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

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## Abstract

The application of laboratory-made zirconium-modified silica gels (Zr-silicas) as cation-exchange stationary phases to ion chromatography with conductimetric detection (IC–CD) for common mono- and divalent cations ( $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{NH}_4^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$ ) was carried out. Zr-silicas were prepared by the reaction of the silanol group on the surface of silica gel with zirconium tetrabutoxide ( $\text{Zr}(\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_3)_4$ ) in ethanol. Zr-silica adsorbed on 10 mg zirconium  $\text{g}^{-1}$  silica gel was a suitable cation-exchange stationary phase in IC–CD for the separation of these mono- and divalent cations. Excellent simultaneous separation and highly sensitive detection for these cations were achieved in 10 min by IC–CD using a Zr-silica column (150×4.6 mm I.D.) and 10 mM tartaric acid containing 10 mM 15-crown-5 (1,4,7,10,13-pentaoxacyclopentadecane) as the eluent. The proposed IC–CD method was successfully applied to the determination of major mono- and divalent cations in natural water samples. © 2001 Elsevier Science B.V. All rights reserved.

**Keywords:** Water analysis; Environmental analysis; Stationary phases, LC; Silica, zirconium-modified; Inorganic cations; Crown ethers

## 1. Introduction

Modification of the silanol group on the surface of silica gel with various metals is an easy and effective way for the preparation of newly advanced silica-based stationary phases in HPLC. Nobuhara et al. [1] prepared magnesium-modified silica gel and Okamoto et al. [2,3] prepared calcium-modified silica gel using the cation-exchange reaction of the dissociated silanol group with the corresponding

metal ions. Nakamura et al. [4] prepared titanium-modified silica gel and zirconium-modified silica gel by the reaction of the silanol group with titanium tetraisopropoxide,  $\text{Ti}[\text{OCH}(\text{CH}_3)_2]_4$ , and zirconium tetrabutoxide,  $\text{Zr}(\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_3)_4$ , respectively. Unfortunately, these metal-modified silica gels were only evaluated as stationary phases in normal-phase HPLC. The ion-exchange characteristics of these metal-modified silica gels in ion chromatography (IC) were not investigated.

On the other hand, it is well known that the presence of certain metals in the silica matrix causes the enhancement of the acidity of the silanol group on the surface of silica gel [5–7]. This suggests that

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modification of silica gel with metals is possible to prepare new silica-based stationary phases with cation-exchange ability under strongly acidic conditions. The authors prepared aluminium-modified silica gel (Al-silica) and evaluated the ion-exchange characteristics in IC [8]. As a result, it was found that the Al-silica acted as a cation exchanger under strongly acidic conditions. The Al-silica was successfully applied to the IC separation of common mono- and divalent cations using a strongly acidic eluent [9].

In a previous study, in order to expand the utility of metal-modified silica gels as stationary phases in IC, the authors prepared zirconium-modified silica gel (Zr-silica) by the reaction of the silanol group on the silica gel with zirconium tetrabutoxide in ethanol [10]. Laboratory-made Zr-silica acted as a cation exchanger under strongly acidic conditions and was successfully applied to the simultaneous separation of monovalent cations ( $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{NH}_4^+$ ,  $\text{K}^+$ ,  $\text{Rb}^+$  and  $\text{Cs}^+$ ) using 10 mM tartaric acid at pH 2.5 as the eluent. Unfortunately, due to the high cation-exchange capacity of the Zr-silica, the simultaneous separation of common mono- and divalent cations ( $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{NH}_4^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$ ) was not achieved.

The aim of this study was to demonstrate the effectiveness of Zr-silica as a cation-exchange stationary phase in IC with conductimetric detection (IC–CD) for the simultaneous separation of these mono- and divalent cations. Zr-silicas adsorbed on various amounts of zirconium were prepared and their cation-exchange characteristics were investigated in detail. Zr-silica adsorbed on 10 mg zirconium  $\text{g}^{-1}$  silica gel was successfully applied to the

simultaneous separation of these cations. Excellent simultaneous separation and highly sensitive detection of these cations were achieved in 10 min by IC–CD using the Zr-silica column (150×4.6 mm I.D.) and 10 mM tartaric acid containing 10 mM 15-crown-5 (1,4,7,10,13-pentaoxacyclopentadecane) as the eluent.

## 2. Experimental

### 2.1. Preparation of zirconium-modified silica gel

A Pia Tec (Suzuka, Japan) Pia Seed 5S-100-SIL high-purity porous spherical silica gel for HPLC was employed as a matrix. The silica gel was dried overnight at 150°C. A 10-g amount of the silica gel was immersed in 100 ml ethanol. While the solution was stirred, 100 ml ethanol solution containing a given amount of zirconium tetrabutoxide solution (~85% (w/w) zirconium tetrabutoxide in butanol) was gradually added to the solution. After adding, the solution was stirring for 1 h and then was filtrated. The resultant gel was washed thoroughly with ethanol and then dried at 150°C followed by calcining at 1000°C for 5 h.

Table 1 shows the physical and chemical properties of Pia Seed 5S-100-SIL and Zr-silicas. The determination of zirconium on Zr-silicas was carried out using a Nippon Jarrel-Ash ICAP-1000 inductively coupled plasma atomic emission spectrometry (ICP-AES) system. The determination of the surface area, pore size and pore volume of Pia Seed 5S-100-SIL and Zr-silicas by using nitrogen adsorption isotherms on the gels at 77 K was carried out using a

Table 1  
Physical and chemical properties of Pia Seed 5S-100-Sil and zirconium-modified silica gels (Zr-silicas)

Gel	Amount of zirconium (mg $\text{g}^{-1}$ silica)	Drying or calcining (°C)	Particle size ( $\mu\text{m}$ )	Surface area ( $\text{m}^2 \text{g}^{-1}$ )	Pore size (Å)	Pore volume ( $\text{ml g}^{-1}$ )	Packing density ( $\text{g ml}^{-1}$ )	Surface area per column <sup>a</sup> ( $\text{m}^2 \text{column}^{-1}$ )
Pia Seed 5S-100-SIL	0	150	6.8	499	102	1.14	0.37	$4.6 \times 10^2$
	0	1000	6.0	250	59	0.54	0.60	$3.7 \times 10^2$
Zr-silica	5.2	1000	5.9	323	82	0.70	0.52	$4.2 \times 10^2$
	10	1000	6.0	313	80	0.69	0.53	$4.1 \times 10^2$
	15	1000	5.8	285	79	0.61	0.58	$4.1 \times 10^2$
	20	1000	5.6	267	78	0.60	0.58	$3.9 \times 10^2$

<sup>a</sup> Column size: 150×4.6 mm I.D.

Beckman-Coulter (Fullerton, CA, USA) Ominisorp 360 gas sorption analyzer. The surface area was calculated from the BET equation.

The separation columns (150×4.6 mm I.D., stainless steel) were packed with Pia Seed 5S-100-SIL and Zr-silicas using the slurry packing method.

## 2.2. Ion chromatograph

The ion chromatograph consisted of a Tosoh (Tokyo, Japan) LC-8020 chromatographic data processor, a Tosoh DP-8020 solvent delivery pump operated at a flow-rate of 1 ml min<sup>-1</sup>, a Tosoh CO-8020 column oven operated at 35°C, a Tosoh CM-8020 conductimetric detector, a Tosoh DS-8023 on-line degasser and a Reodyne (Cotati, CA, USA) Model 9125 injector equipped with a 20-μl sample loop.

## 2.3. Chemicals

All chemicals were of analytical reagent grade. Crown ethers (12-crown-4 (1,4,7,10-tetraoxacyclododecane), 15-crown-5 (1,4,7,10,13-pentaoxacyclopentadecane) and 18-crown-6 (1,4,7,10,13,16-hexaoxacyclooctadecane)) were purchased from Aldrich (Milwaukee, WI, USA) and other chemicals were purchased from Wako (Osaka, Japan). Distilled, deionized water was used for the preparation of eluents and standard solutions.

The pH of eluents was measured with a Toa Denpa (Tokyo, Japan) IM-40S ion meter with a glass electrode.

## 3. Results and discussion

### 3.1. Effect of amount of zirconium adsorbed on silica gel on retention volumes of mono- and divalent cations under acidic conditions

As reported previously [10], modification of silica gel with zirconium was an easy and effective way for the preparation of silica-based cation-exchange stationary phases for IC-CD using strongly acidic eluents. Excellent simultaneous separation and highly sensitive detection for monovalent cations (Li<sup>+</sup>, Na<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, K<sup>+</sup>, Rb<sup>+</sup> and Cs<sup>+</sup>) was achieved in 25

min by IC-CD using a laboratory-made Zr-silica column and 10 mM tartaric acid at pH 2.5 as the eluent. Unfortunately, due to the high cation-exchange capacity of the Zr-silica, divalent cations (Mg<sup>2+</sup>, Ca<sup>2+</sup>, Sr<sup>2+</sup> and Ba<sup>2+</sup>) were not eluted under the above chromatographic conditions. Therefore, the effect of the amount of zirconium adsorbed on silica gel on the retention volumes of common mono- and divalent cations (Li<sup>+</sup>, Na<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup> and Ca<sup>2+</sup>) was investigated for the simultaneous separation of these cations.

First, the effect of the amount of zirconium tetrabutoxide solution (~85% (w/w) zirconium tetrabutoxide in butanol) in 100 ml ethanol solution (coating solution) on the amount of zirconium adsorbed on 10 g silica gel was investigated. As a result, it was found that the amount of zirconium adsorbed on silica gel increased linearly with the amount of the zirconium tetrabutoxide solution in coating solution between 0 and 1 g. When using a coating solution containing 1 g zirconium tetrabutoxide solution, 200 mg zirconium was adsorbed on 10 g silica gel. The amount (200 mg) was almost the same as the amount of zirconium calculated in the coating solution (202 mg). This suggested that almost 100% zirconium tetrabutoxide reacted with silanol groups on the surface of silica gel. The above results also indicated that it was very easy to control the amount of zirconium adsorbed on silica gel.

Next, the effect of the amount of zirconium adsorbed on silica gel on the retention behavior of these mono- and divalent was investigated. Fig. 1 shows the relationship between the amount of zirconium adsorbed on silica gel and the retention volumes of these common mono- and divalent cations using 10 mM tartaric acid as the eluent. The retention volumes of these cations increased with increasing amount of zirconium adsorbed on silica gel. The retention volumes of these monovalent cations increased linearly. The relation indicated that the amount of zirconium adsorbed was directly related to the cation-exchange capacity of Zr-silicas. The retention volumes of the divalent cations drastically increased in comparison with those of the monovalent cations. This is because the retention volumes of divalent cations are strongly influenced by the cation-exchange capacity in comparison with those of monovalent cations [11]. Complete group

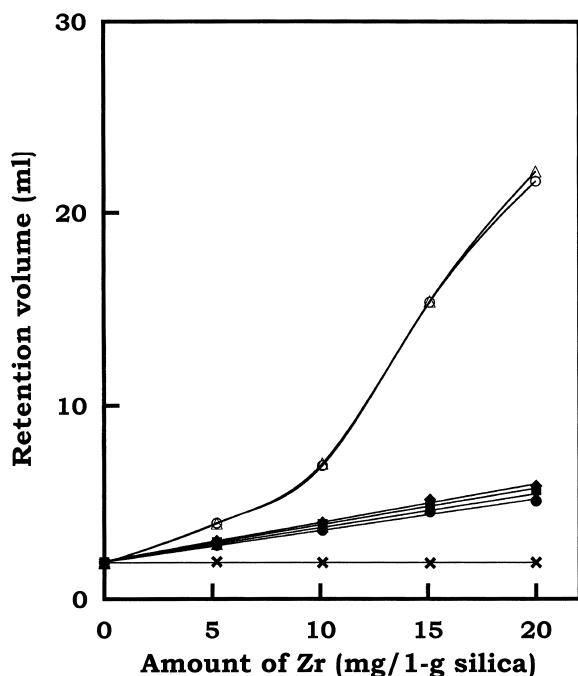


Fig. 1. Effect of amount of zirconium on zirconium-modified silica gels (Zr-silicas) on retention volumes of mono- and divalent cations. Column: Zr-silicas adsorbed on 0–20 mg zirconium  $\text{g}^{-1}$  silica gel; column size: 150 $\times$ 4.6 mm I.D.; column temperature: 35 $^{\circ}\text{C}$ ; eluent: 10 mM tartaric acid at pH 2.5; flow rate: 1 ml  $\text{min}^{-1}$ ; detection: indirect-conductivity; injection volume: 20- $\mu\text{l}$ ; sample concentration: 0.2 mM for monovalent cations and 0.1 mM for divalent cations; symbols: x, water dip; ●,  $\text{Li}^+$ ; ▲,  $\text{Na}^+$ ; ■,  $\text{NH}_4^+$ ; ◆,  $\text{K}^+$ ; ○,  $\text{Mg}^{2+}$ ; △,  $\text{Ca}^{2+}$ .

separation between these mono- and divalent cations was achieved at zirconium  $\geq 10$  mg  $\text{g}^{-1}$  silica gel. However, peak resolution between these monovalent cations and that between divalent cations were not quite satisfactory.

Since a group separation between these mono- and divalent cations was achieved in 10 min, it was decided that Zr-silica adsorbed on 10 g zirconium  $\text{g}^{-1}$  silica gel was a suitable stationary phase for IC-CD separation of these mono- and divalent cations.

### 3.2. Effect of concentration of tartaric acid on retention volumes of mono- and divalent cations

The effect of the concentration of tartaric acid in the eluent on the retention volumes of these mono-

and divalent cations on the Zr-silica (10 mg zirconium  $\text{g}^{-1}$  silica gel) column was investigated for the simultaneous separation of these cations.

Fig. 2 shows the relationship between the concentration of tartaric acid in the eluent and the retention volumes of these mono- and divalent cations. The retention volumes of these cations decreased drastically with increasing concentrations of tartaric acid. This is due to an increase in the concentration of hydronium ion ( $\text{H}^+$ ) as the competing ion in the eluent and perhaps due to a reduction in the cation-exchange capacity of the Zr-silica stationary phase. Since the retention volumes of these cations were still larger than that of water dip when using 50 mM tartaric acid at pH 2.2 as the eluent, it was found that the Zr-silica acted as a cation exchanger under such strongly acidic conditions. The decrease in the retention volume of the divalent cations was much larger than that of the monovalent cations. This is because the retention

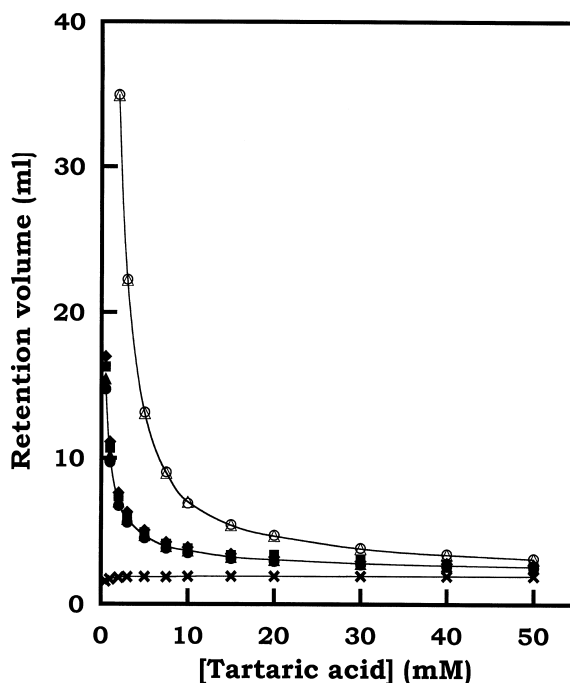


Fig. 2. Effect of concentration of tartaric acid in eluent on retention volumes of mono- and divalent cations on Zr-silica column. Column: Zr-silica (10 mg zirconium  $\text{g}^{-1}$  silica gel); eluent: 0.5–50 mM tartaric acid. Other chromatographic conditions as for Fig. 1.

volumes of divalent cations are strongly influenced by both the cation-exchange capacity and the concentration of eluent ion [11].

Although a complete group separation between these mono- and divalent cations was achieved, peak resolutions between both the monovalent cations and between the divalent cations were incomplete. As shown in Fig. 3, since these mono- and divalent cations were eluted in 10 min, it was concluded that a reasonable concentration of tartaric acid in the eluent was 10 mM.

### 3.3. Effect of crown ethers added to eluent on chromatographic behavior of mono- and divalent cations

It is well known that crown ethers form stable complexes with many cations [12]. On the basis of their unique characteristics, the addition of crown

ethers to acidic eluent was carried out to improve peak resolution between mono- and divalent cations on columns packed with weakly acidic cation exchangers [13,14]. The authors have also reported previously that the addition of crown ethers to eluents was very effective for the improvement of peak resolution between these mono- and divalent cations on a laboratory-made aluminium-modified silica gel (Al-silica) column [9,15]. Therefore, the addition of crown ethers to the eluent was carried out to completely separate these mono- and divalent cations on the Zr-silica column.

#### 3.3.1. 12-Crown-4

Firstly, the effect of 12-crown-4 was investigated. Fig. 4 shows the chromatogram of these mono- and divalent cations using 10 mM tartaric acid containing 20 mM 12-crown-4 as the eluent. As for the mono-

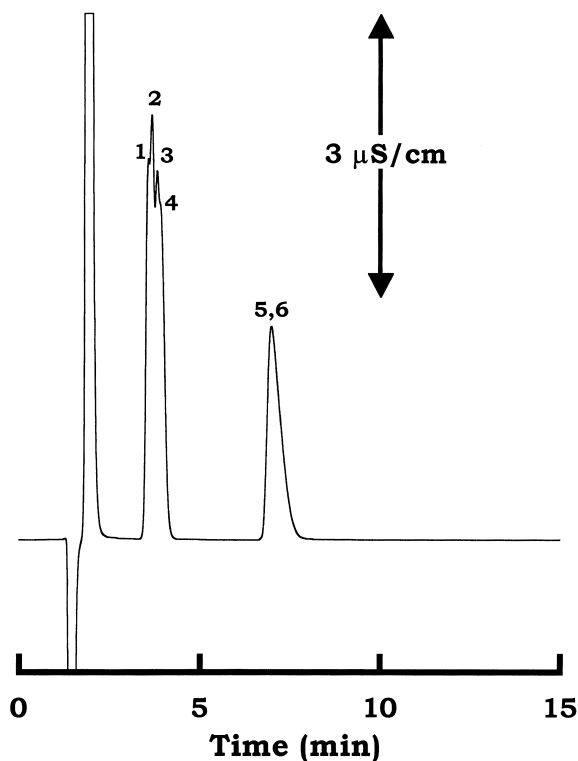


Fig. 3. Chromatogram of mono- and divalent cations on Zr-silica column using 10 mM tartaric acid as eluent. Eluent: 10 mM tartaric acid; peaks: 1,  $\text{Li}^+$ ; 2,  $\text{Na}^+$ ; 3,  $\text{NH}_4^+$ ; 4,  $\text{K}^+$ ; 5,  $\text{Mg}^{2+}$ ; 6,  $\text{Ca}^{2+}$ . Other chromatographic conditions as for Fig. 2.

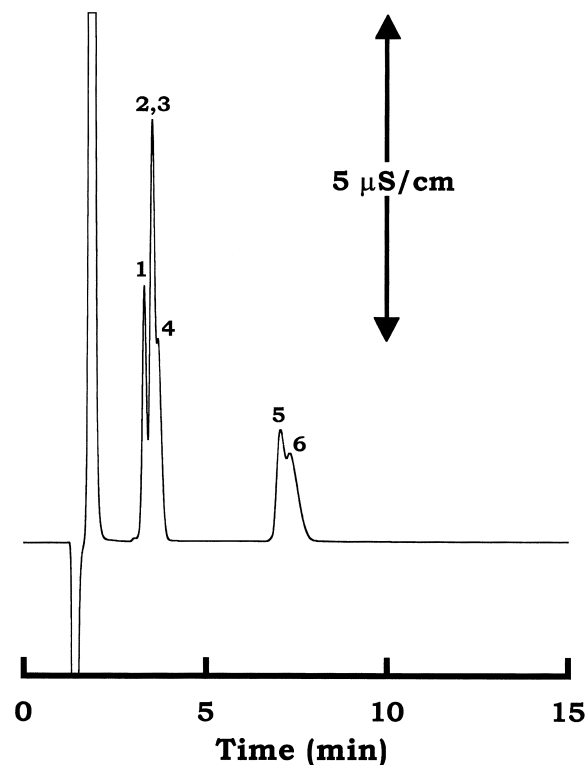


Fig. 4. Chromatogram of mono- and divalent cations on Zr-silica column using 10 mM tartaric acid–20 mM 12-crown-4 as eluent. Eluent: 10 mM tartaric acid containing 20 mM 12-crown-4; peaks: 1,  $\text{Li}^+$ ; 2,  $\text{Na}^+$ ; 3,  $\text{NH}_4^+$ ; 4,  $\text{K}^+$ ; 5,  $\text{Mg}^{2+}$ ; 6,  $\text{Ca}^{2+}$ . Other chromatographic conditions as for Fig. 3.

valent cations, the retention volume of  $\text{Na}^+$  slightly increased and those of other monovalent cations remained almost the same. As a result, peaks of  $\text{Na}^+$  and  $\text{NH}_4^+$  completely overlapped. As for the divalent cations, the retention volume of  $\text{Ca}^{2+}$  slightly increased and that of  $\text{Mg}^{2+}$  remained almost the same. As a result, peak resolution was slightly improved. However, the peak resolution between these mono- and divalent cations was not quite satisfactory. This is mainly due to low stability of complexes formed between these cations and 12-crown-4 [16].

From the above results, it was concluded that the addition of 12-crown-4 was not effective for the improvement of peak resolution between these mono- and divalent cations on the Zr-silica column.

### 3.3.2. 15-Crown-5

The addition of 15-crown-5 to acidic eluent was very effective for the improvement of peak resolution between these mono- and divalent cations on the Al-silica column [9,14]. Hence, secondly, the effect of 15-crown-5 was investigated.

Fig. 5 shows the relationship between the concentration of 15-crown-5 in the eluent and the retention volumes of these mono- and divalent cations. The retention volumes of  $\text{Na}^+$ ,  $\text{NH}_4^+$ ,  $\text{K}^+$  and  $\text{Ca}^{2+}$  increased with increasing concentration of 15-crown-5 in the eluent. The retention volumes of  $\text{Li}^+$  and  $\text{Mg}^{2+}$  remained almost the same. The order of increase in the retention volumes of the monovalent cations was  $\text{Li}^+ < \text{NH}_4^+ < \text{Na}^+ < \text{K}^+$ , while that of the divalent cations was  $\text{Mg}^{2+} < \text{Ca}^{2+}$ . These results were in good agreement with those obtained by IC-CD using the Al-silica column [9]. Complete separation of these mono- and divalent cations was achieved on the Zr-silica column at the concentration of 15-crown-5  $\geq 10$  mM. The concentration of 15-crown-5 in IC-CD was considerably higher than that in IC-CD using an Al-silica column [9]. This is due mainly to differences in chemical and physical properties between the Zr-silica and the Al-silica.

The optimum concentration of 15-crown-5 was concluded to be 10 mM. As shown in Fig. 6, excellent simultaneous separation of these mono- and divalent cations was achieved in 10 min.

### 3.3.3. 18-Crown-6

The addition of 15-crown-5 to acidic eluent was

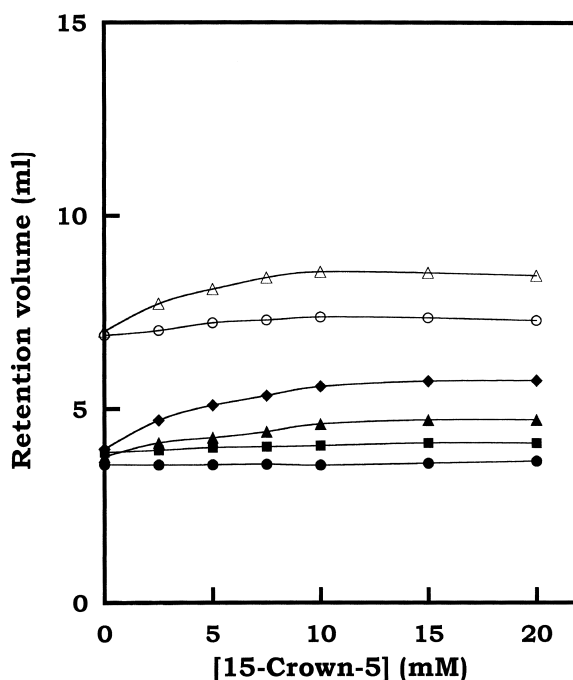


Fig. 5. Effect of concentration of 15-crown-5 in eluent on retention volumes of mono- and divalent cations on Zr-silica column. Eluent: 10 mM tartaric acid containing 0–20 mM 15-crown-5; symbols: ●,  $\text{Li}^+$ ; ▲,  $\text{Na}^+$ ; ■,  $\text{NH}_4^+$ ; ◆,  $\text{K}^+$ ; ○,  $\text{Mg}^{2+}$ ; △,  $\text{Ca}^{2+}$ . Other chromatographic conditions as for Fig. 4.

also effective for the improvement of peak resolution between these mono- and divalent cations in IC-CD using the Al-silica column [9,14]. However, when 18-crown-6 was added to the eluent, the retention volumes of  $\text{K}^+$  increased selectively and the peak shape of  $\text{K}^+$  was strongly tailed. Therefore, it was concluded that the addition of 18-crown-6 was not suitable in IC-CD [9]. However, as mentioned before, the concentration of 15-crown-5 suitable in IC-CD using Zr-silica was considerably higher than that in IC-CD using Al-silica. This result suggested that the simultaneous separation of these mono- and divalent cations could be achieved on the Zr-silica column in a reasonable period of time ( $\leq 15$  min) using 10 mM tartaric acid containing 18-crown-6 as eluent. Hence, thirdly, the effect of 18-crown-6 was investigated.

Fig. 7 shows the relationship between the concentration of 18-crown-6 in the eluent and the

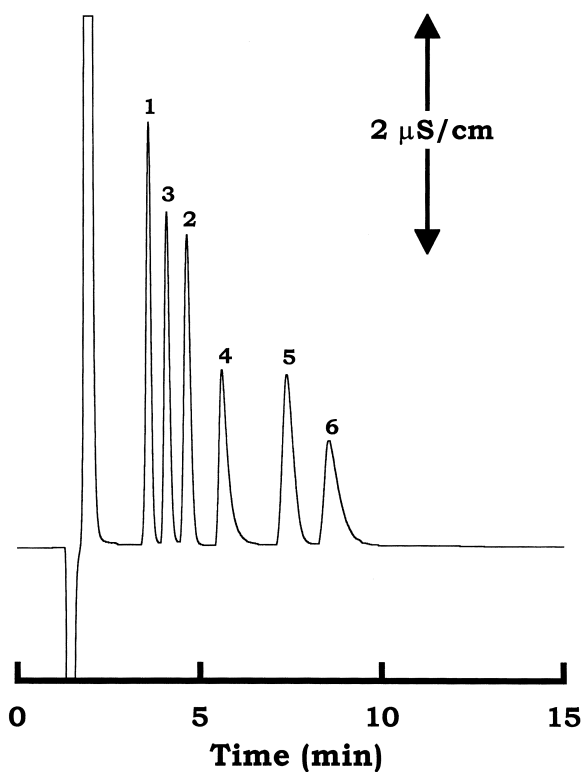


Fig. 6. Chromatogram of mono- and divalent cations on Zr-silica column using 10 mM tartaric acid–10 mM 15-crown-5 as eluent. Eluent: 10 mM tartaric acid containing 10 mM 15-crown-5; peaks: 1,  $\text{Li}^+$ ; 2,  $\text{Na}^+$ ; 3,  $\text{NH}_4^+$ ; 4,  $\text{K}^+$ ; 5,  $\text{Mg}^{2+}$ ; 6,  $\text{Ca}^{2+}$ . Other chromatographic conditions as for Fig. 5.

retention volumes of these mono- and divalent cations. The retention volumes of  $\text{Na}^+$ ,  $\text{NH}_4^+$ ,  $\text{K}^+$  and  $\text{Ca}^{2+}$  increased with increasing concentration of 18-crown-6 in the eluent. The retention volumes of  $\text{Li}^+$  and  $\text{Mg}^{2+}$  remained almost the same. The retention volume of  $\text{K}^+$  increased selectively and the peak was tailed. This is because the internal cavity size of 18-crown-6 (1.38 Å) is the same as that of  $\text{K}^+$  (1.38 Å), and 18-crown-6 forms a very stable metal-in-hole type complex with  $\text{K}^+$  [16]. The order of the increase in the retention volumes of the monovalent cations was  $\text{Li}^+ < \text{Na}^+ < \text{NH}_4^+ \ll \text{K}^+$  and that of the divalent cations was  $\text{Mg}^{2+} < \text{Ca}^{2+}$ . These orders were in good agreement with results obtained by IC-CD with an Al-silica column [9] and those predicted from stability constants of complexes

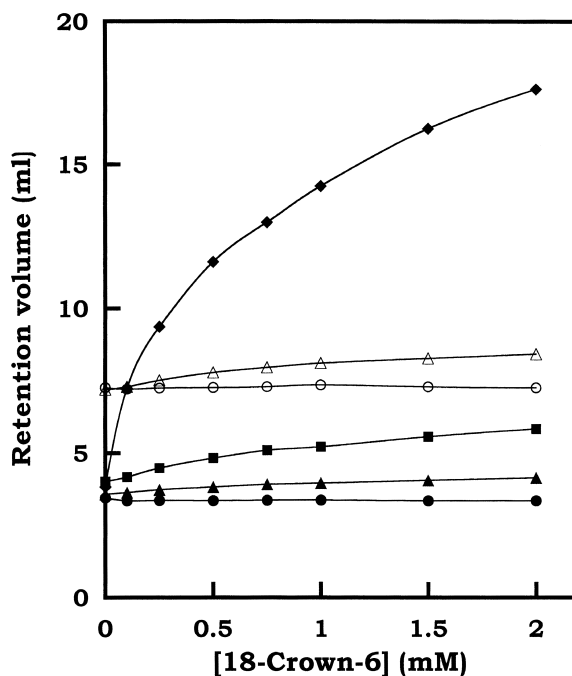


Fig. 7. Effect of concentration of 18-crown-6 in eluent on retention volumes of mono- and divalent cations on Zr-silica column. Eluent: 10 mM tartaric acid containing 0–2 mM 18-crown-6; symbols: ●,  $\text{Li}^+$ ; ▲,  $\text{Na}^+$ ; ■,  $\text{NH}_4^+$ ; ◆,  $\text{K}^+$ ; ○,  $\text{Mg}^{2+}$ ; △,  $\text{Ca}^{2+}$ . Other chromatographic conditions as for Fig. 6.

formed between these cations and 18-crown-6 [16]. Complete separation of these mono- and divalent cations was achieved at the concentration of 18-crown-6  $\geq 1.0$  mM. The concentration was also considerably higher than that in IC-CD using the Al-silica column. This suggested that crown ethers (12-crown-4, 15-crown-5 and 18-crown-5) were strongly adsorbed on the Al-silica stationary in comparison with the Zr-silica. A detailed study of the adsorption behavior of crown ethers to both Zr-silica and Al-silica will be the subject of future work.

The optimum concentration of 18-crown-6 was concluded to be 1 mM. As shown in Fig. 8, complete simultaneous separation of these mono- and divalent cations was achieved in 17 min.

Considering peak resolution, peak shape and separation time, it was concluded that the addition of 15-crown-5 was the most effective for the simulta-

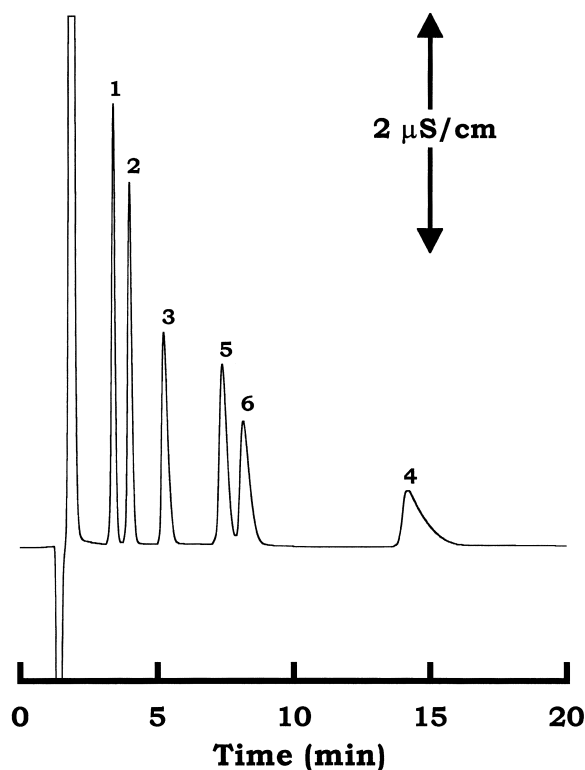


Fig. 8. Chromatogram of mono- and divalent cations on Zr-silica column using 10 mM tartaric acid–1 mM 18-crown-6 as eluent. Eluent: 10 mM tartaric acid containing 1 mM 18-crown-6; peaks: 1,  $\text{Li}^+$ ; 2,  $\text{Na}^+$ ; 3,  $\text{NH}_4^+$ ; 4,  $\text{K}^+$ ; 5,  $\text{Mg}^{2+}$ ; 6,  $\text{Ca}^{2+}$ . Other chromatographic conditions as for Fig. 7.

neous separation of these mono- and divalent cations on the Zr-silica column.

### 3.4. Analytical performance parameters

The optimum column and eluent conditions for the simultaneous separation of these mono- and divalent cations were concluded to be Zr-silica (10 mg zirconium  $\text{g}^{-1}$  silica gel) column and 10 mM tartaric acid containing 10 mM 15-crown-5 as the eluent. Various analytical performance parameters were investigated.

Calibration graphs were obtained by plotting peak area against the concentration of the common mono- and divalent cations. Linear calibration graphs ( $r^2 \geq$

Table 2  
Detection limits of common mono- and divalent cations under optimum chromatographic conditions

Cation	Detection limits <sup>a</sup>	
	$\mu\text{M}$	$\text{ng ml}^{-1}$
$\text{Li}^+$	0.28	1.8
$\text{Na}^+$	0.38	8.6
$\text{NH}_4^+$	0.35	6.3
$\text{K}^+$	0.67	26
$\text{Mg}^{2+}$	0.34	8.3
$\text{Ca}^{2+}$	0.56	22

<sup>a</sup> Signal-to-noise ratio: 3; injection volume: 20  $\mu\text{l}$ .

0.99) were obtained in the concentration range between 0.005 and 1.0 mM for these cations.

The relative standard deviations of the chromatographic peak area of the mono- and divalent cations, whose concentrations were 0.2 mM for monovalent cations and 0.1 mM for divalent cations, were less than 0.9% ( $n=10$ ). Reproducible chromatograms were obtained during repeated chromatographic runs.

Table 2 shows the detection limits of the common mono- and divalent cations at a signal-to-noise ratio of 3. These detection limits compared well with those for non-suppressed IC–CD using an acidic eluent. The result indicated that these mono- and divalent cations were detected by an indirect conductivity mechanism in which they displace the highly conducting hydronium ion ( $\text{H}^+$ ) from the eluent.

### 3.5. Application to cation analysis in natural water samples

The proposed IC–CD method was applied to the determination of major mono- and divalent cations ( $\text{Na}^+$ ,  $\text{NH}_4^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$ ) in rain and river water samples. Samples were analyzed after filtration with a 0.45- $\mu\text{m}$  membrane filter.

Fig. 9A,B shows typical chromatograms of rain and river water samples, respectively. Good separation and detection for these mono- and divalent cations were achieved. These chromatograms indicated that the proposed IC–CD method was a very



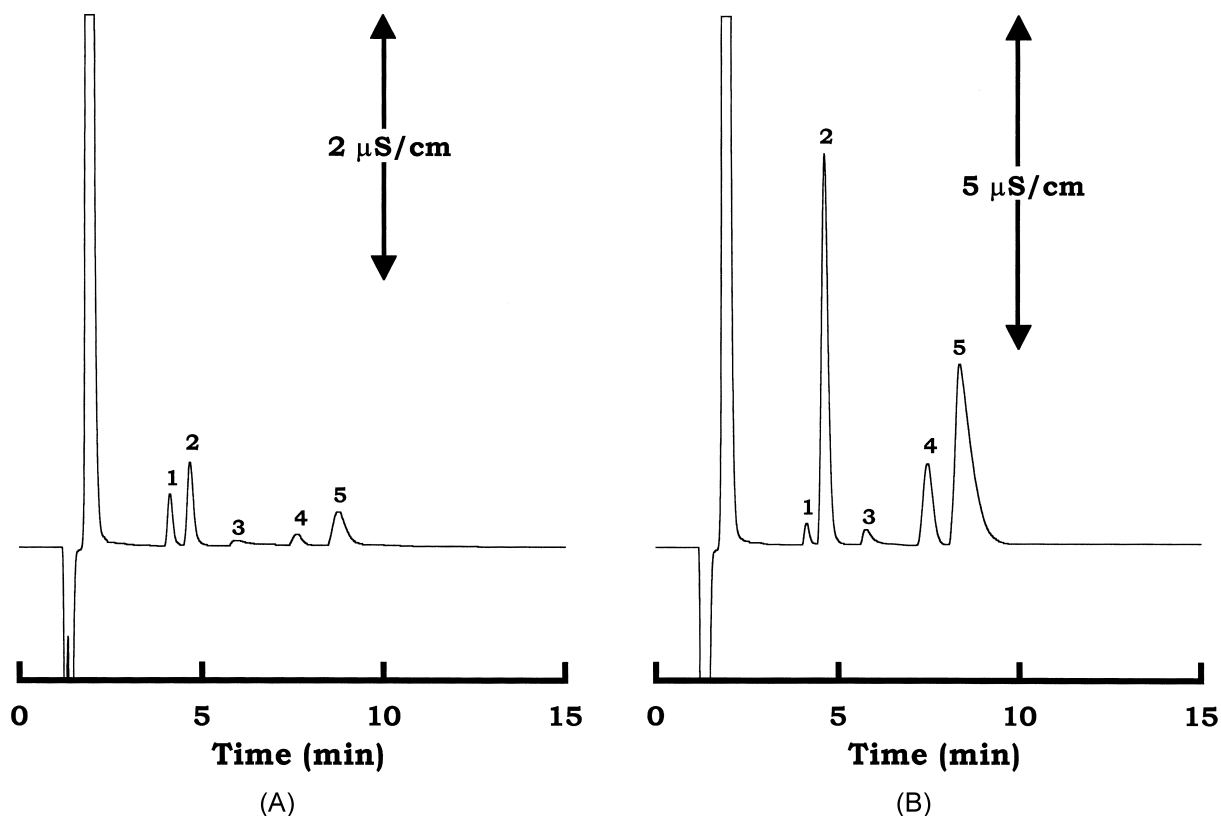


Fig. 9. Chromatograms of rain and river water samples. (A) Rain water: peaks (concentration, mM): 1, NH<sub>4</sub><sup>+</sup> (0.028); 2, Na<sup>+</sup> (0.048); 3, K<sup>+</sup> (0.008); 4, Mg<sup>2+</sup> (0.005); 5, Ca<sup>2+</sup> (0.025). (B) River water: peaks (concentration, mM): 1, NH<sub>4</sub><sup>+</sup> (0.022); 2, Na<sup>+</sup> (0.45); 3, K<sup>+</sup> (0.031); 4, Mg<sup>2+</sup> (0.081); 5, Ca<sup>2+</sup> (0.35). Chromatographic conditions as in Fig. 6.

effective method for the determination of major mono- and divalent cations in natural water samples.

#### 4. Conclusions

The application of Zr-silicas as cation-exchange stationary phases to IC-CD for common mono- and divalent cations (Li<sup>+</sup>, Na<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup> and Ca<sup>2+</sup>) was carried out using tartaric acid as an eluent. Zr-silicas were prepared by the reaction of the silanol group on the surface of silica gel with zirconium tetrabutoxide in ethanol. Excellent simultaneous separation and highly sensitive detection for these mono- and divalent cations were

achieved in 10 min by IC-CD using a laboratory-made Zr-silica (10 mg zirconium g<sup>-1</sup> silica gel) column (150×4.6 mm I.D.) and 10 mM tartaric acid containing 10 mM 15-crown-5 as the eluent. These results strongly confirmed that the modification of silica gel with zirconium was a simple and effective way for the preparation of advanced silica-based cation-exchange stationary phase in IC-CD for cations.

#### References

- [1] K. Nobuhara, M. Kato, M. Nakamura, T. Takami, S. Kaneko, J. Chromatogr. A 704 (1995) 45.

- [2] M. Okamoto, K. Nokuhara, D. Ishii, *J. Chromatogr. A* 697 (1995) 153.
- [3] M. Okamoto, H. Kakamu, K. Nokuhara, D. Ishii, *J. Chromatogr. A* 722 (1996) 181.
- [4] M. Nakamura, T. Nishiyama, M. Takami, K. Nobuhara, S. Kaneko, unpublished results.
- [5] K. Tanabe, T. Sumiyoshi, K. Shibata, T. Kiyoura, J. Kitagawa, *Bull. Chem. Soc. Jpn.* 47 (1974) 1064.
- [6] M. Verzele, D. Depotter, J. Ghysels, *J. High Resolut. Chromatogr. Chromatogr. Commun.* 2 (1979) 151.
- [7] J. Nawrocki, *J. Chromatogr.* 407 (1987) 171.
- [8] K. Ohta, H. Morikawa, K. Tanaka, P.R. Haddad, *J. Chromatogr. A* 804 (1998) 171.
- [9] K. Ohta, K. Tanaka, *J. Chromatogr. A* 850 (1999) 177.
- [10] K. Ohta, H. Morikawa, K. Tanaka, Y. Uwamino, M. Furukawa, M. Sando, *J. Chromatogr. A* 884 (2000) 123.
- [11] P.R. Haddad, P.E. Jackson, *Ion Chromatography: Principles and Applications*, Elsevier, Amsterdam, 1990.
- [12] C.J. Pederson, *J. Am. Chem. Soc.* 89 (1967) 7017.
- [13] M.W. Läubli, B. Kampus, *J. Chromatogr. A* 706 (1995) 103.
- [14] M. Ono, H. Kumagai, T. Sakai, Y. Date, Y. Inoue, *Ind. Water* 469 (1997) 25.
- [15] K. Ohta, *J. Chromatogr. A* 884 (2000) 113.
- [16] R.M. Izatt, J.S. Bradshaw, S.A. Nielsen, L.D. Lamb, J.J. Christensen, *Chem. Rev.* 85 (1985) 271.