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Retention behavior of common mono- and divalent cations on calcinated silica gel columns in ion chromatography with conductimetric detection and the use of nitric acid, containing crown ethers, as eluents

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Abstract

Ion chromatographic behavior of common mono- and divalent cations (Li^+, Na^+, NH_4^+, K^+, Mg^{2+} and Ca^{2+}) on columns packed with silica gels (Super Micro Bead Silica Gel B-5, SMBSG B-5) calcinated at 200, 400, 600, 800 and 1000 °C for 5 h was investigated using nitric acid containing crown ethers [18-crown-6 (1,4,7,10,13,15-hexaoxacyclooctadecane) and 15-crown-5 (1,4,7,10,13-pentaoxacyclopentadecane)] as eluent. When using 0.5 m*M* HNO_3 as the eluent, the calcination had almost no effect on the improvement of peak resolution between these mono- and divalent cations. In contrast, when using 0.5 m*M* HNO_3 containing crown ethers as the eluent, with increasing the calcinating temperature, the amount of crown ethers adsorbed on the corresponding calcinated SMBSG B-5 silica gels columns increased and, as a consequence, peak resolution between these mono- and divalent cations was quite improved. Excellent simultaneous separation of these mono- and divalent cations was achieved on column (150×4.6 mm I.D.) packed with the SMBSG B-5 silica gel calcinated at 1000 °C by elution with 0.5 m*M* HNO_3 containing either 1.0 m*M* 18-crown-6 or 5.0 m*M* 15-crown-5.

Keywords: Retention behaviour; Mobile phase composition; Calcination; Inorganic cations; Crown ethers; Nitric acid

1. Introduction

Since the silanol group on the surface of silica gel behaves as a weak acid at pK_a of ca. 7.1 [1], it is possible to apply unmodified silica gel as cation-exchange stationary phase in ion chromatography with conductimetric detection (IC–CD) for cations. Smith and Pietrzyk [2], Brown and Pietrzyk [3] and Iwachido and co-workers [4–6] have demonstrated the effectiveness of unmodified silica gel in IC–CD for the separation of various cations (alkali, alkaline earth and transition metal cations). Usually, in IC–CD, lithium ion (Li^+) was used as an eluent ion (on the basis of its low limiting equivalent ionic conductance) and the eluent pH was approximately neutral for the separation and detection of analyte cations. The greatest advantage of the IC–CD is that the simultaneous separation of major mono- and divalent cations (Na^+, NH_4^+, K^+, Mg^{2+} and Ca^{2+}) can be achieved easily [5,6], because the affinity of these

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mono- and divalent cations to the dissociated silanol group as cation-exchanger is very similar. Unfortunately, the detection sensitivities of analyte cations in the IC–CD were much lower than those in conventional non-suppressed IC–CD using hydronium ion (H^+) with the highest limiting equivalent ionic conductance as the eluent ion. This is because the detection sensitivity in non-suppressed IC–CD is directly dependent on the difference in limiting equivalent conductance between eluent ion and analyte ion [7]. Therefore, the use of acidic eluent was expected to be one of the best ways for the elimination of the drawback.

In preliminary studies [8–11], the authors have found several commercially available unmodified silica gels [Develosil 30-5, Develosil 60-5, Kaseisorb LC-60-5 and Super Micro Bead Silica gel B-5 (SMBSG B-5)] acted as cation-exchangers under acidic conditions and have applied these silica gels in IC–CD using acidic eluent for the separation of common mono- and divalent (Li^+, Na^+, NH_4^+, K^+, Mg^{2+} and Ca^{2+}). Completely simultaneous separation of these cations was achieved on these silica gels columns using an acidic eluent containing 18-crown-6 (1,4,7,10,13,15-hexaoxacyclooctadecane) [10,11]. This is because 18-crown-6 added to the acidic eluent acts as a selective cation exchanger under the IC–CD conditions. However, the effect of 18-crown-6 on the improvement of peak resolution between these mono- and divalent cations has not been well explained.

The aim of this study was to extent the utility of unmodified silica gel as the cation-exchange stationary phase in IC for cations. Calcination (heat treatment) of silica gel is easy and effective way for the modification of adsorption properties of silica gel for organic compounds [12]. Then, in order to clarify the effect of crown ethers on the ion chromatographic behavior of these mono- and divalent cations, the application of SMBSG B-5 silica gel calcinated at 200–1000 °C for 5 h as cation-exchange stationary phase in IC–CD using nitric acid containing crown ethers [18-crown-6 and 15-crown-5 (1,4,7,10,13-pentaoxacyclopentadecane)] as eluent was carried out for the simultaneous separation of these cations. As a result, it was found that (a) when using nitric acid as the eluent, the calcination had almost no effect on the improvement of peak resolution between these mono- and divalent cations, and (b) when using nitric acid containing crown ethers as the eluent, with increasing the calcinating temperature, the amount of crown ethers adsorbed on the corresponding calcinated SMBSG B-5 silica gels columns increased drastically and, as a consequence, the effect of crown ethers was enhanced largely. The amount of crown ethers adsorbed on silica stationary phase was the predominant factor for the improvement of peak resolution between these mono- and divalent cations under the IC–CD conditions. Excellent simultaneous separation of these mono- and divalent cations was achieved on column (150×4.6 mm I.D.) packed with the SMBSG B-5 silica gel calcinated at 1000 °C by elution with 0.5 m*M* HNO_3 containing either 1.0 m*M* 18-crown-6 or 5.0 m*M* 15-crown-5.

2. Experimental

2.1. Silica gels

A Fuji-Silysia Chemical (Kasugai, Japan) Super Micro Bead Silica Gel B-5 (SMBSG B-5, lot. no. 902530) porous spherical silica gel for HPLC was mainly used in this study. The SMBSG B-5 silica gel was calcinated at 200, 400, 600, 800 and 1000 °C for 5 h. A Nomura Chemical (Seto, Japan) Develosil 60-5 (lot no. 26105) and a Pia Tec (Suzuka, Japan) Pia Seed 5S-60-SIL (lot no. 99060101S-01) porous spherical silica gels for HPLC were also employed in this study. These silica gels were calcinated at 200 and 1000 °C for 5 h.

Table 1 shows the physical properties of calcinated SMBSG B-5 silica gels. The determination of the surface area and pore volume of these silica gels by using nitrogen adsorption isotherms on the gels at 77 K was carried out using a Beckman-Coulter (Fullerton, CA, USA) Omunisorp 360 gas sorption analyzer. The surface area was calculated from the BET equation. The determination of the particle size of these silica gels was carried out using a Horiba (Kyoto, Japan) LA-920 laser scattering particle size distribution analyzer.

The separation columns (150×4.6 mm I.D., stainless steel) were packed with these silica gels using the slurry packing method.

Table 1
Physical properties of calcinated Super Micro Bead Silica Gel B-5 silica gels

Calcinating temperature (°C)	Particle size (μm)	Surface area ($m^2\ g^{-1}$)	Pore size (Å)	Pore volume ($ml\ g^{-1}$)	Packing density ($g\ ml^{-1}$)	Surface area per column[a] ($m^2\ column^{-1}$)
200	5.5	475	60	0.93	0.43	5.1×10^2
400	5.5	487	60	0.89	0.44	5.3×10^2
600	5.5	483	60	0.89	0.44	5.3×10^2
800	5.4	429	59	0.77	0.45	4.8×10^2
1000	5.0	336	57	0.59	0.55	4.6×10^2

[a] Column size: 150×4.6 mm I.D.

2.2. Equipment

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

A Tosoh RI-8023 refractive index detector was also used for the measurement of the amount of crown ethers [18-crown-6 (1,4,7,10,13,15-hexaoxacyclooctadecane) and 15-crown-5 (1,4,7,10,13-pentaoxacyclopentadecane)] adsorbed on calcinated SMBSG B-5 silica gels columns.

2.3. Determination of crown ethers adsorbed on calcinated SMBSG B-5 silica gel columns

The determination of crown ethers adsorbed on calcinated SMBSGB-5 silica gel columns was carried out. The amount of crown ethers adsorbed on calcinated SMBSG B-5 silica gel column (*A*, mmol $column^{-1}$) was calculated from the equation:

$$A = (V_R - V_0)C/1000$$

where V_R is the breakthrough volume (ml), V_0 is the total dead volume (column void volume + connected tube volume, ml) and *C* is the concentration of crown ether in the eluent (m*M*).

First, the column was equilibrated with 0.5 m*M* HNO_3. A sample of 0.2 *M* HNO_3 was injected. Elution volume of peak corresponding to 0.2 *M* HNO_3 was considered as V_0. Next, 0.5 m*M* HNO_3 containing crown ether was passed through the column and the response of refractive index detector (breakthrough curve) was monitored. Volume corresponding to breakthrough point in the detector response curve was considers as V_R.

2.4. Chemicals

All chemicals were of analytical reagent grade. 18-Crown-6 and 15-crown-5 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 the eluents and standard solutions.

3. Results and discussion

3.1. Effect of calcinating temperature of SMBSG B-5 silica gel on ion chromatographic behavior of mono- and divalent cations using nitric acid as eluent

In order to extend the utility of unmodified silica gel as cation-exchange stationary phase in IC for cations, the application of calcinated silica gel (Super Micro Bead Silica Gel B-5, SMBSG B-5) as cation-exchange stationary phase in IC–CD using nitric acid as an eluent was carried out for the simultaneous separation of common mono- and divalent cations (Li^+, Na^+, NH_4^+, K^+, Mg^{2+} and Ca^{2+}). The SMBSG B-5 silica gel was calcinated at 200–1000 °C for 5 h. Fig. 1A–E show chromatograms of these mono- and divalent cations on columns (150× 4.6 mm I.D.) packed with the SMBSG B-5 silica gels

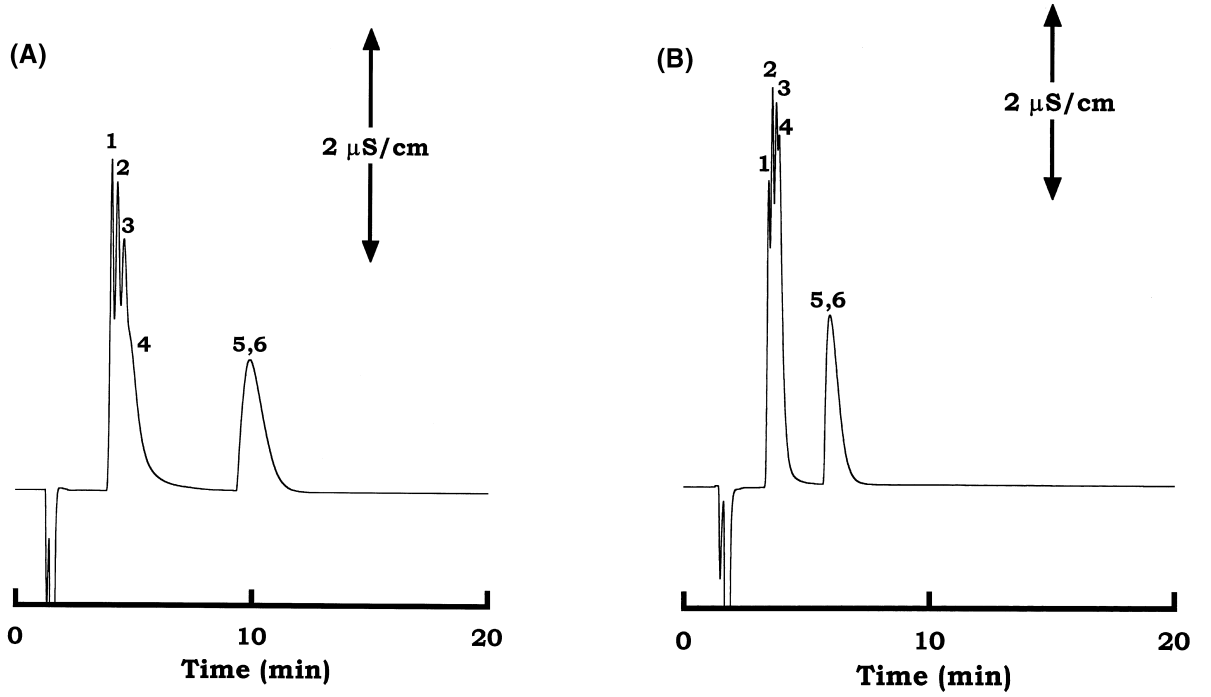

Fig. 1. Chromatograms of mono- and divalent cations on calcinated SMBSG B-5 silica gels columns using 0.5 m*M* HNO_3 as eluent. Conditions: column: SMBSG B-5 silica gel calcinated at (A) 200, (B) 400, (C) 600, (D) 800 and (E) 1000 °C (SMBSG-200, -400, -600, -800 and -1000) at 5 h; column size: 150×4.6 mm I.D.; column temperature: 35 °C; eluent: 0.5 m*M* HNO_3; detection: indirect conductivity; injection volume: 20 μl; sample concentration: 0.1 m*M* for monovalent cations and 0.05 m*M* for divalent cations. Peaks: 1=Li^+, 2=Na^+, 3=NH_4^+, 4=K^+, 5=Mg^{2+} and 6=Ca^{2+}.

calcinated at (A) 200, (B) 400, (C) 600, (D) 800 and (E) 1000 °C (SMBSG-200, -400, -600, -800 and -1000) obtained by using 0.5 m*M* HNO_3 as the eluent.

As shown in Fig. 1A–E, the retention volumes of these mono- and divalent cations changed dramatically, depending on the calcinating temperature. The retention volumes decreased at the calcinating temperature between 200 and 600 °C and then increased at the calcinating temperature ≥600 °C. The change of the retention volumes of the divalent cations was much larger than that of the monovalent cations. In general, the change of the retention volume is due mainly to the change of the cation-exchange capacity [7]. However, as listed in Table 1, since the change of the retention volumes was not dependent on the change of the surface area of these calcinated SMBSG B-5 silica gels columns, it was expected that the main cause of the change of the retention volume was ascribed to change of chemical properties of the SMBSG B-5 silica gel caused by the calcinating procedures.

As shown in Fig. 1A–E, with increasing the calcinating temperature, peak shapes of the monovalent cations were considerably improved. Symmetrical peaks of the monovalent cations were obtained on the SMBSG-1000 column. Additionally, with increasing the calcinating temperature, the difference in the retention volumes between the monovalent cations tended to decrease. These above results also indicated strongly that change of chemical properties of the SMBSG B-5 silica gel occurred. In order to clarify the main cause of the difference in the ion chromatographic behavior of these mono- and divalent cations on these calcinated SMBSG B-5 silica gels columns, the measurement of X-ray diffraction of these SMBSG B-5 silica gels was carried out. Unfortunately, since these silica gels were amorphous, the X-ray diffraction patterns showed almost no variation. Details concerning the

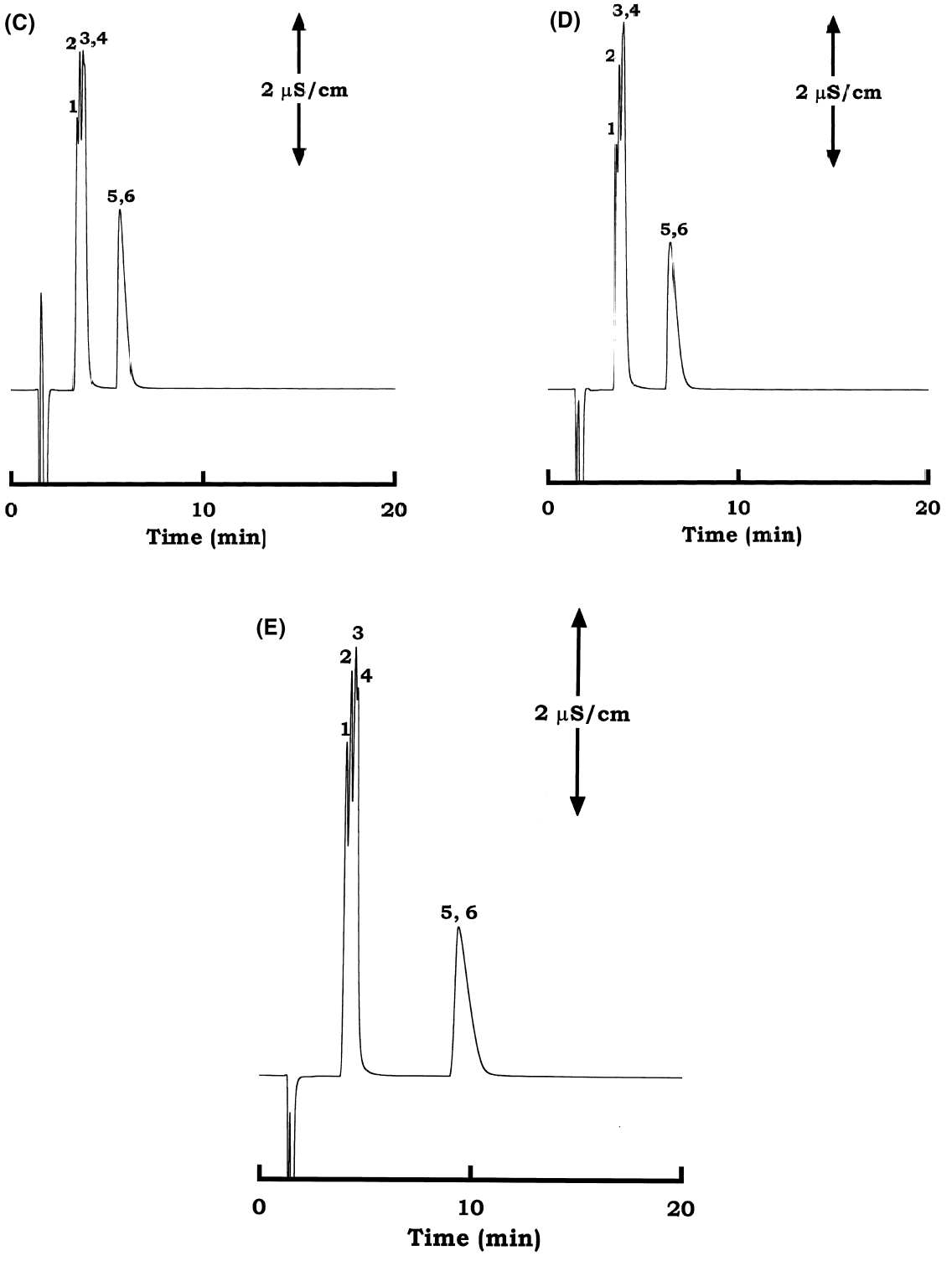

Fig. 1. (*continued*)

effect of the calcinating temperature on chemical properties of the SMBSG B-5 silica gel will be the subject of future work.

From the above results, it was concluded that (a) the calcination was effective for the improvement of peak shapes of these mono- and divalent cations, and (b) the calcination had almost no effect on the improvement of peak resolution between these mono- and divalent cations when using 0.5 m*M* HNO_3 as the eluent.

3.2. Ion chromatographic behavior of mono- and divalent cations on calcinated SMBSG B-5 silica gels columns using nitric acid containing 18-crown-6 as eluent

As reported previously [10], complete simultaneous separation of these mono- and divalent cations was achieved on the SMBSG B-5 silica gel (lot no. 411010) column (4.6 mm I.D.×150 mm) using 1.0 m*M* oxalic acid containing 3 m*M* 18-crown-6 (1,4,7,10,13,15-hexaoxa-cyclooctadecane) at pH 3.0 as the eluent. This is because 18-crown-6 added to the eluent acts as a selective cation-exchanger. However, the retention mechanism of these mono- and divalent cations under IC–CD conditions has not been well explained. It is well known that calcination (heat-treatment) of silica gel is easy and effective way for the modification of adsorption properties of silica gel for organic compounds [12]. Then, the application of these calcinated SMBSG B-5 silica gels in IC–CD using 0.5 m*M* HNO_3 containing 18-crown-6 as the eluent for the simultaneous separation of these mono- and divalent cations was carried out in order to clarify the effect of 18-crown-6 on ion chromatographic behavior of these cations and to extent the utility of the SMBSG B-5 silica gel in IC for cations.

Fig. 2 shows the relationship between the calcinating temperature of the SMBSG B-5 silica gel and the amount of 18-crown-6 adsorbed on corresponding calcinated SMBSG B-5 silica gels columns using 0.5 m*M* HNO_3 containing 5.0 m*M* 18-crown-6 as the eluent. With increasing the calcinating temperature, the amount of 18-crown-6 adsorbed increased drastically. The amount of 18-crown-6 adsorbed on the SMBSG-1000 column (0.093 mmol column^{-1}) was reached about four times as much as that on the SMBSG-200 column (0.025 mmol column^{-1}). This result showed that the calcination was very effective for the increase in the amount of 18-crown-6 adsorbed on SMBSG B-5 silica gel column.

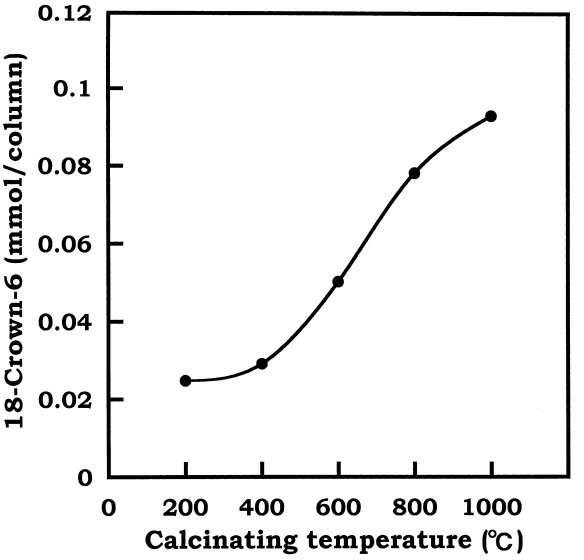

Fig. 2. Effect of calcinating temperature on amount of 18-crown-6 adsorbed on calcinated SMBSG B-5 silica gels columns using 0.5 m*M* HNO_3 containing 5.0 m*M* 18-crown-6 as eluent. Conditions: column: SMBSG-200, -400, -600, -800 and -1000; eluent: 0.5 m*M* HNO_3 containing 5.0 m*M* 18-crown-6; detection: refractive index. Other conditions as in Fig. 1.

Fig. 3A and B show chromatograms of these mono- and divalent cations on the SMBSG-200 and SMBSG-1000 columns, respectively. As shown in Figs. 1A and 3A, and Figs. 1E and 3B, the order of the increase in the retention volumes of the monovalent cations was $Li^+ < Na^+ < NH_4^+ \ll K^+$ and that of the divalent cations was $Mg^{2+} < Ca^{2+}$ on these columns. Since these orders were in good agreement with the stability of complexes form between 18-crown-6 and these cations [13], it was evident that 18-crown-6 acted as a selective cation-exchanger under these IC–CD conditions. The increase in the retention volumes of these mono- and divalent cations on the SMBSG-1000 column was considerably larger than that on the SMBSG-2000 column. As shown in Fig. 3A and B, complete separation of these mono- and divalent cations was achieved on the SMBSG-200 column and incomplete separation was achieved on the SMBSG-1000 column. This is

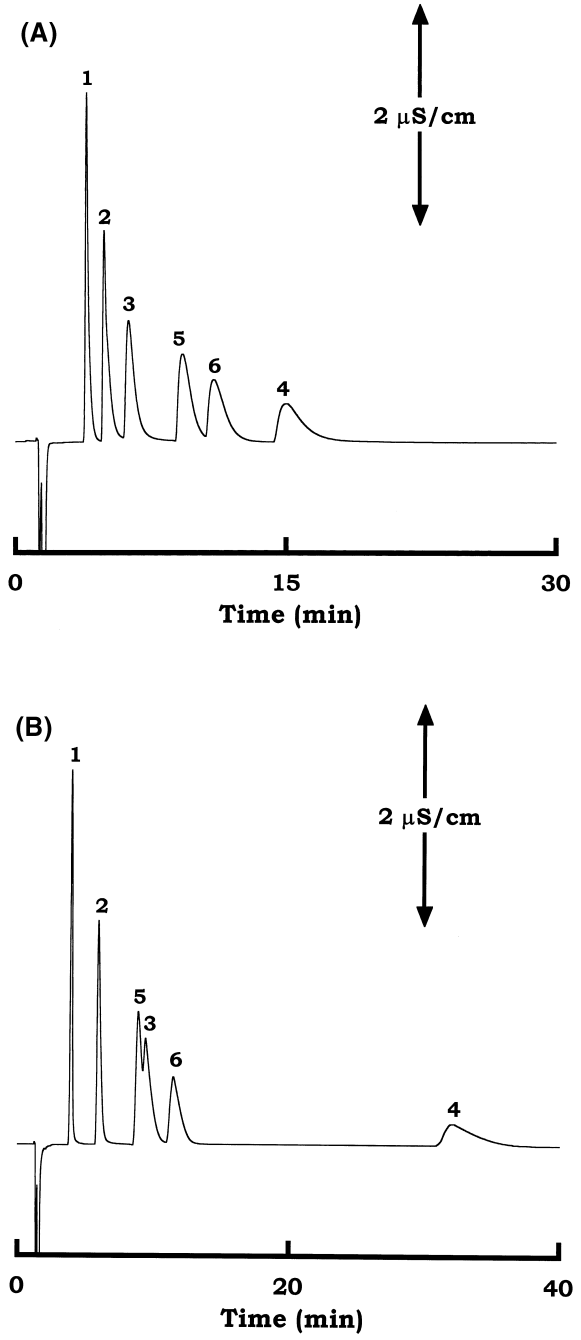

Fig. 3. Chromatograms of mono- and divalent cations on SMBSG-200 and SMBSG-1000 columns using 0.5 m*M* HNO_3 containing 5.0 m*M* 18-crown-6 as eluent. Conditions: column: (A) SMBSG-200, (B) SMBSG-1000; eluent: 0.5 m*M* HNO_3 containing 5.0 m*M* 18-crown-6. Other conditions as in Fig. 1.

because the retention volumes of NH_4^+ increased largely and then peaks of NH_4^+ and Mg^{2+} were somewhat overlapped on the SMBSG-1000 column. These above results strongly suggested that the amount of 18-crown-6 adsorbed on the cation-exchange stationary phase was predominant factor for the improvement of peak resolution between these mono- and divalent cations.

Fig. 4 shows the relationship between the concentration of 18-crown-6 in the eluent on the amount of 18-crown-6 adsorbed on the SMBSG-200 and SMBSG-1000 columns. With increasing the concentration of 18-crown-6 in the eluent, the amount of 18-crown-6 adsorbed increased drastically. As shown in Fig. 5, complete separation of these mono and divalent cations on the SMBSG-1000 column was achieved using 0.5 m*M* HNO_3 containing 1.0 m*M* 18-crown-6 as the eluent. The amount of 18-crown-6 adsorbed on the SMBSG-1000 column was 0.030 mmol $column^{-1}$ when using 0.5 m*M* HNO_3 containing 1.0 m*M* 18-crown-6 as the eluent and was close to that on the SMBSG-200 column when using 0.5 m*M* HNO_3 containing 5.0 m*M* 18-crown-6 as the

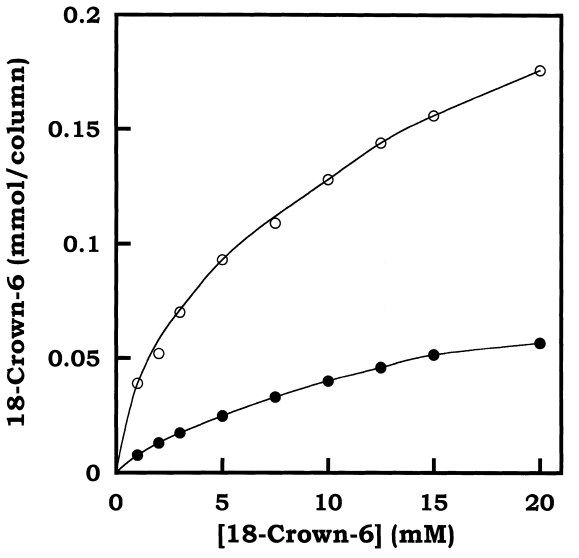

Fig. 4. Effect of concentration of 18-crown-6 in 0.5 m*M* HNO_3 eluent on amount of 18-crown-6 adsorbed on SMBSG-200 and SMBSG-1000 columns. Conditions: column: SMBSG-200 and SMBSG-1000; eluent: 0.5 m*M* HNO_3 containing 0–20 m*M* 18-crown-6; symbols: ●=SMBGS-200, ○=SMBSG-1000. Other conditions as in Fig. 2.

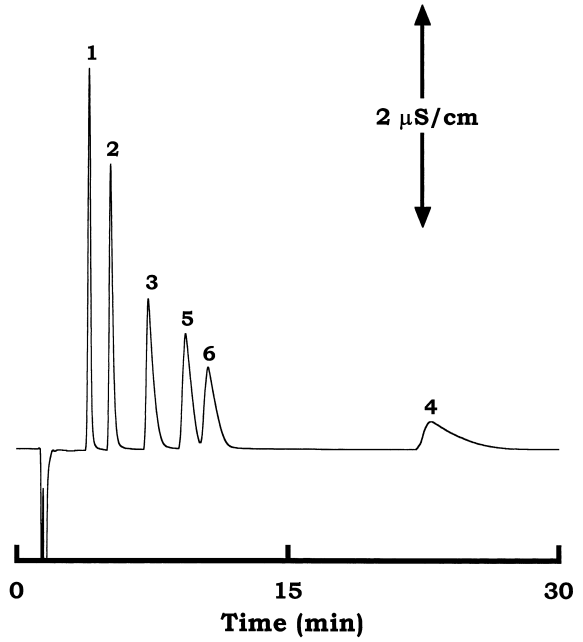

Fig. 5. Chromatogram of mono- and divalent cations on SMBSG-1000 column using 0.5 m*M* HNO_3 containing 1.0 m*M* 18-crown-6 as eluent. Conditions: column: SMBSG-1000; eluent: 0.5 m*M* HNO_3 containing 1.0 m*M* 18-crown-6. Other conditions as in Fig. 3.

eluent (0.025 mmol column^{-1}). This result borne out strongly that the amount of 18-crown-6 adsorbed was the predominant factor for the improvement of peak resolution between these mono- and divalent cations.

From these above results, it was concluded that (a) 18-crown-6 adsorbed on cation-exchange stationary phase mainly acted as a selective cation-exchanger, and (b) the calcination was easy and effective way for the increases in the amount of 18-crown-6 adsorbed on silica stationary phase and, as a consequence, the effect of 18-crown-6 was enhanced largely.

3.3. Ion chromatographic behavior of mono- and divalent cations on calcinated SMBSG B-5 silica gels columns using HNO_3 containing 15-crown-5 as eluent

It is well known that the addition of 15-crown-5 (1,4,7,10,13-pentaoxacyclopentadecane) to acidic eluent is not effective for the improvement of peak resolution between these mono- and divalent cations on weakly acidic cation-exchange column [14,15]. The authors have also reported that incomplete simultaneous separation of these mono- and divalent cations was achieved on the SMBSG B-5 silica gel column using 1.0 m*M* oxalic acid containing 3.0 m*M* 15-crown-5 at pH 3.0 as the eluent [10]. This is because complexes formed between 15-crown-5 and these cations are unstable in comparison to those formed between 18-crown-6 and these cations [13]. However, since the amount of 18-crown-6 adsorbed on the calcinated SMBSG B-5 silica gels columns increased drastically with increasing the calcinating temperature, it was expected that the SMBSG-1000 column would be successfully applied in IC–CD using 0.5 m*M* HNO_3 containing 15-crown-5 as the eluent for the simultaneous separation of these mono- and divalent cations.

Fig. 6 show the relationship between the calcinating temperature and the amount of 15-crown-5 adsorbed on corresponding calcinated SMBSG-B-5 silica gels columns using 0.5 m*M* HNO_3 containing

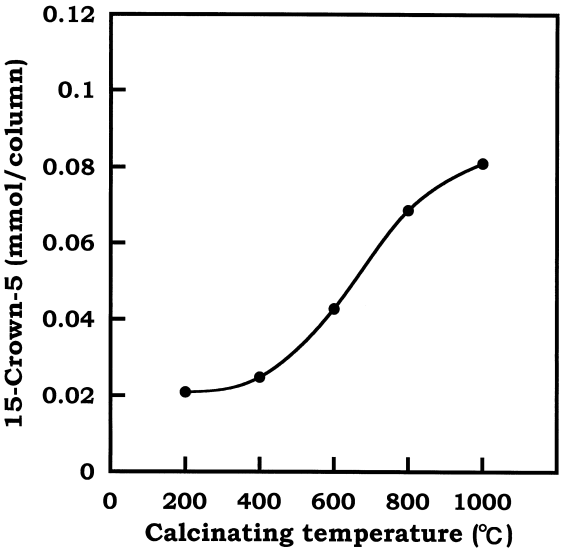

Fig. 6. Effect of calcinating temperature on amount of 15-crown-5 adsorbed on calcinated SMBSG B-5 silica gels columns using 0.5 m*M* HNO_3 containing 5.0 m*M* 15-crown-5 as eluent. Conditions: column: SMBSG-200, -400, -600, -800 and -1000; eluent: 0.5 m*M* HNO_3 containing 5.0 m*M* 15-crown-5. Other conditions as in Fig. 4.

5.0 m*M* 15-crown-5 as the eluent. With increasing the calcinating temperature, the amount of 15-crown-5 adsorbed increased drastically. The amount of 15-crown-5 adsorbed on the SMBSG-1000 column was 0.081 mmol column^{-1} and was reached about four times as much as that on the SMBSG-200 column (0.020 mmol column^{-1}). Fig. 7 shows the relationship between the concentration of 15-crown-5 in the eluent and the amount of 15-crown-5 adsorbed on the SMBSG-200 and SMBSG-1000 columns. With increasing the concentration of 15-crown-5 in the eluent, the amount of 15-crown-5 adsorbed on these columns also increased. The adsorption behavior of 15-crown-5 on these calcinated SMBSG B-5 silica gels columns was almost the same as that of 18-crown-6 on these calcinated SMBSG B-5 silica gels columns. As shown in Fig. 8, complete separation of these mono- and divalent cations was achieved on the SMBSG-1000 column using 0.5 m*M* HNO_3 containing 5.0 m*M* 15-crown-5 as the eluent. In contrast, as shown in Fig. 9, incomplete separation of these mono- and divalent cations was achieved on the SMBSG-200 column using 0.5 m*M* HNO_3 containing 20 m*M* 15-crown-5 as the eluent. This is because the amount of 15-crown-5 adsorbed on the SMBSG-200 column (0.058 mmol column^{-1}) using 0.5 m*M* HNO_3 containing 20 m*M* 15-crown-5 as the eluent was considerable lower than that on the SMBSG-1000 column (0.081 mmol column^{-1}) using 0.5 m*M* HNO_3 containing 5.0 m*M* 15-crown-5 as the eluent.

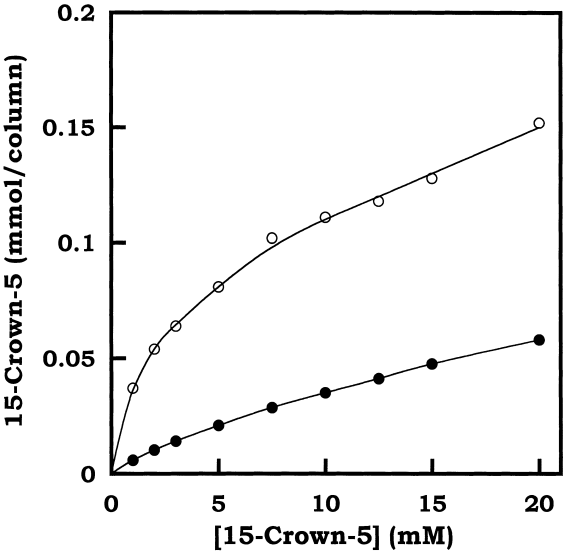

Fig. 7. Effect of concentration of 15-crown-5 in 0.5 m*M* HNO_3 eluent on amount of 15-crown-5 adsorbed on SMBSG-200 and SMBSG-1000 columns. Conditions: eluent: 0.5 m*M* HNO_3 containing 0–20 m*M* 15-crown-5; symbols: ●=SMBGS-200, ○=SMBSG-1000. Other conditions as in Fig. 6.

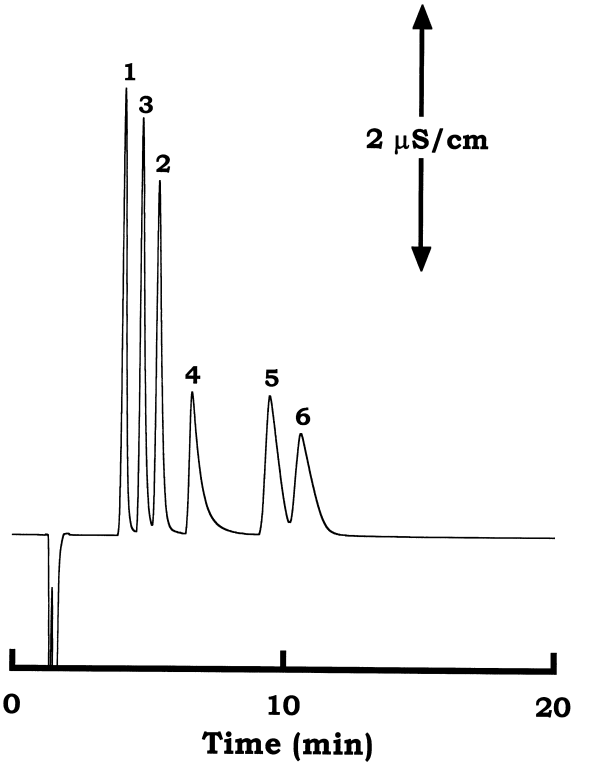

Fig. 8. Chromatogram of mono- and divalent cations on SMBSG-1000 column using 0.5 m*M* HNO_3 containing 5.0 m*M* 15-crown-5 as eluent. Conditions: column: SMBSG-1000; eluent: 0.5 m*M* HNO_3 containing 5.0 m*M* 15-crown-5. Other conditions as in Fig. 5.

From the above results, it was concluded that (a) the amount of 15-crown-5 adsorbed was the predominant factor for the improvement of peak resolution between these mono- and divalent cations, and (b) the calcination was easy and effective way for the increase in the amount of 15-crown-5 adsorbed on silica stationary phase and, as a consequence, the effect of 15-crown-5 was enhanced largely.

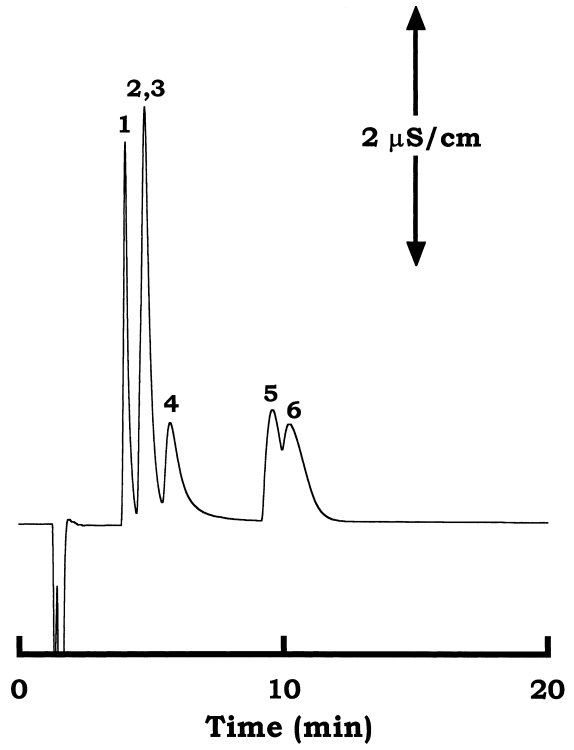

Fig. 9. Chromatogram of mono- and divalent cations on SMBSG-200 column using 0.5 m*M* HNO_3 containing 20 m*M* 15-crown-5 as eluent. Conditions: column: SMBSG-200; eluent: 0.5 m*M* HNO_3 containing 20 m*M* 15-crown-5. Other conditions as in Fig. 8.

3.4. Ion chromatographic behavior of mono- and divalent cations on calcinated Develosil 60-5 and Pia Seed 5S-60-SIL silica gels columns

In order to demonstrate the effectiveness of calcinated silica gel as cation-exchange stationary phase in IC for cations, the application of calcinated Develosil 60-5 and Pia Seed 5S-60-SIL silica gels in IC–CD using nitric acid containing crown ethers as the eluent was carried out for the simultaneous separation of these mono- and divalent cations. The Pia Seed 5S-60-SIL silica gel is pure silica gel synthesized by the hydrolysis of pure tetraethoxysilane [$Si(OCH_2CH_3)_4$]. These silica gels were calcinated at 200 and 1000 °C for 5 h.

Figs. 10 and 11 show chromatograms of these mono- and divalent cations on columns packed with Develosil 60-5 silica gels calcinated at 200 and 1000 °C (Develosil-200 and -1000), respectively. As shown in Figs. 10A and 11A, when using 1.0 m*M* HNO_3 as the eluent, the chromatograms of these mono- and divalent cations on the Develosil-200 column and that on Develosil-1000 column were almost without variation, it was evident that the calcination had no effect for the improvement of peak resolution between these mono- and divalent cations. As shown in Figs. 10B and 11B, complete separation of these mono- and divalent cations was achieved on the Develosil-1000 column using 1.0 m*M* HNO_3 containing 5 m*M* 15-crown-5 as the eluent and incomplete separation was achieved on the Develosil-200 column using 1.0 m*M* HNO_3 containing 20 m*M* 15-crown-5 as the eluent. This might be because the amount of 15-crown-5 adsorbed on the Develosil-200 column was considerable lower than that on the Develosil-1000 column. As shown in Figs. 10C and 11C, although complete simultaneous separation of these mono- and divalent cations was achieved on the Develosil-200 and Develosil-1000 columns, a suitable concentration of 18-crown-6 in IC–CD using the Develosil-200 column (5 m*M*) was much higher than that in IC–CD using the Develosil-1000 column (1 m*M*). These above results were in good agreement with those on the calcinated SMBSG B-5 silica gel columns.

Figs. 12 and 13 show chromatograms of these mono- and divalent cations on columns packed with Pia Seed 5S-60-SIL silica gels calcinated at 200 and 1000 °C, respectively. The ion chromatographic behavior of these mono- and divalent cations on calcinated Pia Seed 5S-60-SIL silica gels columns was also almost the same as that on the calcinated SMBSG B-5 silica gels columns.

From the above results, it was evident that the calcination was an easy and effective way for the preparation of advanced silica stationary phase in IC–CD using HNO_3 containing crown ethers as the eluent for the simultaneous separation of these mono- and divalent cations.

4. Conclusion

In order to extend the utility of silica gel as cation-exchange stationary phase in IC for cations,

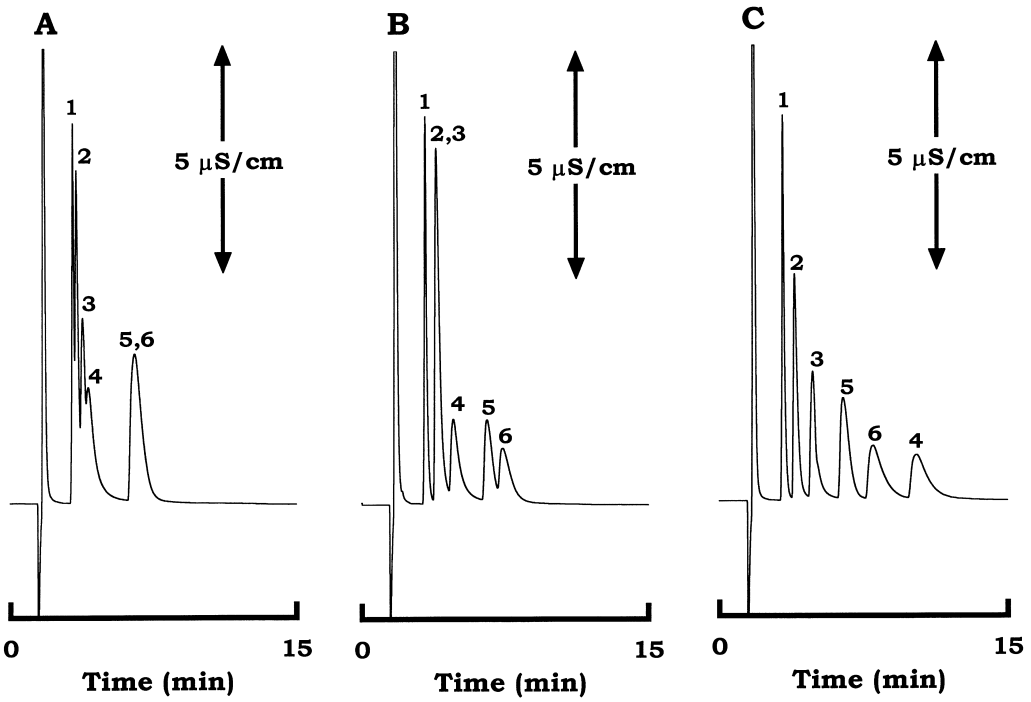

Fig. 10. Chromatograms of mono- and divalent cations on column packed with Develosil 60-5 silica gel calcinated at 200 °C. Conditions: column: Develosil 60-5 silica gel calcinated at 200 °C for 5 h; eluent: (A) 1.0 m*M* HNO_3, (B) 1.0 m*M* HNO_3 containing 20 m*M* 15-crown-5, (C) 1.0 m*M* HNO_3 containing 5.0 m*M* 18-crown-6; sample concentration: 0.2 m*M* for monovalent cations and 0.1 m*M* for divalent cations. Other conditions as in Fig. 9.

the application of unmodified silica gel (Super Micro Bead Silica Gel B-5, SMBSG B-5) calcinated at 200–1000 °C for 5 h in IC–CD using HNO_3 containing crown ethers [18-crown-6 (1,4,7,10,13,15-hexaoxacyclooctadecane) and 15-crown-5 (1,4,7,10, 13-pentaoxacyclopentadecane)] as the eluent was carried out for the simultaneous separation of common mono and divalent cations (Li^+, Na^+, NH_4^+, K^+, Mg^{2+} and Ca^{2+}). When using 0.5 m*M* HNO_3 as the eluent, the calcination had almost no effect for the improvement of peak resolution between these cations. In contrast, when using 0.5 m*M* HNO_3 containing crown ethers as the eluent, with increasing the calcinating temperature, the amount of crown ethers adsorbed on the corresponding calcinated SMBSG B-5 silica gels columns increased drastically and, as a consequence, the effect of crown ethers was enhanced largely. These results indicate that crown ethers adsorbed on silica stationary phase mainly acts as a selective cation-exchanger. Excellent simultaneous separation of these mono- and divalent cations was achieved on column (150×4.6 mm I.D.) packed with the SMBSG B-5 silica gel calcinated at 1000 °C by elution with 0.5 m*M* HNO_3 containing either 1.0 m*M* 18-crown-6 or 5.0 m*M* 15-crown-5.

Calcination (heat treatment) is proved to be an easy and effective way for the preparation of advanced silica stationary phases in IC–CD for cations. These results largely extend the utility of silica gel as cation-exchange stationary phase in IC–CD for cations.

Acknowledgements

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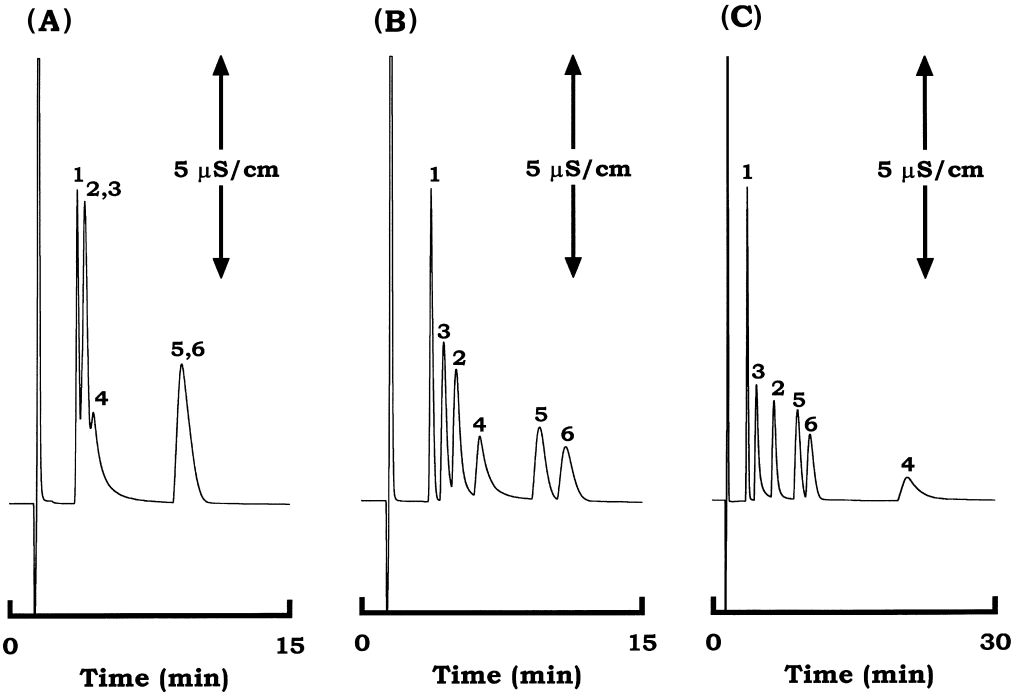

Fig. 11. Chromatograms of mono- and divalent cations on column packed with Develosil 60-5 silica gel calcinated at 1000 °C. Conditions: column: Develosil 60-5 silica gel calcinated at 1000 °C for 5 h; eluent: (A) 1.0 m*M* HNO_3, (B) 1.0 m*M* HNO_3 containing 5.0 m*M* 15-crown-5, (C) 1.0 m*M* HNO_3 containing 1.0 m*M* 18-crown-6. Other conditions as in Fig. 10.

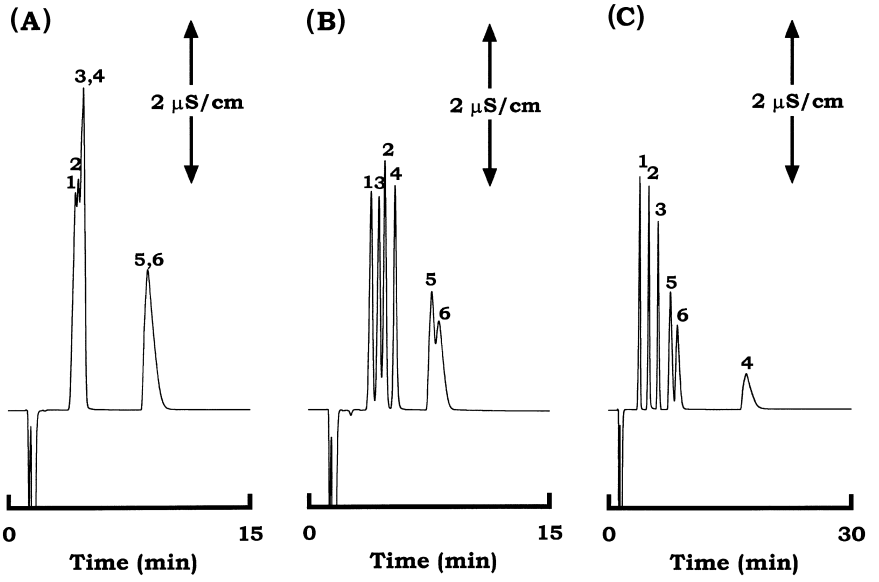

Fig. 12. Chromatograms of mono- and divalent cations on column packed with Pia Seed 5S-60-SIL silica gel calcinated at 200 °C. Conditions: column: Pia Seed 5S-60-SIL silica gel calcinated at 200 °C for 5 h; eluent: (A) 0.25 m*M* HNO_3, (B) 0.25 m*M* HNO_3 containing 20 m*M* 15-crown-5, (C) 0.25 m*M* HNO_3 containing 5.0 m*M* 18-crown-6; sample concentration: 0.1 m*M* for monovalent cations and 0.05 m*M* for divalent cations. Other conditions as in Fig. 11.

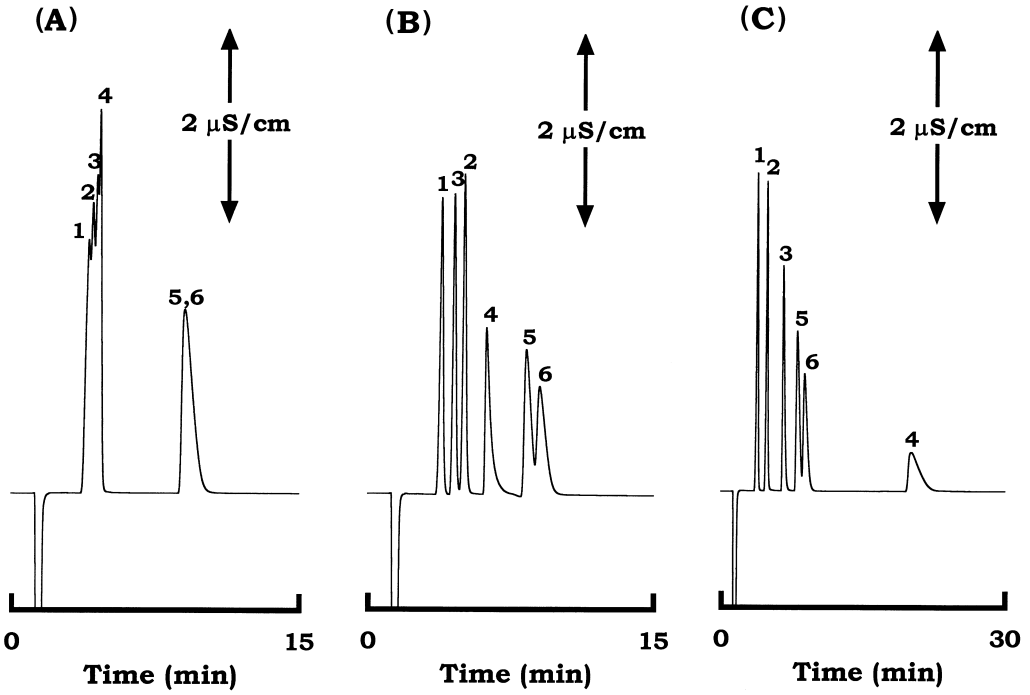

Fig. 13. Chromatograms of mono- and divalent cations on column packed with Pia Seed 5S-60-SIL silica gel calcinated at 1000 °C. Conditions: column: Pia Seed 5S-60-SIL silica gel calcinated at 1000 °C for 5 h; eluent: (A) 0.25 m*M* HNO_3, (B) 0.25 m*M* HNO_3 containing 5.0 m*M* 15-crown-5, (C) 0.25 m*M* HNO_3 containing 1.0 m*M* 18-crown-6. Other conditions as in Fig. 12.

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