Focusing Review

Pure silica gel as cation−exchange stationary phase in ion chromatography for mono− and divalent cations

Kazutoku Ohta

Inhomogeneity Analysis Research Group

Research Institute of Instrumentation Frontier (RIIF)

National Institute of Advanced Industrial Science and Technology (AIST)

2266−98 Anagahora, Simoshidami, Moriyama−ku, Nagoya 463−8560, Japan

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Abstract

The review article describes the application of a pure silica gel (Pia Seed 5S−60−SIL), synthesized by the hydrolysis of pure teratraetoxysilane [$Si(OCH_2CHG_3)_4$], as a cation−exchange stationary phase in ion chromatography for common mono− and divalent cations (Li^+, Na^+, NH_4^+, K^+, Mg^{2+} and Ca^{2+}). Using aromatic monoamines at pH 5.0 as eluents, the Pia Seed 5S−60−SIL silica gel acted as an advanced cation−exchange stationary phase for these mono− and divalent cations. Excellent simultaneous separation and highly sensitive indirect−photometric detection at 275 nm for these cations were achieved on a Pia Seed 5S−60−SIL column (150 × 4.6 mm i. d.) in 20 min with 0.75 mM tyramine [4−(2−aminoethyl)phenol]−0.25 mM oxalic acid at pH 5.0 containing 1.5 mM 18−crown−6 (1,4,7,10,13,16−hexaoxacyclooctadecane) as the eluent. Using dilute oxalic acid (0.2 mM oxalic acid) as the eluent, the Pia Seed 5S−60−SIL silica gel also behaved as an advanced cation−exchange stationary phase for these mono− and divalent cations. Excellent simultaneous separation and highly sensitive indirect−conductimetric detection for these cations were also achieved on the column in 20 min with 0.2 mM oxalic acid at pH 3.6 containing 1.5 mM 18−crown−6 as the eluent. The review article also describes the chromatographic behavior of these mono− and divalent cations on the calcinated Pia Seed 5S −60−SIL silica gel columns.

Key words: Pure silica gel, Ion Chromatography, Cations, Indirect−photometric detection, Tyramine, Indirect−conductimetric detection, Oxalic acid, Crown ethers, Calcination.

1. Introduction

Ion chromatography (IC) developed by Small *et al*. [1] is widely recognized as a simple, powerful and convenient analytical technique for the determination of various low−molecular−weight ionic compounds [2, 3]. Firstly, IC with conductimetric detection (IC−CD) was mainly applied for the determination of inorganic anions. This is because a lightly sulfonated styrene−divinylbenzene co−polymer (S−DVB) resin was used as the cation−exchange stationary phase in IC−CD for cations and, as a consequence, the simultaneous separation of common mono− and divalent cations (Li^+, Na^+, NH_4^+, K^+, Mg^{2+}, and Ca^{2+}) could not be achieved easily on this type resin column with acidic solution as the eluent [1−3]. Kolla *et al*. [4], and Kondratjonok and Schwedt [5] applied carboxylated silica gel (polybutadiene−maleic acid on silica gel), as the cation−exchange stationary phase in IC−CD for these mono− and divalent cations [4, 5]. The greatest advantage of the use of this type resin in IC−CD is that the simultaneous separation and highly sensitive conductimetric detection for these mono− and divalent cations can be achieved easily with acidic solution as the eluent. Now, IC−CD with carboxylated silica column or carboxylated S−DVB resin column is widely utilized for the determination of these mono− and divalent cations in various real sample waters.

Silica gel is physically stable, unreactive towards organic solvents and its particle size, pore size, pore volume, and surface area

Phone: +81−52−736−7363, Facsimile: +81−52−736−7224
E−mail: kazu.ohta@aist.go.jp

can be controlled easily. The silanol group on the surface of silica gel is easily bonded chemically to various kinds of functional groups. For these reasons, both unmodified and modified silica gels are widely employed as stationary phases in liquid chromatography for various organic compounds [6]. Furthermore, since the silanol group behaves as a weak acid [7], it is possible to utilize unmodified silica gel as a cation−exchange stationary phases in IC−CD for various cations [8−13]. The most advantage of the use of unmodified silica gel in 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 with lithium oxalate as the eluent [11−13]. However, due to very small difference in the equivalent conductivity between lithium ion (Li^+) as the eluent ion and the analyte cations, the conductimetric detection sensitivities result in very low.

The use of hydronium ion (H^+) having the largest equivalent conductivity as the eluent ion was expected to be one of the most effective ways for the enhancement of the detection sensitivities for the analyte cations in IC−CD. Then, chromatographic behavior of common mono− and divalent cations (Li^+, Na^+, NH_4^+, K^+, Mg^{2+}, and Ca^{2+}) on various commercially available unmodified silica gel columns was investigated with 2 mM nitric acid at pH 2.7 as the eluent [14−17]. Some silica gels (Develosil 30−5, Kaseisorb LC−60−5, and Zorbax BP−SIL) showed cation−exchange behavior and could be successfully applied in IC−CD for these mono− and divalent cations using acidic solution as the eluent. The main cause of the cation−exchange behavior was attributed to be polyvalent metals as impurities in silica matrix [18, 19]. However, it should be kept in mind that all silica gels could not be utilized as cation−exchange stationary phase in the IC−CD for these cations with acidic solution as the eluent.

The use of protonated aromatic monoamines having high molar extinction coefficients as the eluent ions is very effective way for the achievement of higher detection sensitivities for these mono− and divalent cations in IC with indirect−photometric detection (IC−IPD) [20, 21]. However, since commercially available silica gels, except for pure silica gel, synthesized by the hydrolysis of pure tetraethoxysilane [$Si(OCH_2CH_3)_4$] contains various polyvalent metals as impurities in silica matrix, strongly unfavorable interaction occurs frequently between protonated aromatic monoamines as the eluent ions and polyvalent metals in the silica matrix [22−25]. Therefore, the use of aromatic monoamines as the eluent in the IC−IPD with unmodified silica gel column has not been so popular [26, 27].

The article describes the application of a pure silica gel (Pia Seed−5S−60−SIL) as a cation−exchange stationary phase in IC for common mono− and divalent cations (Li^+, Na^+, NH_4^+, K^+, Mg^{2+}, and Ca^{2+}), in order to demonstrate the effectiveness of the Pia Seed 5S−60−SIL silica gel in IC for cations. The Pia Seed−5S−60−SIL silica gel acted as an advanced cation−exchange stationary phase for these cations both (a) in IC−IPD with aromatic monoamines as the eluents and (b) in IC−CD with dilute oxalic acid as the eluent [28, 29]. The article also describes the effect of calcination (heat treatment) of the Pia Seed−5 S−60−SIL silica gel on chromatographic behavior of these mono− and divalent cations [30, 31].

2. Experiment

2.1. Instruments

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 CO−8020 column oven operated at 35 ℃, a Tosoh UV−8020 UV−Vis spectrophotometric detector, a Tosoh CM−8020 conductimetric detector, a Tosoh SD−8023 on−line degasser, and a Reodyne (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 determination of the amounts of crown ethers [18−crown−6 (1,4,7,10,13,16−hexaoxacyclooctadecane) and 15−crown−5 (1,4,7,10,13−pentaoxacyclopentadecane)] adsorbed on calcinated pure silica gel columns.

A Toa Electronics (Tokyo, Japan) IM−40S ion meter with a glass electrode was used for the measurements of the pH of eluents. A Toa Electronics CM−20 conductimetric detector was used for the measurements of conductivities of eluents.

A Perkin−Elmer (Shelton, CT, USA) Lambda 18NS double beam UV−Vis spectrometer was employed for the measurements of UV spectra of aromatic monoamine eluents.

2.2. Silica gels

Various commercially available unmodified silica gels [Macherey−Nargel (Düren, Germany) Nucleosil 50−5, Fuji−Silysia Chemical (Kasugai, Japan) Super Micro Bead Silica Gel B−5, Nomura Chemical (Seto, Japan) Develosil 60−5, and Pia Tec (Suzuka, Japan) Pia Seed 5S−60−SIL silica gels] were used in this work. The Pia Seed 5S−60−SIL silica gel is pure silica gel, synthesized by the hydrolysis of pure tetraethoxysilane [$Si(OCH_2CH_3)_4$].

Table 1 shows physical properties of these silica gels. The determination of the surface area and pore volume by nitrogen adsorption isotherms at 77 K was carried out by 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 was carried out by using a Horiba (Kyoto, Japan) LA−920 laser scattering particle size distribution analyzer.

Table 2 shows analytical results of polyvalent metals in these silica gels. Firstly, the main polyvalent metals were qualitatively defined as Fe, Al, Ti, Zr, Mg, and Ca by using a Cameca (Cour-

Table 1. Physical properties of various silica gels

Silica gel	Form	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* ($m^2\ column^{-1}$)
Nucleosil 50−5	Spherical	4.8	365	65	0.90	0.51	4.6×10^2
Super Micro Bead Silica Gel B−5	Spherical	5.5	475	60	0.93	0.43	5.1×10^2
Develosil 60−5	Spherical	5.9	417	65	1.04	0.45	4.7×10^2
Pia Seed 5S−60−SIL	Spherical	7.0	619	58	1.04	0.41	6.3×10^2

* Column size : 150 mm × 4.6 mm i.d.
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Table 2. Analytical results of polyvalent metal in various silica gels

Silica gel	Content (μmol g^{-1}−silica gel)					
	Mg	Al	Ca	Ti	Fe	Zr
Nucleosil 50−5	0.99	1.5	3.1	2.1	0.20	1.1
Super Micro Bead Silica Gel B−5	0.08	1.2	0.25	1.3	0.27	0.13
Develosil 60−5	1.7	4.9	12	1.5	0.10	0.16
Pia Seed 5S−60−SIL	0.10	< 0.004	0.10	0.01	0.01	0.01

Table 3. Physical properties of calcinated Pia Seed 5S−60−SIL silica gels

Calcinated temperature (℃)	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* ($m^2\ column^{-1}$)
200	7.0	618	58	1.04	0.41	6.3×10^2
400	6.8	581	60	0.94	0.42	6.1×10^2
600	6.7	551	59	0.88	0.45	6.2×10^2
800	6.4	460	56	0.76	0.49	5.6×10^2
1000	5.0	269	42	0.39	0.71	4.8×10^2

* Column size : 150 mm × 4.6 mm i.d.
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bevoie Cedex, France) IMS−3F secondary ion−mass spectrometer (SIMS) system. Next, the amounts of the above metals were determined quantitatively by using a Nippon Jarrel−Ash (Kyoto, Japan) ICAP−1000 inductively coupled plasma−atomic emission spectrometer (ICP−AES) system [18].

Table 3 shows physical properties of the Pia Seed 5S−60−SIL silica gels calcinated at 200, 400, 600, 800 and 1000 ℃ for 5 h.

The separation columns (150 × 4.6 mm i.d., stainless steel) were packed with these silica gels by the use of the slurry−packing method.

The determination of the amounts of crown ethers (18−crown−6 and 15−crown−5) adsorbed on calcinated Pia Seed 5S−60−SIL columns was carried out. The amount of crown ether (A, μmol $column^{-1}$) was calculated by use of the equation:

$$A = (V_R - V_0) \times C$$

where V_R is the breakthrough volume (ml), V_0 is the total dead volume (column void volume and connected tube volume, ml) and C is the concentration of crown ether in the eluent (mM). Firstly, column was equilibrated with 0.75 mM tyramine [4−(2−aminoethyl) phenol]−0.25 mM oxalic acid at pH 5.0 as the eluent. A sample of 75 mM tyramine−25 mM oxalic acid at pH 5.0 was injected. Elution volume of peak corresponding to 75 mM tyramine was regarded as V_0. Next, 0.75 mM tyramine−0.25 mM oxalic acid at pH 5.0 containing crown ether as the eluent was passed through column and the response of refractive index detector (breakthrough curve) was monitored. Volume corresponding to breakthrough

point in the detector response curve was regarded as V_R.

2.3. Chemicals

All chemicals were analytical regent grade. Tyramine, 18−crown−6, and 15−crown−5 were purchased from Aldrich Chemicals (Milwaukee, WI. USA), and other chemicals were purchased from Wako Pure Chemicals (Osaka, Japan) or Tokyo Kasei Kogyo (Tokyo, Japan). Distilled, de−ionized water was used for the preparation of eluents and standard solutions.

3. Results and discussion

3.1. Separation and indirect−photometric detection of mono− and divalent cations on Pia Seed 5S−60−SIL column with aromatic monoamines as eluents

The application of a pure silica gel (Pia Seed 5S−60−SIL), synthesized by the hydrolysis of pure tetraethoxysilane [$Si(OCH_2CH_3)_4$], as a cation−exchange stationary phase in ion chromatography with indirect−photometric detection (IC−IPD) for common mono− and divalent cations (Li^+, Na^+, NH_4^+, K^+, Mg^{2+}, and Ca^{2+}) was attempted with aromatic monoamines as eluents. Firstly, chromatographic behavior of these cations on various commercially available unmodified silica gel columns (150 × 4.6 mm i.d.) was investigated with tyramine [4−(2−aminoethyl)phenol] as the eluent. Table 1 shows physical properties of silica gels used in this work. Table 2 shows analytical results of polyvalent metals as impurities in these silica gels. Figures 1A−D show chromatograms of these cations on (A) Nucleosil 50−5 column with 1.0 mM tyramine−0.25 mM oxalic acid at pH 5.0 as the eluent, (B) Super Micro Bead Silica Gel B−5 column with 0.75 mM tyramine−0.25 mM oxalic acid at pH 5.0 as the eluent, (C) Develosil 60−5 column with 1.5 mM tyramine−0.25 mM oxalic acid at pH 5.0 as the eluent, and (D) Pia Seed 5S−60−SIL column with 0.75 mM tyramine−0.25 mM oxalic acid at pH 5.0 as the eluent. The pH of these eluents was adjusted with 1 M HNO_3. This is because nitrate ion (NO_3^-) has almost no effects on the retention behavior of these cations.

As shown in Figures 1A−D, it was very easy to elute these mono− and divalent cations in a reasonable period of time (< 20 min). This is because the affinity of these mono− and divalent cations to the dissociated silanol group as cation−exchanger was very similar. The elution order of the monovalent cations was $Li^+ < Na^+ < NH_4^+ < K^+$. The order indicated that these silica gels acted as cation−exchange stationary phases under the individual eluent conditions. Incomplete separation of the monovalent cations and complete separation of the divalent cations were achieved. The complete separation was due mainly to oxalate in the eluent, which acted as a complexing agent for the divalent cations [12, 13]. As shown in Figures 1A−C, largely destroyed peaks of the monovalent cations were obtained on conventional silica gel columns, whereas, as shown in Figure 1D, symmetrical peaks of the monovalent cations were obtained on the Pia Seed 5S−60−SIL column. The peak destruction was due mainly to strong interaction between protonated tyramine as eluent ion and polyvalent metals as impurities in silica matrix [22−25]. These chromatograms suggested that the Pia Seed 5S−60−SIL silica gel could be applied successfully as the cation−exchange stationary phase in the IC−IPD for these cations.

Secondly, chromatographic behavior of these mono− and divalent cations on the Pia Seed 5S−60−SIL column was investigated with various aromatic monoamines as the eluents. Figures 2A−D show chromatograms of these cations with (A) 0.5 mM benzylamine−0.25 mM oxalic acid at pH 5.0, (B) 0.5 mM pheylethylamine−0.25 mM oxalic acid at pH 5.0, (C) 0.25 mM 2−methylpyridine−0.1 mM oxalic acid at pH 5.0, and (D) 0.25 mM 2,6−dimethylpyridine−0.1 mM oxalic acid at pH 5.0, as the eluents. The pH of these eluents was adjusted with 1 M HNO_3.

As shown in Figure 1D and Figures 2A and B, using protonated tyramine, benzylamine or phenylethylamine as the eluent ions, although symmetrical peaks of these mono− and divalent were obtained, peak resolution between the monovalent cations was very poor. The detection sensitivities of these cations obtained with protonated tyramine as the eluent ion were much higher than those obtained with protonated benzylamine and phenylethylamine as the eluent ions. This is because molar extinction coefficient of protonated tyramine [1.5×10^3 $(mol\ cm)^{-1}$ at 275 nm] was much higher than those of protonated benzylamine [2.6×10^2 $(mol\ cm)^{-1}$ at 256 nm] and phenylethylamine [2.1×10^2 $(mol\ cm)^{-1}$ at 257 nm]. Molar extinction coefficients of protonated 2−methylpyridine [4.2×10^3 $(mol\ cm)^{-1}$ at 253 nm] and 2,6−dimethylpyridine [4.3×10^3 $(mol\ cm)^{-1}$ at 253 nm] were considerably higher than that of protonated tyramine. Unfortunately, as shown in Figures 2C and D, largely fronted peaks of the divalent cations were obtained with 0.25 mM 2−methylpyridine−0.1 mM oxalic acid at pH 5.0 and 0.25 mM 2,6−dimethylpyridine−0.1 mM oxalic acid at pH 5.0, as the eluents. This might be due to low concentrations of protonated 2−methylpyridine (0.25 mM) and 2,6−dimethylpyridine (0.25 mM) in the eluent in comparison to those of protonated tyramine (0.75 mM), benzylamine (0.5 mM), and phenylethylamine (0.5 mM) in the eluent. These chromatograms meant that protonated tyramine was the most favorable eluent ion in the IC−IPD for these mono− and divalent cations. However, a further study was required for complete separation of these cations on the Pia Seed 5S−60−SIL column.

18−Crown−6 (1,4,7,10,13,16−hexaoxacyclooctadecane) forms stable complexes with many cations [32, 33]. The addition of 18−crown−6 to acidic solution as the eluent is often carried out, for improving peak resolution between these mono− and divalent cations on weakly acidic cation−exchange resin columns [34, 35].

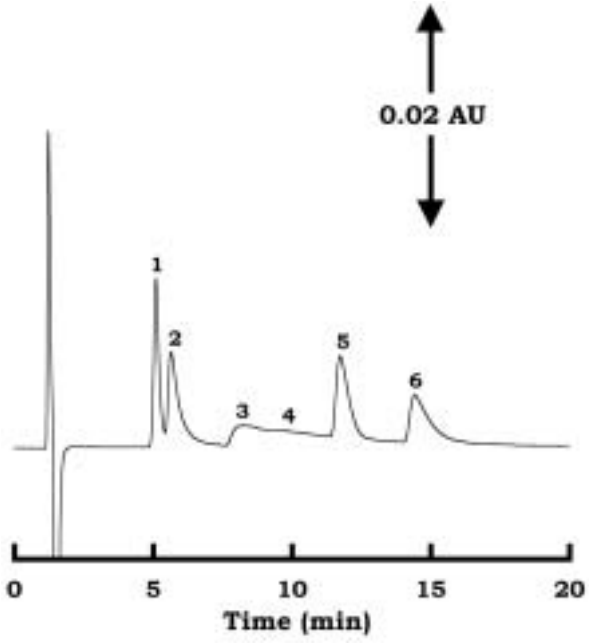

Figure 1 A

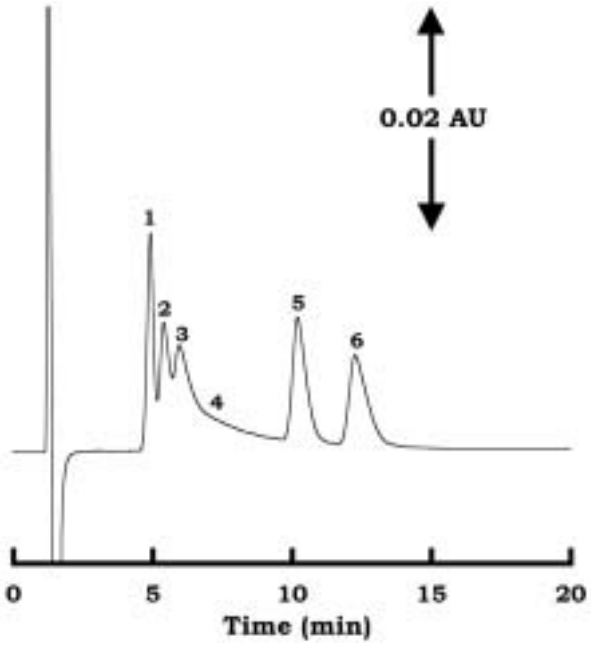

Figure 1 B

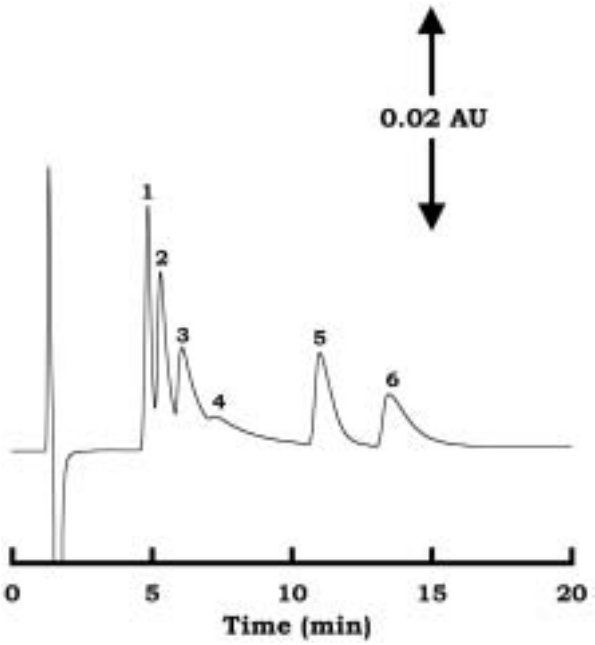

Figure 1 C

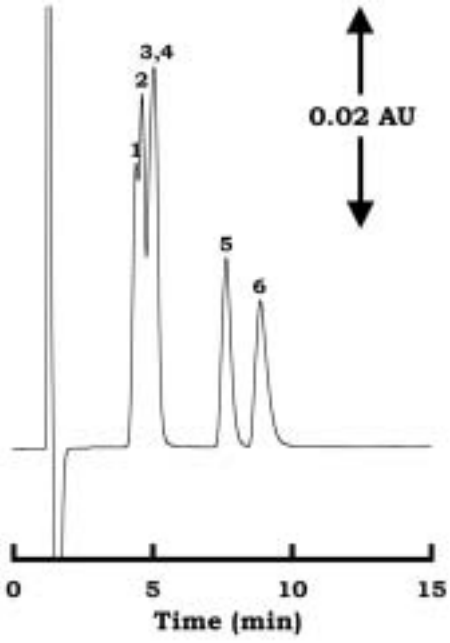

Figure 1 D

Figure 1. Chromatograms of mono− and divalent cations on various silica gel columns with tyramine as eluent

Column : (A) Nucleosil 50−5, (B) Super Micro Bead Silica Gel B−5, (C) Develosil 60−5, (D) Pia Seed 5 S−60−SIL,

Column size: 150 mm × 4.6 mm i.d., Column temperature : 35 ℃,

Eluent : (A) 1.0 mM tyramine−0.25 mM oxalic acid at pH 5.0, (B) 0.75 mM tyramine−0.25 mM oxalic acid at pH 5.0, (C) 1.5 mM tyramine−0.25 mM oxalic acid at pH 5.0, (D) 0.75 mM tyramine−0.25 mM oxalic acid at pH 5.0, The pH of eluents was adjusted using 1 M HNO_3.

Flow rate : 1 ml min^{-1}, Detection : Indirect−UV at (A) 270, (B) 275, (C) 265, and (D) 275 nm, Injection volume : 20 μl,

Sample concentration : (A), (B) and (D) 0.2 mM for monovalent cations and 0.1 mM for divalent cations, (C) 0.4 mM for monovalent cations and 0.2 mM for divalent cations

Peaks : 1 = Li^+, 2 = Na^+, 3 = NH_4^+, 4 = K^+, 5 = Mg^{2+}, and 6 = Ca^{2+}

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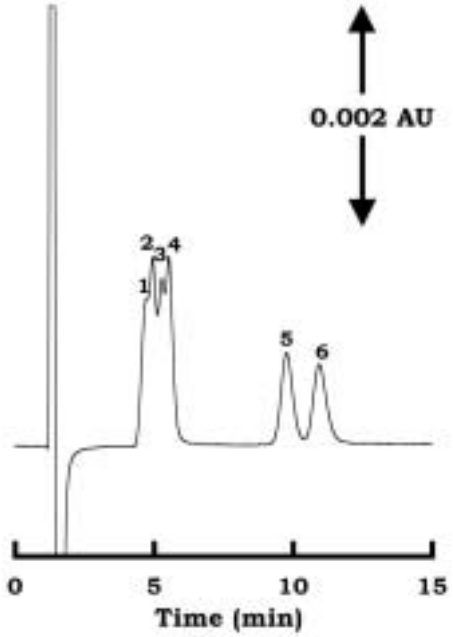

Figure 2 A

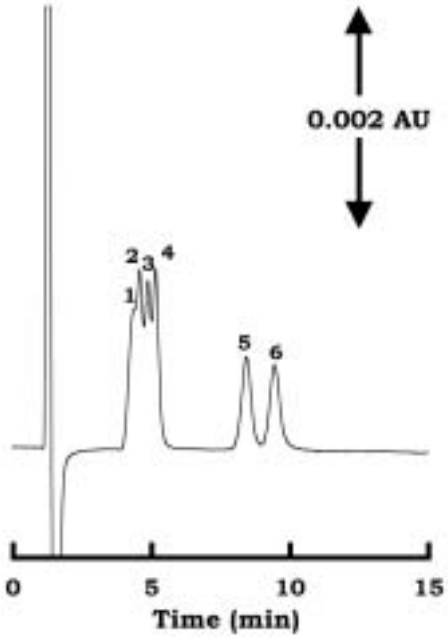

Figure 2 B

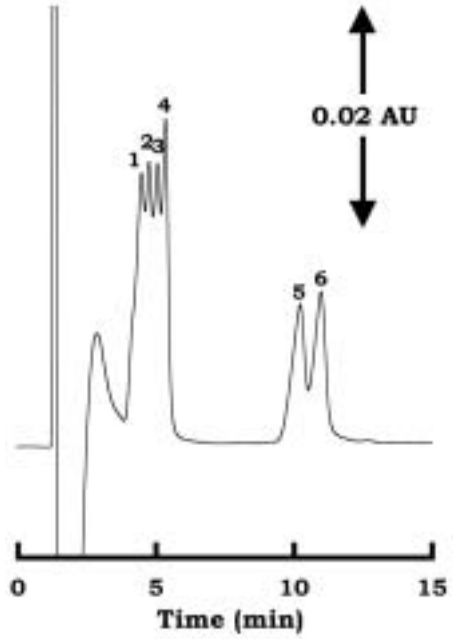

Figure 2 C

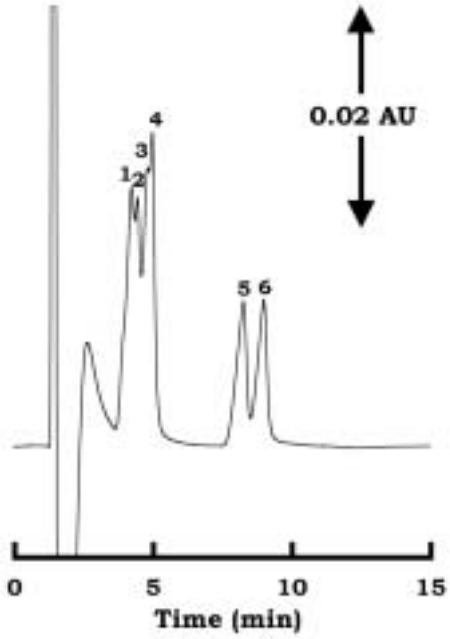

Figure 2 D

Figure 2. Chromatograms of mono− and divalent cations on Pia Seed 5S−60−SIL column with various aromatic monoamines as eluents

Column: Pia Seed 5S−60−SIL

Eluent : (A) 0.5 mM benzylamine−0.25 mM oxalic acid at pH 5.0, (B) 0.5 mM phenylethylamine−0.25 mM oxalic acid at pH 5.0, (C) 0.25 mM 2−methylpyridine−0.1 mM oxalic acid at pH 5.0, (D) 0.25 mM 2,6−dimethylpyridine−0.1 mM oxalic acid at pH 5.0,

The pH of eluents was adjusted using 1 M HNO_3.

Detection : Indirect−UV at (A) 256, (B) 257, (C) 253, (D) 257 nm,

Sample concentration : (A) and (B) 0.2 mM for monovalent cations and 0.1 mM for divalent cations, (C) and (D) 0.1 mM for monovalent cations and 0.05 mM for divalent cations,

Peaks : 1 = Li^+, 2 = Na^+, 3 = NH_4^+, 4 = K^+, 5 = Mg^{2+}, and 6 = Ca^{2+}.

Other chromatographic conditions are as for in Figure 1.

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Therefore, the addition of 18−crown−6 to 0.75 mM tyramine−0.25 mM oxalic acid at pH 5.0 as the eluent was carried out for complete separation of these mono− and divalent cations on the Pia Seed 5S−60−SIL column. Figure 3 shows the relationship between the concentration of 18−crown−6 in the eluent and the retention volumes of these cations. Figure 4 shows chromatogram of these cations with 0.75 mM tyramine−0.25 mM oxalic acid at pH 5.0 containing 1.5 mM 18−crown−6 as the eluent.

As shown in Figure 3, with changing the concentration of 18−crown−6 in the eluent, the retention volumes of these cations also changed. As for the monovalent cations, with increasing the concentration of 18−crown−6, (a) the retention volumes of Li^+ slightly decreased, (b) the retention volumes of NH_4^+ and Na^+ increased initially and then remained almost the same, and (C) the retention volumes of K^+ increased drastically. The order of the increase in the retention volumes of the monovalent cations ($Li^+ < Na^+ < NH_4^+ << K^+$) was good agreement with that of the stabilities of complexes formed between the monovalent cations and 18−crown−6 (log K_{Na^+}= 0.8, Log K_{NH4^+} = 1.23, and Log K_{K^+} = 2.03) [33]. This result meant that 18−crown−6 seemed to act as a selective cation−exchanger (selective retention modifier) for the monovalent cations. Complete separation of the monovalent cations was achieved at the concentration of 18−crown−6 ≥ 1.5 mM. In contrast, as for the divalent cations, with increasing the concentration of 18−crown−6, the retention volumes slightly decreased. The decrease might be due mainly to both (a) low stabilities of complexes formed between the divalent cations and 18−crown−6 (Log $K_{Ca^{2+}} < 0.8$) [33], and (b) slight decrease in the cation−exchange capacity caused by 18−crown−6 adsorbed on the surface of the silica gel. As shown in Figure 4, complete separation of these mono− and divalent cations was achieved in 20 min with 0.75 mM tyramine−0.25 mM oxalic acid at pH 5.0 containing 1.5 mM 18−crown−6 as the eluent.

Various analytical performance parameters were investigated under the optimum IC−IPD conditions (eluent : 0.75 mM tyramine −0.25 mM oxalic acid−1.5 mM 18−crown−6 at pH 5.0). Table 4 lists the detection limits (signal−to−noise ratio of 3, injection volume of 20 μl) of these mono− and divalent cations. Highly sensitive indirect−photometric detection at 275 nm was achieved. This is because these cations were detected by indirect−photometrically mechanism, in which they displace the protonated tyramine, having high molar extinction coefficient [1.5×10^3 $(mol\ cm)^{-1}$ at 275 nm],

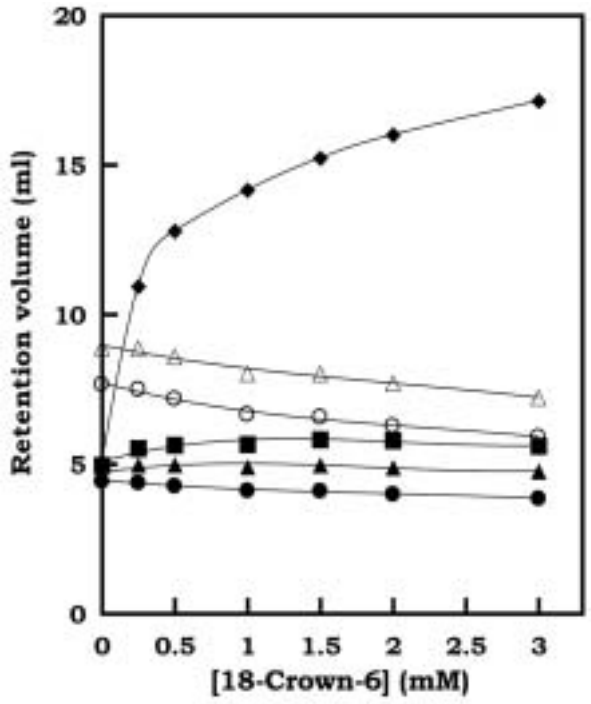

Figure 3. Effect of concentration of 18−crown−6 in 0.75 mM tyramine−0.25 mM oxalic acid at pH 5.0 as eluent on retention volumes of mono− and divalent cations on Pia Seed 5S−60−SIL column

Column : Pia Seed 5S−60−SIL, Eluent: 0−3 mM 18−crown−6 in 0.75 mM tyramine−0.25 mM oxalic acid at pH 5.0, Detection : Indirect−UV at 275 nm, Sample : 0.2 mM for monovalent cations and 0.1 mM for divalent cations, Symbols : ●= Li^+, ▲= Na^+, ■= NH_4^+, ◆= K^+, ○= Mg^{2+}, and △= Ca^{2+}.

Other chromatographic conditions are as for in Figure 2.

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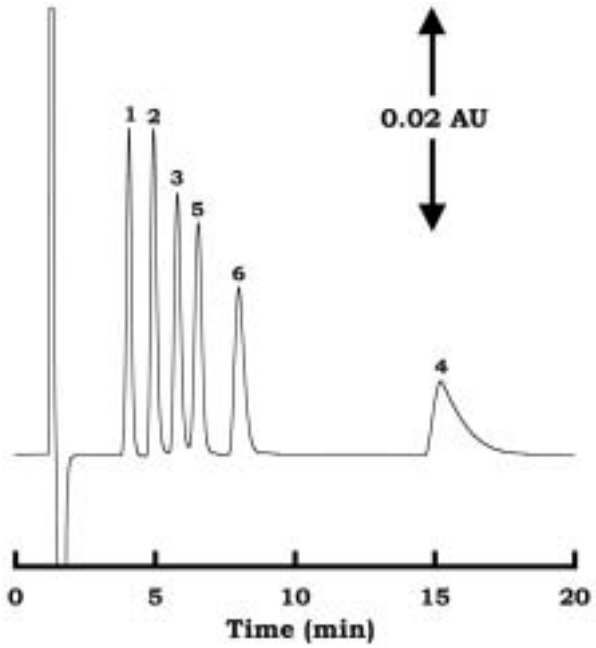

Figure 4. Chromatograms of mono− and divalent cations on Pia Seed 5S−60−SIL column with 0.75 mM tyramine−0.25 mM oxalic acid−1.5 mM 18−crown−6 at pH 5.0 as eluent

Eluent : 0.75 mM tyramine−0.25 mM oxalic acid−1.5 mM 18−crown−6 at pH 5.0, Peaks : 1 = Li^+, 2 = Na^+, 3 = NH_4^+, 4 = K^+, 5 = Mg^{2+}, and 6 = Ca^{2+}.

Other chromatographic conditions are as for in Figure 3.

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Table 4. Detection limits (injection volume of 20 μl, signal−to noise ratio of 3) of mono− and divalent cations with 0.75 mM tyramine−0.25 mM oxalic acid−1.5 mM 18−crown −6 at pH 5.0 as eluent

Cation	Detection limits	
	(μM)	(ng ml^{-1})
Li^+	0.31	2.2
Na^+	0.32	7.3
NH_4^+	0.40	7.1
K^+	1.4	55
Mg^{2+}	0.22	5.4
Ca^{2+}	0.31	12

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from the eluent. Calibration graphs obtained by plotting peak area against the concentration of these cations were linear ($r^2 \geq 0.99$) in the concentration range between 0.005 and 1.0 mM. The relative standard deviations of the chromatographic peak areas, whose concentrations were 0.2 mM for the monovalent cations and 0.1 mM for the divalent cations, were < 0.7 % (n=8). Reproducible chromatograms were obtained during repeated chromatographic runs.

From these above results, it was demonstrated that the pure silica gel (Pia Seed 5S−60−SIL) acted as the advanced cation−exchange stationary phase in the IC−IPD for common mono− and divalent cations using tyramine−oxalic acid containing 18−crown−6 as the eluent.

3.2. Separation and indirect−conductimetric detection mono− and divalent cations on Pia Seed 5S−60−SIL column with dilute oxalic acid as eluent

A silica gel (Develosil 30−3) was successfully applied as a cation−exchange stationary phase in IC with conductimetric detection (IC−CD) for major mono− and divalent cations (Na^+, NH_4^+, K^+, Mg^{2+} and Ca^{2+}) with lithium oxalate as the eluent [13]. Then, chromatographic behavior of the cations on the Pia Seed 5S−60−SIL column was investigated with lithium oxalate as the eluent. Figures 5A and B show chromatograms of the cations with (A) 0.5 mM lithium oxalate at pH 5.0, and (B) 0.5 mM lithium oxalate at pH 5.0 containing 0.75 mM 18−crown−6, as the eluents. The pH of the eluents was adjusted with 1 M HNO_3.

As shown in Figure 5A, both incomplete separation of the monovalent cations and complete separation of the divalent cations were achieved. The complete separation was due mainly to oxalate in the eluent [12, 13]. The incomplete separation was due mainly to physical properties (particle size, pore size and surface area, etc.) of the Pia Seed 5S−60−SIL silica gel. Unfortunately, complete separation of the mono− and divalent cations could not be achieved in a

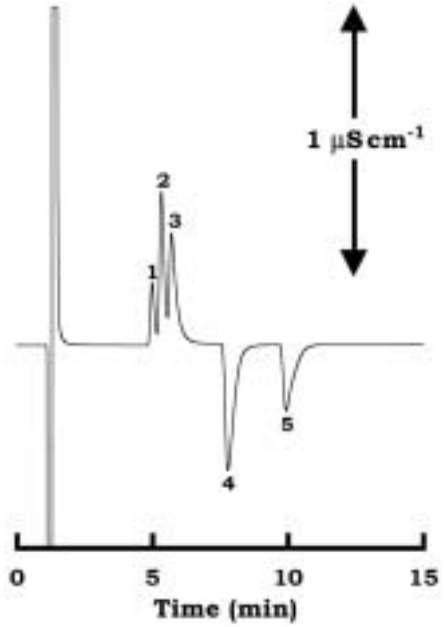

Figure 5 A

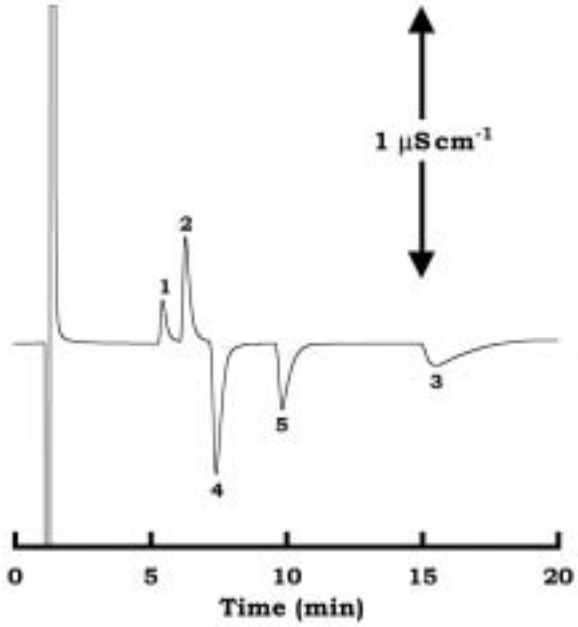

Figure 5 B

Figure 5. Chromatograms of mono− and divalent cations on Pia Seed 5S−60−SIL column with (A) 0.5 mM lithium oxalate at pH 5.0, and (B) 0.5 mM lithium oxalate−0.75 mM 18−crown−6 at pH 5.0, as eluents

Eluent: (A) 0.5 mM lithium oxalate at pH 5.0, (B) 0.5 mM lithium oxalate −0.75 mM 18−crown−6 at pH 5.0, The pH of eluents was adjusted using 1 M HNO_3.

Detection: Conductivity, Sample concentration: 0.2 mM for monovalent cations and 0.1 mM for divalent cations, Peaks: 1 = Na^+, 2 = NH_4^+, 3 = K^+, 4 = Mg^{2+}, and 5 = Ca^{2+}.

Other chromatographic conditions are as for in Figure 4.

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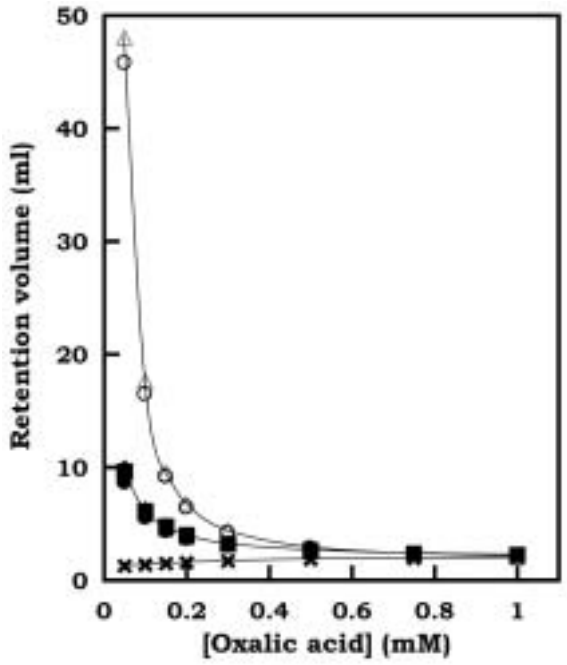

Figure 6. Effect of concentration of oxalic acid in eluent on retention volumes of mono− and divalent cations on Pia Seed 5S−60−SIL column

Eluent : 0.05−1 mM oxalic acid, Detection : Indirect−conductivity, Sample concentration : 0.1 mM for monovalent cations and 0.05 mM for divalent cations, Symbols : ✖= water dip, ●= Li^+, ▲= Na^+, ■= NH_4^+, ◆= K^+, ○= Mg^{2+}, and △= Ca^{2+}.

Other chromatographic conditions are as for in Figure 5.

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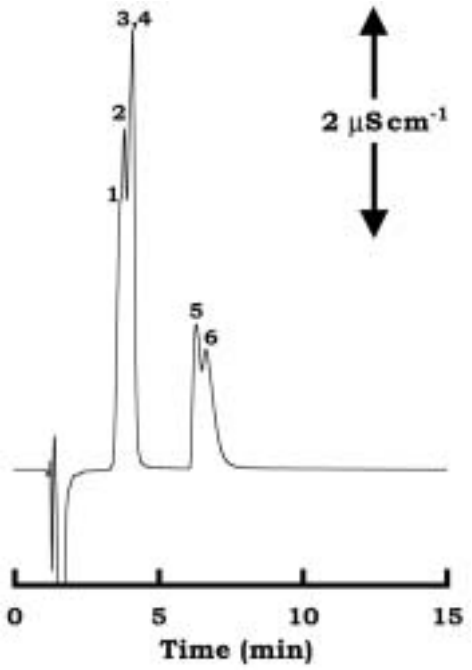

Figure 7. Chromatograms of mono− and divalent cations on Pia Seed 5S−60−SIL column with 0.2 mM oxalic acid at pH 3.6 as eluent

Eluent : 0.2 mM oxalic acid at pH 3.6, Peaks : 1 = Li^+, 2 = Na^+, 3 = NH_4^+, 4 = K^+, 5 = Mg^{2+}, and 6 = Ca^{2+}.

Other chromatographic conditions are as for in Figure 6.

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reasonable period of time (< 20 min) with lithium oxalate at pH 5.0 as the eluent. The addition of 18−crown−6 to 0.5 mM lithium oxalate at pH 5.0 as the eluent was very effective way for improving peak resolution between the monovalent cations. As shown in Figure 5B, complete separation of the cations was achieved in 20 min with 0.5 mM lithium oxalate at pH 5.0 containing 0.75 mM 18−crown−6 as the eluent. However, since Na^+, and NH_4^+ were detected direct−conductimetrically, and K^+, Mg^{2+}, and Ca^{2+} were detected indirect−conductimetrically, chromatogram was very complicated. Furthermore, due to very small difference in equivalent conductivity between lithium ion (Li^+) as the eluent ion and the analyte cations, the conductimetric detection sensitivities resulted in very low.

Dilute oxalic acid was tested as the eluent in the IC−CD with the Pia Seed 5S−60−SIL column for common mono− and divalent cations (Li^+, Na^+, NH_4^+, K^+, Mg^{2+}, and Ca^{2+}), in order to eliminate these above drawbacks. Figure 6 shows the relationship between the concentration of oxalic acid in the eluent and the retention volumes of these cations. Figure 7 shows chromatogram of these cations with 0.2 mM oxalic acid at pH 3.6 as the eluent.

As shown in Figure 6, the Pia Seed 5S−60−SIL silica gel showed cation−exchange behavior at the concentration of oxalic acid in the eluent < 1 mM. With increasing the concentration of oxalic acid, the retention volumes of these cations decreased drastically. This is due to both (a) a decrease in the cation−exchange capacity caused by suppressing the dissociation of the silanol group on the surface of the silica gel as cation−exchanger, and (b) an increase in the concentration of hydronium ion (H^+) as eluent ion in the eluent. As shown in Figure 7, using 0.2 mM oxalic acid at pH 3.6 as the eluent, although complete group separation between these mono− and divalent cations was achieved in 10 min, peak resolutions between the monovalent cations and between the divalent cations were very poor. These results suggested that the Pia Seed 5S−60−SIL column could be utilized in the IC−CD for these cations with dilute oxalic acid as the eluent. However, a further study was required for the complete separation of these cations on the Pia Seed 5S−60−SIL column.

The addition of 18−crown−6 to 0.2 mM oxalic acid as the eluent was carried out for improving peak resolution between these mono− and divalent cations. Figure 8 shows the relationship between the concentration of 18−crown−6 in the eluent and the retention volumes of these cations. Figure 9 shows chromatogram of these cations with 0.2 mM oxalic acid at pH 3.6 containing 4 mM 18−crown−6 as the eluent.

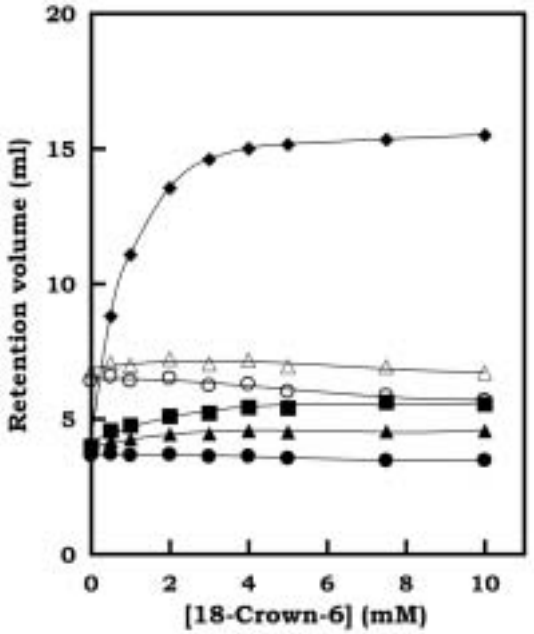

Figure 8. Effect of concentration of 18−crown−6 in 0.2 mM oxalic acid at pH 3.6 as eluent on retention volumes of mono− and divalent cations on Pia Seed 5S−60−SIL column

Eluent : 0−10 mM 18−crown−6 in 0.2 mM oxalic acid, Symbols : ●= Li^+, ▲= Na^+, ■= NH_4^+, ◆= K^+, ○= Mg^{2+}, and △= Ca^{2+}.

Other chromatographic conditions are as for in Figure 7.

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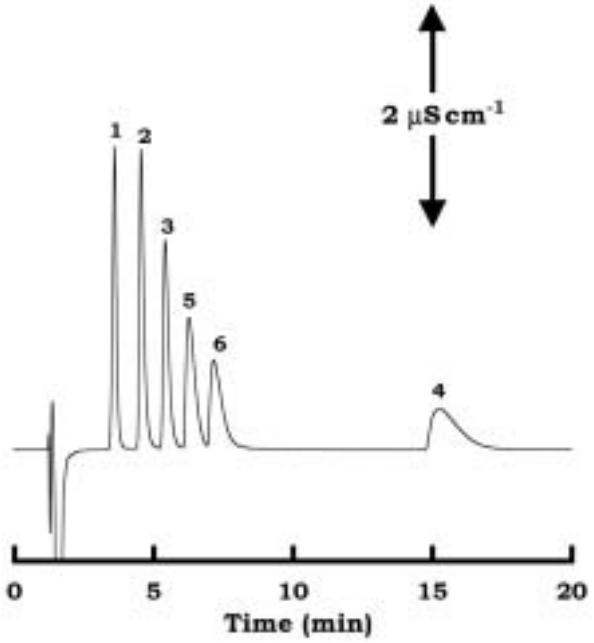

Figure 9. Chromatograms of mono− and divalent cations on Pia Seed 5S−60−SIL column with 0.2 mM oxalic acid−4 mM 18−crown−6 at pH 3.6 as eluent

Eluent : 0.2 mM oxalic acid−4 mM 18−crown−6 at pH 3.6, Peaks : 1 = Li^+, 2 = Na^+, 3 = NH_4^+, 4 = K^+, 5 = Mg^{2+}, and 6 = Ca^{2+}.

Other chromatographic conditions are as for in Figure 8.

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Table 5. Detection limits (injection volume of 20 μl, signal−to noise ratio of 3) of mono− and divalent cations with 0.2 mM oxalic acid−4 mM 18−crown−6 at pH 3.6 as eluent

Cation	Detection limits	
	(μM)	(ng ml^{-1})
Li^+	0.15	0.99
Na^+	0.16	3.7
NH_4^+	0.21	3.9
K^+	1.0	39
Mg^{2+}	0.17	4.2
Ca^{2+}	0.25	10

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As shown in Figure 8, with changing the concentration of 18−crown−6 in the eluent, the retention volumes of these cations changed individually. This result meant that 18−crown−6 seemed to act as a selective cation−exchanger (selective retention modifier) for these cations under the IC−CD conditions. With increasing the concentration of 18−crown−6, the peak resolutions were improved largely. As a result, as shown in Figure 9, complete separation of these mono− and divalent cations was achieved in 20 min with 0.2 mM oxalic acid at pH 3.6 containing 4 mM 18−crown−6 as the eluent.

Various analytical performance parameters were investigated under the optimum IC−CD conditions (eluent : 0.2 mM oxalic acid −4 mM 18−crown−6 at pH 3.6). Table 5 lists the detection limits (signal−to−noise ratio of 3, injection volume of 20 μl) of these mono− and divalent cations. Highly sensitive indirect−conductimetric detection was achieved. This is because these cations were detected by indirect−conductivity mechanism, in which they displace the hydronium ion, having the highest limiting equivalent ionic conductance, from the eluent. Calibration graphs obtained by plotting peak area against the concentration of these cations were linear ($r^2 \geq 0.99$) in the concentration range between 0.005 and 0.5 mM for the monovalent cations and between 0.005 and 0.3 mM for the divalent cations. Somewhat narrow linear range was attributed to be very low cation−exchange capacity of the Pia Seed 5S−60−SIL column under the optimum IC−CD conditions. The relative standard deviations of the chromatographic peak areas, whose concentration were 0.1 mM for monovalent cations and 0.05 mM for the divalent cations, were < 1.2 % (n=10). Reproducible chromatograms were obtained during repeated chromatographic runs.

From these above results, it was demonstrated that the pure silica gel (Pia Seed 5S−60−SIL) also acted as the advanced cation−

exchange stationary phase in the IC−CD for common mono− and divalent cations with dilute oxalic acid containing 18−crown−6 as the eluent.

3.3. Separation of mono− and divalent cations on calcinated Pia Seed 5S−60−SIL columns

Calcination (heat treatment) is easy and effective way for the modification of adsorption properties of silica gel for organic compounds [36]. Then, chromatographic behavior of common mono− and divalent cations (Li^+, Na^+, NH_4^+, K^+, Mg^{2+}, and Ca^{2+}) on columns (150 × 4.6 mm i.d.) packed with the Pia Seed 5S−60−SIL silica gels calcinated at 200, 400, 600, 800 and 1000 ℃ for 5 h (denoted Pia−Seed−200, −400, −600, −800, and −1000) was investigated, for the expansion the utility of the pure silica gel in IC for cations. Table 3 shows physical properties of the calcinated Pia Seed 5S−60−SIL silica gels. Firstly, chromatographic behavior of these mono− and divalent cations on the calcinated Pia Seed 5S−60−SIL columns was investigated with 0.75 mM tyramine−0.25 mM oxalic acid at pH 5.0 as the eluent. Figures 10A−C show chroma-

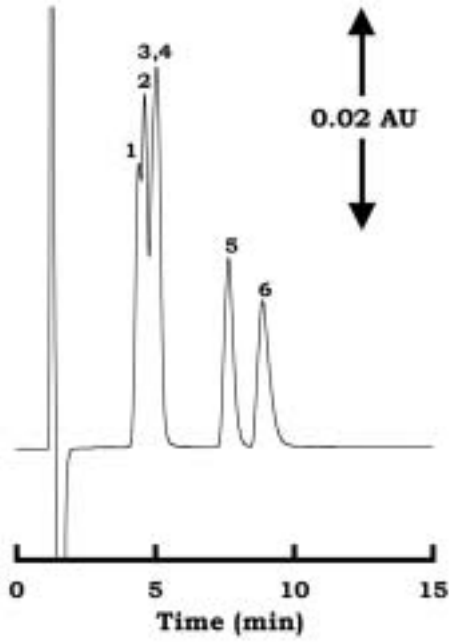

Figure 10 B

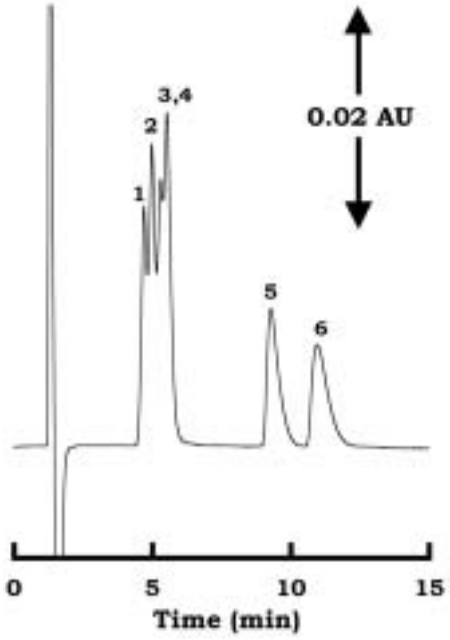

Figure 10 A

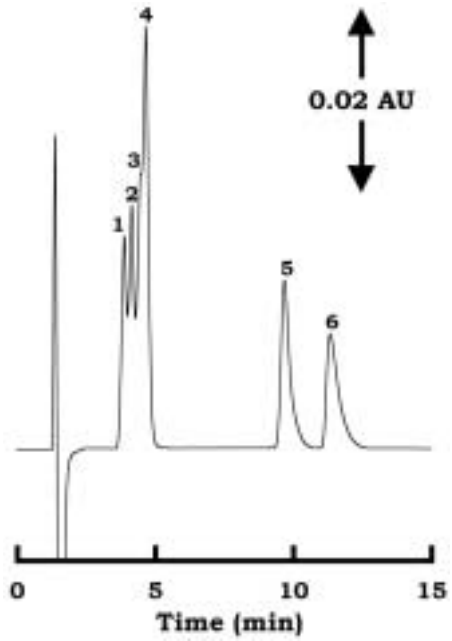

Figure 10 C

Figure 10. Chromatograms of mono− and divalent cations on calcinated Pia Seed 5S−60−SIL silica gel columns with 0.75 mM tyramine−0.25 mM oxalic acid at pH 5.0 as eluent.

Column : (A) Pia Seed 5S−60−SIL calcinated at 200 ℃ for 5 h (Pia Seed−200), (B) Pia Seed 5S−60−SIL calcinated at 600 ℃ for 5 h (Pia Seed−600), (C) Pia Seed 5S−60−SIL calcinated at 1000 ℃ for 5 h (Pia Seed−1000),

Eluent : 0.75 mM tyramine−0.25 mM oxalic acid at pH 5.0, The pH of eluents was adjusted with 1 M HNO_3.

Detection : Indirect−UV at 275 nm, Sample concentration : 0.2 mM for monovalent cations and 0.1 mM for divalent cations,

Peaks : 1 = Li^+, 2 = Na^+, 3 = NH_4^+, 4 = K^+, 5 = Mg^{2+}, and 6 = Ca^{2+}.

Other chromatographic conditions are as for in Figure 9.

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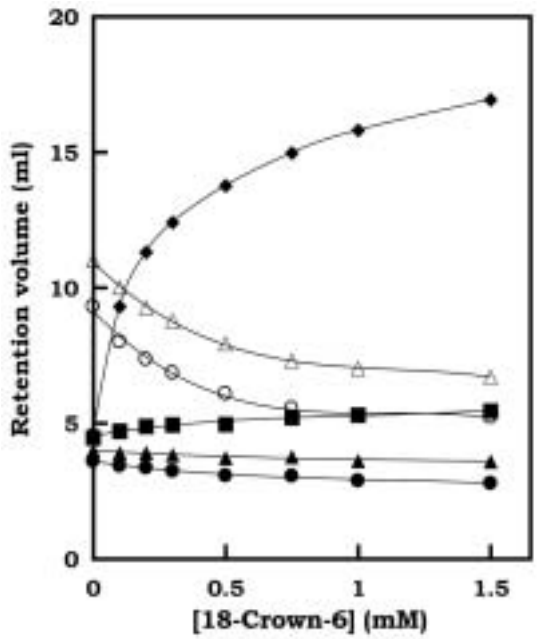

Figure 11. Effect of concentration of 18−crown−6 in 0.75 mM tyramine−0.25 mM oxalic acid at pH 5.0 as eluent on retention volumes of mono− and divalent cations on Pia Seed−1000 column

Column : Pia Seed−1000, Eluent 0−1.5 mM 18−crown−6 in 0.75 mM tyramine−0.25 mM oxalic acid at pH 5.0, Symbols : ●= Li^+, ▲= Na^+, ■= NH_4^+, ◆= K^+, ○= Mg^{2+}, and △= Ca^{2+}.
Other chromatographic conditions are as for in Figure 10.
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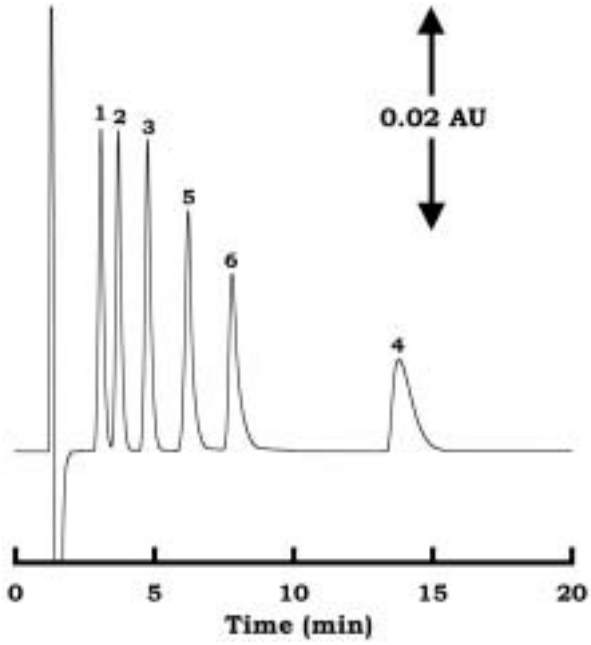

Figure 12. Chromatograms of mono− and divalent cations on Pia Seed−1000 column with 0.75 mM tyramine−0.25 mM oxalic acid−0.5 mM 18−crown−6 at pH 5.0 as eluent

Eluent : 0.75 mM tyramine−0.25 mM oxalic acid−0.5 mM 18−crown−6 at pH 5.0, Peaks : 1 = Li^+, 2 = Na^+, 3 = NH_4^+, 4 = K^+, 5 = Mg^{2+}, and 6 = Ca^{2+}.
Other chromatographic conditions are as for in Figure 11.
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tograms of these cations on (A) Pia Seed−200, (B) Pia Seed−600, and (C) Pia Seed−1000 columns.

As shown in Figures 10A−C, both incomplete separation of the monovalent cations and complete separation of the divalent cations were achieved on these columns in 13 min. Chromatographic behavior of these cations on these columns was very similar. These chromatograms indicated that the calcination was almost no effect for improving peak resolution between these cations with 0.75 mM tyramine−0.25 mM oxalic acid at pH 5.0 as the eluent.

Next, chromatographic behavior of these cations on the Pia Seed−1000 column was investigated in detail with 0.75 mM tyramine−0.25 mM oxalic acid at pH 5.0 containing 18−crown−6 as the eluent. Figure 11 shows the relationship between the concentration of 18−crown−6 in the eluent and the retention volumes of these cations. Figure 12 shows chromatogram of these cations with 0.75 mM tyramine−0.25 mM oxalic acid at pH 5.0 containing 0.5 mM 18−crown−6 as the eluent.

As shown in Figure 11, with changing the concentration of 18−crown−6 in the eluent, the retention volumes of these cations also changed. With increasing the concentration of 18−crown−6 (in the concentration range of 18−crown−6 between 0 and 0.5 mM), peak resolution between these cations was improved. As a result, as shown in Figure 12, complete separation of these cations was achieved with 0.75 mM tyramine−0.25 mM oxalic acid at pH 5.0 containing 0.5 mM 18−crown−6 as the eluent. The suitable concentration of 18−crown−6 on the Pia Seed−1000 column (0.5 mM) was considerably lower than that on the Pia Seed 5S−60−SIL column (1.5 mM), as shown in Figure 4. These results suggested that the effect of 18−crown−6 as the retention modifier for these cations enhanced on the Pia Seed−1000 column. Then, the amounts of 18−crown−6 adsorbed on the calcinated Pia Seed 5S−60−SIL columns were determined with 0.75 mM tyramine−0.25 mM oxalic acid at pH 5.0 containing 1.5 mM 18−crown−6 as the eluent. Figure 13 show breakthrough curves of the calcinated Pia Seed 5S−60−SIL columns.

As shown in Figure 13, with arising calcination temperature, breakthrough volume of corresponding calcinated Pia Seed 5 S−60−SIL column increased largely. The amounts of 18−crown−6 adsorbed on the Pia Seed−200, −400, −600, −800, and −1000 columns were 9.9, 19, 24, 28, and 30 μmol $column^{-1}$, respectively. The amount of 18−crown−6 adsorbed on the Pia Seed−1000 column reached three times larger than that on the Pia Seed−200 column. This result revealed that (a) the calcination enhanced the affinity of the Pia Seed 5S−60−SIL silica gel for 18−crown−6, and (b) the predominant factor in the effect of 18−crown−6 as the re-

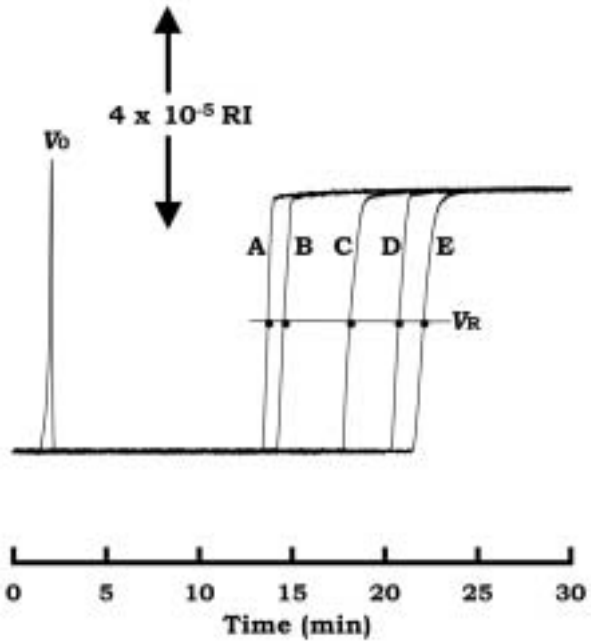

Figure 13. Breakthrough curves of calcinated Pia Seed 5 S−60−SIL columns with 0.75 mM tyramine−0.25 mM oxalic acid at pH 5.0 containing 1.5 mM 18−crown−6 as eluent

Column : (A) Pia Seed−200, (B) Pia Seed−400, (C) Pia Seed−600, (D) Pia Seed−800, (E) Pia Seed−1000

Eluent : 0.75 mM tyramine−0.25 mM oxalic acid−1.5 mM 18−crown−6 at pH 5.0, Detection : Refractive index, Sample : 7.5 mM tyramine−2.5 mM oxalic acid at pH 5.0,

Other chromatographic conditions are as for in Figure 12.

Vo : total dead volume (column void volume + connected tube volume)

V_R : breakthrough volume

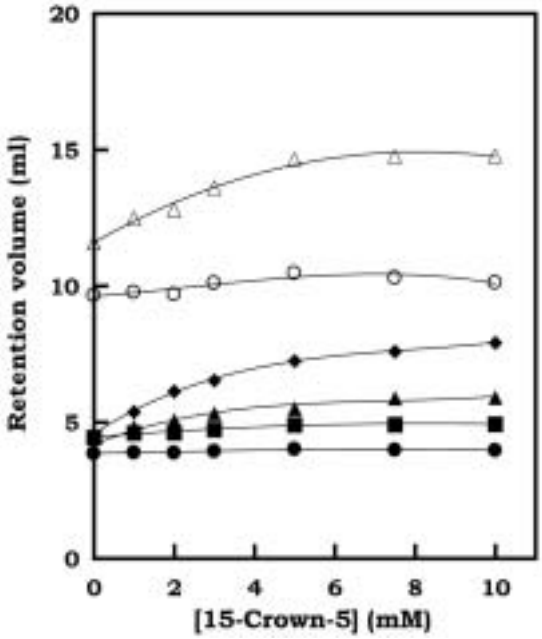

Figure 14. Effect of concentration of 15−crown−5 in 0.75 mM tyramine−0.25 mM oxalic acid at pH 5.0 as eluent on retention volumes of mono− and divalent cations on Pia Seed−1000 column

Column : Pia Seed−1000, Eluent : 0−10 mM 15−crown−5 in 0.75 mM tyramine−0.25 mM oxalic acid at pH 5.0, Detection : Indirect−UV at 275 nm, Sample concentration: 0.2 mM for monovalent cations and 0.1 mM for divalent cations, Symbols : ●= Li^+, ▲= Na^+, ■= NH_4^+, ◆= K^+, ○= Mg^{2+}, and △= Ca^{2+}.

Other chromatographic conditions are as for in Figure 13.

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tention modifier for these cations was not the concentration of 18−crown−6 in the eluent but the amount of 18−crown−6 adsorbed on silica stationary phase under the IC−IPD conditions.

15−Crown−5 also forms complex with many cations [32, 33]. Due to low stabilities of complexes formed with 15−crown−5 and these mono− and divalent cations, the addition of 15−crown−6 to acidic solution as the eluent is not effective for improving peak resolution between these cations on weakly acidic cation−exchange resin columns [35]. Therefore, chromatographic behavior of these cations on the Pia Seed−200 and −1000 columns was investigated with 0.75 mM tyramine−0.25 mM oxalic acid at pH 5.0 containing 15−crown−5 as the eluent. Figure 14 shows the relationship between the concentration of 15−crown−5 in the eluent on the retention volumes of these cations on the Pia Seed−1000 column. Figures 15 A and B show chromatograms of these cations on (A) the Pia Seed−1000, and (B) the Pia Seed−200 columns with 0.75 mM tyramine− 0.25 mM oxalic acid at pH 5.0 containing 5 mM 15−crown−5 as the eluent.

As shown in Figure 14, with increasing the concentration of 15−crown−5 in the eluent, the retention volumes of these cations increased. The order of the increase in the retention volumes of the monovalent cations was $Li^+ < NH_4^+ < Na^+ < K^+$ and that of the divalent cations was $Mg^{2+} < Ca^{2+}$. These orders meant that 15−crown−5 also behaved as a selective cation−exchanger (selective retention modifier) for these cations in the IC−IPD conditions. With increasing the concentration of 15−crown−5, peak resolution between these cations was improved effectively. As a result, as shown in Figure 15 A, excellent separation of these cations was achieved on the Pia Seed−1000 column in 20 min with 0.75 mM tyramine−0.25 mM oxalic acid at pH 5.0 containing 5 mM 15−crown−5 as the eluent. In contrast, as shown in Figure 15 B, the complete separation of the monovalent cations was not achieved on the Pia Seed−200 column with 0.75 mM tyramine−0.25 mM oxalic acid at pH 5.0 containing 5 mM 15−crown−5 as the eluent. When using 0.75 mM tyramine−0.25 mM oxalic acid at pH 5.0 containing 20 mM 15−crown−5 as the eluent, peak resolution between the monovalent cations remained unsatisfactory on the Pia Seed−200 column. Then, the amounts of 15−crown−5 adsorbed on the calcinated Pia Seed 5S−60−SIL columns were determined with 0.75

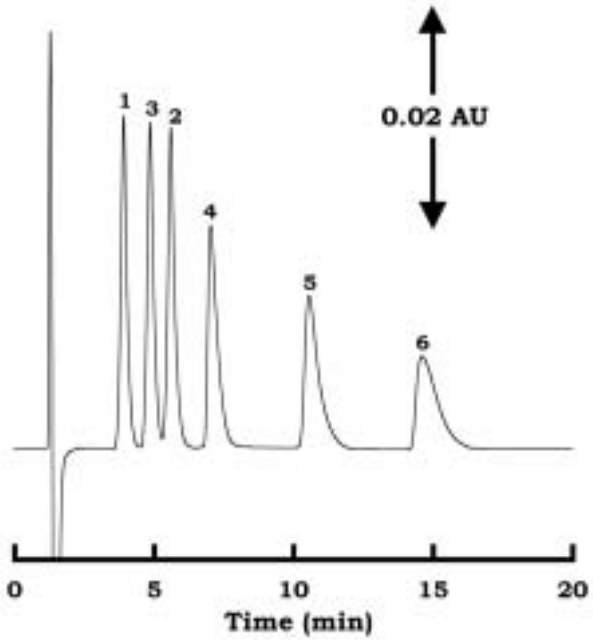

Figure 15 A

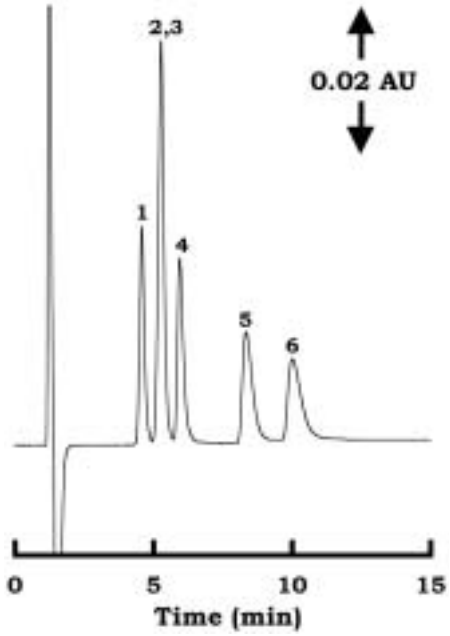

Figure 15 B

Figure 15. Chromatograms of mono− and divalent cations on (A) Pia Seed−1000, and (B) Pia Seed−200 columns with 0.75 mM tyramine−0.25 mM oxalic acid−5 mM 15−crown−5 at pH 5.0 as eluent

Column : (A) Pia Seed−1000, (B) Pia Seed−200, Eluent : 0.75 mM tyramine−0.25 mM oxalic acid−0.5 mM 18−crown−6 at pH 5.0, Peaks : 1 = Li^+, 2 = Na^+, 3 = NH_4^+, 4 = K^+, 5 = Mg^{2+}, and 6 = Ca^{2+}.

Other chromatographic conditions are as for in Figure 14.

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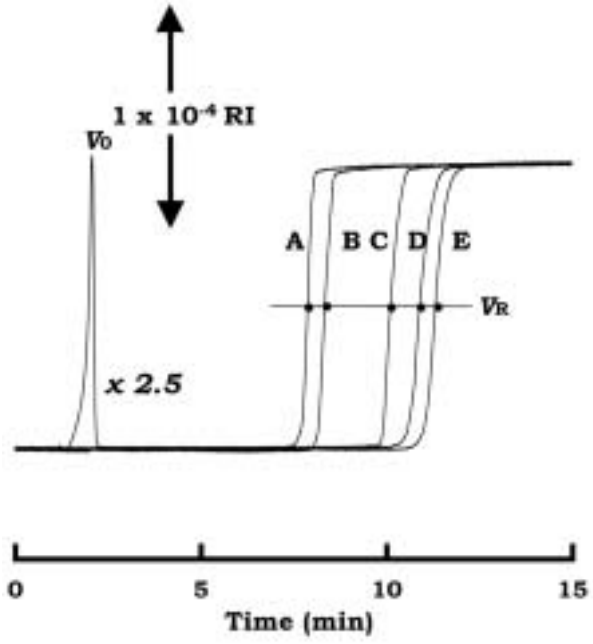

Figure 16. Breakthrough curves of calcinated Pia Seed 5 S−60−SIL columns with 0.75 mM tyramine−0.25 mM oxalic acid−5 mM 15−crown−5 at pH 5.0 as eluent

Column: (A) Pia Seed−200, (B) Pia Seed−400, (C) Pia Seed−600, (D) Pia Seed−800, (E) Pia Seed−1000, Eluent: 0.75 mM tyramine−0.25 mM oxalic acid−5 mM 15−crown−5 at pH 5.0, Detection: Refractive index, Sample: 7.5 mM tyramine−2.5 mM oxalic acid at pH 5.0,

Other chromatographic conditions are as for in Figure 15.

Vo: total dead volume (column void volume + connected tube volume)

V_R: breakthrough volume.

mM tyramine−0.25 mM oxalic acid at pH 5.0 containing 5 mM 15−crown−5 as the eluent. Figure 16 show breakthrough curves of the calcinated Pia Seed 5S−60−SIL columns.

As shown in Figure 16, with arising calcination temperature, breakthrough volume of corresponding calcinated Pia Seed 5S−60−SIL column increased largely. The amounts of 15−crown−5 adsorbed on the Pia Seed−200, −400, −600, −800, and −1000 columns were 19, 32, 40, 44, and 50 μmol $column^{-1}$, respectively. The amount of 15−crown−5 adsorbed on the Pia Seed−1000 column was much larger than that on the Pia Seed−200 column. This result also bore out strongly that the amount of crown ethers adsorbed on the silica stationary phase was the predominant factor in the effect of crown ethers as the retention modifiers for these mono− and divalent cations under the IC−IPD conditions.

Finally, chromatographic behavior of these mono− and divalent on the calcinated Pia Seed 5S−60−SIL columns was investigated with dilute oxalic acid (0.2 mM, pH 3.6) containing crown ethers (18−crown−6 and 15−crown−5) as the eluent. Figures 17 A−C show chromatograms of these cations on the Pia Seed−1000 column with (A) 0.2 mM oxalic acid, (B) 0.2 mM oxalic acid containing 0.4 mM 18−crown−6, and (C) 0.2 mM oxalic acid containing 4

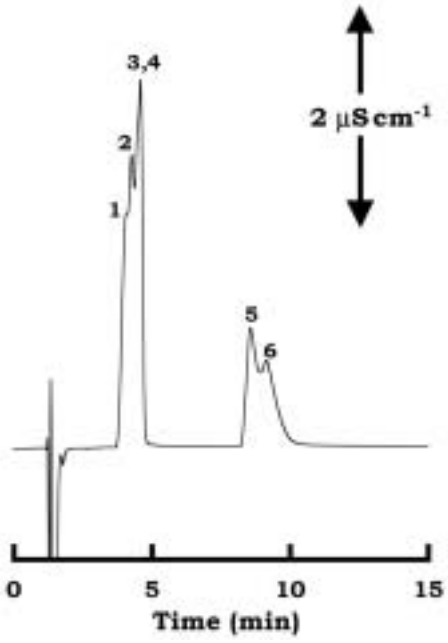

Figure 17 A

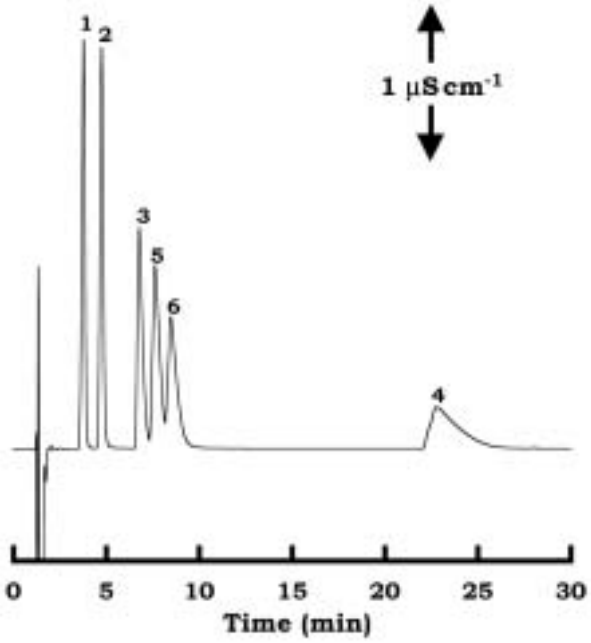

Figure 17 B

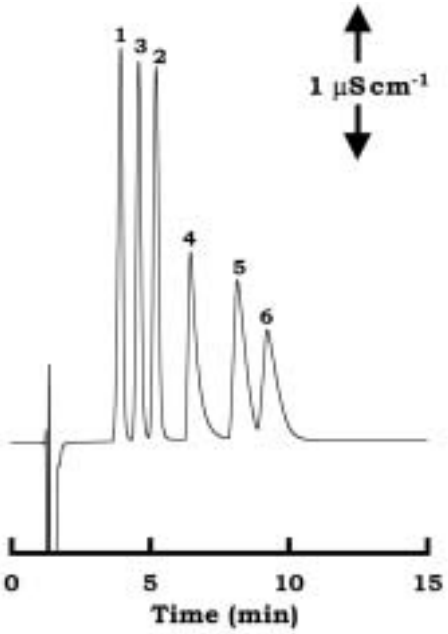

Figure 17 C

Figure 17. Chromatograms of mono− and divalent cations on Pia Seed−1000 column with (A) 0.2 mM oxalic acid, (B) 0.2 mM oxalic acid−0.4 mM 18−crown−6, and (C) 0.2 mM oxalic acid−4 mM 15−crown−5, as eluents.

Column : Pia Seed−1000, Eluent: (A) 0.2 mM oxalic acid at pH 3.6, (B) 0.2 mM oxalic acid−0.4 mM 18−crown−6 at pH 3.6, (C) 0.2 mM oxalic acid−4 mM 15−crown−5 at pH 3.6, Detection : Indirect−conductivity, Sample concentration : 0.1 mM for monovalent cations and 0.05 mM for divalent cations, Peaks : 1 = Li^+, 2 = Na^+, 3 = NH_4^+, 4 = K^+, 5 = Mg^{2+}, and 6 = Ca^{2+}.

Other chromatographic conditions are as for in Figure 16.

mM 15−crown−5, as the eluents.

As shown in Figure 17 A, poor peak resolutions between the monovalent cations and between the divalent cations were obtained with 0.2 mM oxalic acid as the eluent. The addition of crown ethers to 0.2 mM oxalic acid as the eluent was very effective for improving the peak resolutions. This is because crown ethers was adsorbed on the silica stationary phase at first and then acted as selective cation−exchangers (selective retention modifiers) for these cations. As shown in Figure 17 B, good separation of these cations was achieved with 0.2 mM oxalic acid containing 0.4 mM 18−crown−6 as the eluent. The concentration of 18−crown−6 on the Pia Seed−1000 column (0.4 mM) was much lower than that on the Pia Seed 5S−60−SIL column (4 mM), as shown in Figure 9. As shown in Figure 17 C, excellent separation of these cations was also achieved with 0.2 mM oxalic acid containing 4 mM 15−crown −5 as the eluent. In contrast, the addition of 40 mM 15−crown−5 to the eluent was requited for good separation of these cations on the Pia Seed−200 column.

From these above results, it was revealed that the calcinated Pia Seed 5S−60−SIL silica gels, especially Pia Seed−1000, acted as advanced cation−exchange stationary phases for common mono− and divalent cations in both (a) IC−IPD with aromatic monoamine (tyramine)−oxalic acid at pH 5.0 containing crown ethers as the eluent, and (b) IC−CD with dilute oxalic acid containing crown ethers as the eluent.

4. Conclusions

Effectiveness of a pure silica gel (Pia Seed 5 S−60−SIL), synthesized by the hydrolysis of pure tetraethoxysiliane [$Si(OCH_2CH_3)_4$] as a cation−exchange stationary phase in ion chromatography (IC) for common mono− and divalent cations (Li^+, Na^+, NH_4^+, K^+, Mg^{2+}, and Ca^{2+}) was described. Due to the inert nature of the pure silica gel for aromatic monoamines, the Pia Seed 5S−60−SIL silica gel acted as an advanced cation−exchange stationary phase in IC with indirect−photometric detection for these cations using aromatic monoamines as the eluents. The Pia Seed 5S−60−SIL silica gel also behaved as an advanced cation−exchange stationary phase in IC with conductimetric detection for these cations using dilute oxalic acid as the eluent. Excellent simultaneous separation and highly sensitive detection for these cations were achieved in 20 min on a Pia Seed 5S−60−SIL column (150 mm × 4.6 mm i.d.) with (a) 0.75 mM tyramine [4−(2−aminoethyl)phenol]−0.25 mM oxalic acid at pH 5.0 containing 1.5 mM 18−crown−6 (1,4,7,10,13,16−hexaoxacyclooctadecane) as the eluent, or (b) 0.2 mM oxalic acid at pH 3.6 containing 4 mM 18−crown−6 as the eluent.

Effectiveness of calcinated Pia Seed 5S−60−SIL silica gels as cation−exchange stationary phases in IC for common mono− and divalent cations was also described. Calcination enhanced the affinity of the Pia Seed 5S−60−SIL silica gel for crown ethers [18−crown−6 and 15−crown−5 (1,4,7,10,13,16−hexaoxacyclooctadecane)] and, as a consequence, the effect of crown ethers as the selective cation−exchangers (selective retention modifiers) for these cations enhanced effectively. Calcination expanded largely the utility of the Pia Seed 5S−60−SIL silica gel in IC for these mono− and divalent cations.

The pure silica gel (Pia Seed 5S−60−SIL) is one of the most favorable cation−exchange stationary phases in IC for common mono− and divalent cations.

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