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Application of zirconium-modified silica gel as a stationary phase in the ion-exclusion chromatography of carboxylic acids

I. Separation of benzenecarboxylic acids with tartaric acid as eluent and with UV-photometric detection

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Abstract

The application of zirconium-modified silica gels (Zr–Silicas) as stationary phases for ion-exclusion chromatography with UV-photometric detection (IEC–PD) for mono-, di-, tri- and tetrabenzenecarboxylic acids (pyromellitic, trimellitic, hemimellitic, *o*-phthalic, salicylic and benzoic acids) and phenol was carried out using tartaric acid as the eluent. Zr–Silicas were prepared by the reaction of the silanol group on the surface of silica gel with zirconium tetrabutoxide [$\text{Zr}(\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_3)_4$] in ethanol solution. The effect of the amount of zirconium adsorbed on silica gel on chromatographic behavior of these benzenecarboxylic acids and phenol was investigated. As a result, Zr–Silica adsorbed on 20 mg zirconium g^{-1} silica gel was the most suitable stationary phase in the IEC–PD for the simultaneous separation of these benzenecarboxylic acids and phenol. Excellent simultaneous separation and highly sensitive UV detection at 254 nm for these benzenecarboxylic acids and phenol were achieved in 20 min by the IEC–PD using the Zr–Silica column (250×4.6 mm I.D.) and a 10 mM tartaric acid at pH 2.5 as eluent. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Zirconized silica; Stationary phases, LC; Mobile phase composition; Silica, zirconized; Benzenecarboxylic acids; Carboxylic acids; Tartaric acid

1. Introduction

Ion-exclusion chromatography (IEC) developed by Wheaton and Bauman [1] is commonly used for the separation of various kinds of carboxylic acids. High-capacity sulfonated styrene–divinylbenzene copolymer resins are exclusively employed as cation-exchange stationary phases in IEC for carboxylic acids [2]. However, due to the largely hydrophobic nature, the application of these resins for the ion-

exclusion chromatographic separation of hydrophobic carboxylic acids, such as higher aliphatic carboxylic acids and aromatic carboxylic acids, was very difficult. The addition of organic modifiers to the eluents in IEC is carried out for both reduction of retention times and improvement of peak shapes of hydrophobic carboxylic acids [3–5]. Unfortunately, the use of higher concentration of organic modifiers is limited, because shrinking of these resins occurs. One of the best ways for the ion-exclusion chromatographic separation of largely hydrophobic carboxylic acids was to use cation-exchange resins having a largely hydrophobic nature.

Since the silanol group on the surface of silica gel

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behaves as a weak acid with a pK_a of ca. 7.1 [6], it is possible to apply unmodified silica gel as a cation-exchange stationary phase for IEC for carboxylic acids. Zenki et al. have applied unmodified silica gel to the determination of hydrogen carbonate (HCO_3^-) in river water samples using borate buffer at pH 7.1 as the eluent [7]. Strongly acidic eluents are very effective for the improvement of peak shapes of carboxylic acids in IEC [8]. However, strongly acidic eluents cause the suppression of the dissociation of silanol group on the surface of silica gel as the cation exchanger. Therefore, the application of unmodified silica gel as the stationary phase in IEC for the separation of carboxylic acids has been not carried out.

Fortunately, the author has found that a commercially available unmodified silica gel (Develosil 30-5) acted as a cation exchanger under strongly acidic conditions [9]. The Develosil 30-5 silica gel was successfully applied for the ion-exclusion chromatographic separation of various kinds of carboxylic acids using strongly acidic eluent [10,11]. The advantage of using the Develosil 30-5 silica gel in IEC was that the separation of hydrophobic carboxylic acids, such as higher aliphatic carboxylic acids and aromatic carboxylic acids, could be easily achieved. This is due mainly to the largely hydrophilic nature of the silica material. The main cause of the cation-exchange characteristics was found to be aluminum present as a metal impurity in the silica matrix [12]. Then, the modification of the silanol group on the surface of silica gel with aluminum was carried out. Laboratory-made aluminum-modified silica gel (Al-Silica) acted as a cation exchanger under strongly acidic conditions [13] and was successfully applied for the ion-exclusion chromatographic separation of hydrophobic carboxylic acids [14]. Since certain polyvalent cations in the silica gel cause the enhancement of the acidity of the silanol group on the surface of silica gel [15–18], the modification of silica gel with metals was expected to be a very effective way for the preparation of newly advanced silica-based cation-exchange stationary phase in IEC for carboxylic acids.

In a previous study [19], the author has prepared zirconium-modified silica gel (Zr-Silica) by the reaction of silanol group on silica gel with zirconium tetrabutoxide [$\text{Zr}(\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_3)_4$] in ethanol

solution. Laboratory-made Zr-Silica acted as a cation exchanger under strongly acidic conditions and was successfully applied for the simultaneous separation of monovalent cations (Li^+ , Na^+ , NH_4^+ , K^+ , Rb^+ and Cs^+) using a 10 mM tartaric acid at pH 2.5 as eluent. However, the application of the Zr-Silica as a stationary phase in IEC for the separation of carboxylic acids has not been carried out yet.

The aim of this study was to demonstrate the effectiveness of Zr-Silicas as stationary phases in IEC for carboxylic acids. Then, Zr-Silicas adsorbed on various amount of zirconium were prepared and were applied as stationary phases in IEC with UV-photometric detection (IEC-PD) for the separation of benzenecarboxylic acids using tartaric acid as the eluent. A Zr-Silica adsorbed on 20 mg zirconium g^{-1} silica gel was the most suitable stationary phase in IEC for the separation of benzenecarboxylic acids. Excellently simultaneous separation and highly sensitive UV detection at 254 nm 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 were achieved in 20 min by the IEC-PD using the Zr-Silica column (250×4.6 mm I.D.) and a 10 mM tartaric acid at pH 2.5 as the eluent.

2. Experimental

2.1. Preparation of zirconium-modified silica gel

A Pia Tec (Suzuka, Japan) Pia Seed 5S-100-SIL high-purity porous spherical silica gel for HPLC was employed as a matrix. The silica gel was dried overnight at 150°C. A 10 g sample of the silica gel was immersed in 100 ml ethanol. Stirring the solution, 100 ml ethanol solution containing given amount of zirconium tetrabutoxide [$\text{Zr}(\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_3)_4$] solution [ca. 85% (w/w) zirconium tetrabutoxide in butanol] was gradually added to the solution. After adding, the solution was stirred for 1 h and then filtrated. The resultant gel was washed thoroughly with ethanol and then dried at 150°C followed by calcining at 1000°C for 5 h.

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

Gel	Amount of zirconium (mg g ⁻¹ silica)	Drying or calcining (°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)
Pia Seed 5S-100-SIL	0	150	6.9	499	102	1.14	0.37	7.7×10 ²
	0	1000	6.0	250	59	0.54	0.60	6.3×10 ²
Zr-Silica	5.2	1000	5.9	323	82	0.70	0.52	7.0×10 ²
	10	1000	6.0	313	80	0.69	0.53	6.9×10 ²
	15	1000	5.8	285	79	0.61	0.58	6.9×10 ²
	20	1000	5.6	267	78	0.60	0.58	6.4×10 ²
	39	1000	5.5	230	80	0.50	0.63	6.0×10 ²
	57	1000	5.3	223	78	0.48	0.66	6.1×10 ²
	87	1000	5.3	216	73	0.47	0.71	6.3×10 ²
	100	1000	5.2	204	67	0.47	0.76	6.4×10 ²
	101	1000	5.2	207	66	0.47	0.76	6.5×10 ²

^a Column size: 250×4.6 mm I.D.

Table 1 shows the physical and chemical properties of Pia Seed 5S-100-SIL and prepared zirconium-modified silica gels (Zr-Silicas). The determination of zirconium on Zr-Silicas was carried out using a Nippon Jarrel-Ash ICAP-1000 inductively coupled plasma atomic emission spectrometry (ICP-AES) system. The determination of the surface area, pore size and pore volume of Pia Seed 5S-100-SIL and Zr-Silicas by using nitrogen adsorption isotherms on the gels at 77 K was carried out using a Beckman-Coulter (Fullerton, CA, USA) Ominisorp 360 gas sorption analyzer. The surface area was calculated from the BET equation.

The separation columns (250×4.6 mm I.D., stainless steel) were packed with Pia Seed 5S-100-SIL and Zr-Silicas using the slurry-packing method.

2.2. Instrument

The ion chromatograph consisted of a Tosoh (Tokyo, Japan) LC-8020 chromatographic data processor, a Tosoh DP-8020 solvent delivery pump operated at a flow-rate of 0.35 or 1.0 ml min⁻¹, a Tosoh CO-8020 column oven operated at 35°C, a Tosoh CM-8020 conductimetric detector, a Tosoh UV-8020 UV-Vis spectrophotometric detector operated at 254 and 270 nm, a Tosoh DS-8023 on-line degasser and a Reodyne (Cotati, CA, USA) Model 9125 injector equipped with a 20 μl sample loop.

2.3. Chemicals

All chemicals were of analytical reagent grade and purchased from Aldrich (Milwaukee, WI, USA), Wako (Osaka, Japan) and Tokyo Kasei (Tokyo, Japan). Distilled, deionized water was used for the preparation of eluents and standard solutions.

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

3. Results and discussion

3.1. Cation-exchange characteristics of zirconium-modified silica gels under acidic condition

Cation-exchange characteristics of laboratory-made zirconium-modified silica gels (Zr-Silicas) were investigated for the application of Zr-Silicas as stationary phases for IEC-PD for benzenecarboxylic acids.

Fig. 1 shows the relationship between the amount of zirconium tetrabutoxide solution [ca. 85% (w/w) zirconium tetrabutoxide in butanol] in 100 ml ethanol solution (coating solution) and the amount of zirconium adsorbed on 10 g silica gel. With increasing amounts of zirconium tetrabutoxide in the coating solution, the amount of zirconium adsorbed on silica gel increased at first and then remained almost

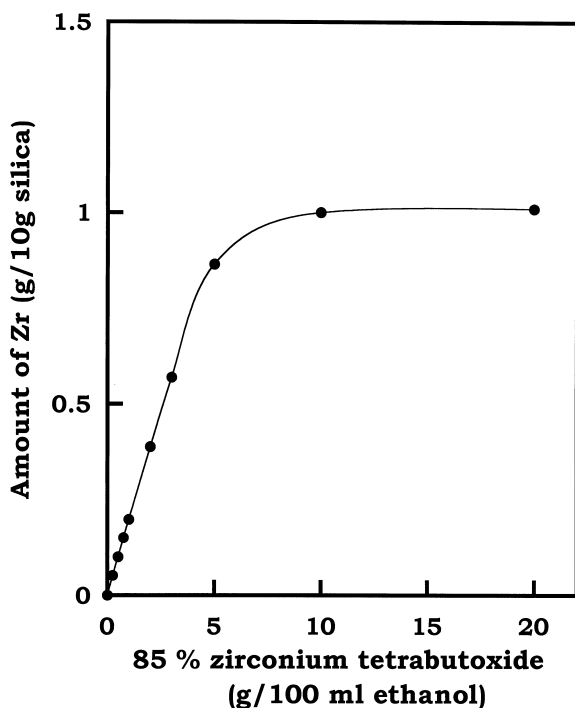


Fig. 1. Effect of amount of zirconium tetrabutoxide in ethanol on amount of zirconium adsorbed on silica gel.

the same. The amount of zirconium adsorbed on silica gel increased linearly at the amount of zirconium butoxide solution in the coating solution between 0 and 3 g. The amount of zirconium adsorbed was saturated at the amount of the zirconium tetrabutoxide solution in the coating solution ≥ 10 g. The maximum amount of zirconium adsorbed was 100 mg g^{-1} silica gel. This indicated that ca. 30% silanol group on the surface of the silica gel reacted with zirconium tetrabutoxide. These results also suggested that zirconium tetrabutoxide reacted with only silanol group on the surface of silica gel and the reaction was interfered by the already reacted zirconium tetrabutoxide.

Fig. 2 shows the relationship between the amount of zirconium adsorbed on silica gel and the retention volumes of monovalent cations (Li^+ , Na^+ , NH_4^+ , K^+ , Rb^+ and Cs^+) using 10 mM tartaric acid at pH 2.5 as an eluent. With increasing amount of zirconium, the retention volumes of these cations increased. The retention volumes increased linearly at the range of the amount of zirconium between 0

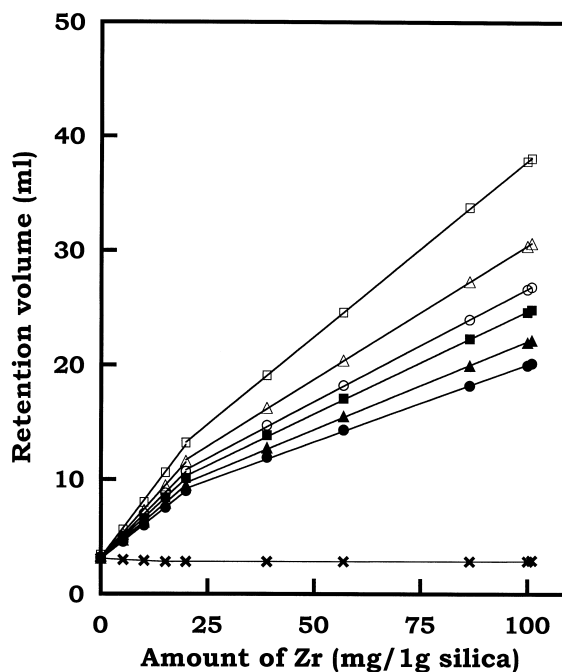


Fig. 2. Effect of amount of zirconium on zirconium-modified silica gels (Zr-Silicas) on retention volumes of monovalent cations. Column: Zr-Silicas adsorbed on 0–101 mg zirconium g^{-1} silica gel; column size: 250×4.6 mm I.D.; column temperature: 35°C; eluent: 10 mM tartaric acid at pH 2.5; flow-rate: 1 ml min^{-1} ; detection: indirect-conductivity; injection volume: 20 μ l; sample concentration: 1 mM; symbols: \times =water dip, \bullet = Li^+ , \blacktriangle = Na^+ , \blacksquare = NH_4^+ , \circ = K^+ , \triangle = Rb^+ , \square = Cs^+ .

and 20 mg g^{-1} silica gel and those also increased linearly at the range of the amount of zirconium between 20 and 100 mg g^{-1} silica gel. Although no conclusive reasons for the relationships were found, it was evident that the modification was very useful for the preparation of Zr-Silicas with various cation-exchange capacities under strongly acidic conditions.

3.2. Effect of amount of zirconium adsorbed on silica gel on chromatographic behavior of benzenecarboxylic acids

It is well known that the retention times of carboxylic acids in IEC are strongly influenced by the cation-exchange capacity of the stationary phase. Lee and Lord have demonstrated that there is an optimum ion-exchange capacity of sulfonated resins as stationary phase in IEC for the separation of

carboxylic acids [20]. Therefore, the effect of the amount of zirconium adsorbed on silica gel (0–100 mg zirconium g^{-1} silica gel) on chromatographic behavior of 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 investigated for the ion-exclusion chromatographic separation of these benzenecarboxylic acids and phenol on Zr–Silica as the stationary phase.

Fig. 3A–E show chromatograms of these benzenecarboxylic acids and phenol on Zr–Silicas adsorbed on 0, 10, 20, 39 and 101 mg zirconium g^{-1} silica gel as stationary phases, respectively. As shown in Fig. 3A, both complete separation of *o*-phthalic, salicylic and benzoic acids and phenol and incomplete separation of pyromellitic, trimellitic and hemimellitic acids were achieved on Zr–Silica adsorbed on 0 mg zirconium g^{-1} silica gel (Pia Seed 5S-100-SIL calcined at 1000°C) as the stationary phase. Since the Pia Seed 5S-100-SIL had little cation-exchange capacity under the ion-exclusion chromatographic conditions, these benzenecarboxylic acids were mainly separated by hydrophobic adsorption process. Therefore, the chromatogram indicated that complete separation of hydrophilic polyvalent benzenecarboxylic acids (pyromellitic, trimellitic and hemimellitic acids) was very difficult on the Pia Seed 5S-100-SIL column. As shown in Fig. 3B and C, complete separation of these benzenecarboxylic acids and phenol was achieved on Zr–Silicas adsorbed on 10 and 20 mg zirconium g^{-1} silica gel as the stationary phases. Since these Zr–Silicas acted as a cation exchanger under the ion-exclusion chromatographic conditions, complete separation of these hydrophilic polyvalent benzenecarboxylic acids were achieved by both ion-exclusion process and hydrophobic adsorption process. In contrast, as shown in Fig. 3D and E, with increasing the amount of zirconium adsorbed on silica gel (>20 mg zirconium g^{-1} silica gel), peak shapes of these benzenecarboxylic acids were largely destroyed. The peak shape of phenol remained the same. Peak shapes of polyvalent benzenecarboxylic acids (pyromellitic, trimellitic, hemimellitic and *o*-phthalic acids) were destroyed largely in comparison with those of monovalent

benzenecarboxylic acids (salicylic and benzoic acids). However, although no conclusive reasons for the peak destruction were found, it was evident that strong interactions between carboxylic group of benzenecarboxylic acids and zirconium on the surface of the Zr–Silica occurred. A detailed study on retention behavior of benzenecarboxylic acids on Zr–Silica stationary phase will be the subject of future work.

Considering peak shapes, peak resolution and separation time, it was concluded that Zr–Silica adsorbed on 20 mg zirconium g^{-1} silica gel was the most suitable stationary phase in the IEC–PD for the simultaneous separation of these benzenecarboxylic acids and phenol.

3.3. Effect of concentration of tartaric acid in eluent on chromatographic behavior of benzenecarboxylic acids

The use of acidic eluent in IEC is very effective for the improvement of both peak shapes of carboxylic acids and the resolution between carboxylic acids [8]. Therefore, the effect of the concentration of tartaric acid in the eluent on chromatographic behavior of these benzenecarboxylic acids on the Zr–Silica (20 mg zirconium g^{-1} silica gel) as the stationary phase was investigated for the simultaneous separation of these benzenecarboxylic acids and phenol with good peak shapes.

Fig. 4 shows the relationship between the concentration of tartaric acid in the eluent and the retention times of these benzenecarboxylic acids and phenol. The retention times of these benzenecarboxylic acids drastically increased at first and then remained almost the same. The retention time of phenol remained almost the same. This is due mainly to both a decrease in an electrostatic repulsion and an increase in hydrophobic interaction between these benzenecarboxylic acids and the Zr–Silica stationary phase by suppressing the dissociation of both these acids and the silanol group on the surface of the Zr–Silica. Table 2 shows the dissociation constants ($\text{p}K_{\text{a}}$) of these benzenecarboxylic acids and phenol in aqueous solution at 25°C. The degree to which the retention times varied with the concentration of tartaric acid in the eluent was dependent on the $\text{p}K_{\text{a}}$ values and the hydrophobicity of individual solutes.

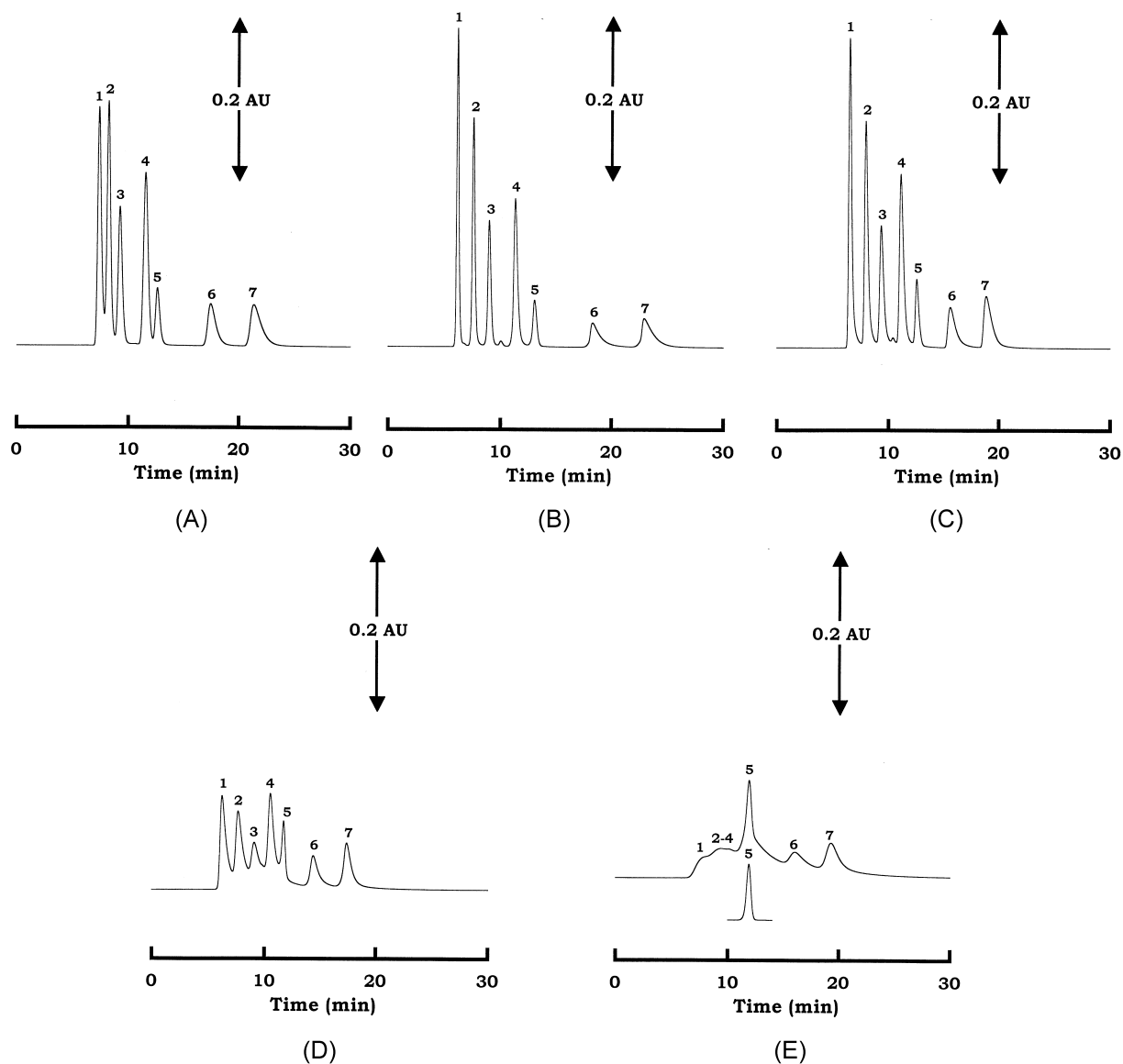


Fig. 3. Chromatograms of benzenecarboxylic acids and phenol on various Zr-Silica columns using 10 mM tartaric acid as eluent. (A) Zr-Silica adsorbed on 0 mg zirconium g^{-1} silica gel (Pia Seed 5S-100-SIL calcined at 1000°C); (B) Zr-Silica adsorbed on 10 mg zirconium g^{-1} silica gel; (C) Zr-Silica adsorbed on 20 mg zirconium g^{-1} silica gel; (D) Zr-Silica adsorbed on 39 mg zirconium g^{-1} silica gel; (E) Zr-Silica adsorbed on 101 mg zirconium g^{-1} silica gel. Flow rate: 0.35 ml min^{-1} ; detection: UV at 254 nm; sample concentration: 0.025 mM for pyromellitic and trimellitic acid and 0.1 mM for other benzenecarboxylic acid and phenol. Peaks: 1, pyromellitic acid; 2, trimellitic acid; 3, hemimellitic acid; 4, *o*-phthalic acid; 5, phenol; 6, salicylic acid; 7, benzoic acid. Other conditions as for Fig. 2.

Fig. 5A–C show chromatograms of these benzenecarboxylic acids and phenol using 0 mM tartaric acid (water) at pH 5.5, 1 mM tartaric acid at pH 3.2, and 50 mM tartaric acid at pH 2.2 as eluents,

respectively. (The chromatogram using 10 mM tartaric acid as the eluent has already been shown in Fig. 3C.) As shown in Fig. 5A, when using 0 mM tartaric acid (water) as the eluent, these benzenecar-

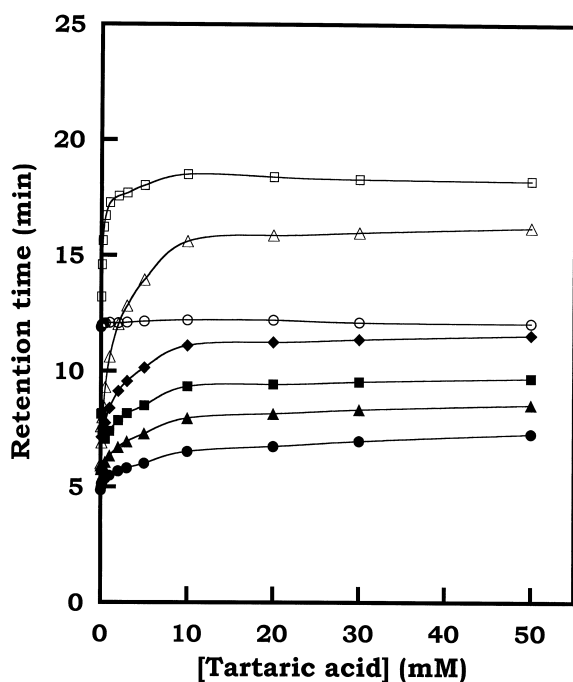


Fig. 4. Effect of concentration of tartaric acid in eluent on retention times of benzenecarboxylic acid and phenol on Zr–Silica column. Column: Zr–Silica adsorbed on 20 mg zirconium g^{-1} silica gel; eluent: 0–50 mM tartaric acid. Symbols: ●=pyromellitic acid, ▲=trimellitic acid, ■=hemimellitic acid, ◆=o-phthalic acid, ○=phenol, △=salicylic acid, □=benzoic acid. Other conditions as for Fig. 3.

boxylic acids were not separated and the peak shapes of these carboxylic acids were strongly tailed or fronted. This is because these benzenecarboxylic acids and the silanol group on the Zr–Silica were well dissociated and then these benzenecarboxylic acids were strongly excluded from dissociated silanol

Table 2

Dissociation constants of benzenecarboxylic acids and phenol in aqueous solution at 25°C

Benzenecarboxylic acid	$\text{p}K_{\text{a}1}$	$\text{p}K_{\text{a}2}$	$\text{p}K_{\text{a}3}$	$\text{p}K_{\text{a}4}$
Pyromellitic acid	1.92	2.82	4.49	5.64
Hemimellitic acid	2.62	3.82	5.51	
Trimellitic acid	2.52	3.85	5.20	
o-Phthalic acid	3.14	5.40		
Salicylic acid	2.75	12.4		
Benzoic acid	4.20			
Phenol	9.70			

group on the Zr–Silica stationary phase. As shown in Figs. 5B, C and 3C, with increasing the concentration of tartaric acid in the eluent, both the peak shapes and peak resolution of these benzenecarboxylic acids were improved. This is due to both a decrease in an electrostatic repulsion and an increase in hydrophobic adsorption between these benzenecarboxylic acids and the Zr–Silica by suppressing the dissociation of these acids and the silanol group on the Zr–Silica.

Considering peak shape, peak resolution and separation time, it was concluded that the optimum concentration of tartaric acid was a 10 mM. As shown in Fig. 3C, excellently simultaneous separation of these benzenecarboxylic acids and phenol was achieved in 20 min.

3.4. Analytical performance parameters

The optimum column and eluent conditions in the IEC–PD for the simultaneous separation of these benzenecarboxylic acids and phenol were concluded to the Zr–Silica (20 mg zirconium g^{-1} silica gel) column and a 10 mM tartaric acid as the eluent. Various analytical performance parameters were investigated.

Calibration graphs were obtained by plotting peak area versus the concentration of these benzenecarboxylic acids and phenol. Linear calibration graphs ($r^2 \geq 0.99$) were obtained in the concentration range between 0.001 and 2.0 mM for pyromellitic acids and trimellitic acid at 270 nm. Linear calibration graphs ($r^2 \geq 0.99$) were also obtained in the concentration range between 0.001 and 2.0 mM for the other benzenecarboxylic acids and phenol at 254 nm.

The relative standard deviations of the chromatographic peak area of these benzenecarboxylic acids and phenol, whose concentrations were 0.025 mM for pyromellitic and trimellitic acids and 0.1 mM for other benzenecarboxylic acid and phenol, were less than 0.5% ($N=10$) at 254 nm. Reproducible chromatograms were obtained during repeated chromatographic runs.

Table 3 shows the detection limits of these benzenecarboxylic acids and at a signal-to-noise ratio of 3 at 254 nm. Highly sensitive detection was achieved by the proposed method.

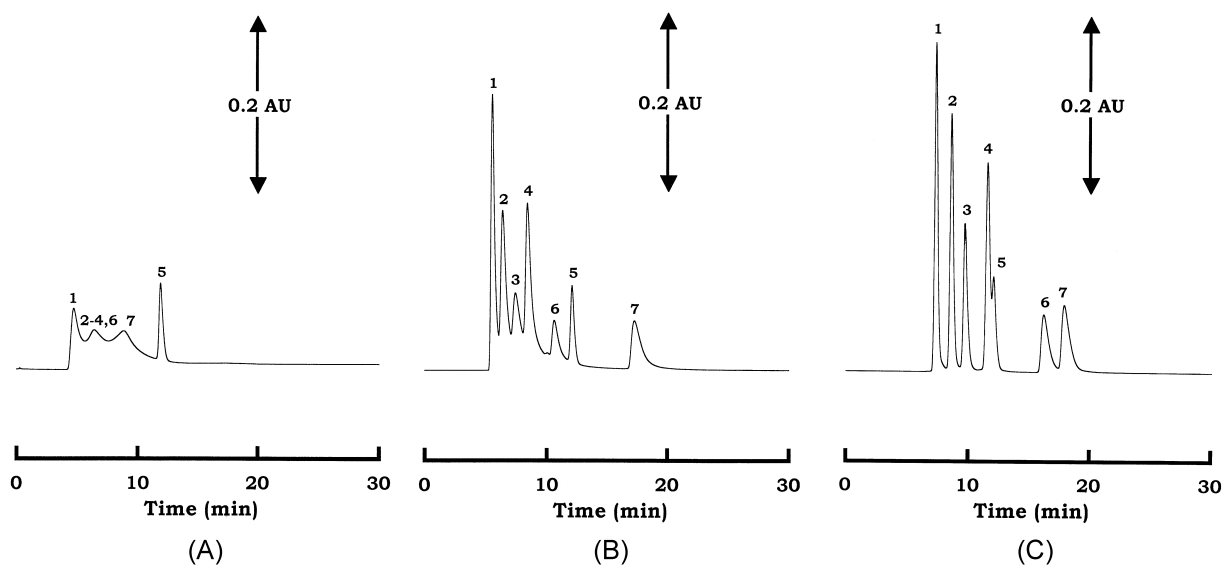


Fig. 5. Chromatograms of benzenecarboxylic acids and phenol on Zr–Silica column using various concentration of tartaric acid as eluent. (A) 0 mM tartaric acid at pH 5.5 (water); (B) 1 mM tartaric acid at pH 3.2; (C) 50 mM tartaric acid at pH 2.2. Peaks: 1, pyromellitic acid; 2, trimellitic acid; 3, hemimellitic acid; 4, *o*-phthalic acid; 5, phenol; 6, salicylic acid; 7, benzoic acid. Other conditions as for Fig. 4.

4. Conclusion

In order to expand the utility of laboratory-made zirconium-modified silica gels (Zr–Silicas) as stationary phases in IEC for carboxylic acids, the application of Zr–Silicas as cation-exchange stationary phase in IEC–PD for the separation of several benzenecarboxylic acids (pyromellitic, trimellitic, hemimellitic, *o*-phthalic, salicylic and benzoic acids)

Table 3

Detection limits of benzenecarboxylic acids and phenol under optimum chromatographic conditions

Benzenecarboxylic acid	Detection limits ^a	
	μM	ng ml^{-1}
Pyromellitic acid	0.036	9.1
Trimellitic acid	0.049	10
Hemimellitic acid	0.36	76
<i>o</i> -Phthalic acid	0.26	43
Salicylic acid	1.1	152
Benzoic acid	0.85	104
Phenol	0.65	61

^a Signal-to-noise ratio=3. Injection volume: 20 μl . Detection: UV at 254 nm.

and phenol was carried out using tartaric acid as eluent. Zr–Silicas were prepared by the reaction of the silanol group on the surface of silica gel with zirconium tetrabutoxide [$\text{Zr}(\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_3)_4$] in ethanol solution. A Zr–Silica adsorbed on 20 mg zirconium g^{-1} silica gel was the most suitable stationary phase in IEC–PD for the simultaneous separation of these benzenecarboxylic acids and phenol. Excellent simultaneous separation and highly sensitive UV detection at 254 nm for these benzenecarboxylic acids and phenol were achieved in 20 min by IEC–PD using the Zr–Silica column (250×4.6 mm I.D.) and a 10 mM tartaric acid at pH 2.5 as the eluent. This result strongly confirmed that Zr–Silica was a very useful cation-exchange stationary phase not only in ion chromatography for cations but also in IEC for benzenecarboxylic acids.

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