonly used as an organic modifier in HPLC, added in 0.15 mM pyromellitate eluent at pH 6.25 was investigated.

As shown in Fig. 4, when methanol was added to the eluent, the  $V_R$  values of  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$  increased owing to the decrease in the eluent strength of pyromellitate. Especially the  $V_R$  value of  $\text{SO}_4^{2-}$  increased drastically owing to the low solvation in methanol–water media. The  $V_R$  values of  $\text{NO}_2^-$  and  $\text{NO}_3^-$  with hydrophobic characteristics decreased owing to the decrease in the hydrophobic interaction. The  $V_R$  value of  $\text{HCO}_3^-$  also slightly decreased owing to the suppression of the dissociation.

On the other hand, the  $V_R$  values of  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  increased drastically. This might be because the stability of the complexes was enhanced and

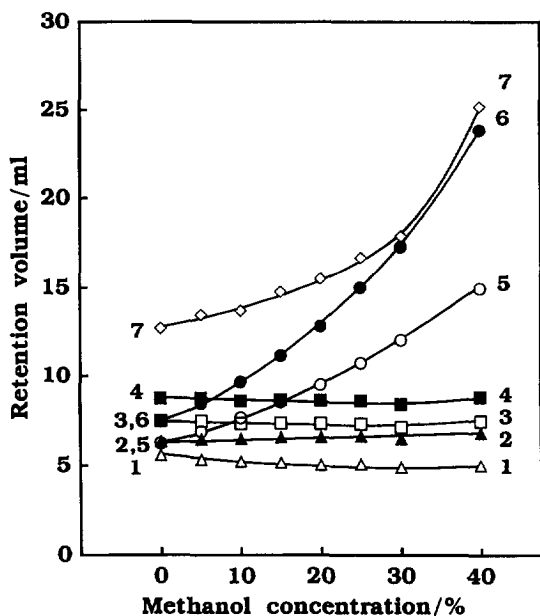


Fig. 4. Effect of concentration of methanol in the eluent on the retention volumes of the common anions,  $\text{HCO}_3^-$ ,  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$ . Eluent, 0.15 mM pyromellitate–methanol–water at pH 6.25. Other chromatographic conditions as in Fig. 1. Lines: 1 =  $\text{HCO}_3^-$ ; 2 =  $\text{Cl}^-$ ; 3 =  $\text{NO}_2^-$ ; 4 =  $\text{NO}_3^-$ ; 5 =  $\text{Mg}^{2+}$ ; 6 =  $\text{Ca}^{2+}$ ; 7 =  $\text{SO}_4^{2-}$ .

thus the complexes were strongly retained on the column.

As shown in Fig. 5, when using 0.15 mM pyromellitate–22.5% methanol–water as eluent at pH 6.25, an excellent chromatogram of the common inorganic anions,  $\text{HCO}_3^-$ ,  $\text{Mg}^{2+}$ , and  $\text{Ca}^{2+}$  was obtained in 20 min.

### 3.4. Calibration graphs

Calibration graphs were obtained by plotting peak area against the concentration of  $\text{HCO}_3^-$ , the anions,  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$ . Linear calibration graphs were obtained over at least the concentration ranges 0–2.0 mM for  $\text{HCO}_3^-$ , monovalent anions,  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  and 0–1.5 mM for  $\text{SO}_4^{2-}$ .

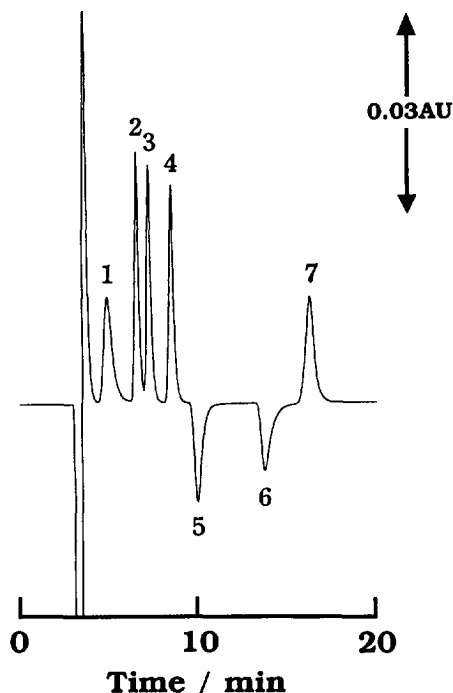


Fig. 5. Chromatogram of the common anions,  $\text{HCO}_3^-$ ,  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$ . Eluent, 0.15 mM pyromellitate–22.5% methanol–water at pH 6.25; detection, UV at 262 nm; sample, mixture of 0.5 mM  $\text{NaHCO}_3$ , 0.1 mM  $\text{MgSO}_4$  and  $\text{Ca}(\text{NO}_3)_2$  and 0.2 mM  $\text{NaCl}$  and  $\text{NaNO}_2$ . Other chromatographic conditions as in Fig. 1. Peaks (concentration): 1 =  $\text{HCO}_3^-$  (0.5 mM); 2 =  $\text{Cl}^-$  (0.2 mM); 3 =  $\text{NO}_2^-$  (0.2 mM); 4 =  $\text{NO}_3^-$  (0.2 mM); 5 =  $\text{Mg}^{2+}$  (0.1 mM); 6 =  $\text{Ca}^{2+}$  (0.1 mM); 7 =  $\text{SO}_4^{2-}$  (0.1 mM).

Table 1

Detection limits of the common inorganic anions,  $\text{HCO}_3^-$ ,  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  under the optimum chromatographic conditions (injection volume 20  $\mu\text{l}$ )

Ion	Detection limit <sup>a</sup>	
	$\mu\text{M}$	ppb
$\text{HCO}_3^-$	2.4	140
$\text{Cl}^-$	0.42	15
$\text{NO}_2^-$	0.43	20
$\text{NO}_3^-$	0.48	30
$\text{SO}_4^{2-}$	0.50	48
$\text{Mg}^{2+}$	0.45	11
$\text{Ca}^{2+}$	0.67	27

<sup>a</sup> Signal-to-noise ratio = 3.

### 3.5. Detection limits

The detection limits of  $\text{HCO}_3^-$ , the anions,  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  at a signal-to-noise ratio of 3 are given in Table 1. The detection limits are reasonable for the determination of the common inorganic anions,  $\text{HCO}_3^-$ ,  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  in various environmental waters.

### 3.6. Reproducibilities

The relative standard deviations of the chromatographic peak areas of  $\text{HCO}_3^-$ , the anions,  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  under the optimum conditions described above were less than 1% ( $n=8$ ). Reproducible chromatograms were obtained during repeated chromatographic runs.

### 3.7. Retention volumes of inorganic anions, organic acids and di- and trivalent cations

Table 2 lists the  $V_R$  values of inorganic anions, organic acids and di- and trivalent metal cations under the optimum conditions described above.

Several divalent metal cations also formed UV-absorbing complexes with pyromellitate and the complexes might be determined under the same conditions.

Some inorganic anions and organic acids could

Table 2

Retention volumes ( $V_R$ ) of anions, organic acids and di- and trivalent cations under the optimum chromatographic conditions

Ion	$V_R$ (ml)	Ion	$V_R$ (ml)
$\text{HCO}_3^-$	5.0	Malic acid	14.6
$\text{H}_2\text{PO}_4^-$	5.9	Tartaric acid	16.3
$\text{F}^-$	6.1	Phthalic acid	20.8
$\text{Cl}^-$	6.6	Oxalic acid	21.1
$\text{NO}_2^-$	7.3	Fumaric acid	22.1
$\text{Br}^-$	8.2	Citric acid	37.0
$\text{NO}_3^-$	8.6		
$\text{I}^-$	12.5	$\text{Mg}^{2+}$	9.9
$\text{SCN}^-$	15.8	$\text{Ca}^{2+}$	13.5
$\text{SO}_4^{2-}$	16.5	$\text{Sr}^{2+}$	11.3
$\text{S}_2\text{O}_3^{2-}$	24.9	$\text{Ba}^{2+}$	13.3
		$\text{Mn}^{2+}$	20.1
Lactic acid	5.2	$\text{Co}^{3+}$	23.1
Formic acid	5.9	$\text{Ni}^{2+}$	29.5
Acetic acid	5.5	$\text{Cd}^{2+}$	69.3
Propionic acid	5.4	$\text{Fe}^{2+}$	ND
Butyric acid	5.6	$\text{Zn}^{2+}$	ND
Valeric acid	5.8	$\text{Pb}^{2+}$	ND
Benzoic acid	9.3	$\text{Cu}^{2+}$	ND
Maleic acid	9.6	$\text{Fe}^{3+}$	ND
Malonic acid	12.3	$\text{Al}^{3+}$	ND
Succinic acid	13.0		

ND = not detected.

be also determined together with the common inorganic anions,  $\text{HCO}_3^-$ ,  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$ .

### 3.8. Application to river waters

The proposed IC method was applied to the simultaneous determination of the common inorganic anions,  $\text{HCO}_3^-$ ,  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  in various river waters. The monovalent cations ( $\text{Na}^+$ ,  $\text{NH}_4^+$  and  $\text{K}^+$ ) were determined by using the conventional non-suppressed IC. River water samples were collected near the city of Nagoya, in central Japan. The samples were analyzed after filtration with a 0.45- $\mu\text{m}$  membrane filter.

Fig. 6A and B show typical chromatograms of river waters obtained by the proposed IC method. The peak resolution for both chromatograms was satisfactory.

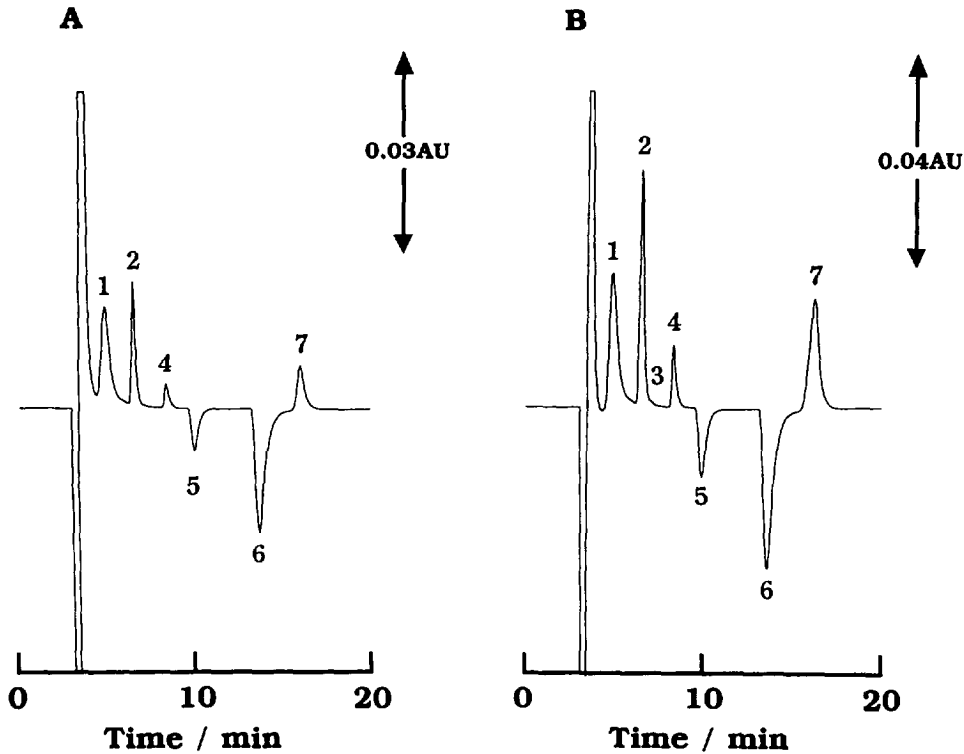


Fig. 6. Chromatograms of river water samples. Chromatographic conditions as in Fig. 5. (A) Upper stream of Nagara river. Peaks (concentration, mM): 1 =  $\text{H}_2\text{CO}_3$  (total carbonate) (0.430); 2 =  $\text{Cl}^-$  (0.096); 4 =  $\text{NO}_3^-$  (0.021); 5 =  $\text{Mg}^{2+}$  (0.041); 6 =  $\text{Ca}^{2+}$  (0.179); 7 =  $\text{SO}_4^{2-}$  (0.042). (B) Mid-stream of Nagara river. Peaks (concentration, mM): 1 =  $\text{H}_2\text{CO}_3$  (total carbonate) (0.810); 2 =  $\text{Cl}^-$  (0.253); 3 =  $\text{NO}_2^-$  (0.001); 4 =  $\text{NO}_3^-$  (0.070); 5 =  $\text{Mg}^{2+}$  (0.089); 6 =  $\text{Ca}^{2+}$  (0.310), 7 =  $\text{SO}_4^{2-}$  (0.145).

Table 3  
Determination of major anions and cations in various river water samples

Sample	pH	Concentration (mequiv./l)										Ion balance <sup>b</sup>
		$\text{HCO}_3^-$ <sup>a</sup>	$\text{Cl}^-$	$\text{NO}_2^-$	$\text{NO}_3^-$	$\text{SO}_4^{2-}$	$\text{Mg}^{2+}$	$\text{Ca}^{2+}$	$\text{Na}^+$	$\text{NH}_4^+$	$\text{K}^+$	
Nagara River 1	7.12	0.367	0.096	ND <sup>c</sup>	0.021	0.084	0.082	0.358	0.131	ND	0.015	1.03
Nagara River 2	7.34	0.396	0.105	ND	0.024	0.098	0.080	0.394	0.147	ND	0.015	1.02
Nagara River 3	7.18	0.458	0.143	ND	0.043	0.130	0.116	0.456	0.174	ND	0.017	0.99
Nagara River 4	7.21	0.711	0.253	0.001	0.070	0.290	0.178	0.620	0.436	0.018	0.037	0.97
Yada River	7.15	1.03	0.790	0.002	0.134	2.30	0.242	2.04	1.72	0.040	0.144	0.98
Shonai River	7.00	0.906	1.061	ND	0.115	1.77	0.208	1.57	1.87	0.049	0.127	0.99

<sup>a</sup> The concentration of  $\text{HCO}_3^-$  was calculated from the concentration of total carbonate determined by the proposed IC method and the sample pH.

<sup>b</sup> Ion balance = total concentration of cations/total concentration of anions.

<sup>c</sup> ND = not detected.

Table 3 gives the analytical results for anions and cations in various river waters. The other ions were not determined in the samples. The concentration of  $\text{HCO}_3^-$  was calculated from the

concentration of total carbonate determined by the proposed IC method and the sample pH. Since the ion balance (total charge of cations/total charge of anions) value ranged from 0.97 to

1.03, the proposed IC method was concluded to be useful for evaluating approximately environmental water quality.

### Acknowledgement

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