Indirect ultraviolet spectrophotometric detection in the ion chromatography of common mono- and divalent cations on an aluminium adsorbing silica gel column with tyramine-containing crown ethers as eluent

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Abstract

The application of laboratory-made aluminium-adsorbing silica gel (Al–Silica) as a cation-exchange stationary phase to ion chromatography–indirect photometric detection (IC–IPD) for common mono- and divalent cations (Li^+, Na^+, NH_4^+, K^+, Mg^{2+} and Ca^{2+}) was carried out by using protonated tyramine (4-aminoethylphenol) as eluent ion. When using 1.2 mM tyramine–0.2 mM oxalic acid at pH 4.5 as eluent, incomplete separation of the monovalent cations and complete separation of the divalent cations were achieved in 17 min. Then, the addition of crown ethers in the eluent was carried out for the complete separation of the mono- and divalent cations. As a result, when using 1.2 mM tyramine–0.2 mM oxalic acid at pH 4.5 containing either 5 mM 15-crown-5 (1,4,7,10,13-pentaoxacyclopentadecane) or 0.5 mM and 18-crown-6 (1,4,7,10,13,16-hexaoxacyclooctadecane) as eluent, excellently simultaneous separation of these cations was achieved in 21 min. The proposed IC–IPD was successfully applied to the determination of major cations in natural water samples. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Indirect detection; Mobile phase composition; Silica, aluminium adsorbing; Stationary phases, LC; Water analysis; Environmental analysis; Inorganic cations; Crown ethers; Tyramine

1. Introduction

The modification of silica gel with aluminium by a coating method is simple and effective way for the preparation of advanced silica-based cation-exchanger for ion chromatography (IC) [1–3]. The most unique characteristics is that the silica gel modified with aluminium (aluminium-adsorbing silica gel, Al–Silica) behaves as a cation-exchanger under strongly acidic conditions. On the basis of the characteristics, the author has developed highly

sensitive IC-conductimetric detection for common mono- and divalent cations (Li^+, Na^+, NH_4^+, K^+, Mg^{2+} and Ca^{2+}) with the Al–Silica column and nitric acid-15-crown-5 (1,4,7,10,13-pentaoxacyclopentadecane) as eluent [3]. In this study, in order to expand the utility of the Al–Silica in IC, the application of the Al–Silica column to IC-indirect photometric detection (IC–IPD) for these mono- and divalent cations was carried out.

IC–IPD developed by Small and Miller [4] is recognized as simple and convenient method for the determination of various kind of anions and cations. In IPD for cations, the simultaneous separation of these mono- and divalent cations could be achieved

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by using both copper(II) ion as eluent ion and columns packed with strongly acidic cation-exchangers, such as sulfonated styrene–divinylbenzene copolymer and sulfonated silica [5–7]. However, the determination of these cations is often interfered with organic compounds coexisting in analytical samples, because the detection wavelength was at 220–240 nm.

Protonated aromatic monovalent amines (PAMA) with strongly UV-adsorption could be applied as eluent ion to IC–IPD for cations. Haddad and Foley [8] have reported the application of various protonated aromatic monovalent amines as the eluent ion to IC–IPD with column packed with a lightly sulfonated styrene–divinylbenzene copolymer. However, since the eluent strength of PAMA was weaker that that of Cu^{2+}, it was very difficult to elute these mono- and divalent cations under the same eluent conditions. Additionally, strongly hydrophobic interaction between PAMA and the stationary phase caused poor peak resolution between monovalent cations. Therefore, another approach was required in IC–IPD using PAMA as eluent ion for the simultaneous separation of these mono- and divalent cations. One of the best ways is to utilize weakly acidic cation-exchangers with large hydrophobicity as stationary phase, because the affinity of mono- and divalent cations to weakly acidic cation-exchanger is very similar [9,10]. Unmodified silica gel is expected to be one of the most suitable cation-exchange stationary phases in the IC–IPD with PAMA as the eluent ion, because silica gel is weakly acidic cation-exchanger and has large hydrophobicity. Munaf et al. [11,12] have applied an unmodified silica gel (Develosil 30-5) to IC–IPD with the benzyltrimethylanmonium ion as the eluent ion for the simultaneous separation of these cations. Unfortunately, the peak resolution between these cations was moderate.

In this study, the author has examined the applica-

tion of the Al–Silica to IC–IPD for the mono- and divalent cations using protonated tyramine (4-aminoethylphenol) as eluent ion. As a result, excellently simultaneous separation of these cations was achieved in 21 min by using 1.2 mM tyramine–0.2 mM oxalic acid at pH of 4.5 containing either 5 mM 15-crown-5 or 0.5 mM 18-crown-6 (1,4,7,10,13,16-hexaoxacyclooctadecane) as eluent.

2. Experimental

2.1. Preparation of aluminium-absorbing silica gel

A Fuji-Silysia Chemical (Kasugai, Japan) Super Micro Bead Silica Gel B-5 (SMBSG B-5) porous spherical silica gel was employed as a matrix. A 10-g amount of the silica gel was immersed in 200 ml of $Al_2(SO_4)_3$ solution [1 g $Al_2(SO_4)_3 \cdot 14$–$18H_2O/100$ ml distilled, deionized water (DIW)]. After stirring for 1 h, the solution was filtered. The resultant gel was washed with DIW thoroughly and then was dried overnight at 120°C followed by calcining at 1000°C for 5 h.

The determination of aluminium on Al–Silica was carried out by using a Nippon Jarrell-Ash (Kyoto, Japan) ICAP-1000 inductively coupled plasma-atomic emission spectrometry (ICP–AES) system [1]. The amount of aluminium adsorbed on 1 g of silica gel was ca. 500 μg.

Table 1 shows physical properties of the Al–Silica and SMBSG B-5 silica gel. The determination of the surface area and pore volume by the nitrogen adsorption isotherms on the gels at 77 K was carried out by using a Carlo Erba (Milan, Italy) Sorptomatic 2400 surface analyzer. The surface area was calculated from the BET equation. The pore volume was obtained from the liquid nitrogen volume evaluated from the nitrogen adsorption volume at $P/P_0 = 0.95$.

Table 1
Physical properties of Super Micro Beads Silica Gel B-5 (SMBSG B-5) and aluminium-adsorbing silica gel (Al–Silica)

Packing	Form	Particle size (μm)	Surface area ($m^2 \ g^{-1}$)	Pore size (Å)	Pore volume (ml g^{-1})	Packing density (g ml^{-1})
SMBSG B-5	Spherical	6.1	541	68	0.83	0.44
Al–Silica	Spherical	5.3	310	64	0.48	0.65

The decrease in the surface area and pore volume and the increase in the packing density were due mainly to shrinkage of silica matrix.

The separation columns (250×4.6 mm I.D, stainless steel) were packed with the Al–Silica by using slurry packing method.

2.2. Ion chromatograph

The ion chromatograph consisted of a Tosoh (Tokyo, Japan) SC-8020 chromatographic data-processor, a Tosoh CCPM-II solvent delivery pump operated at a flow-rate of 1 ml min^{-1}, a Tosoh CO-8020 column oven operated at 35°C, a Tosoh SD-8023 on-line degasser, a Shimadzu (Kyoto, Japan) SPD-10AV UV–Vis spectrophotometric detector operated at 265 nm and a Rheodyne (Cotati, CA, USA) model 9125 injector equipped with 20 μl or 100 μl sample loops.

2.3. Reagents

All reagents were of analytical reagent grade. Tyramine (4-aminoethylphenol) and crown ethers [12-crown-4 (1,4,7,10-tetraoxacyclododecane), 15-crown-5 and 18-crown-6 were purchased from Aldrich (Milwaukee, WI, USA) and other reagents were purchased from Wako (Osaka, Japan). DIW was used for the preparation of the eluents and standard solutions.

A Toa Denpa (Tokyo, Japan) IM-40S ion meter with a glass electrode was used for the measurement of pH of eluents and natural water samples.

3. Result and discussion

3.1. Effect of pH of tyramine-oxalic acid eluent on retention behavior of mono- and divalent cations

Since laboratory-made aluminium-adsorbing silica gel (Al–Silica) is weakly acidic cation-exchanger, a cation-exchange capacity of the Al–Silica column is strongly influenced by pH of eluent. Then, for the simultaneous separation of common mono- and divalent cations (Li$^+$, Na$^+$, NH$_4^+$, K$^+$, Mg^{2+} and Ca^{2+}) on the Al–Silica column, the effect of pH of

1.2 mM tyramine–0.2 mM oxalic acid eluent on the retention behavior of these cations was investigated in detail. Oxalic acid added to the eluent was expected to act both as buffer agent and complexation agent for the divalent cations [13,14]. The pH of eluents was adjusted with 1 mM nitric acid.

Fig. 1 shows the relationship between the pH of eluent and the retention volumes of the mono- and divalent cations. The retention volumes of these cations increased with increasing the pH of eluent. This is due mainly to an increase in the cation-exchange capacity of the Al–Silica column by promoting the dissociation of silanol groups on the surface of the Al–Silica. The degree of the increases in the retention volumes of the divalent cations was much larger than that of the monovalent cations. This is because the retention volumes of divalent cations are strongly influenced by cation-exchange
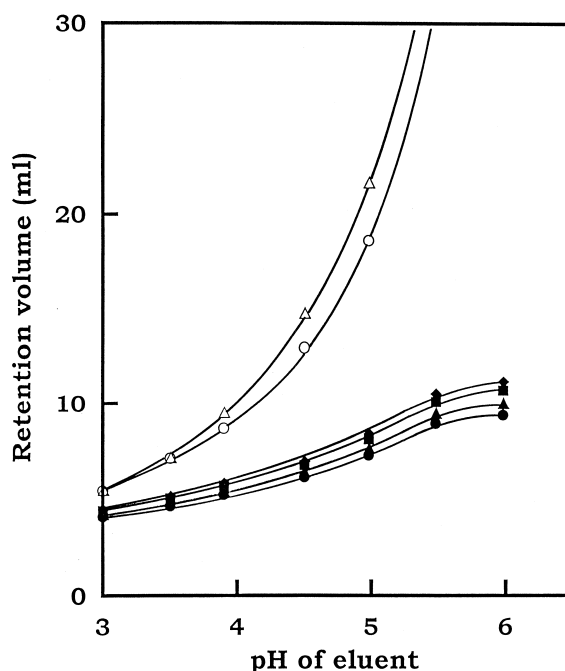

Fig. 1. Effect of pH of 1.2 mM tyramine–0.2 mM oxalic acid eluent on retention volumes of common mono- and divalent cations. Column: Al–Silica; column size: 250×4.6 mm I.D.; column temperature: 35°C; eluent: 1.2 mM tyramine–0.2 mM oxalic acid, the pH of eluent was adjusted with 1 M nitric acid; flow-rate: 1 ml min^{-1}; detection: indirect UV at 265 nm; injection volume: 20 μl; sample concentration: 0.2 mM. Symbols: ●=Li$^+$, ▲=Na$^+$, ■=NH$_4^+$, ♦=K$^+$, ○=Mg^{2+} and △=Ca^{2+}.

capacity when compared to those of monovalent cations. As for the monvalent cations, the elution order was $Li^+ < Na^+ < NH_4^+ < K^+$. The order indicated that the monovalent cations were mainly separated by cation-exchange process. However, incomplete separation of the monovalent cations was achieved under the chromatographic conditions. On the other hands, as for these divalent cations, the elution order was $Mg^{2+} < Ca^{2+}$ and complete separation was achieved at the pH ≥ 4.0. The order and the separation was mainly ascribed to oxalic acid, because the divalent cations were co-eluted when using 1.2 mM tyramine as eluent.

From above results, it was decided that the reasonable pH of the eluent was ca. 4.5. As shown in Fig. 2, the mono- and divalent cations could be eluted in 17 min by using 1.2 mM tyramine–0.2 mM oxalic acid at pH 4.5 as eluent.
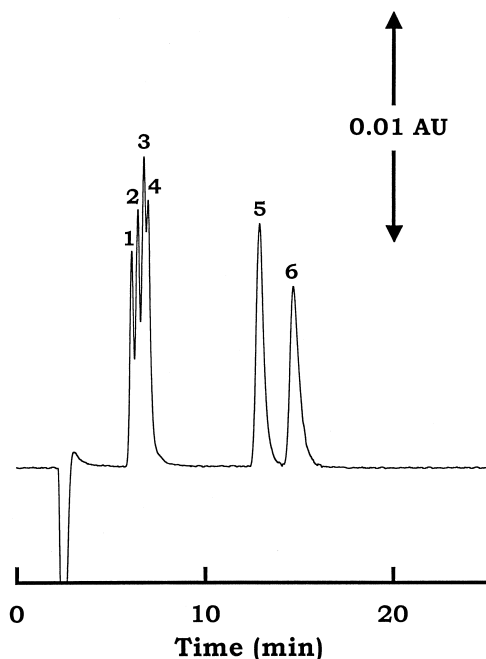

Fig. 2. Chromatogram of common mono- and divalent cations obtained by 1.2 mM tyramine–0.2 mM oxalic at pH 4.5 as eluent. Eluent: 1.2 mM tyramine–0.2 mM oxalic acid at pH 4.5; other chromatographic conditions as for Fig. 1. Peaks: 1 = Li^+, 2 = Na^+, 3 = NH_4^+, 4 = K^+, 5 = Mg^{2+} and 6 = Ca^{2+}.

3.2. Effect of crown ethers added to tyramine–oxalic acid eluent on retention behavior of mono- and divalent cations

It is well known that the addition of crown ethers in acidic eluents is very effective for the improvement of peak resolution between mono- and divalent cations in IC–conductimetric detection (IC–CD) with a column packed with a weakly acidic cation-exchanger [15,16]. In preliminary study [3], the author has also demonstrated the effectiveness of crown ethers added in strongly acidic eluent for the improvement of peak resolution between these cations on the Al–silica column in IC–CD. Then, the addition of various crown ethers (12-crown-4, 15-crown-5 and 18-crown-6) in 1.2 mM tyramine–0.2 mM oxalic acid eluent at pH 4.5 was carried out for the complete separation of the mono- and divalent cations on the Al–Silica column.

3.2.1. Effect of 12-crown-4

First, the effect of 12-crown-4 was investigated.

Fig. 3 shows a chromatogram of the mono- and divalent cations obtained by 1.2 mM tyramine–0.2 mM oxalic acid–20 mM 12-crown-4 at pH 4.5 as eluent. As for the monovalent cations, the peak resolution was not improved. The peaks of Na^+ and NH_4^+ were completely overlapped, because the order of the increase in the retention volumes was $Li^+ \leq NH_4^+ < Na^+ < K^+$. In contrast, as for the divalent cations, the peak resolution was quite improved, because the order of the increase in the retention volumes was $Mg^{2+} < Ca^{2+}$. These results suggested that 12-crown-4 seemed to act as a selective-cation-exchanger under the chromatographic conditions. However, since the separation of the mono- and divalent cations was incomplete when using 1.2 mM tyramine–0.2 mM oxalic acid–20 mM 12-crown-4 at pH 4.5, it was concluded that 12-crown-4 was not suitable for the simultaneous separation of these cations by IC–IPD.

3.2.2. Effect of 15-crown-5

In a previous study [3], the author has reported that the addition of 15-crown-5 to strongly acidic eluent was very effective for the improvement peak
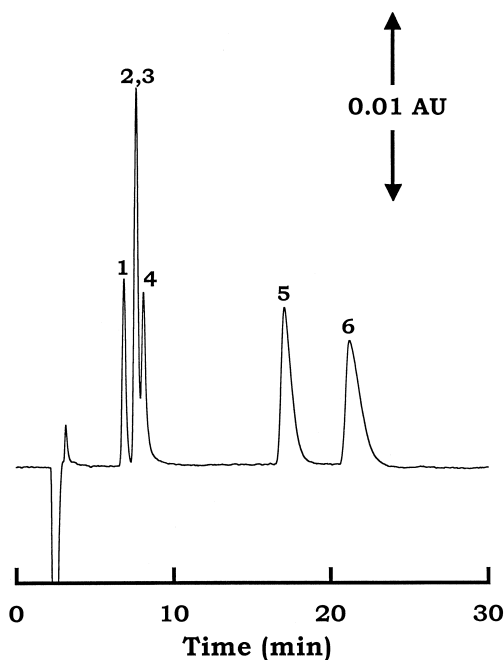
Fig. 3. Chromatogram of common mono- and divalent cations obtained by 1.2 mM tyramine–0.2 mM oxalic acid–20 mM 12-crown-4 at pH 4.5 as eluent. Eluent: 1.2 mM tyramine–0.2 mM oxalic acid–20 mM 12-crown-4 at pH 4.5. Other chromatographic conditions as for Fig. 2.
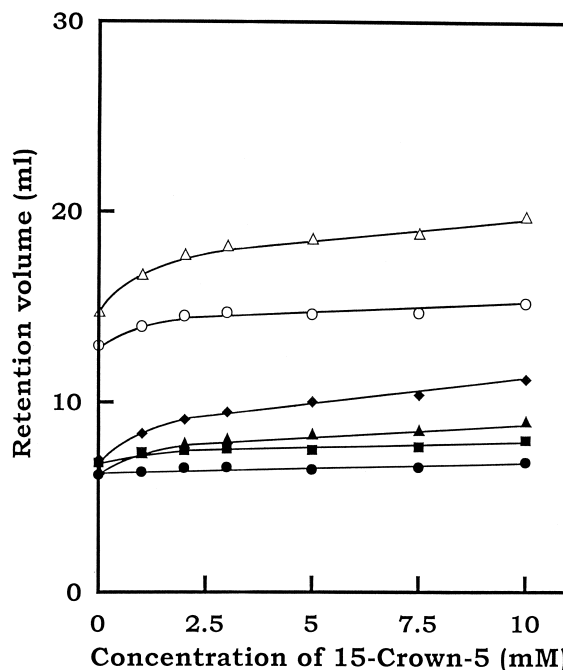

Fig. 4. Effect of concentration of 15-crown-5 in 1.2 mM tyramine–0.2 mM oxalic acid eluent at pH 4.5 on retention volumes of common mono- and divalent cations. Eluent: 0–10 mM 15-crown-5 in 1.2 mM tyramine–0.2 mM oxalic acid at pH 4.5; other chromatographic conditions as for Fig. 3 Symbols: ●=Li$^+$, ▲=Na$^+$, ■=NH$_4^+$, ♦=K$^+$, ○=Mg^{2+} and △=Ca^{2+}.

resolution between these mono- and divalent cations in the IC–CD with the Al–Silica column. Second, the effect of 15-crown-5 was investigated in detail.

Fig. 4 shows the relationship between the concentration of 15-crown-5 in the eluent and the retention volumes of the mono- and divalent cations. The retention volumes of these cations increased with increasing the concentration of 15-crown-5 in the eluent. As for the monovalent cations, the order of the increase in the retention volumes was Li$^+$ ≤ NH$_4^+$ < Na$^+$ < K$^+$ and then the peak resolution was remarkably improved. Good separation of the monovalent cations were achieved at the concentration of 15-crown-5 ≥ 5 mM. As for the divalent cations, the order of the increase in the retention volumes was Mg^{2+} < Ca^{2+} and then the peak resolution was also improved. Since these orders were in good agree-

ment with those obtained by the CD–IC with the Al–Silica column and nitric acid-15-crown-5 as eluent [3], it was evident that 15-crown-5 seemed to act as selective cation-exchanger under the IC–IPD conditions. Complete separation of the mono- and divalent cations was achieved at the concentration of 15-crown-5 ≥ 5 mM. The concentration of 15-crown-5 in the IC–IPD was higher than that in the IC–CD [3]. This suggested that the effect of 15-crown-5 was interfered with tyramine, which was also adsorbed on the Al–Silica strongly.

From above results, it was concluded that the optimum concentration of 15-crown-5 was 5 mM. As shown in Fig. 5, excellently simultaneous separation of the mono- and divalent cations were achieved in 21 min by elution with 1.2 mM tyramine–0.2 mM oxalic acid–5 mM 15-crown-5 at pH 4.5 (Eluent A).
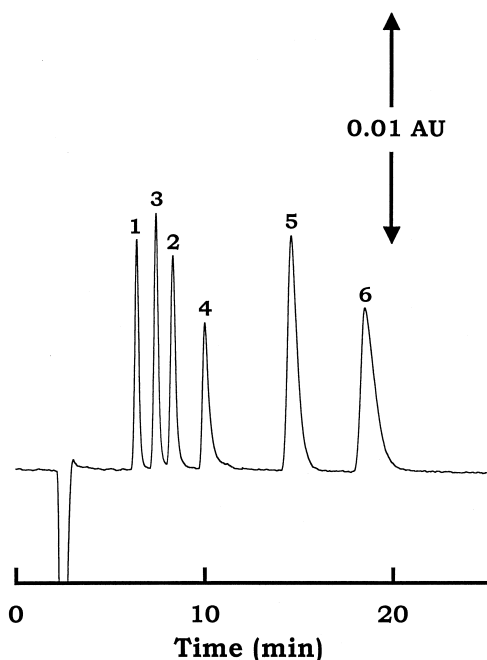
Fig. 5. Chromatogram of common mono- and divalent cations obtained by 1.2 mM tyramine–0.2 mM oxalic acid–5 mM 15-crown-5 at pH 4.5 as eluent. Eluent: 1.2 mM tyramine–0.2 mM oxalic acid–5 mM 15-crown-5 at pH 4.5 (Eluent A); other chromatographic conditions are as for Fig. 4. Peaks: 1=Li$^+$, 2=Na$^+$, 3=NH$_4^+$, 4=K$^+$, 5=Mg^{2+} and 6=Ca^{2+}.

Fig. 6. Effect of concentration of 18-crown-6 in 1.2 mM tyramine–0.2 mM oxalic acid eluent at pH 4.5 on retention volumes of common mono- and divalent cations. Eluent: 0–1 mM 18-crown-6 in 1.2 mM tyramine–0.2 mM oxalic acid at pH 4.5; other chromatographic conditions as for Fig. 5. Symbols: ●=Li$^+$, ▲=Na$^+$, ■=NH$_4^+$, ♦=K$^+$, ○=Mg^{2+} and △=Ca^{2+}.

3.2.3. Effect of 18-crown-6

The addition of 18-crown-6 to acidic eluent was also effective for the improvement peak resolution between the mono- and divalent cations in the IC–CD with the Al–Silica column. The retention volumes of K$^+$ increased selectively and the peak shape of K$^+$ was strongly tailed, because 18-crown-6 forms very stable complex with K$^+$. Therefore, it was concluded that the addition of 18-crown-6 was not suitable in the IC–CD [3]. However, as mentioned before, the effect of 15-crown-5 was expected to be suppressed by tyramine under the IC–IPD conditions. This finding suggested that good separation of these cations could be achieved in the IC–IPD by using 1.2 mM tyramine–0.2 mM oxalic acid at pH 4.5 containing 18-crown-6 as eluent. Third, the effect of 18-crown-6 was investigated in detail.

Fig. 6 shows the relationship between the concentration of 18-crown-6 in the eluent and the retention volumes of the mono- and divalent cations.
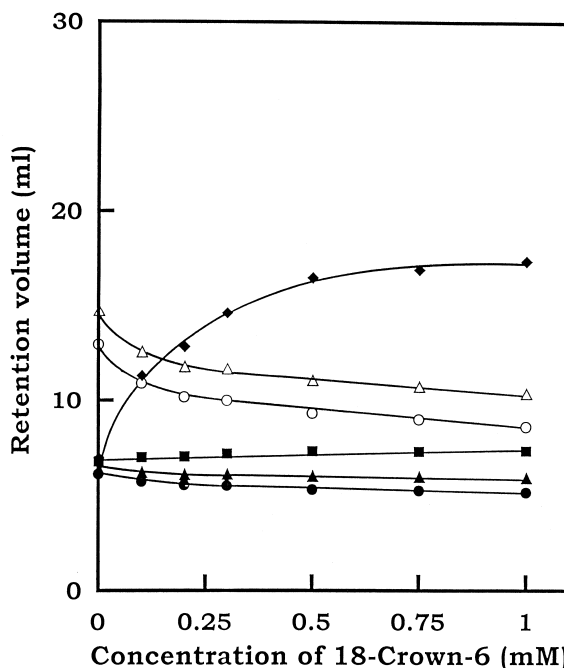
As for the monovalent cations, the retention volume of NH$_4^+$ and K$^+$ increased and those of Li$^+$ and Na$^+$ slightly decreased with increasing the concentration of 18-crown-6 in the eluent. The retention volume of K$^+$ increased drastically, because 18-crown-6 forms very stable complex with K$^+$ [17]. The order of the increase in the retention volume was Li$^+$<Na$^+$< NH$_4^+$<K$^+$ and then peak resolution between the monovalent cations was quite improved. Good separation was achieved at the concentration of 18-crown-6≧0.5 mM. As for the divalent cations, the retention volumes decreased with increasing the concentration of 18-crown-6 in the eluent. The order of the decrease in the retention volume was Ca^{2+}< Mg^{2+}. (In other words, the order of the increase in the retention volume was Mg^{2+}<Ca^{2+}.) These orders were in good agreement with both those obtained by the IC–CD [3] and these predicted from stability constants of complexes formed between

these cations and 18-crown-6 [17]. Although no conclusive reasons for the changes of the retention volumes of the mono- and divalent cations were found, it was evident that 18-crown-6 seemed to act as a selective cation-exchanger in the IC–IPD. The detailed study for the clarification of the changes will be subject of future work.

Complete separation of the mono- and divalent cations was achieved at the concentration of 18-crown-6$\geq$0.5 mM. The concentration of 18-crown-6 was ten times lower than that of 15-crown-5. This is because 18-crown-6 is strongly retained on the Al–Silica stationary phase and forms more stable complexes with these cations when compared to 15-crown-5.

From above results, it was concluded that the optimum concentration of 18-crown-6 was 0.5 mM. As shown in Fig. 7, excellently simultaneous separation of the mono- and divalent cations were achieved in 20 min by elution with 1.2 mM
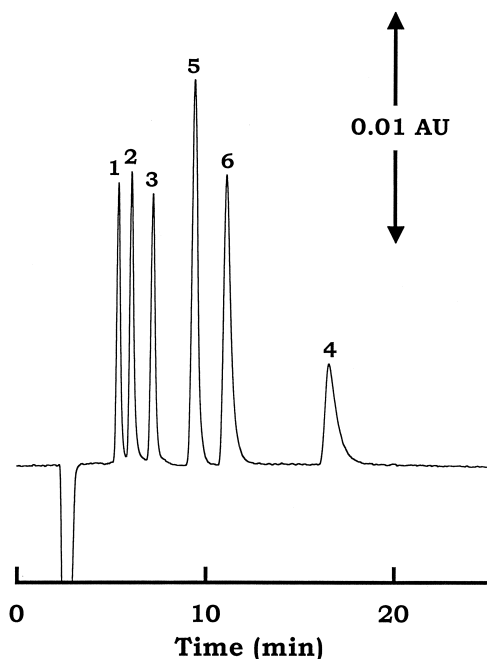
Table 2
Detection limits of comon mono- and divalent cations obtained by 1.2 mM tyramine–0.2 mM oxalic acid–5 mM 15-crown-5 at pH of 4.5 (Elunt A) and 1.2 mM tyramine–0.2 mM oxalic aid–0.5 mM 18-crown-6 at pH 4.5 (Eluent B) as eluent[a]

Cation	Eluent A		Eluent B	
	μM	ng ml^{-1}	μM	ng ml^{-1}
Li$^+$	3.7	26	3.1	22
Na$^+$	4.0	92	3.2	74
NH$_4^+$	4.0	72	3.5	62
K$^+$	9.0	350	9.4	370
Mg^{2+}	4.1	99	2.3	55
Ca^{2+}	6.0	240	3.0	120

[a] Signal-to-noise ratio=3. Injection volume: 20 μl.

tyramine–0.2 mM oxalic acid–0.5 mM 18-crown-6 at pH 4.5 (Eluent B).

3.3. Analytical parameters

Various analytical performance parameters ob-

Fig. 7. Chromatogram of common mono- and divalent cations obtained by 1.2 mM tyramine–0.2 mM oxalic acid–0.5 mM 18-crown-6 at pH 4.5 as eluent. Eluent: 1.2 mM tyramine–0.2 mM oxalic acid–0.5 mM 18-crown-6 at pH 4.5 (eluent B); other chromatographic conditions are as for Fig. 6. Peaks: 1=Li$^+$, 2=Na$^+$, 3=NH$_4^+$, 4=K$^+$, 5=Mg^{2+} and 6=Ca^{2+}.

Table 3
Retention volumes of various cations obtained by 1.2 mM tyramine–0.2 mM oxalic acid–5 mM 15-crown-5 at pH of 4.5 (Eluent A) and 1.2 mM tyramine–0.2 mM oxalic acid–0.5 mM 18-crown-6 at pH of 4.5 (Eluent B)

Cation	Retention volume (ml)	
	Eluent A	Eluent B
Li$^+$	6.4	5.3
Na$^+$	8.4	6.0
NH$_4^+$	7.5	7.3
K$^+$	10.1	16.5
Rb$^+$	9.3	9.4
Cs$^+$	9.2	8.2
Mg^{2+}	14.6	9.4
Ca^{2+}	18.6	11.1
Sr^{2+}	SR[a]	SR[a]
Ba^{2+}	SR[a]	SR[a]
Ni^{2+}	4.3	3.8
Pb^{2+}	SR[a]	SR[a]
Zn^{2+}	5.4	4.4
Co^{2+}	5.9	4.6
Fe^{2+}	8.8	6.4
Mn^{2+}	12.0	7.8
Cd^{2+}	11.7	7.8
Cu^{2+}	ND[b]	ND[b]
Fe^{3+}	ND[b]	ND[b]

[a] Strongly retained (retained volume$\geq$60 ml).
[b] Not detected.

tained by the Eluent A and Eluent B as eluent were investigated.

Table 2 shows the detection limits (signal-to-noise ratio of 3) of the mono- and divalent cations at injection volume of 20 µl. The detection limits obtained by the IC–IPC were about 10 times higher than those obtained by the IC–CD [3].

Calibration graphs were obtained by plotting peak area against various concentration of the mono- and divalent cations (0.01, 0.02, 0.03, 0.05, 0.075, 0.1, 0.15, 0.2, 0.3, 0.5, 0.75 and 1.0 mM) at injection volume of 20 µl. Linear calibration graphs ($r^2 \geq$ 0.99) were obtained in the concentration range of 0.01–1.0 mM for these mono- and divalent cations.

The relative standard deviations of the chromatographic peak areas of the mono- and divalent cations, whose concentrations were 0.2 mM, was less than 1.5% ($n = 8$). Reproducible chromatograms were obtained during repeated chromatographic runs.

Interference effects were determined for the mono- and divalent cations. Table 3 show the retention volumes of various cations obtained by the Eluent A

and Eluent B as eluent. The retention volumes of several cations, such as Rb^+, Cs^+, Fe^{2+}, Mn^{2+} and Cd^{2+}, were closed to those of the mono- and divalent cations. Although the concentration of these cations were very low in natural water samples, it was concluded that the determination of the mono- and divalent cations were not affected by these cations.

3.4. Application to cation analysis in natural water samples

The proposed IC–IPD method was applied to the determination of major mono- and divalent cations (Na^+, NH_4^+, K^+, Mg^{2+} and Ca^{2+}) in river and rain water samples. Samples were analyzed after filtration with a 0.45-µm membrane filter.

Fig. 8A and B show typical chromatograms of river water sample obtained by the Eluent A and Eluent B as eluent, respectively. Good separation and detection for these mono- and divalent cations were achieved at the injection volume of 20 µl. In
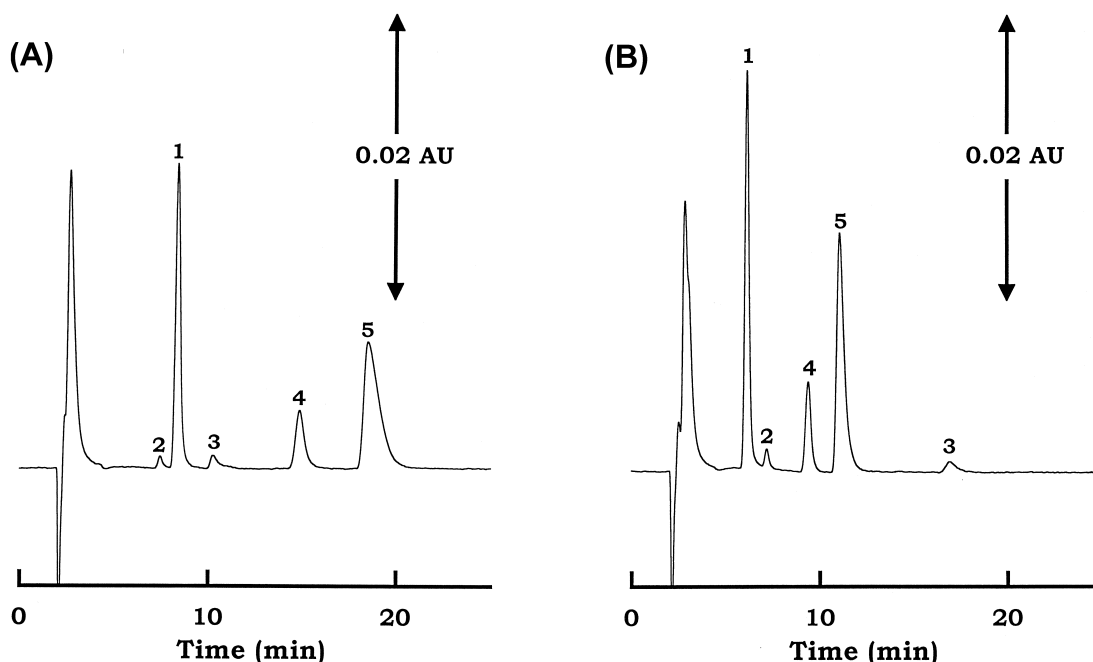

Fig. 8. Chromatograms of river water sample (Mid-stream of Nagara River) obtained by (A) Eluent A and (B) Eluent B as eluent at injection volume 20 µl. Peaks (concentration, mM): 1 = Na^+ (0.47), 2 = NH_4^+ (0.015), 3 = K^+ (0.027), 4 = Mg^{2+} (0.056), 5 = Ca^{2+} (0.27).
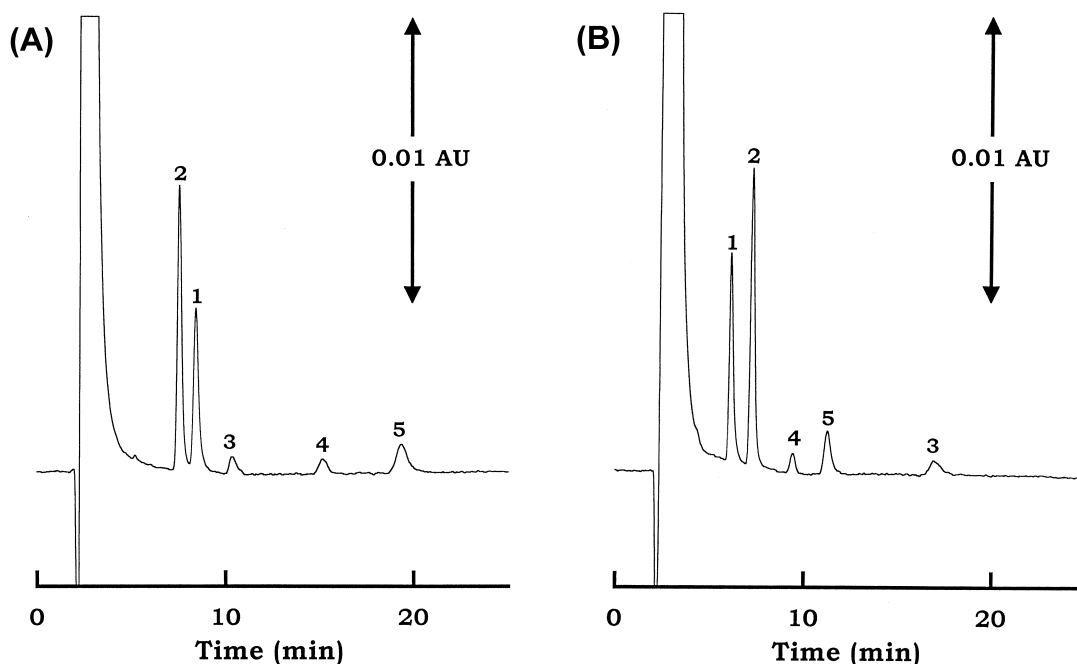
Fig. 9. Chromatograms of rain water sample at pH 4.19 obtained by (A) Eluent A and (B) Eluent B as eluent at injection volume 100 μl. Peaks (concentration, mM): $1 = Na^+$ (0.023), $2 = NH_4^+$ (0.036), $3 = K^+$ (0.005), $4 = Mg^{2+}$ (0.002), $5 = Ca^{2+}$ (0.005).

contrast, since the concentrations of these cations, especially K^+, in rain water sample was much lower than those in river water sample, it was very difficult to determine these cations at injection volume of 20-μl. However, as shown in Fig. 9A and B, good separation and detection for these cations were achieved at injection volume of 100-μl.

From the above results, it was proved that the proposed IC–IPD method was very effective for the determination of major mono- and divalent cations in natural water samples.

4. Conclusion

In this work, in order to expand the utility of laboratory-made Al–Silica in IC for cations, the application of the Al–Silica column to IC–IPD for common mono- and divalent cations (Li^+, Na^+, NH_4^+, K^+, Mg^{2+} and Ca^{2+}) was carried out by using protonated tyramine (4-aminoethylphenol) as eluent ion. As a result, excellently simultaneous separation

of these cations were achieved in 21 min by using 1.2 mM tyramine–0.2 mM oxalic acid at pH 4.5 containing either 0.5 mM 15-crown-5 or 0.5 mM 18-crown-6 as eluent,. The proposed IC–IPD method was successfully applied to the determination of major mono- and divalent cations in various natural water samples. As reported before [3], the Al–Silica was very effective cation-exchange stationary phase in IC–CD for these mono- and divalent cations. These results were strongly confirmed that the modification of silica gel with aluminium was simple and effective way for the preparation of advanced silica-based cation-exchanger in IC for cations.

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