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Ion-chromatographic behavior of alkali metal cations and ammonium ion on zirconium-adsorbing silica gel

Kazutoku Ohta*, Hisashi Morikawa, Kazuhiko Tanaka, Yoshinnori Uwamino, Masamichi Furukawa, Mutsuo Sando

National Industrial Research Institute of Nagoya, 1-1 Hirate-cho, Kita-ku, Nagoya 462-8510, Japan

Abstract

The preparation and evaluation of zirconium-adsorbing silica gel (Zr-Silica) as an ion-exchange stationary phase in ion chromatography for inorganic anions and cations was carried out. The Zr-Silica was prepared by the reaction of silanol groups on the surface of the silica gel with zirconium butoxide ($\text{Zr}(\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_3)_4$) in ethanol. The ion-exchange characteristics of the Zr-Silica were evaluated using 10 mM tartaric acid at pH 2.5 as eluent. The Zr-Silica was found to act as a cation-exchanger under the eluent conditions. The retention behavior of alkali and alkaline earth metal cations was then investigated. The Zr-Silica column was proved to be suitable for the simultaneous separation of alkali metal cations and ammonium ion. Excellent separation of the cations on a 15 cm Zr-Silica column was achieved in 25 min using 10 mM tartaric acid as eluent. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Ion chromatography (IC), developed by Small et al. [1], is now commonly used as a simple and powerful analytical tool for the determination of various kinds of anions and cations. Many types of functionalized polymer resins and silicas are employed as ion-exchange stationary phase in IC [2,3]. Since the ion-exchange characteristics of many metal oxides have been well evaluated [4], it is also possible to utilize metal oxides as ion-exchange stationary phases in IC. Smith and Pietrzyk [5] and

Iwachido et al. [6] applied unmodified silica gel as a cation-exchange stationary phase to IC for common mono- and divalent cations. Pietrzyk and Brown [7] and Takeuchi et al. [8] applied alumina as an anion-exchange stationary phase to IC for common inorganic anions. However, metal oxides have not yet been applied as ion-exchange stationary phases in IC. This is because the manufacturing processes of these metal oxides for HPLC use, except for silica gel and alumina, are not well established.

The modification of silica gel with various metals is a simple and effective way for the preparation of inorganic packing materials in HPLC. The advantage is that the control of physical properties, such as particle size, pore size, surface area, pore volume, etc., is very easy and control of the amount of metal adsorbed on the silica gel is also possible. In

*Corresponding author. Tel.: +81-52-911-3596; fax: +81-52-911-2428.

E-mail address: kazuoha@nirin.go.jp (K. Ohta)

contrast, the chemical properties of metal-adsorbing silica gels are not always the same as those of the corresponding metal oxides. Nobuhara et al. [9] prepared magnesium-adsorbing silica gel and Okamoto et al. [10,11] prepared calcium-adsorbing and silver-adsorbing silica gels using the cation-exchange reaction of silanol groups on the surface of silica gel with the corresponding metal ions. Nakamura et al. [12] prepared titanium-adsorbing and zirconium-adsorbing silica gels by reaction of silanol groups on the surface of silica gel with titanium isopropoxide and zirconium butoxide, respectively. Unfortunately, in these studies, the characteristics of these metal-adsorbing silica gels was only evaluated as stationary phase in normal-phase HPLC.

In preliminary studies [13–15], the authors prepared aluminium-adsorbing silica gel (Al-Silica) and evaluated the characteristics of Al-Silica as an ion-exchange stationary phase in IC. The authors demonstrated that laboratory-made Al-Silica was very effective for the simultaneous separation of common mono- and divalent cations in conductimetric detection IC (IC–CD) using strongly acidic eluent. In this study, the preparation and evaluation of zirconium-adsorbing silica gel (Zr-Silica) were carried out for the development of a new ion-exchange stationary phase in IC. Laboratory-made Zr-Silica was found to act as a cation-exchanger under strongly acidic conditions (pH >2). Excellent simultaneous separation of alkali metal cations and ammonium ion on a 15 cm Zr-Silica column was achieved in 25 min using 10 mM tartaric acid as eluent.

2. Experimental

2.1. Preparation of zirconium-adsorbing silica gels

A Pia Tec (Suzuka, Japan) Pia Seed 5S-100-SIL high-purity porous spherical silica gel for HPLC was employed as a matrix. Ninety grams of the silica gel was immersed in 1000 ml of zirconium butoxide ($\text{Zr}(\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_3)_4$) solution (200 g zirconium butoxide in 1000 ml ethanol). After stirring for 1 h, the solution was filtered. The resultant gel was washed thoroughly with ethanol and then dried overnight at 120°C followed by calcining at 400–1000°C for 5 h.

The determination of zirconium on zirconium-adsorbing silica gel (Zr-Silica) was carried out using a Nippon Jarrell-Ash (Kyoto, Japan) ICAP-1000 inductively coupled plasma atomic emission spectrometry (ICP-AES) system. The amount of zirconium adsorbed on 1 g of the silica gel was ca. 120 mg.

Table 1 shows the physical properties of Pia Seed 5S-100-SIL and the Zr-Silicas. Determination of the surface area and pore volume by 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 separation columns (150×4.6 mm I.D., stain-

Table 1
Effect of calcining temperature on the physical properties of Pia Seed 5S-100-SIL and zirconium-adsorbing silica gels (Zr-Silica)

Gel	Drying or calcining (°C)	Particle size (μm)	Surface area per weight ($\text{m}^2 \text{g}^{-1}$)	Pore size (Å)	Pore volume (ml g^{-1})	Packing density (g ml^{-1})	Surface area per column ^a ($\text{m}^2 \text{column}^{-1}$)
Pia Seed 5S-100-SIL (untreated)	120	5.3	332	124	0.93	0.35	289
Zr-Silica	120	5.3	304	108	0.84	0.38	288
	400	5.2	298	118	0.87	0.41	305
	600	5.2	278	120	0.83	0.43	298
	800	5.2	249	122	0.79	0.45	279
	1000	4.3	178	104	0.52	0.64	284

^a Column size: 150×4.6 mm I.D.

less 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) 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 CM-8020 conductimetric detector, a Tosoh SD-8023 on-line degasser and a Rheodyne (Cotati, CA, USA) Model 9125 injector equipped with 20 or 100 µl sample loops.

2.3. Reagents

All reagents were of analytical reagent grade and were purchased from Wako (Osaka, Japan). Distilled, deionized water was used for the preparation of the 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. Result and discussion

3.1. Evaluation of ion-exchange characteristics of zirconium-adsorbing silica gel

For the evaluation of the ion-exchange characteristics of laboratory-made zirconium-adsorbing silica gel (Zr-Silica), the elution behavior of common inorganic anions and cations on a column packed with Zr-Silica calcined at 1000°C (Zr-Silica 1000) was investigated using 10 mM tartaric acid at pH 2.5 as eluent

Table 2 shows the retention volumes of inorganic anions and cations on the Pia Seed 5S-100-SIL and Zr-Silica 1000 columns. For the Pia Seed 5S-100-SIL column, the retention volumes of anions, water dip (tartaric acid) and cations were almost the same. This indicates that the Pia Seed 5S-100-SIL gel had no charge under the eluent condition. In contrast, for

Table 2

Retention volumes of inorganic anions and cations on columns packed with (A) Pia Seed 5S-100-SIL and (B) Zr-Silica calcined at 1000°C obtained using 10 mM tartaric acid as eluent^a

Ion	Retention volume (ml)	
	A	B
F ⁻	ND ^b	ND
Cl ⁻	2.0	1.3
NO ₂ ⁻	2.1	1.3
Br ⁻	2.0	1.3
NO ₃ ⁻	2.1	1.3
I ⁻	1.9	1.6
SCN ⁻	2.0	1.3
SO ₄ ²⁻	1.8	1.8
S ₂ O ₃ ²⁻	1.8	1.3
PO ₄ ³⁻	2.0	ND
Water dip	2.1	2.0
Li ⁺	2.1	11.9
Na ⁺	2.2	13.0
NH ₄ ⁺	2.2	14.4
K ⁺	2.2	15.4
Rb ⁺	2.3	17.4
Cs ⁺	2.4	21.5
Mg ²⁺	2.1	SR ^c
Ca ²⁺	2.1	SR
Sr ²⁺	2.1	SR
Ba ²⁺	2.1	SR

^a Column, (A) Pia Seed 5S-100-SIL, (B) Zr-Silica calcined at 1000°C; column size, 150×4.6 mm I.D.; column temperature, 35°C; eluent, 10 mM tartaric acid; flow-rate, 1 ml min⁻¹; detection, conductivity; injection volume, 20 µl; sample concentration, 0.5 mM.

^b ND, not detected.

^c SR, strongly retained.

the Zr-Silica 1000 column, the elution order was anions < water dip < cations. This order indicates that these anions were retained by an ion-exclusion process and cations were retained by a cation-exchange process. That is to say, Zr-Silica 1000 had a negative charge and acted as a cation-exchanger under the eluent condition.

As shown in Table 2, fluoride and phosphate ions were not detected on the Zr-Silica 1000 column. This is mainly due to the strong affinity between these anions and Zr-Silica 1000. Alkaline earth metal cations were not eluted from the Zr-Silica 1000 column in a reasonable time. This was mainly due to the high cation-exchange capacity of the Zr-Silica

1000 column. The ion-exchange characteristics of the Zr-Silicas calcined at 120, 400, 600 and 800°C (Zr-Silica 120, 400, 600 and 800) were also evaluated. The ion-exchange characteristics of Zr-Silica 120, 400, 600 and 800 were very similar to that of Zr-Silica 1000.

From the above results, it is demonstrated that Zr-Silica acts as a cation-exchanger and is very suitable for the simultaneous separation of alkali metal cations and ammonium ion under strongly acidic conditions.

3.2. Effect of calcining temperature of Zr-Silica on retention behavior of alkali metal cations and ammonium ion

The effect of the calcining temperature of Zr-Silica on the chromatographic behavior of alkali metal cations and ammonium ion using 10 mM tartaric acid as eluent was investigated in detail.

Fig. 1 show the relationship between the calcining temperature and the retention volumes of these cations. The retention volumes changed dramatically depending on the calcining temperature. As shown in Table 1, since the surface area per column showed no variation between 120 and 1000°C, it was assumed that the chemical structural change of Zr-Silica occurred due to the elevated calcining temperature. Fig. 2A–E show chromatograms of these cations on Zr-Silica 120, 400, 600, 800 and 1000, respectively. The peak shapes of these cations also changed dramatically. With increasing calcining temperature, the peak shapes of late-eluting cations (K^+ , Rb^+ and Cs^+) initially decreased and then improved. As shown in Fig. 2E, good separation of these cations was achieved on the Zr-Silica 1000 column. However, no conclusive reason for the change of the peak shape was found; it was evident that the phenomenon could largely be attributed to chemical structural changes of the Zr-Silica due to the elevated calcining temperature. Details concerning the effect of the calcining temperature will be the subject of future work.

Considering the chromatographic behavior of these cations, it was concluded that the optimum calcining temperature was 1000°C.

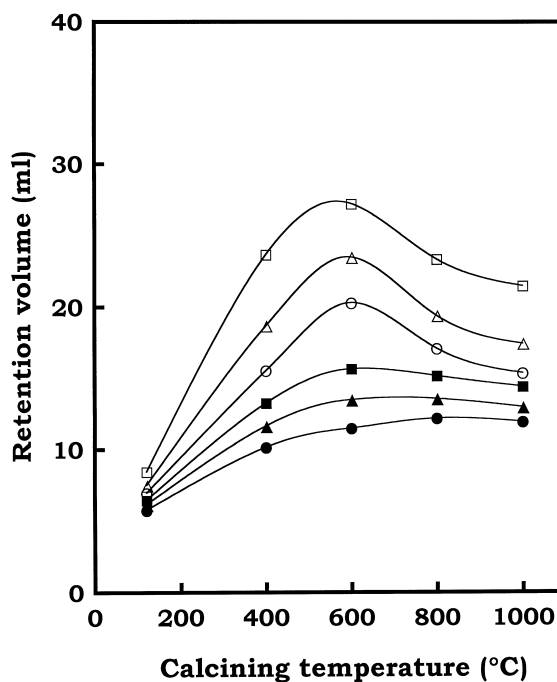


Fig. 1. Effect of the calcining temperature of zirconium-adsorbing silica gel (Zr-Silica) on retention volumes of alkali metal cations and ammonium ion. Column, Zr-Silica calcined at 120–1000°C; column size, 150×4.6 mm I.D.; column temperature, 35°C; eluent, 10 mM tartaric acid; flow-rate, 1 ml min⁻¹; detection, indirect conductivity; injection volume, 20 μl; sample concentration, 0.5 mM. Symbols: (●) Li⁺, (▲) Na⁺, (■) NH₄⁺, (○) K⁺, (△) Rb⁺, (□) Cs⁺.

3.3. Retention behavior of alkali metal cations and ammonium ion on the Zr-Silica 1000 column using tartaric acid as eluent

A detailed investigation of the retention behavior of alkali metal cations and ammonium ion on the Zr-Silica 1000 column was carried out using tartaric acid as eluent.

Fig. 3 shows the relationship between the concentration of tartaric acid in the eluent and the retention volumes of these cations. The retention volumes of the cations decreased drastically with increasing concentration of tartaric acid in the eluent. This is mainly due to an increase in the concentration of hydronium ion (H^+) as the competing ion and perhaps due to a decrease in the cation-exchange capacity of the Zr-Silica 1000 column. Since the

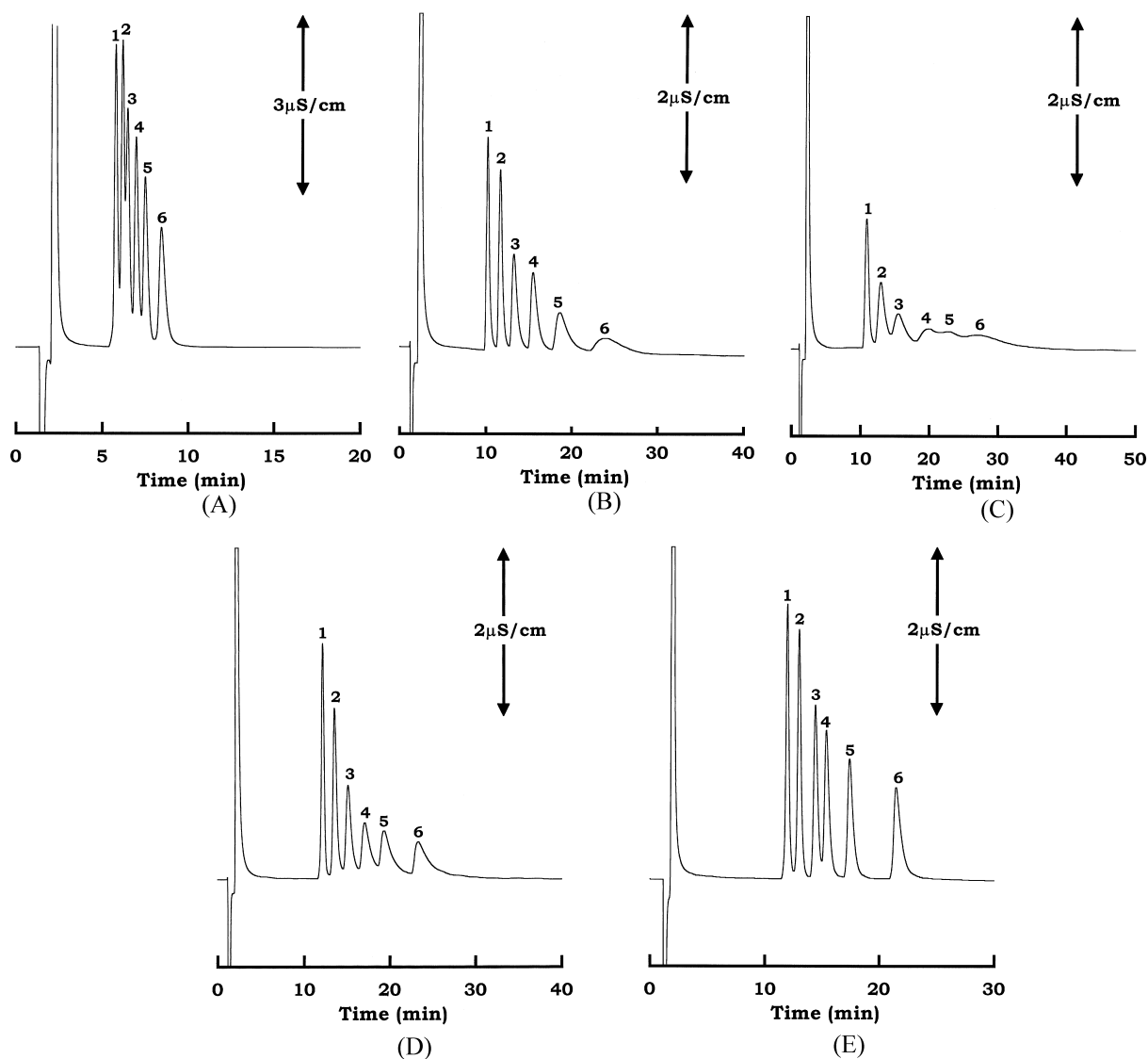


Fig. 2. Effect of calcining temperature of Zr-Silica on chromatographic behavior of alkali metal cations and ammonium ion. (A) 120°C, (B) 400°C, (C) 600°C, (D) 800°C, (E) 1000°C. Peaks: 1=Li⁺, 2=Na⁺, 3=NH₄⁺, 4=K⁺, 5=Rb⁺ and 6=Cs⁺. Other conditions as for Fig. 1.

retention volumes of these cations were larger than that of the water dip (V_0) when using 100 mM tartaric acid at pH 2.0 as eluent, Zr-Silica 1000 was found to behave as a cation-exchanger under such strongly acidic eluent conditions. The optimum concentration of tartaric acid was investigated for the simultaneous separation of these cations in a reasonable time. It was concluded that the optimum con-

centration was 10 mM. As shown in Fig. 2E, good separation of these cations was achieved in 25 min.

3.4. Analytical performance

Various analytical performance parameters obtained under optimum conditions were investigated. Table 3 shows the detection limits (signal-to-noise

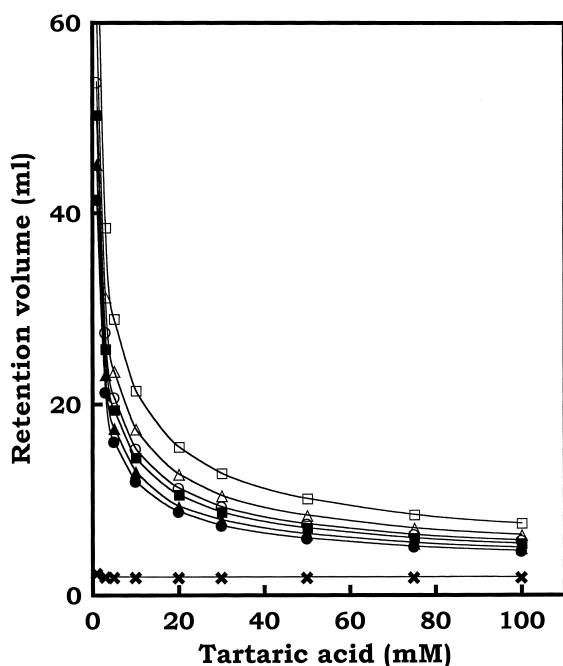


Fig. 3. Effect of the concentration of tartaric acid on retention volumes of alkali metal cations and ammonium ion. Column, Zr-Silica calcined at 1000°C (Zr-Silica 1000); eluent, 0–100 mM tartaric acid. Symbols: (×) water dip (V_0), (●) Li^+ , (▲) Na^+ , (■) NH_4^+ , (○) K^+ , (△) Rb^+ , (□) Cs^+ . Other conditions as for Fig. 2.

ratio 3) of these cations at an injection volume of 20 μl . Highly sensitive conductimetric detection was achieved. This indicates that these cations were detected by an indirect conductivity mechanism where they displace the high-conducting hydronium ion from the eluent.

Table 3

Detection limits of alkali metal cations and ammonium ion obtained under optimum chromatographic conditions (injection volume, 20 μl)

Cation	Detection limit ^a	
	μM	ng ml^{-1}
Li^+	0.28	1.9
Na^+	0.30	7.0
NH_4^+	0.44	7.9
K^+	0.51	20
Rb^+	0.63	54
Cs^+	0.83	109

^a Signal-to-noise ratio 3.

Calibration graphs were obtained by plotting peak area against the concentration of these cations at an injection volume of 20 μl . Linear calibration graphs ($r^2 \geq 0.99$) were obtained in the concentration range 0.005–5.0 mM for these cations.

The relative standard deviation of the chromatographic peak areas of the cations, at a concentration of 0.5 mM, was <1.2% ($n = 8$). Reproducible chromatograms were obtained during repeated chromatographic runs.

The long-term stability of the Zr-Silica 1000 column was investigated. As shown in Fig. 4A, when using 10 mM tartaric acid as eluent, the retention volumes of the cations gradually decrease. This is mainly due to the instability of the silica matrix in aqueous solution. Since the daily decrease in retention volume was very small and good separation was maintained, it was concluded that Zr-Silica 1000 was very suitable for practical use when using 10 mM tartaric acid as eluent. In contrast, as shown in Fig. 4B, when using 2 mM nitric acid as eluent, the retention volumes of the cations decreased drastically. After 20 days, the cations were not retained on the Zr-Silica 1000 column. This indicates that zirconium was removed from the surface of Zr-Silica 1000 by nitric acid and Zr-Silica lost its cation-exchange ability. However, the detailed mechanism concerning the difference in column stability is not clear and will be the subject of future work.

3.5. Application to cation analysis of natural water samples

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

For river water samples, as shown in Fig. 5, good separation and detection of the cations were achieved at an injection volume of 20 μl . In contrast, for rain water samples, since the concentration of the cations, especially K^+ , was very low, accurate determination of the cations was somewhat difficult. As shown in Fig. 6, when 100 μl of a rain water sample was injected, good separation and detection of the cations were achieved.

The above results demonstrate that IC is useful for

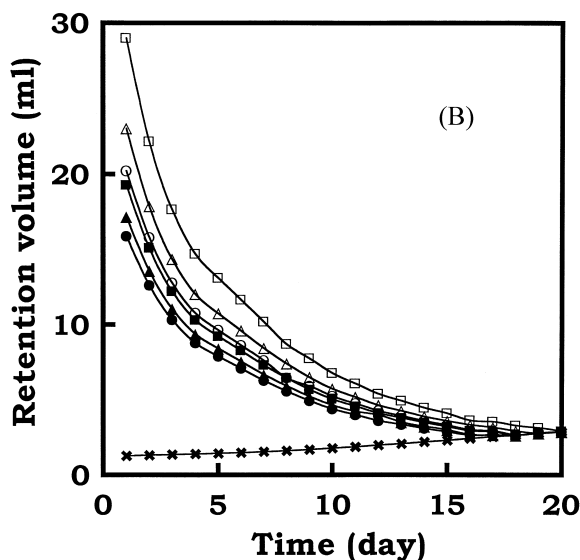
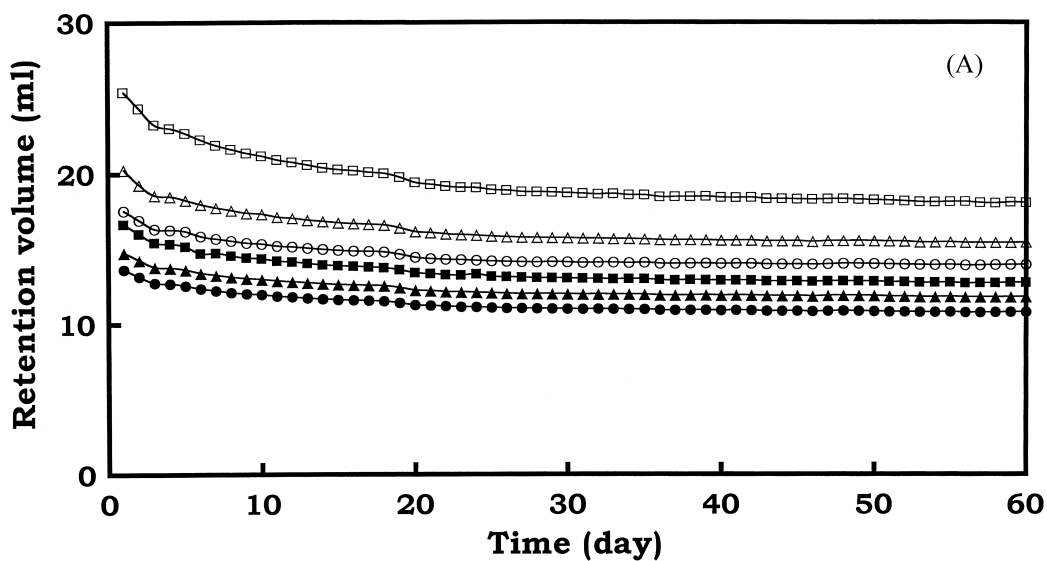


Fig. 4. Long-term stability of the Zr-silica 1000 column. (A) 10 mM tartaric acid as eluent, (B) 2 mM nitric acid as eluent. Symbols: (×) water dip (V_0), (●) Li^+ , (▲) Na^+ , (■) NH_4^+ , (○) K^+ , (△) Rb^+ , (□) Cs^+ . Other conditions as for Fig. 3.

the determination of major monovalent cations in natural water samples.

4. Conclusion

In this work, the modification of silica gel with zirconium was carried out for the preparation of a

new silica-based stationary phase in ion chromatography. The silica gel modified with zirconium (zirconium-adsorbing silica gel, Zr-Silica) prepared here was found to act as a cation-exchanger under strongly acidic conditions. Excellent simultaneous separation of alkali metal cations and ammonium ion on a 15 cm column packed with Zr-Silica calcined at 1000°C was achieved in 25 min using 10 mM tartaric

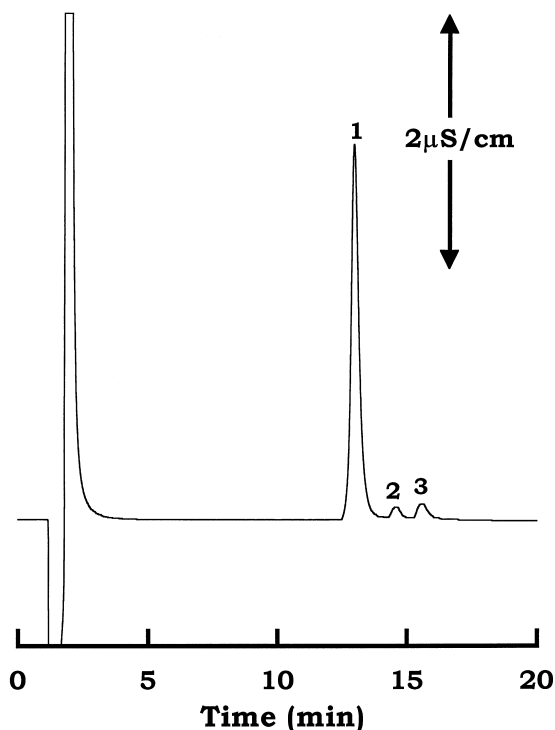


Fig. 5. Chromatogram of river water sample. Eluent, 10 mM tartaric acid. Peaks (concentration, mM): 1=Na⁺ (0.47), 2=NH₄⁺ (0.015), 3=K⁺ (0.028). Other conditions as for Fig. 4.

acid as eluent. However, since the cation-exchange capacity of Zr-Silica was too high, the simultaneous elution of alkali earth metal cations was very difficult. Development of a procedure for controlling the amount of zirconium adsorbed on the silica gel is required for the simultaneous separation of alkali and alkaline earth metal cations. This will be the subject of future work.

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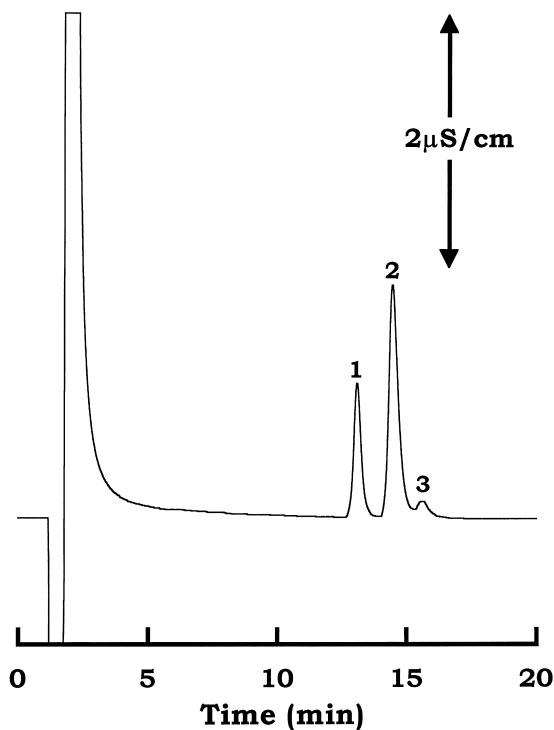


Fig. 6. Chromatogram of a rain water sample. Injection volume, 100 μl. Peaks (concentration, mM): 1=Na⁺ (0.020), 2=NH₄⁺ (0.043), 3=K⁺ (0.005). Other conditions as for Fig. 5.

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