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Simultaneous separation of common mono- and divalent cations on silica gel modified with aluminium by non-suppressed ion chromatography with conductimetric detection and nitric acid–15-crown-5 as eluent

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Abstract

The modification of silica gel with aluminium by a coating method was very effective for the preparation of silica-based stationary phases which acted as a cation exchanger under strongly acidic conditions. However, the separation of common mono- and divalent cations (Li^+ , Na^+ , NH_4^+ , K^+ , Mg^{2+} and Ca^{2+}) on an aluminium-adsorbing silica (Al-Silica) column was moderate by a conductimetric detection ion chromatography (IC) with strongly acidic eluents. Then, the addition of various crown ethers (12-crown-4, 15-crown-5 and 18-crown-6) in acidic eluent was carried out. As a result, it was found that 15-crown-5 was most effective for the improvement of peak resolution. Excellent separation of these cations was achieved in 20 min by elution with 2 mM nitric acid–2 mM 15-crown-5. The proposed IC was successfully applied to the determination of major cations in various natural waters. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Stationary phases, LC; Mobile phase composition; Water analysis; Environmental analysis; Inorganic cations; Crown ethers

1. Introduction

Since the presence of certain metals in silica matrix causes the enhancement of acidity of silanol group on the surface of silica gel [1–3], it is possible to prepare silica gel with cation-exchange ability under strongly acidic conditions by the modification of silica gel with metals. There are two major advantages in the application of the silica gel with cation-exchange ability under strongly acidic con-

ditions to a conductimetric detection ion chromatography (IC) for cations. First, the simultaneous separation of common mono- and divalent cations could be achieved, because the affinity of mono- and divalent cations to dissociated silanol group as a cation-exchanger is very similar. Second, highly sensitive indirect-conductimetric detection of cations could be achieved, because hydronium ion (H^+) with the largest equivalent conductance is generally employed as eluent ion. However, the modification of silica gel with metals has not yet been investigated for the preparation of silica-based stationary phase in IC for cations.

In previous studies [4–6], we have found that a commercially available unmodified silica gel (Develosil 30-5) acted as a cation-exchanger under

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strongly acidic conditions and the main cause of the cation-exchange characteristics was attributed to be a trace amount of aluminium present in the silica gel. However, the silica gel was developed as a stationary phase for normal-phase HPLC, the appearance of the cation-exchange characteristics of the Develosil 30-5 is not necessarily reproducible. Then, in order to prepare silica gel with cation-exchange ability under strongly acidic conditions, the modification of silica gel with aluminium by a coating method was carried out [7]. As a result, home-made aluminium-adsorbing silica gel (Al-Silica) acted as a cation-exchanger under strong acidic conditions and the moderate separation of common mono- and divalent cations was achieved on the Al-Silica column.

It is well known that crown ethers form stable complexes with many cations [8]. On the basis of the characteristics, the modification of HPLC stationary phase with various crown ether derivatives was carried out for the separation of cations [9–14]. Recently, the addition of crown ethers to acidic eluents was carried out for the improvement of peak resolution among common mono- and divalent cations on weakly acidic cation-exchange columns [15,16].

The aim of this study was to demonstrate the effectiveness of the home-made Al-Silica stationary phase in conductimetric detection IC for cations with strongly acidic eluents. Therefore, the effect of various crown ethers added in strongly acidic eluents was investigated for the achievement of high resolution separation of common mono- and divalent cations (Li^+ , Na^+ , NH_4^+ , K^+ , Mg^{2+} and Ca^{2+}). As a result, when using 2 mM nitric acid–2 mM 15-crown-5 as eluent, excellent separation and highly sensitive detection for these mono- and divalent cations were achieved in 20 min on a 25-cm Al-Silica column.

2. Experimental

2.1. Preparation of aluminium-adsorbing silica gel

A Fuji-Silysia Chemical (Kasugai, Japan) Super Micro Bead Silica Gel B-5 (SMBS 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 $\text{Al}_2(\text{SO}_4)_3$ solution [1 g $\text{Al}_2(\text{SO}_4)_3 \cdot 14\text{--}18 \text{ H}_2\text{O}/100 \text{ ml}$ 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 130°C followed by calcining at 1000°C for 5 h.

The determination of aluminium on aluminium-adsorbing silica gel (Al-Silica) was carried out by using a Nippon Jarrell-Ash (Kyoto, Japan) ICAP-1000 inductively coupled plasma–atomic emission spectrometer (ICP–AES) [7]. The amount of aluminium adsorbed on the 1 g silica gel was ca. 500 μg .

Table 1 shows physical properties of Al-Silica and SMBS 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 using a Carlo Erba Instruments (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 $P/P_0=0.95$. The decrease of surface area and pore volume and the increase of packing density were due mainly to shrinkage of the silica matrix.

2.2. Ion chromatograph

The ion chromatograph consisted of a Tosoh (Tokyo, Japan) SC-8020 chromatographic data-pro-

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

Packing	Form	Particle size (μ)	Surface area ($\text{m}^2 \text{g}^{-1}$)	Pore size (\AA)	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

cessor, 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 CM-8020 conductimetric detector, a Tosoh SD-8023 on-line degasser, and a Rheodyne (Cotati, CA, USA) model 9125 injector equipped with a $20 \mu\text{l}$ sample loop.

The separation columns ($250 \times 4.6 \text{ mm I.D.}$, stainless steel) were packed with the Al-Silica by using a slurry packing method.

2.3. Reagents

All reagents were of analytical reagent grade. Crown ethers [1,4,7,10-tetraoxacyclododecane (12-crown-4), 1,4,7,10,13-pentaoxacyclopentadecane (15-crown-5) and 1,4,7,10,13,16-hexaoxacyclooctadecane (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.

3. Results and discussion

3.1. Retention behavior of common mono- and divalent cations on the Al-Si column under strongly acidic conditions

The retention behavior of common mono- and divalent cations (Li^+ , Na^+ , NH_4^+ , K^+ , Mg^{2+} and Ca^{2+}) under strongly acidic conditions was investigated on the SMBSG B-5 and the Al-Silica columns. Fig. 1(a) and (b) show chromatograms of these mono- and divalent cations on the SMBSG B-5 and the Al-Si columns by elution with 2 mM nitric acid (pH 2.7), respectively.

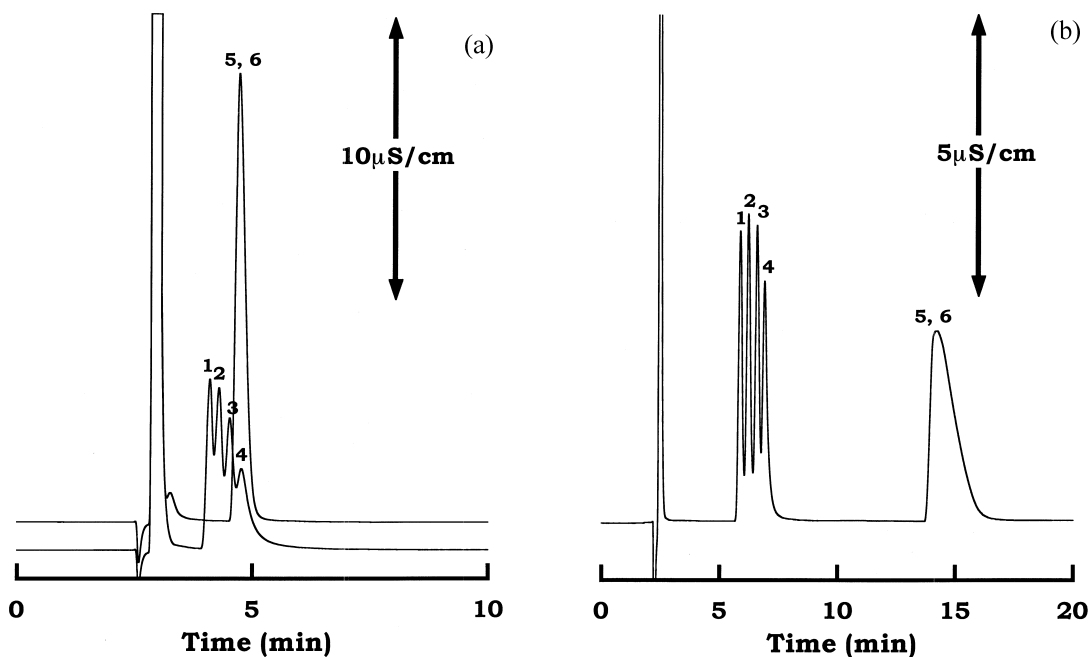


Fig. 1. Chromatograms of common mono- and divalent cations on (a) Super Micro Bead Silica Gel B-5 and (b) aluminium-adsorbing silica gel columns by elution with 2 mM nitric acid (pH 2.7). Column: (a) Super Micro Bead Silica Gel B-5, (b) aluminium-adsorbing silica gel ($500 \mu\text{g}$ aluminium/g silica gel) calcined at 1000°C for 5 h. Column size: $250 \times 4.6 \text{ mm I.D.}$; column temperature: 35°C ; eluent: 2 mM nitric acid (pH 2.7); flow-rate: 1 ml min^{-1} ; detection: indirect-conductivity; injection volume: $20 \mu\text{l}$; sample concentration: 0.2 mM . Peaks: 1= Li^+ , 2= Na^+ , 3= NH_4^+ , 4= K^+ , 5= Mg^{2+} , 6= Ca^{2+} .

As shown in Fig. 1(a), since the retention times of these cations were larger than that of the water dip, the SMBSG B-5 was found to act as a cation-exchanger under the strongly acidic eluent conditions. However, since the retention times of these cations were very similar and were close to that of the water dip, it was found that the simultaneous separation of these mono- and divalent cations on the SMBSG B-5 column was very difficult under the strongly acidic eluent conditions. In contrast, as shown in Fig. 1(B), the retention times of these cations on the Al-Silica column were much larger than those on the SMBSG B-5 column and complete group separation between mono- and divalent cations was achieved on the Al-Silica column. These results indicated that the modification of silica gel with aluminum was very effective for the preparation of silica-based stationary phase for IC, which acted as a cation-exchanger under strongly acidic eluent conditions.

The improvement of peak resolution between these divalent cations (Mg^{2+} and Ca^{2+}) on the Al-Silica column was relatively easy. As shown in Fig. 2(a) and (b), good separation of these divalent cations was achieved by elution with 2 mM nitric acid–0.5 mM 2,6-pyridinedicarboxylic acid (PDCA) and 2 mM oxalic acid, respectively. This is because Mg^{2+} and Ca^{2+} form complexes with PDCA ($\log K_{Mg^{2+}}=2.7$ and $\log K_{Ca^{2+}}=4.2$ at 25°C) [17] and oxalic acid ($\log K_{Mg^{2+}}=3.43$ and $\log K_{Ca^{2+}}=3.00$ at 18°C) [17] and the stability between the Mg^{2+} complex and the Ca^{2+} complex formed is relatively different. On the other hand, the improvement of peak resolution among these monovalent cations (Li^+ , Na^+ , NH_4^+ and K^+) was extremely difficult. This is because these monovalent cations are inert for almost complexing agents.

3.2. Effect of crown ethers on the retention behavior of mono- and divalent cations

Crown ethers form stable complexes with many cations, especially in monovalent cations. On the basis of the unique characteristics, the addition of crown ethers in acidic eluents was carried out for the improvement of peak resolution among mono- and divalent cations on weakly acidic cation-exchange stationary phases. Therefore, in order to achieve

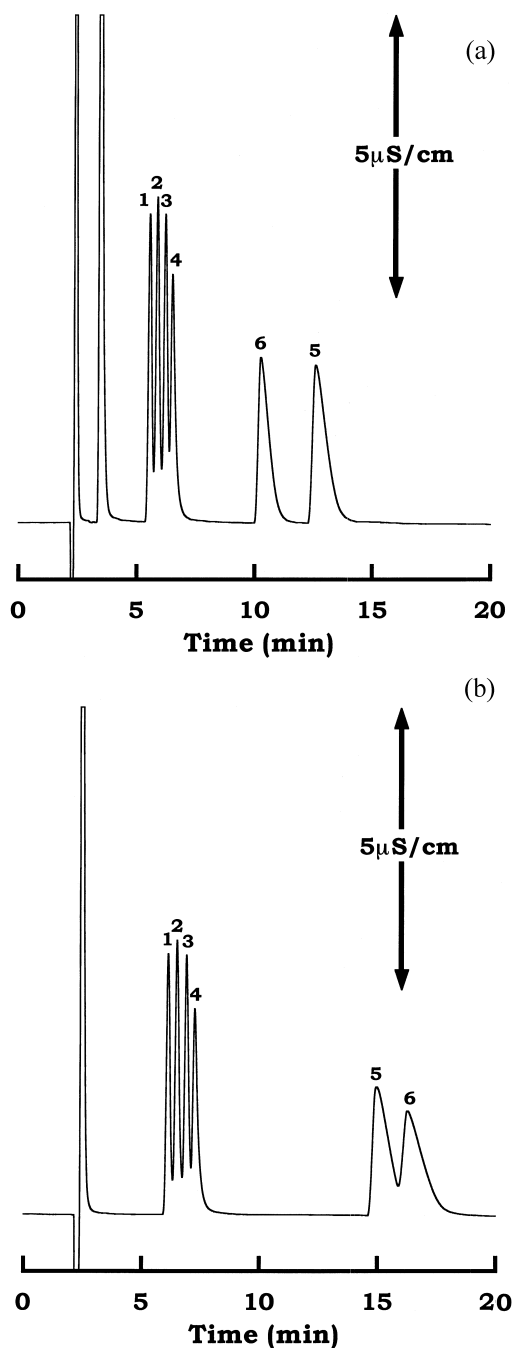


Fig. 2. Chromatograms of common mono- and divalent cations on the aluminium-adsorbing silica gel column by elution with (a) 2 mM nitric acid–0.5 mM 2,6-pyridinedicarboxylic acid and (b) 2 mM oxalic acid. Column: aluminium-adsorbing silica gel; eluent: (a) 2 mM nitric acid–0.5 mM 2,6-pyridinedicarboxylic acid, (b) 2 mM oxalic acid. Chromatographic conditions are as for Fig. 1.

complete 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 various crown ethers (12-crown-5, 15-crown-5 and 18-crown-6) added in 2 mM nitric acid eluent was investigated in detail.

3.2.1. Effect of 12-crown-4

First, the effect of 12-crown-4 was investigated. As shown in Fig. 3, with increasing the concentration of 12-crown-4 in the eluent, the retention times of Na^+ and Ca^{2+} increased and those of other cations were almost the same. This result indicated that 12-crown-4 in the eluent was adsorbed on the surface of the Al-Silica stationary phase and acted as a selective cation-exchanger. Although the peak resolution between Mg^{2+} and Ca^{2+} was improved, the peak resolution among monovalent cations was not improved. As shown in Fig. 4, complete separation

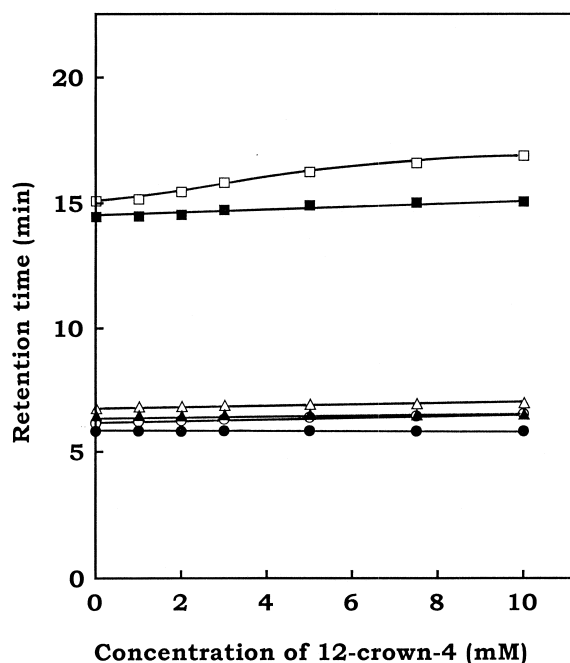


Fig. 3. Effect of concentration of 12-crown-4 in 2 mM nitric acid eluent on retention volumes of common mono- and divalent cations on the aluminium-adsorbing silica gel column. Column: aluminium-adsorbing silica gel; eluent: 0–10 mM 12-crown-4 in 2 mM nitric acid. Symbols: ●= Li^+ , ○= Na^+ , ▲= NH_4^+ , △= K^+ , ■= Mg^{2+} , □= Ca^{2+} . Other chromatographic conditions are as for Fig. 1.

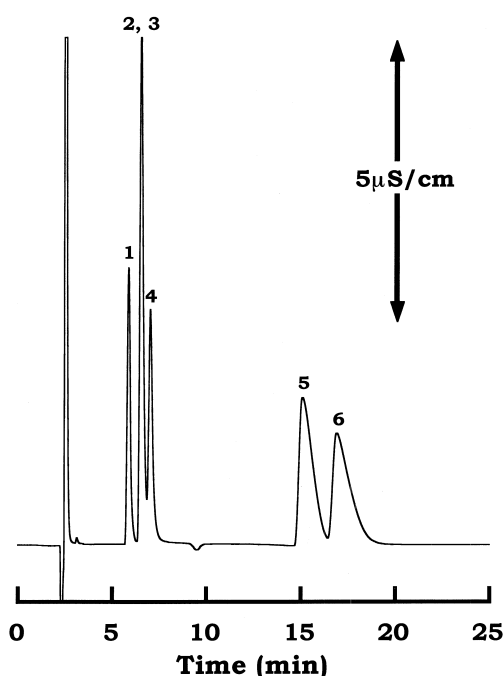


Fig. 4. Chromatograms of common mono- and divalent cations on the aluminium-adsorbing silica gel column by elution with 2 mM nitric acid–10 mM 12-crown-4. Column: aluminium-adsorbing silica gel; eluent: 10 mM 12-crown-4 in 2 mM nitric acid. Peaks: 1= Li^+ , 2= Na^+ , 3= NH_4^+ , 4= K^+ , 5= Mg^{2+} , 6= Ca^{2+} . Other chromatographic conditions are as for Fig. 1.

of Mg^{2+} and Ca^{2+} and incomplete separation of these monovalent cations were achieved in 20 min by elution with 2 mM nitric acid–10 mM 12-crown-4.

3.2.2. Effect of 15-crown-5

It is well known that 15-crown-5 forms more stable complexes with cations when compared to 12-crown-4. Second, the effect of 15-crown-5 was investigated. As shown in Fig. 5, with increasing the concentration of 15-crown-5, the retention times of Na^+ , K^+ and Ca^{2+} increased and those of other cations were almost the same. The degree of the increase of retention times by using 15-crown-5 was considerably larger than that by using 12-crown-4. This is because 15-crown-5 is adsorbed strongly on the Al-Silica stationary phase and form stable complexes with these cations compared to 12-crown-4. As shown in Fig. 6, complete separation of these mono- and divalent cations with good peak shapes

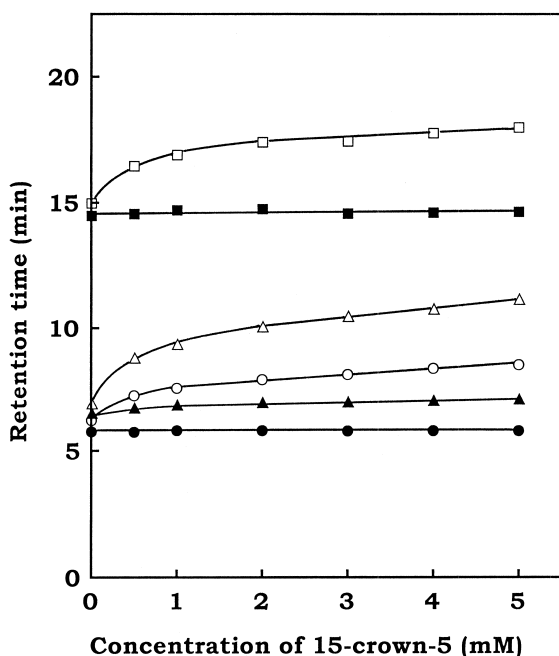


Fig. 5. Effect of concentration of 15-crown-5 in 2 mM nitric acid eluent on retention volumes of common mono- and divalent cations on the aluminium-adsorbing silica gel column. Column: aluminium-adsorbing silica gel; eluent: 0–5 mM 15-crown-5 in 2 mM nitric acid. Symbols: ●=Li⁺, ○=Na⁺, ▲=NH₄⁺, △=K⁺, ■=Mg²⁺, □=Ca²⁺. Other chromatographic conditions are as for Fig. 1.

was achieved in 20 min by elution with 2 mM nitric acid–2 mM 15-crown-5.

3.2.3. Effect of 18-crown-6

Finally, the effect of 18-crown-6 was investigated. As shown in Fig. 7, with increasing the concentration of 18-crown-6, the retention times of Na⁺, NH₄⁺, K⁺ and Ca²⁺ increased and those of Li⁺ and Mg²⁺ were almost the same. Table 2 shows the stability constants of complexes formed between crown ethers (15-crown-5 and 18-crown-6) and mono- and divalent cations [18]. The degree of increasing retention times by using 18-crown-6 was much larger than those by using 15-crown-5. This is because 18-crown-6 is strongly adsorbed on the Al-Silica stationary phase and forms more stable complexes with these cations when compared to 15-crown-5.

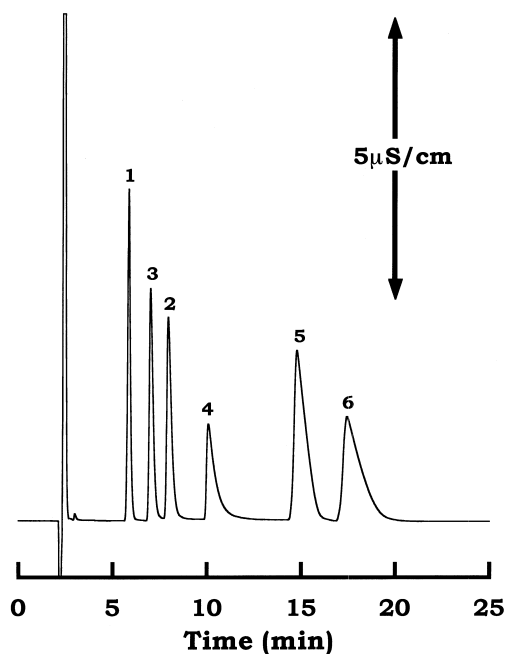


Fig. 6. Chromatograms of common mono- and divalent cations on the aluminium-adsorbing silica gel column by elution with 2 mM nitric acid–2 mM 15-crown-5. Column: aluminium-adsorbing silica gel; eluent: 2 mM 15-crown-5 in 2 mM nitric acid. Peaks: 1=Li⁺, 2=Na⁺, 3=NH₄⁺, 4=K⁺, 5=Mg²⁺, 6=Ca²⁺. Other chromatographic conditions are as for Fig. 1.

The degree of increasing retention times of these monovalent cations was Li⁺ < Na⁺ < NH₄⁺ < K⁺. The elution order was in good agreement with that predicted from their stability constants in Table 2. The retention time of K⁺ remarkably increased. This is because the internal cavity size of 18-crown-6 (1.38 Å) is the same as the size of K⁺ (1.38 Å) and then 18-crown-6 forms a very stable metal-in-hole type complex with K⁺. As shown in Fig. 8, although good separation of these mono- and divalent cations were achieved by elution with 2 mM nitric acid–0.2 mM 18-crown-6, the peak shape of K⁺ was strongly tailed and the separation time required was twice when compared to that using 15-crown-5.

When considering peak resolution, peak shape and separation time, it was concluded that 15-crown-5 was the most effective for the simultaneous separation of these mono- and divalent cations on the Al-Silica column.

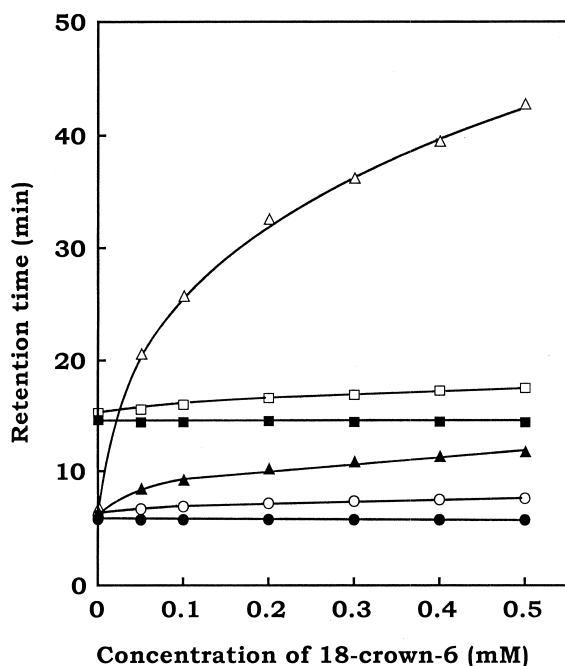


Fig. 7. Effect of concentration of 18-crown-6 in 2 mM nitric acid eluent on retention volumes of common mono- and divalent cations on the aluminium-adsorbing silica gel column. Column: aluminium-adsorbing silica gel; eluent: 0–0.5 mM 18-crown-6 in 2 mM nitric acid. Symbols: ●=Li⁺, ○=Na⁺, ▲=NH₄⁺, △=K⁺, ■=Mg²⁺, □=Ca²⁺. Other chromatographic conditions are as for Fig. 1.

3.3. Analytical parameters

As shown in Fig. 6, the optimum eluent condition was found to be 2 mM nitric acid–2 mM 15-crown-

Table 2

Stability constants (log *K*) binding for mono- and divalent cations to 15-crown-5 and 18-crown-6 in water at 25°C [18]

Cation	log <i>K</i>	
	15-Crown-5	18-Crown-6
Li ⁺	–	–
Na ⁺	0.70	0.80
NH ₄ ⁺	1.71	1.23
K ⁺	0.74	2.03
Rb ⁺	0.62	1.56
Cs ⁺	0.8	0.99
Mg ²⁺	–	–
Ca ²⁺	–	<0.5
Sr ²⁺	1.95	2.82
Ba ²⁺	1.71	3.87

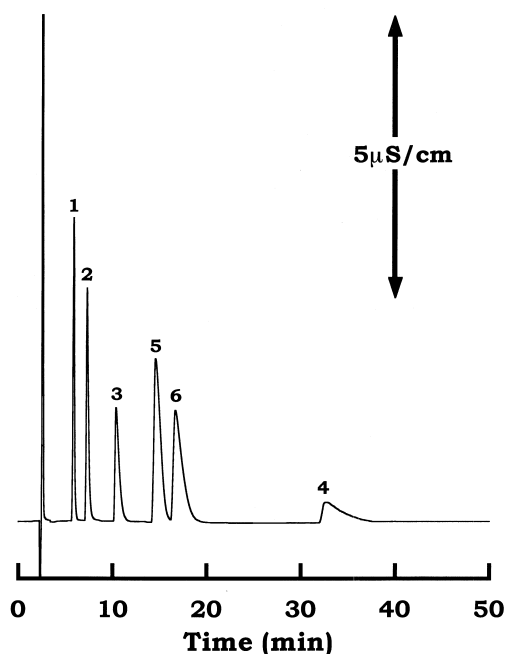


Fig. 8. Chromatograms of common mono- and divalent cations on the aluminium-adsorbing silica gel column by elution with 2 mM nitric acid–0.2 mM 18-crown-6. Column: aluminium-adsorbing silica gel; eluent: 0.2 mM 18-crown-6 in 2 mM nitric acid. Peaks: 1=Li⁺, 2=Na⁺, 3=NH₄⁺, 4=K⁺, 5=Mg²⁺, 6=Ca²⁺. Other chromatographic conditions are as for Fig. 1.

5. Various analytical parameters were investigated.

Calibration graphs were obtained by plotting peak area against the concentration of the common mono- and divalent cations. Linear calibration graphs ($r^2 \geq 0.99$) were obtained in the concentration range of 0.005–1.0 mM for these cations.

Table 3

Detection limits of common mono- and divalent cations under the optimum chromatographic conditions (injection volume, 20 μl)

Cation	Detection limits ^a	
	μM	ng ml ⁻¹
Li ⁺	0.17	1.1
Na ⁺	0.28	6.4
NH ₄ ⁺	0.24	4.1
K ⁺	0.61	24
Mg ²⁺	0.34	8.3
Ca ²⁺	0.57	23

^a Signal-to-noise ratio=3.

Table 4
Retention times of various cations on the Al-Silica column by elution with (A) 2 mM nitric acid–2 mM 15-crown-5 and (B) 2 mM nitric acid

Cation	Retention volume (min)	
	A	B
Li ⁺	5.9	5.9
Na ⁺	7.9	6.2
NH ₄ ⁺	7.0	6.6
K ⁺	10.1	6.9
Rb ⁺	8.7	7.4
Cs ⁺	9.0	8.2
Mg ²⁺	14.8	14.5
Ca ²⁺	17.4	14.9
Sr ²⁺	29.3	15.2
Ba ²⁺	SR ^a	15.5
Cd ²⁺	14.8	14.3
Co ²⁺	15.0	14.5
Cu ²⁺	15.0	14.5
Mn ²⁺	15.1	14.4
Ni ²⁺	14.9	14.5
Zn ²⁺	15.1	14.5
Fe ²⁺	ND ^b	14.5
Pb ²⁺	ND ^b	15.3
Fe ³⁺	ND ^b	SR ^a

^a SR: Strongly retained.

^b ND: Not detected.

Table 3 shows the detection limits of the common mono- and divalent cations at a signal-to-noise ratio of 3 (injection volume of 20 μ l). The detection limits are sufficiently low to allow the determination of the common mono- and divalent cations in various natural waters.

The relative standard deviations of the chromatographic peak areas of the mono- and divalent cations, whose concentrations were 0.2 mM, were less than 1.0% ($n=10$).

Table 4 shows the retention times of mono-, di- and trivalent cations. As listed in Table 4, the degree of increasing retention times of monovalent cations was Li⁺ < NH₄⁺ < Na⁺ < Cs⁺ < Rb⁺ < K⁺ and that of alkaline earth metal cations was Mg²⁺ < Ca²⁺ < Sr²⁺ < Ba²⁺. Since these orders were not in good agreement with that predicted from their stability constants in Table 2, the detailed study for retention mechanism is required and will be the subject of future work. As listed in Table 4, most transition metal cations, except for Fe²⁺ and Pb²⁺ were co-eluted, it was found that the addition of 15-crown-5 had no effect for the separation of these cations.

A long-term stability of the Al-Silica column was

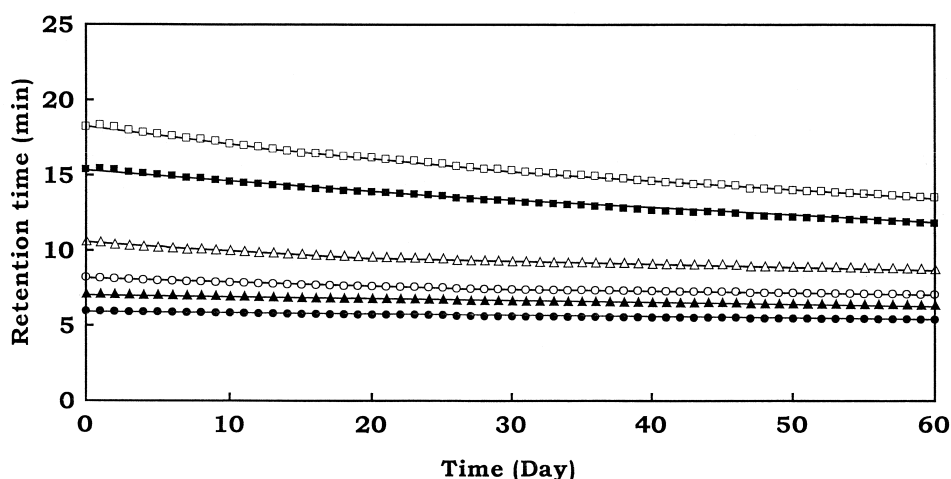


Fig. 9. Long-term stability of aluminium-adsorbing silica gel. Symbols: ●=Li⁺, ○=Na⁺, ▲=NH₄⁺, △=K⁺, ■=Mg²⁺, □=Ca²⁺. Chromatographic conditions are as for Fig. 6.

investigated in order to apply the Al-Silica column to practical use. As shown in Fig. 9, the retention times of these common mono- and divalent cations were gradually decreased. This is due mainly to an instability of the silica matrix in aqueous solution.

However, the amount of decrease of retention times was very little in a day. For instance, the amount of decrease of retention times of Ca^{2+} was less than 0.07 min in a day. Additionally, simultaneous separation of these mono- and divalent cations was successfully achieved over a period of 1500 h.

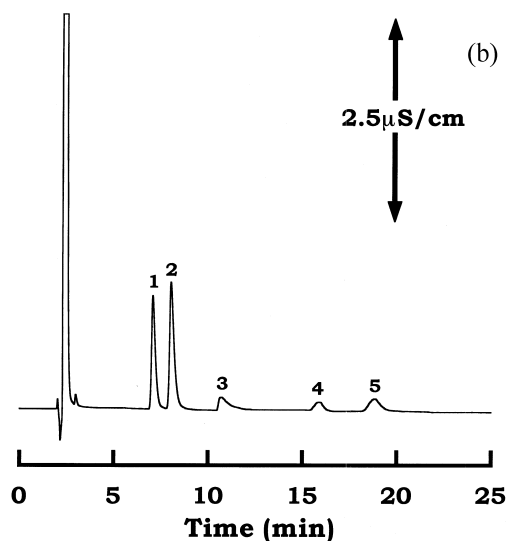
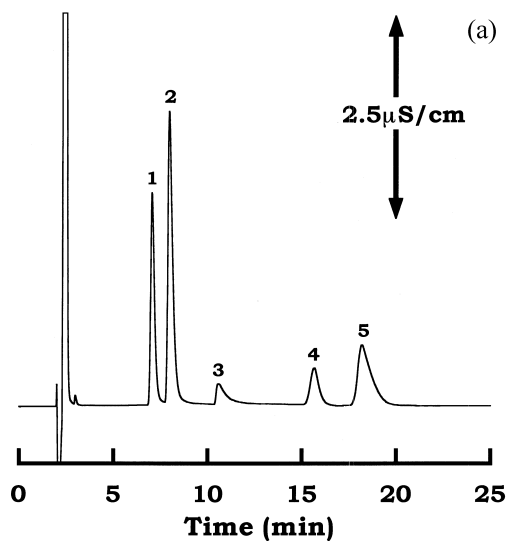


Fig. 10. Chromatograms of acid rain water samples. (a) pH 4.09; peaks (concentration, mM): 1= NH_4^+ (0.14), 2= Na^+ (0.21), 3= K^+ (0.037), 4= Mg^{2+} (0.025), 5= Ca^{2+} (0.063). (b) pH 4.29; peaks (concentration, mM): 1= NH_4^+ (0.073), 2= Na^+ (0.094), 3= K^+ (0.023), 4= Mg^{2+} (0.005), 5= Ca^{2+} (0.012). Chromatographic conditions are as for Fig. 6.

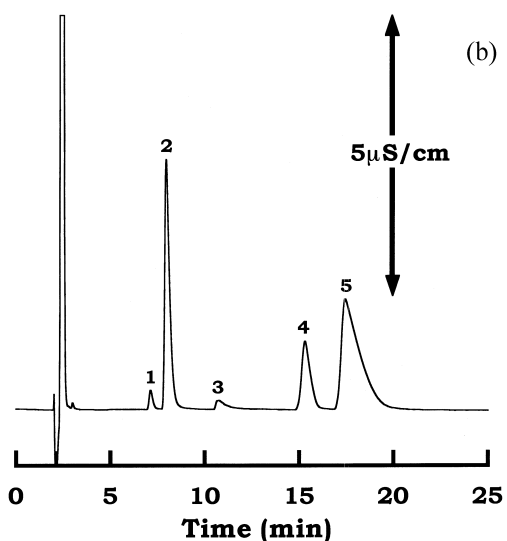
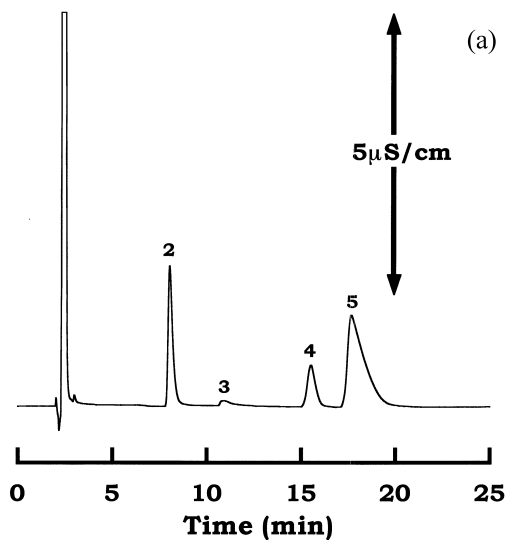


Fig. 11. Chromatograms of river water samples. (a) Upper-stream of Nagara River; peaks (concentration, mM): 2= Na^+ (0.14), 3= K^+ (0.012), 4= Mg^{2+} (0.041), 5= Ca^{2+} (0.17). (b) Mid-stream of Nagara River; peaks (concentration, mM): 1= NH_4^+ (0.016), 2= Na^+ (0.25), 3= K^+ (0.021), 4= Mg^{2+} (0.066), 5= Ca^{2+} (0.24). Chromatographic conditions are as for Fig. 6.

Considering these results, it was proved that the Al-Silica column was well suitable for practical use.

3.4. Application to cation analysis in natural water samples

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

Figs. 10 and 11 show typical chromatograms of rain and river water samples. When analyzing natural waters by the conventional conductimetric detection IC with weakly acidic cation-exchange column, it has been pointed out that peaks of Na^+ and NH_4^+ are partly overlapped and the determination of NH_4^+ is often interfered. However, excellent separation of these cations was achieved by the proposed IC method. This result strongly indicated that the proposed IC was very effective for the determination of major cations in natural water samples.

4. Conclusion

In this work, the application of laboratory-made aluminium-adsorbing silica gel (Al-Silica) as a stationary phase to IC separation of common mono- and divalent cations (Li^+ , Na^+ , NH_4^+ , K^+ , Mg^{2+} and Ca^{2+}) on the Al-Si column was carried out. As a result, it was found that the addition of crown ether was very effective for the improvement of peak resolution among common mono- and divalent cations. An excellent separation of common mono- and divalent cations was achieved in 20 min by elution with 2 mM nitric acid–2 mM 15-crown-5. The proposed IC was successfully applied to cation analysis in various natural waters. The addition of crown ethers to acidic eluents was demonstrated to

expand the utility of the Al-Silica in conductimetric detection IC for mono- and divalent cations

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