Focusing Review

Separation of Cationic Species by Ion Chromatography Using Zirconium−Modified Silica Gel as Stationary Phase

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Abstract

This review article demonstrates the effectiveness of zirconium−modified silica gels (Zr−Silicas) as cation−exchange stationary phases in ion chromatography (IC) for various cationic species. Zr−Silicas were prepared by the reaction of silanol group on the surface of silica gel with zirconium tetrabutoxide [Zr $(OC_4H_9)_4$] in ethanol solution. Laboratory−made Zr−Silicas behaved as cation−exchangers under strongly acidic conditions. Zr−Silica adsorbed on 10 mg zirconium g^{-1} silica was applied successfully as the cation−exchange stationary phase in ion chromatography for both simultaneous separation and highly sensitive indirect−conductimetric detection of common monovalent and divalent cations (Li^+, Na^+, NH_4^+, K^+, Mg^{2+} and Ca^{2+}) using tartaric acid containing either 15−crown−5 (1, 4, 7, 10, 13−pentaoxacyclopentadecane) or 18−crown −6 (1, 4, 7, 10, 13, 16−hexaoxacyclooctadecane) as the eluent. Zr−Silicas could be also applied successfully as the cation−exchange stationary phases in ion−exclusion chromatography for the separation of aliphatic carboxylic acids and benzenecarboxylic acids.

Keywords: Zirconium−modified silica gel, Ion chromatography, Cations, Crown ethers, Ion−exclusion chromatography, Aliphatic carboxylic acids, Benzenecarboxylic acids

1. Introduction

Ion chromatography (IC), developed by Small et al. [1], is widely recognized as a simple and powerful analytical technique for the determination of various inorganic and organic anions and cations [2]. Sulfonated and carboxylated polymer resins and silicas are commonly employed as cation−exchange stationary phases in IC for cationic species. The application of unmodified silica gels as cation−exchange stationary phases in IC with conductimetric detection (IC−CD) for various cationic species (alkali, alkaline earth and transition metal cations) is also possible [3−8], because the silanol group on the surface of silica gel behaves as a weak acid with a *p*Ka of 7.1 [9]. The greatest advantage of the use of unmodified silica gels in IC−CD is that the simultaneous separation of major monovalent and divalent cations (Na^+, NH_4^+, K^+, Mg^{2+} and Ca^{2+}) can be achieved [8]. In the IC−CD, lithium ion (Li^+) with the lowest limiting equivalent ionic conductance was mainly utilized as the eluent competing ion and the eluent pH was approximately neutral, in order to separate and detect these monovalent and divalent cations. Unfortunately, the IC conditions resulted in very low detection sensitivities of these analyte cations and short lifetime of silica gel column [10]. The use of acidic eluent was expected to be one of the best ways for eliminating these above drawbacks.

It is well known that commercially available silica gels, except for pure silica gel synthesized by the hydrolysis of high purity tetraethoxysilane [Si $(OC_2H_5)_4$], contain various metals as impurities in the silica matrix and several polyvalent metals cause the enhancement of the acidity of the silanol group on the surface of silica gel [11−14]. The cation−exchange properties of various unmodified silica gels under acidic condition (2 mM HNO_3 at pH 2.7) were evaluated. Some silica gels (Develosil 30−5, Kaseisorb LC−60−5 and Zorbax BP−SIL silica gels) showed cation−exchange behavior under the acidic condition. These silica substrates were ap-

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plied successfully as the cation−exchange stationary phases in IC−CD using acidic eluent for the simultaneous separation and highly sensitive indirect−conductimetric detection of common monovalent and divalent cations (Li^+, Na^+, NH_4^+, K^+, Mg^{2+} and Ca^{2+}) [15−18]. Subsequent studies revealed that the cation−exchange properties of the Develosil 30−5 and Kaseisorb LC 60−5 silica gels could be attributed to aluminium [19] and that of the Zorbax BP−SIL silica gel could be attributed to zirconium [20], present as impurities in the silica matrix. Hence, deliberate modification of silica gel with aluminum and zirconium was expected to be a very effective way to prepare advanced silica−based cation−exchange stationary phases in IC−CD for these monovalent and divalent cations.

The modification of silica gel with various metals has been already attempted for the preparation of newly advanced silica−based stationary phase in high performance liquid chromatography (HPLC). Various metal−modified silica gels, such as magnesium−modified silica gel [21], calcium−modified silica gel [22], silver−modified silica gel [23] and titanium− and zirconium−modified silica gels [24], were prepared. However, the characteristics of these metal−modified silica gels were only evaluated as stationary phases in normal phase HPLC. The preparation of aluminium−modified silica gel (Al−Silica) has been also carried out by using the cation−exchange reaction of silanol group on the surface of silica gel with aluminum ion in aquatic solution. The Al−Silica showed cation−exchange behavior under strongly acidic condition [25] and was applied successfully in IC−CD for the simultaneous separation of these monovalent and divalent cations [26]. Fortunately, due to the large hydrophilicity, the Al−Silica could be also applied successfully as the cation−exchange stationary phase in ion−exclusion chromatography (IEC) for the separation of hydrophobic carboxylic acids (higher aliphatic carboxylic acids and benzenecarboxylic acids) [27].

In this article, easy preparation of zirconium−modified silica gel (Zr−Silica) and the application of prepared Zr−Silica as the cation−exchange stationary phase in both IC−CD for common monovalent and divalent cations (Li^+, Na^+, NH_4^+, K^+, Mg^{2+} and Ca^{2+}) and IEC for C_1−C_8 aliphatic carboxylic acids and benzenecarboxylic acids are described, in order to demonstrate the effectiveness of Zr−Silica as the stationary phase for the separation of various cationic species [20, 28−33].

2. Instruments

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

The ion−exclusion chromatograph for benzenecarboxylic acids consisted of a Tosoh LC−8020 data processor, CCPM−II eluent delivery pump operated at a flow rate of 0.35 ml min^{-1}, CO−8020 column oven operated at 35℃, UV−8020 UV−Vis spectrophotometer detector operated at 254 nm and DS−8023 on−line degasser and a Reodyne Model 9125 injector equipped with a 20 μl of sample loop.

The ion−exclusion chromatograph for aliphatic carboxylic acids consisted of a Tosoh LC−8020 data processor, CCPM−II eluent delivery pump operated at a flow rate of 0.35 ml min^{-1}, CCPD regenerant delivery pump operated at a flow rate of 0.7 ml min^{-1}, CO−8020 column oven operated at 35℃, CM−8020 conductimetric detector and DS−8023 on−line degasser, a Reodyne Model 9125 injector equipped with a 20 μl of sample loop and a Dionex (Sunnyvale, CA. USA) ASRS−ULTRA (2−mm) anion self−regenerating suppressor.

3. Zirconium−modified silica gels

3.1. Preparation of zirconium−modified silica gels

Zirconium−modified silica gels (Zr−Silicas) were prepared using the following steps. A Pia Tec (Suzuka, Japan) Pia Seed 5S−100−SIL pure silica gel for HPLC, synthesized by the hydrolysis of high purity tetraethoxysilane [Si $(OC_2H_5)_4$] was employed as a matrix. The silica gel was dried overnight at 150℃. 10 g of the silica gel was immersed in 100 ml ethanol. Whilst stirring the solution, 100 ml ethanol solution containing given amount of zirconium tetrabutoxide [Zr $(OC_4H_9)_4$] solution (ca. 85% (w/w) zirconium tetrabutoxide in butanol solution) was gradually added to the solution. After adding, the solution was stirring for 1 h and then was filtrated. The resultant gel was washed thoroughly with ethanol and then dried at 150℃, followed by calcinating at 1000℃ for 5 h. Table 1 shows the physical and chemical properties of prepared Zr−Silicas.

Figure 1 shows the relationship between the amount of the zirconium tetrabutoxide solution in 100 ml ethanol solution (coating solution) and the amount of zirconium adsorbed on 10 g silica gel. The amount of zirconium adsorbed on silica gel increased linearly at the range of the amount of the zirconium tetrabutoxide solution in the coating solution between 0 and 3 g. The degree of the increase in the amount of zirconium adsorbed decreased drastically at the amount of the zirconium tetrabutoxide solution in the coating solution $\geq$3 g. The amount of zirconium adsorbed was saturated at the amount of the zirconium tetrabutoxide solution in the coating solution $\geq$10 g. The maximum amount of zirconium adsorbed was ca. 100 mg g^{-1} silica gel. This meant that ca. 30% silanol group on the surface of the silica gel reacted with zirconium tetrabutoxide.
The modification was easy and effective way to prepare Zr−Silicas

Table 1. Physical properties of Pia Seed 5S−100−SIL silica gel and zirconium−modified silica gels (Zr−Silicas).

Gel	Amount of Zirconium (mg g^{-1} silica)	Drying or calcinating (℃)	Particle size (μm)	Surface area ($m^2 g^{-1}$)	Pore size (Å)	Pore volume (ml g^{-1})	Packing density (g ml^{-1})
Pia Seed 5S−100−SIL	0	150	6.9	499	102	1.14	0.37
	0	1000	6.0	250	59	0.54	0.60
Zr−Silica	5.2	1000	5.9	323	82	0.70	0.52
	10	1000	6.0	313	80	0.69	0.53
	15	1000	5.8	285	79	0.61	0.58
	20	1000	5.6	267	78	0.60	0.58
	39	1000	5.5	230	80	0.50	0.63
	57	1000	5.3	223	78	0.48	0.66
	87	1000	5.3	216	73	0.47	0.71
	100	1000	5.2	204	67	0.47	0.76
	101	1000	5.2	207	66	0.47	0.76

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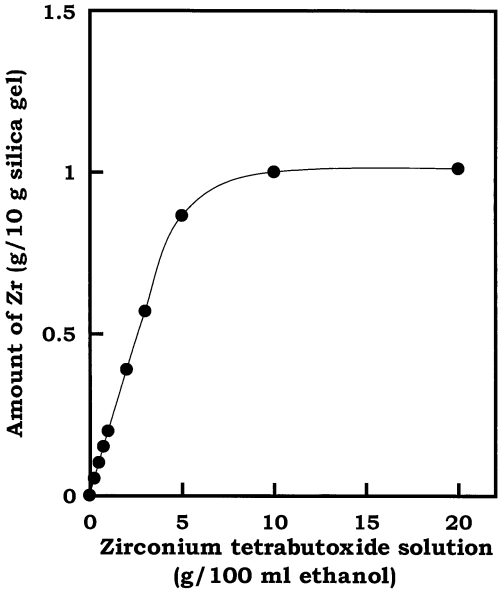

Figure 1. Effect of amount of zirconium tetrabutoxide in ethanol on amount of zirconium adsorbed on silica gel.
(Conditions)
Zirconium tetrabutoxide solution: ca. 85% (w/w) zirconium tetrabutoxide in butanol solution.
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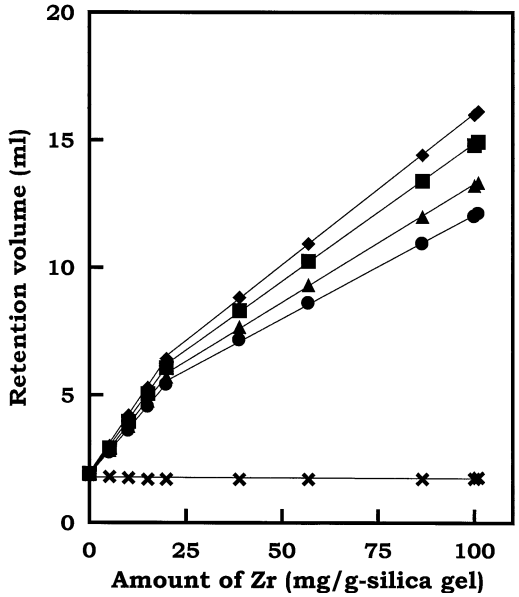

Figure 2. Effect of amount of zirconium on zirconium−modified silica gels (Zr−Silicas) on retention volumes of monovalent and divalent cations.
(Conditions)
Column: Zr−Silicas adsorbed on 0−101 mg zirconium g^{-1} silica gel;
Column size: 150 x 4.6 mm i.d.;
Column temperature: 35℃;
Eluent: 10 mM tartaric acid at pH 2.5;
Flow rate: 1 ml min^{-1};
Detection: indirect−conductivity;
Injection volume: 20 μl;
Sample concentration: 0.2 mM;
Symbols: ×=water dip, ●=Li^+, ▲=Na^+, ■=NH_4^+ and◆=K^+.
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adsorbed on 0−100 mg zirconium g^{-1} silica gel.

3.2. Cation−exchange properties of Zr−Silicas under acidic condition

Figure 2 shows the relationship between the amount of zirconium adsorbed on silica gel and the retention volumes of monovalent cations (Li^+, Na^+, NH_4^+ and K^+) using 10 mM tartaric acid at pH 2.5 as the eluent. Zr−Silica adsorbed on 0 mg zirconium g^{-1} silica gel (Pia Seed 5S−100−SIL silica gel calcinated at 1000℃) showed no cation−exchanger behavior under the acidic eluent condition. With increasing the amount of zirconium adsorbed, the retention volumes of the monovalent cations increased. The retention volumes increased linearly at the range of the amount of zirconium ad-

sorbed between 0 and 20 mg g^{-1} silica gel and those also increased linearly at the range of the amount of zirconium adsorbed between 20 and 100 mg g^{-1} silica gel. The slopes between 0 and 20 mg g^{-1} silica gel were larger than those between 20 and 100 mg g^{-1} silica gel. Although no conclusive reasons for the explanation on these relationships were found, it was evident that the cation−exchange capacities of prepared Zr−Silicas increased significantly by the inclusion of zirconium in the silica gel, which caused the enhancement of the acidity of silanol group.

The modification was easy and effective way to prepare Zr−Silicas with various cation−exchange capacities under strongly acidic conditions.

4. Application of Zr−Silica for separation of various cationic species

4.1. Separation of monovalent and divalent cations on Zr−Silica column

The application of Zr−Silica adsorbed on 10 mg zirconium g^{-1} silica gel as the cation−exchange stationary phase in ion chromatography with conductimetric detection (IC−CD) for common monovalent and divalent cations (Li^+, Na^+, NH_4^+, K^+, Mg^{2+} and Ca^{2+}) was attempted with tartaric acid as the eluent.

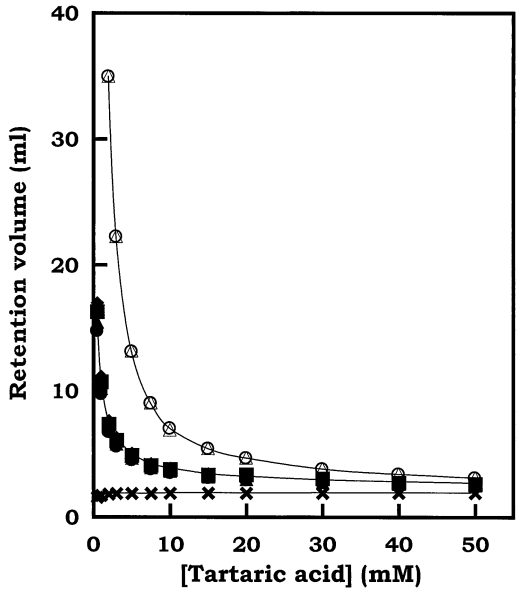

Figure 3. Effect of concentration of tartaric acid in eluent on retention volumes of monovalent and divalent cations on Zr−Silica column.
(Conditions)
Column: Zr−Silica adsorbed on 10 mg zirconium g^{-1} silica gel;
Eluent: 0.5−50 mM tartaric acid;
Sample concentration: 0.2 mM for monovalent cations and 0.1 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 2.
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Figure 3 shows the relationship between the concentration of tartaric acid in the eluent and the retention volumes of these monovalent and divalent cations on the Zr−Silica column (150 x 4.6 mm i.d.). With increasing the concentration of tartaric acid, the retention volumes of these monovalent and divalent cations decreased drastically. This is due to both an increase in the concentration of hydronium ion (H^+) as the competing ion in the eluent and a decrease in the cation−exchange capacity of the Zr−Silica column. The retention volumes of the divalent cations decreased largely in comparison with those of the monovalent cations. This is because retention volumes of divalent cations are strongly influenced with both cation−exchange capacity and concentration of competing ion, in comparison with those of monovalent cations [2]. Since the retention volumes of these monovalent and divalent cations were still larger than that of water dip when using 50 mM tartaric acid at pH 2.2 as the eluent, it was revealed that the Zr−Silica functioned as cation−exchanger under such strongly acidic eluent conditions. As shown in Figure 4, when using 10 mM tartaric acid as the eluent, although complete group separation of these monovalent and divalent cations was achieved in 10 min, peak resolution between the monovalent cations and that between the divalent cations were very poor.

Crown ethers [15−crown−5 (1, 4, 7, 10, 13−pentaoxacyclopentadecane) and 18−crown−6 (1, 4, 7, 10, 13, 16−hexaoxacyclooctadecane)] form stable complexes with these monovalent and

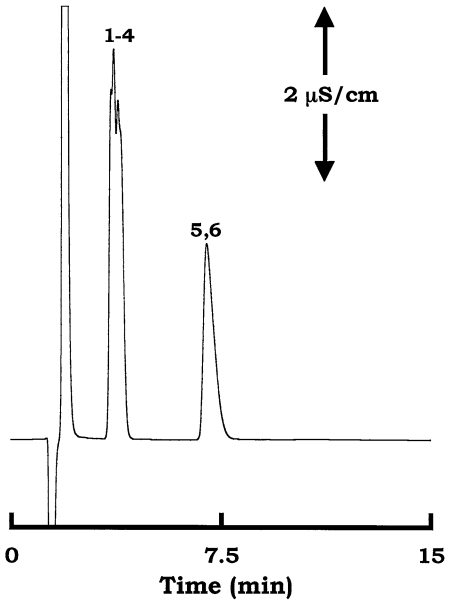

Figure 4. Chromatogram of monovalent and divalent cations on Zr−Silica column with tartaric acid as eluent.
(Conditions)
Eluent: 10 mM tartaric acid;
Peaks: 1=Li^+, 2=Na^+, 3=NH_4^+, 4=K^+, 5=Mg^{2+} and 6=Ca^{2+}.
Other chromatographic conditions are as for in Figure 3.
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divalent cations [34−37]. The addition of these crown ethers to 10 mM tartaric acid as the eluent was carried out for improving peak resolution between these monovalent and divalent cations.

Figure 5 shows the relationship between the concentration of 15−crown−5 in the eluent and the retention volumes of these monovalent and divalent cations. With increasing the concentration of 15−crown−5, the retention volumes of these monovalent and divalent cations increased. The order of the increase in the retention volumes for the monovalent cations was $Li^+ < NH_4^+ < Na^+ < K^+$ and that of the divalent cations was $Mg^{2+} < Ca^{2+}$. The orders indicated that 15−crown−5 in the eluent was adsorbed on the Zr−Silica stationary phases and then seemed to behave as a selective cation−exchanger for these monovalent and divalent cations [38]. Peak resolution between these monovalent and divalent cations was improved greatly. Complete separation was achieved at the concentration of 15−crown−5≥10 mM. As shown in Figure 6, excellent simultaneous separation of these monovalent and divalent cations was achieved in 10 min using 10 mM tartaric acid containing 10 mM 15−crown−5 as the eluent (Eluent A).

Figure 7 shows the relationship between the concentration of 18−crown−6 in the eluent and the retention volumes of these monovalent and divalent cations. With increasing the concentration of 18−crown−6 in the eluent, the retention volumes of Na^+, NH_4^+, K^+ and Ca^{2+} increased and those of Li^+ and Mg^{2+} remained almost the same. The order of the increase in the retention volumes for the

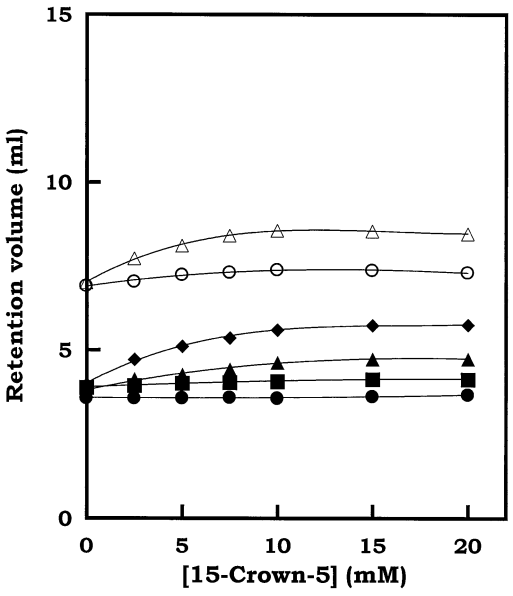

Figure 5. Effect of concentration of 15−crown−5 in eluent on retention volumes of monovalent and divalent cations on Zr−Silica column.
(Conditions)
Eluent: 10 mM tartaric acid containing 0−20 mM 15−crown−5;
Symbols:●=Li^+, ▲=Na^+, ■=NH_4^+, ◆=K^+, ○=Mg^{2+} and△=Ca^{2+}.
Other chromatographic conditions are as for in Figure 4.
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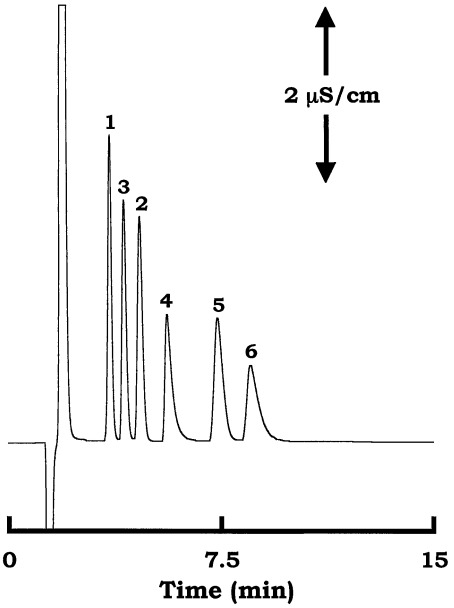

Figure 6. Chromatogram of monovalent and divalent cations on Zr−Silica column with tartaric acid containing 15−crown−5 as eluent.
(Conditions)
Eluent: 10 mM tartaric acid containing 10 mM 15−crown−5;
Peaks: 1=Li^+, 2=Na^+, 3=NH_4^+, 4=K^+, 5=Mg^{2+} and 6=Ca^{2+}.
Other chromatographic conditions are as for in Figure 5.
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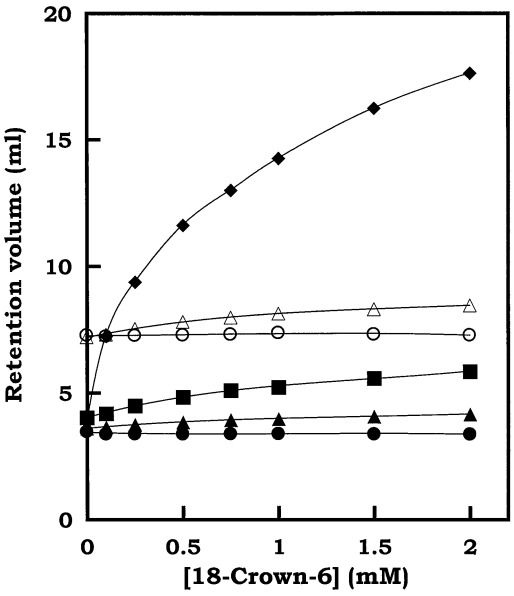

Figure 7. Effect of concentration of 18−crown−6 in eluent on retention volumes of monovalent and divalent cations on Zr−Silica column.
(Conditions)
Eluent: 10 mM tartaric acid containing 0−2 mM 18−crown−6;
Symbols:●=Li^+, ▲=Na^+, ■=NH_4^+, ◆=K^+, ○=Mg^{2+} and△=Ca^{2+}.
Other chromatographic conditions are as for in Figure 6.
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monovalent cations was $Li^+ < Na^+ < NH_4^+ << K^+$ and that of the divalent cations was $Mg^{2+} < Ca^{2+}$. The retention volume of K^+ in-

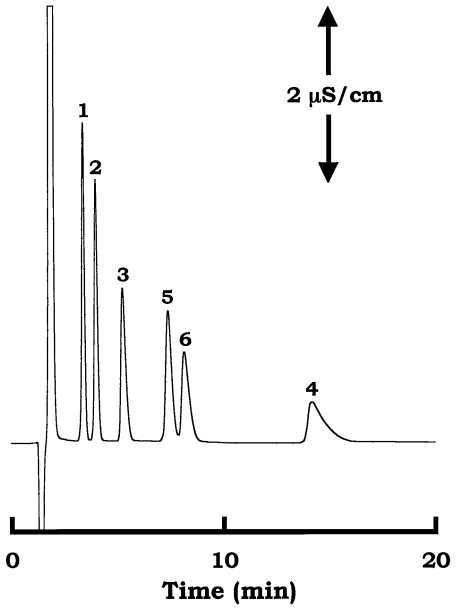

Figure 8. Chromatogram of monovalent and divalent cations on Zr−Silica column with tartaric acid containing 18−crown−6 as eluent.
(Conditions)
Eluent: 10 mM tartaric acid containing 1 mM 18−crown−6;
Peaks: 1=Li^+, 2=Na^+, 3=NH_4^+, 4=K^+, 5=Mg^{2+} and 6=Ca^{2+}.
Other chromatographic conditions are as for in Figure 7.
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creased drastically, because 18−crown−6 forms very stable metal−in−hole type complex with K^+. The orders also indicated that 18−crown−6 in the eluent was adsorbed on the Zr−Silica stationary phase and then seemed to behave as a selective cation−exchanger for these monovalent and divalent cations [38]. Peak resolution between these monovalent and divalent cations was also improved. Complete separation was achieved at the concentration of 18−crown−6≥1 mM. As shown in Figure 8, excellent simultaneous separation of these monovalent and divalent cations was achieved in 17 min using 10 mM tartaric acid containing 1 mM 18−crown−6 as the eluent (Eluent B). The optimum concentration of 18−crown−6 (1 mM) was much lower than that of 15−crown−5 (10 mM). This is because complexes formed between 18−crown−6 and these cations are much stable in comparison with those formed between 15−crown−5 and these cations [35].

Table 2 shows the detection limits (signal−to−noise ratio of 3, injection volume of 20 μl) of these monovalent and divalent cations obtained by using Eluent A and Eluent B. These detection limits compared well those obtained by conventional non−suppressed IC−CD with dilute strong acid as the eluent. This is because these monovalent and divalent cations were detected by an indirect−conductivity mechanism, in which they displaced the highly conducting hydronium ion (H^+) from the eluent.

Zr−Silica adsorbed on 10 mg zirconium g^{-1} silica gel was the advanced cation−exchange stationary phase in the IC−CD for the simultaneous separation of these monovalent and divalent cations using tartaric acid containing either 15−crown−5 or 18−crown−6 as the eluent.

Table 2. Detection limits (signal−to−noise ratio of 3, injection volume of 20 μl) of monovalent and divalent cations obtained by using Eluent A and Eluent B.

Cation	Eluent A*		Eluent B**	
	μM	ng ml^{-1}	μM	ng ml^{-1}
Li^+	0.28	1.8	0.26	1.7
Na^+	0.38	8.6	0.31	7.1
NH_4^+	0.35	6.3	0.51	9.1
K^+	0.67	26	2.0	78
Mg^{2+}	0.34	8.3	0.31	7.7
Ca^{2+}	0.56	22	0.47	18

* 10 mM tartaric acid containing 10 mM 15−crown−5.
**10 mM tartaric acid containing 1 mM 18−crown−6.
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4.2. Separation of benzenecarboxylic acids on Zr−Silica column

The application of the Zr−Silicas as cation−exchange stationary phases in ion−exclusion chromatography with UV photometric detection (IEC−PD) for benzenecarboxylic acids [pyromellitic acid (1, 2, 4, 5−benzenetetracarboxylic acid), hemimellitic acid (1, 2, 3−benzenetricarboxylic acid), trimellitic acid (1, 2, 4−benzenetricarboxylic acid), o−phthalic acid, salicylic acid and benzoic acid] and phenol was attempted with tartaric acid as the eluent.

Figure 9 A−D show chromatograms of these benzenecarboxylic acids and phenol on columns (250 x 4.6 mm i.d.) packed with Zr−Silicas adsorbed on 0, 20, 39 and 100 mg zirconium g^{-1} silica gel, obtained by using 10 mM tartaric acid at pH 2.5 as the eluent, respectively. As shown in Figure 9 A, both complete separation of o−phthalic, salicylic and benzoic acids and phenol and incomplete separation of pyromellitic, trimellitic and hemimellitic acids were achieved on column packed with Zr−Silica adsorbed on 0 mg zirconium g^{-1} silica gel (Pia Seed 5S−100−SIL silica gel calcinated at 1000℃). Since the Zr−Silica showed almost no cation−exchange behavior under the acidic eluent condition, these benzenecarboxylic acids were mainly separated by the hydrophobic adsorption process. This chromatogram also suggested that complete separation of these benzenecarboxylic acids and phenol would not be very difficult on the Zr−Silica column in a reasonable period of time (< 30 min) with tartaric acid as the eluent. As shown in Figure 9 B, complete separation of these benzenecarboxylic acids and phenol was achieved in 20 min on column packed with Zr−Silica adsorbed on 20 mg zirconium g^{-1} silica gel. Since the Zr−Silica showed cation−exchange behavior under the acidic eluent condi-

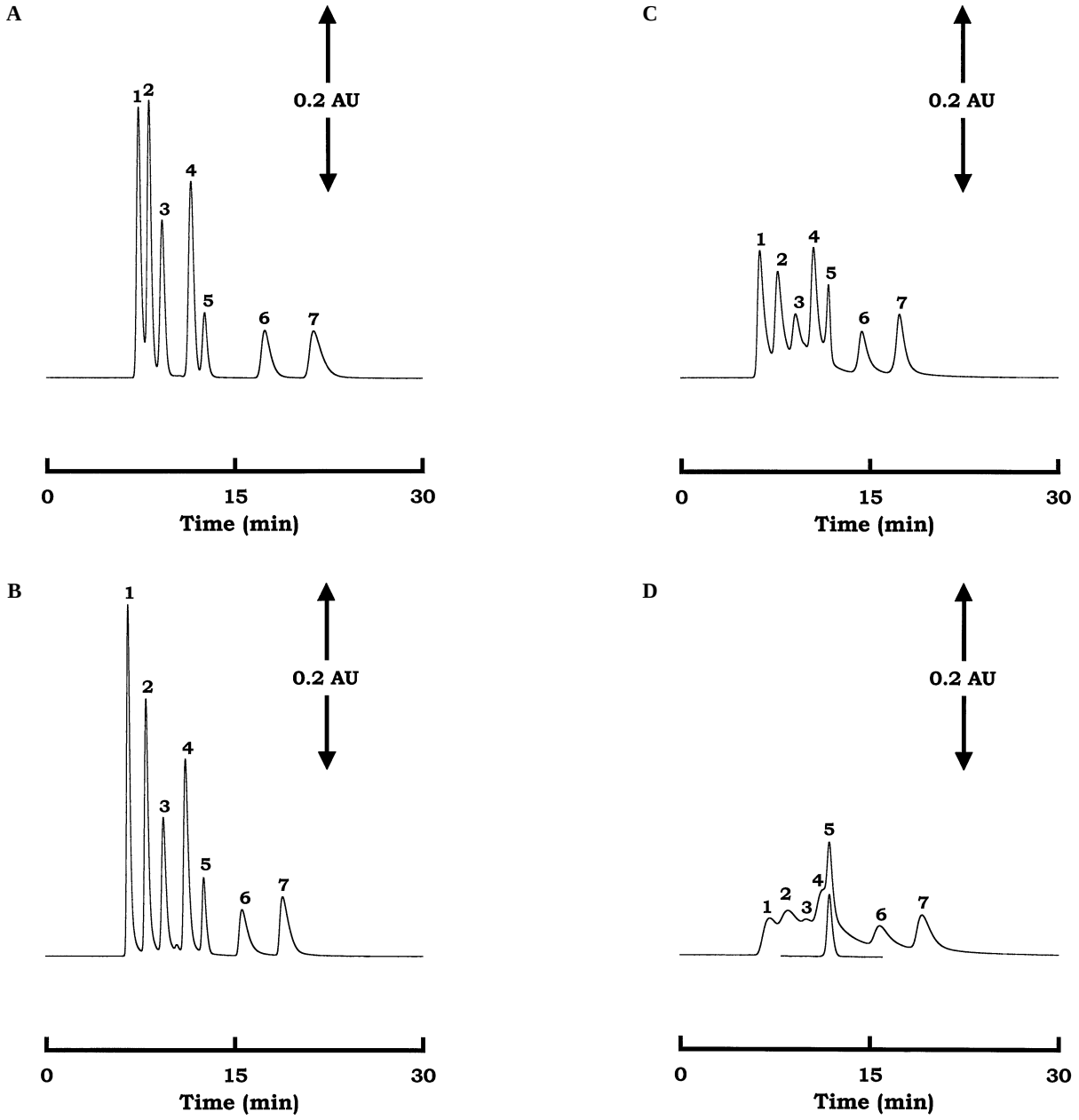

Figure 9. Chromatograms of benzenecarboxylic acids and phenol on various Zr−Silica columns with tartaric acid as eluent.
(Conditions)
Column: (A) Zr−Silica adsorbed on 0 mg zirconium g^{-1} silica gel;
(B) Zr−Silica adsorbed on 20 mg zirconium g^{-1} silica gel;
(C) Zr−Silica adsorbed on 39 mg zirconium g^{-1} silica gel;
(D) Zr−Silica adsorbed on 100 mg zirconium g^{-1} silica gel;
Column size: 250 x 4.6 mm i.d.;
Column temperature: 35℃;
Eluent: 10 mM tartaric acid;
Flow rate: 0.35 ml min^{-1};
Detection: UV at 254 nm;
Injection volume: 20 μl;
Sample concentration: 0.025 mM for pyromellitic and trimellitic acid and 0.1 mM for other benzenecarboxylic acids and phenol;
Peaks: 1=pyromellitic acid, 2=trimellitic acid, 3=hemimellitic acid, 4=o−phthalic acid, 5=phenol, 6=salicylic acid and 7=benzoic acid.
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tions, the complete separation was achieved by both the IEC process and hydrophobic adsorption process. On the other hand, as shown in Figure 9 C and D, with increasing the amount of zirconium adsorbed on silica gel (> 20 mg zirconium g^{-1} silica gel), peak shapes of these benzenecarboxylic acids were destroyed largely. The peak shape of phenol remained the same. The large peak destruction suggested that strong interaction occurred between carboxylic group of benzenecarboxylic acids and zirconium adsorbed on the surface of these Zr−Silicas stationary phases.

Zr−Silica adsorbed on 20 mg zirconium g^{-1} silica gel could be applied successfully as the advanced cation−exchange stationary phase in the IEC−PD for the separation of these benzenecarboxylic acids with tartaric acid as the eluent.

4.3. Separation of C_1−C_8 aliphatic carboxylic acids on Zr−Silica column

The application of the Zr−Silicas as cation−exchange stationary phases in IEC with suppressed−conductimetric detection (IEC−SCD) for C_1−C_8 aliphatic carboxylic acids (formic acid, acetic acid, propionic acid, butyric acid, valeric acid, caproic acid, heptanoic acid and caplyric acid) was attempted with pyromellitic acid as the eluent.

Figure 10 A−D show chromatograms of these aliphatic carboxylic acids on columns (250 x 4.6 mm i.d.) packed with Zr−Silicas adsorbed on 0, 10, 20 and 100 mg zirconium g^{-1} silica gel, obtained by using 0.2 mM pyromellitic acid at pH 3.5 as the eluent, respectively. As shown in Figure 10 A, good separation of these aliphatic carboxylic acids was achieved on column packed with Zr −Silica adsorbed on 0 mg zirconium g^{-1} silica gel (Pia Seed 5S−100 −SIL silica gel calcinated at 1000℃). Unfortunately, due mainly to very low cation−exchange capacity of the Zr−Silica column, peaks of cations co−existing in the sample solution appeared and, as a consequence, the determination of these aliphatic carboxylic acids was interfered seriously. As shown in Figure 10 B, although complete separation of these aliphatic carboxylic acids, without any interference from co−existing cations, was achieved on column packed with Zr−Silica adsorbed on 10 mg zirconium g^{-1} silica gel, it took a very long time for the elution of higher aliphatic carboxylic acids (caproic, heptanoic and caprylic acids) and their peaks were tailed strongly. This is due mainly to strongly hydrophobic interaction between these higher aliphatic carboxylic acids and the surface of the Zr−Silica stationary phase. On the other hand, as shown in Figure 10 C and D, with increasing the amount of zirconium adsorbed on silica gel (> 10 mg zirconium g^{-1} silica gel), peak shapes of C_1−C_8 aliphatic carboxylic acids were destroyed largely. The large peak destruction might be due to strong interaction between carboxylic group of aliphatic carboxylic acids and zirconium adsorbed on the surface of these Zr−Silicas stationary phases. Hence, the most suitable stationary phase was Zr−Silica adsorbed on 10 mg zirconium g^{-1} silica gel in the IEC−SCD for these C_1−C_8 aliphatic carboxylic acids

The addition of organic solvents, especially higher alcohols, to the eluent in IEC is very effective way for improving peak shapes and reducing retention times for hydrophobic carboxylic acids [2, 27, 39, 40]. The effect of C_1−C_7 alcohols as elution modifiers in the IEC−SCD was evaluated. Alcohols > C_7 (heptanol) were not applicable, due to their limited solubility. The concentration of alcohols added to the eluent was determined for the elution of these C_1−C_8 aliphatic carboxylic acids within 30 min. Figure 11 A−C show chromatograms of these C_1−C_8 aliphatic carboxylic acids on column packed with Zr−Silica adsorbed on 10 mg zirconium g^{-1} silica gel, obtained by using 0.2 mM pyromellitic acid containing (A) 10% methanol, (B) 2% propanol, (C) 0.3% pentanol and (D) 0.15% heptanol as the eluent. These chromatograms indicated clearly that higher alcohols (pentanol and heptanol) were more effective elution modifiers than lower alcohols (methanol and propanol) for improving peak shapes and reducing elution times of higher aliphatic carboxylic acids under the IEC−SCD conditions. The higher alcohols in the eluent were believed to be adsorbed on the Zr−Silica stationary phase strongly and then reduced the hydrophobicity of the Zr−Silica stationary phase. Heptanol was the most effective elution modifier in the IEC−SCD. As shown in Figure 11 D, excellent simultaneous separation of these C_1−C_8 aliphatic carboxylic acids was achieved in 25 min using 0.2 mM pyromellitic acid containing 0.15% heptanol as the eluent.

Zr−Silica adsorbed on 10 mg zirconium g^{-1} silica gel could be also applied successfully as the advanced cation−exchange stationary phase in the IC−SCD for the separation of these C_1−C_8 aliphatic carboxylic acids with pyromellitic acid containing heptanol as the eluent.

5. Conclusion

The preparation of zirconium−modified silica gels (Zr−Silicas) and the application of prepared Zr−Silicas as cation−exchange stationary phases in ion chromatography (IC) for common monovalent and divalent cations and ion−exclusion chromatography (IEC) for C_1−C_8 aliphatic carboxylic acids and several benzenecarboxylic acids were described in the article. Laboratory−made Zr−Silicas acted as cation−exchange stationary phases under strongly acidic eluent conditions and were applied successfully for the separation of various cationic species. The modification of silica gel with zirconium is easy and effective way to prepare advanced silica −based stationary phases in not only IC and IEC for cationic species but also HPLC for various organic compounds.

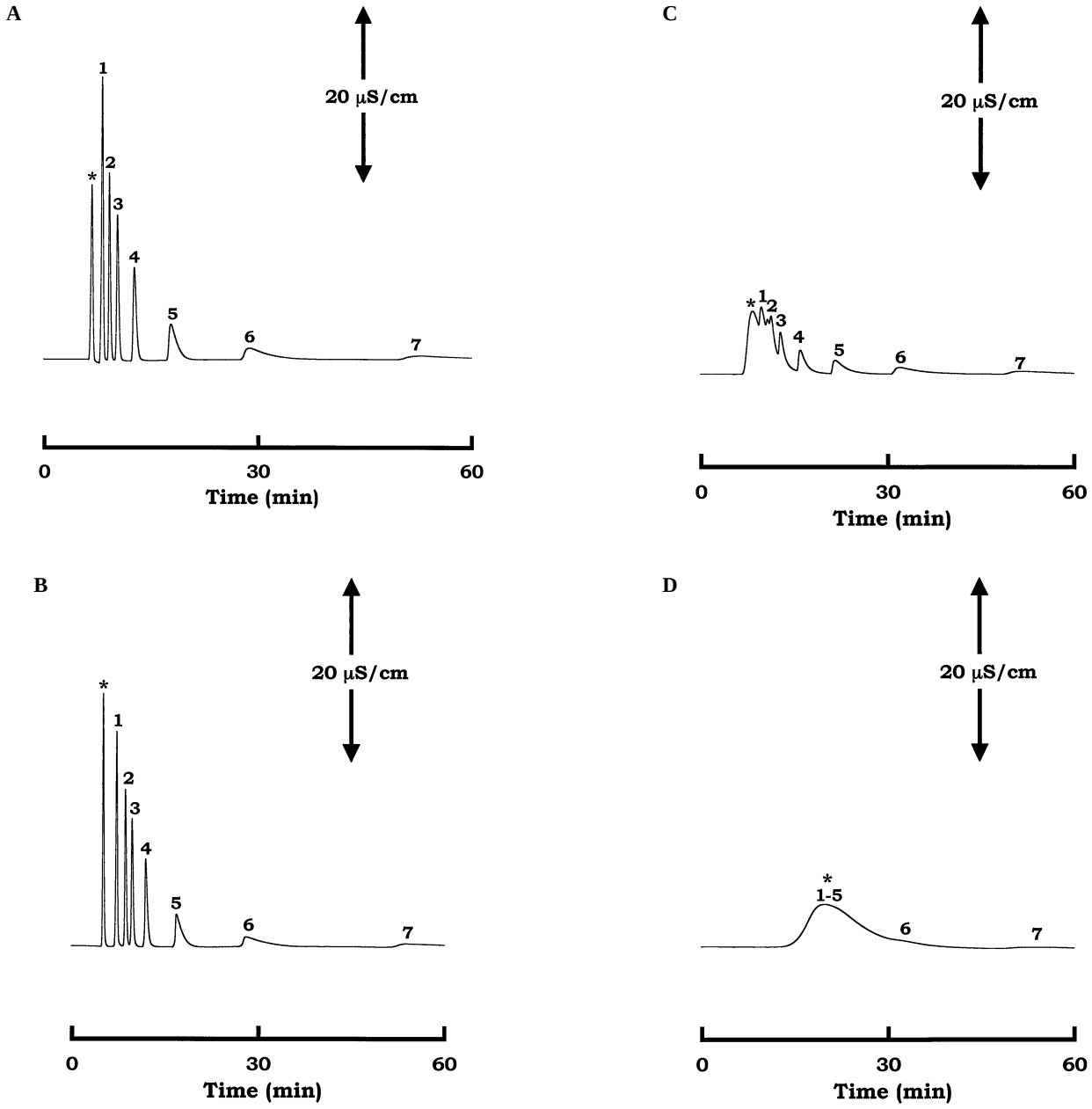

Figure 10. Chromatograms of C_1−C_8 aliphatic carboxylic acids on various Zr−Silica columns with using pyromellitic acid as eluent (Conditions)
Column: (A) Zr−Silica adsorbed on 0 mg zirconium g^{-1} silica gel;
(B) Zr−Silica adsorbed on 10 mg zirconium g^{-1} silica gel;
(C) Zr−Silica adsorbed on 20 mg zirconium g^{-1} silica gel;
(D) Zr−Silica adsorbed on 100 mg zirconium g^{-1} silica gel;
Eluent: 0.2 mM pyromellitic acid at pH 3.5;
Flow rate: 0.35 ml min^{-1};
Regenerant: 20 mM K_2SO_4;
Regenerant flow rate: 0.7 ml min^{-1};
Detection: suppressed−conductivity;
Injection volume: 20 μl;
Sample concentration: 1 mM;
Peaks: *=pyromellitic acid, 1=formic acid, 2=acetic acid, 3=propionic acid, 4=butyric acid, 5=valeric acid, 6= caproic acid, 7=heptanoic acid and 8=caprylic acid.
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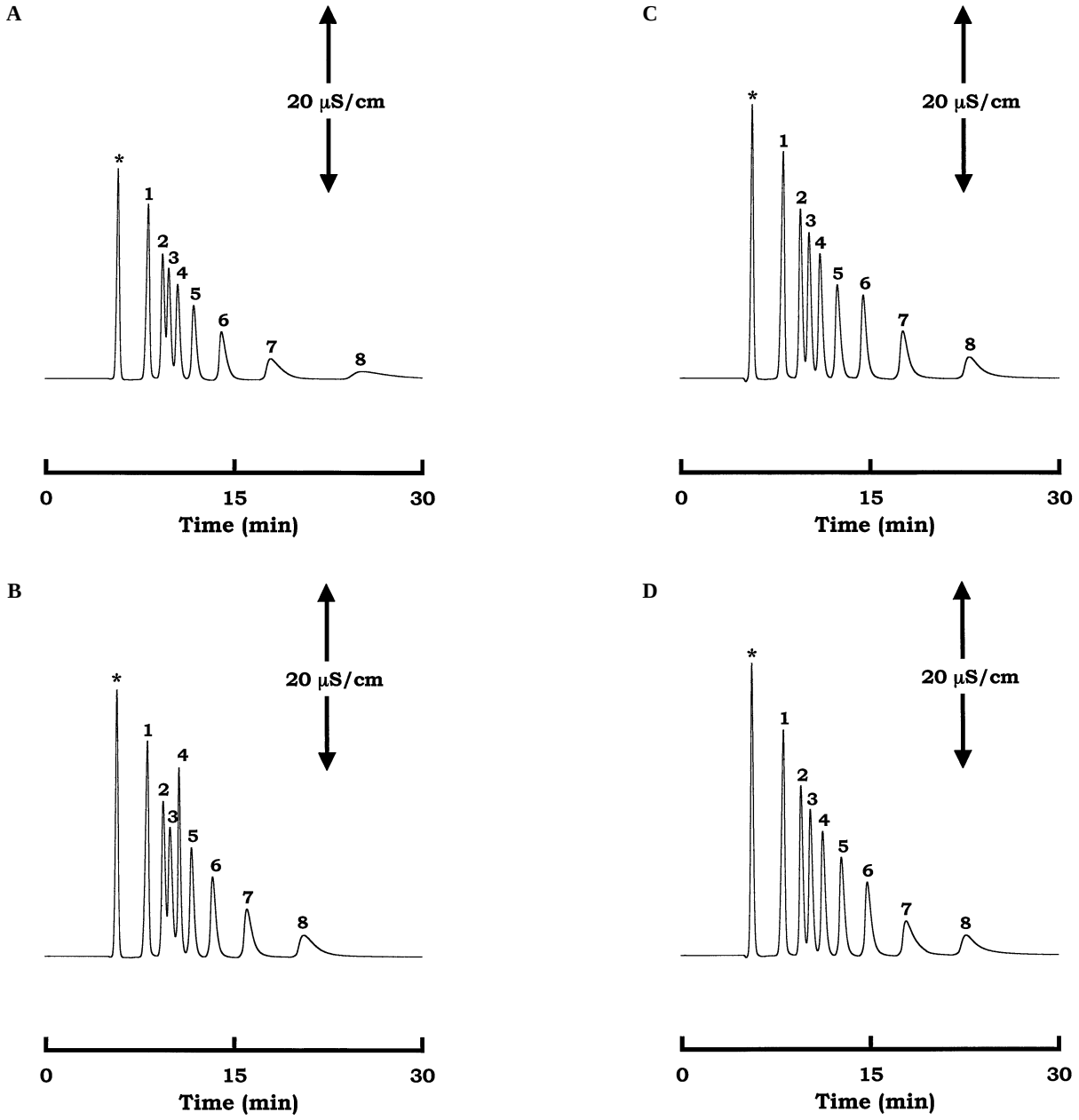

Figure 11. Chromatograms of C_1−C_8 aliphatic carboxylic acids on Zr−Silica column with pyromellitic acid containing various alcohols as eluent.
(Conditions)
Eluent: (A) 0.2 mM pyromellitic acid containing 10% methanol;
(B) 0.2 mM pyromellitic acid containing 2% propanol;
(C) 0.2 mM pyromellitic acid containing 0.3% pentanol;
(D) 0.2 mM pyromellitic acid containing 0.15% heptanol;
Column: Zr−Silica adsorbed on 10 mg zirconium g^{-1} silica gel.
Other chromatographic conditions are as for in Figure 10.
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