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Non-suppressed ion chromatography of cations on silica gel modified with aluminium

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Abstract

The presence of aluminium in the silica matrix causes an enhancement of the acidity of the silanol group on silica gel. Therefore, in order to prepare silica-based cation-exchangers for ion chromatography (IC) under strongly acidic eluent conditions, modification of silica gel with aluminium using a coating method was carried out. As a result, aluminium-adsorbing silica gels were found to act as a cation-exchangers under strongly acidic eluent conditions and were successfully applied to the conductimetric detection IC for the separation of common mono- and divalent cations using nitric acid–2,6-pyridinedicarboxylic acid eluent. These results strongly indicate that the modification is a simple and effective way for the preparation of advanced silica-based cation-exchangers for IC. © 1998 Elsevier Science B.V.

Keywords: Aluminium-modified silica; Silica; Stationary phases, LC; Metal cations

1. Introduction

It is well known that the silanol group on the surface of silica gel behaves as a weak acid with a pK_a of ca. 7.1 [1]. On the basis of cation-exchange characteristics, Smith et al. [2], Brown et al. [3] and Iwachido et al. [4–6] have applied unmodified silica gel as a cation-exchanger for the conductimetric detection ion chromatography (IC) of alkali and alkaline earth metal cations. In these works, the lithium ion (Li^+) was mainly employed as the eluent ion and the pH of eluent was kept approximately neutral to achieve both conductimetric detection and separation of these cations. Under these chromatographic conditions, it is pointed out that there are serious disadvantages, such as the low conductimetric detection sensitivity and the instability of silica gel matrix. Using strongly acidic eluent is one of the

best ways to improve upon these disadvantages of IC.

In our preliminary works [7,8], we have found that one commercially available unmodified silica gel (Develosil 30-5) can act as a cation-exchanger under strongly acidic eluent conditions and have demonstrated the effectiveness of the Develosil 30-5 silica gel in the conductimetric detection IC for cations under strongly acidic eluent conditions. We have also revealed that the main cause of cation-exchange characteristics of the Develosil 30-5 silica gel under strongly acidic conditions is attributed to aluminium present as an impurity in the silica gel [9]. These findings strongly indicate that the modification of silica gel with aluminium is very effective for the preparation of silica-based cation-exchangers for IC. However, the preparation of aluminium-containing silica gels by sol-gel reaction was very difficult. This is because the optimum concentration of aluminium in silica gel for IC is extremely low and the

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manufacturing process of aluminium-containing silica gel for HPLC is not well established.

Therefore, in this work, in order to demonstrate the effectiveness of silica gel modified with aluminium in IC, a simple approach for the modification, using a coating method, was investigated.

2. Experimental

2.1. Preparation of aluminium-adsorbing silica gels

A Fuji–Silysia Chemical (Kasugai, Japan) Super Micro Bead Silica Gel B-5 porous spherical silica gel was employed as a matrix. A 10 g amount of the silica gel was immersed in 200 ml of a given concentration of $\text{Al}_2(\text{SO}_4)_3$ solution. The solution was prepared by dissolving $\text{Al}_2(\text{SO}_4)_3 \cdot 14\text{--}18\text{H}_2\text{O}$ in distilled and deionized water (DIW). After stirring for 1 h, the solution was filtered. The resultant gel was washed with a 300 ml DIW and then was dried overnight at 130°C , followed by calcining at $200\text{--}800^\circ\text{C}$ for 5 h.

2.2. Determination of amount of aluminium on aluminium-adsorbing silica gels

The determination of aluminium on aluminium-adsorbing silica gels was carried out using a Nippon Jarrell–Ash (Kyoto, Japan) ICAP-1000 inductively coupled plasma-atomic emission spectrometry (ICP-AES) system. Fig. 1 shows the analytical procedure employed for the dissolution of aluminium-adsorbing silica gels prior to their analysis using ICP-AES.

2.3. Measurement of physical properties of aluminium adsorbing silica gels

The determination of the surface area and pore volume of aluminium-adsorbing silica gels by the nitrogen adsorption isotherms on the gels at 77 K was carried out using a Carlo Erba Instruments (Milano, Italy) Sorptomatic 1800 surface analyser. The surface area was calculated from the BET equation. The pore volume was obtained from the

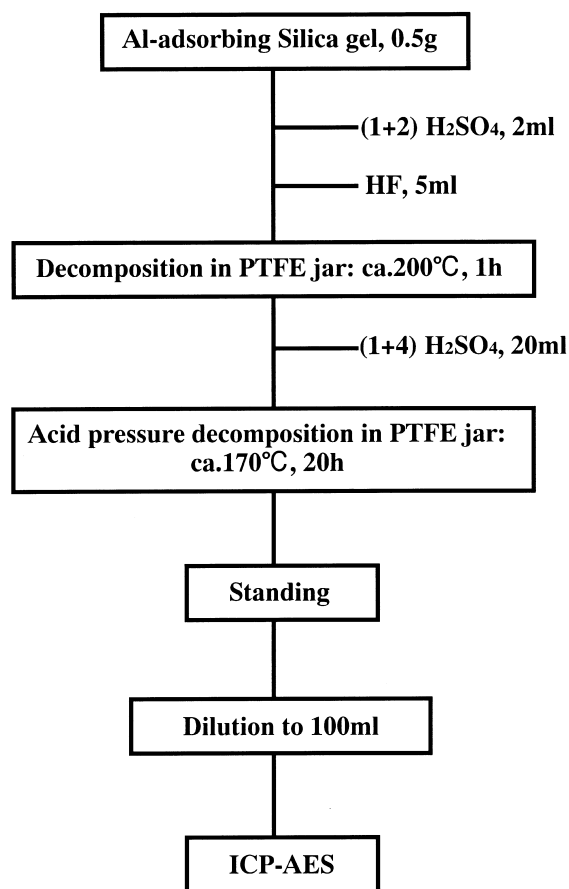


Fig. 1. Dissolution procedure for the determination of aluminium on aluminium-adsorbing silica gels using ICP-AES.

liquid nitrogen volume evaluated from the nitrogen adsorption volume at $P/P_0=0.95$.

2.4. Ion chromatograph

The ion chromatograph consisted of a Tosoh (Tokyo, Japan) SC-8020 chromatographic data-processor, a Tosoh CCPM-II solvent delivery pump operated at a flow-rate of 1 ml min^{-1} , a Tosoh CO-8020 column oven operated at 35°C , a Tosoh CM-8020 conductimetric detector, a Tosoh SD-8023 on-line degasser, and a Rheodyne (Cotati, CA, USA) model 9125 injector equipped with a $50\text{-}\mu\text{l}$ sample loop.

The separation columns ($250 \text{ mm} \times 4.6 \text{ mm I.D.}$,

stainless steel) were packed with aluminium-adsorbing silica gels using the slurry packing method.

2.5. Reagents

All reagents, except for H_2SO_4 and HF were of analytical reagent grade and were purchased from Wako (Osaka, Japan). H_2SO_4 and HF were of ultra-pure grade and were purchased from Wako and Tama (Tokyo, Japan), respectively. DIW was used for the preparation of the eluents and standard solutions.

3. Results and discussion

3.1. Effect of the amount of aluminium on aluminium-adsorbing silica gels on retention behaviour of mono- and divalent cations under strongly acidic conditions

Firstly, the effect of the concentration of $\text{Al}_2(\text{SO}_4)_3$ in the solution on the amount of aluminium on aluminium-adsorbing silica gel was investigated.

As shown in Fig. 2, although the amount of aluminium increased with increasing the concentration of $\text{Al}_2(\text{SO}_4)_3$, the degree of the increase

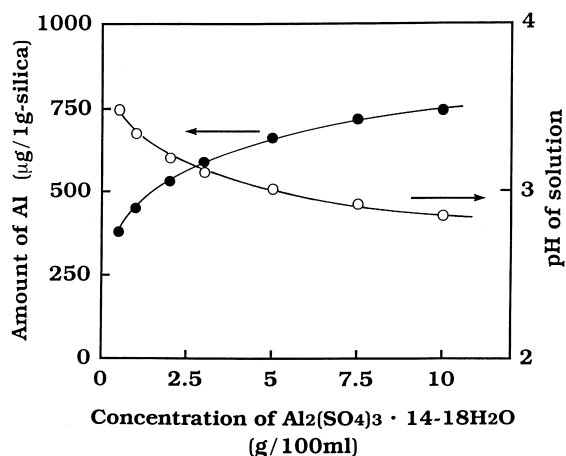


Fig. 2. Effect of concentration of $\text{Al}_2(\text{SO}_4)_3 \cdot 14-18\text{H}_2\text{O}$ in the solution on the amount of aluminium adsorbed on silica gels. Symbols: ●=Amount of Al, ○=pH of solution.

gradually decreased. This indicated that the amount of aluminium was strongly dependent on the concentration of aluminium under these coating conditions. On the other hand, since the pH of the solutions decreased with increasing concentration of $\text{Al}_2(\text{SO}_4)_3$ and the silica gel has a little cation-exchange ability under the acidic eluent conditions [9], it might be expected that the amount of aluminium adsorbed was also somewhat influenced on the pH of the solution under these coating conditions.

Secondly, the effect of the amount of aluminium on the retention behaviour of mono- and divalent cations (Li^+ , Na^+ , NH_4^+ , K^+ , Rb^+ , Cs^+ , Mg^{2+} , Ca^{2+} and Ba^{2+}) was investigated using a 2 mM nitric acid eluent. Aluminium-adsorbing silica gels calcined at 600°C for 5 h were employed.

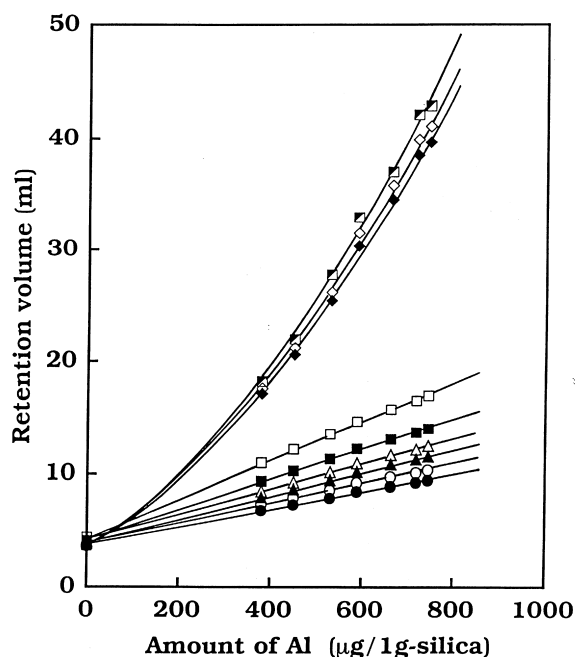


Fig. 3. Effect of the amount of aluminium on aluminium-adsorbing silica gels on retention volumes of common mono- and divalent cations. Column: Aluminium-adsorbing silica gels calcined at 600°C for 5 h; column size: 250×4.6 mm I.D.; column temperature: 35°C ; eluent: 2 mM HNO_3 ; flow-rate: 1 ml min^{-1} ; detection: indirect conductivity; injection volume: $50 \mu\text{l}$; sample concentration: 0.1 mM; symbols: ●= Li^+ , ○= Na^+ , ▲= NH_4^+ , △= K^+ , ■= Rb^+ , □= Cs^+ , ◆= Mg^{2+} , ◇= Ca^{2+} , ▣= Ba^{2+} .

As shown in Fig. 3, the retention volumes of these cations increased with increasing the amount of aluminium adsorbed on the silica gel. The retention volumes of divalent cations drastically increased. This is because the retention volumes of divalent cations are more strongly dependent on the cation-exchange capacity compared to those of monovalent cations. In other words, the result meant that the cation-exchange capacity of aluminium-adsorbing silica gels under strongly acidic eluent conditions was strongly dependent on the amount of aluminium.

From the above results, it was concluded that the modification of silica gel using the coating method with aluminium was simple and effective for the preparation of silica-based cation-exchanger for IC under strongly acidic eluent conditions.

3.2. Effect of the calcining temperature on retention behaviour of mono- and divalent cations under strongly acidic conditions

The effect of calcining temperature on the retention behaviour of mono- and divalent cations was investigated. The aluminium-adsorbing silica gel (450 μg aluminium g^{-1} silica) prepared using $\text{Al}_2(\text{SO}_4)_3$ solution (1 g $\text{Al}_2(\text{SO}_4)_3 \cdot 14\text{-}8\text{H}_2\text{O}$ 100 ml^{-1}) was employed after the calcining at 200–800°C for 5 h.

As shown in Fig. 4, the retention volumes of these cations were dramatically changed depending on the calcining temperature. As shown in Table 1, since the physical properties (surface area and pore volume) of aluminium-adsorbing silica gels demonstrated no variation up to 600°C, the increase of retention volumes of these cations might be mainly due to the structural change of aluminium-adsorbing silica gels caused by the elevated calcining temperature. In contrast, the retention volumes of these cations decreased at temperatures above 600°C. The decrease was mainly due to a decrease of surface area, causing a decrease of the cation-exchange capacity. The details concerning the effect of calcining temperature will be the subject of future work.

Considering retention behaviour of mono- and divalent cations, the optimum calcining temperature was concluded to be ca. 600°C.

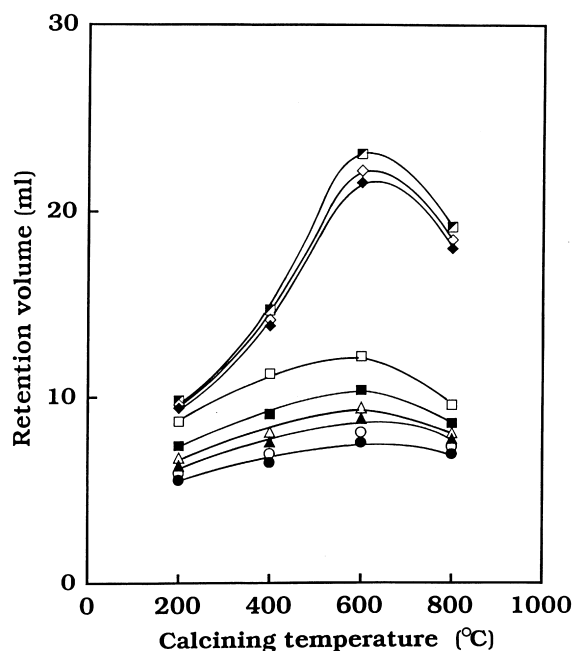


Fig. 4. Effect of calcining temperature on retention volumes of common mono- and divalent cations. Column: Aluminium-adsorbing silica gels (450 μg aluminium g^{-1} silica gel) calcined at 200–800°C for 5 h. Other chromatographic conditions and symbols as for Fig. 3.

3.3. Retention behaviour of mono- and divalent cations on the aluminium-adsorbing silica gel under strongly acidic eluent conditions

The detailed investigation of the retention behaviour of mono- and divalent cations on aluminium-adsorbing silica gel column was carried out under strongly acidic eluent conditions. The aluminium-adsorbing silica gel (450 μg aluminium g^{-1} silica) was employed after the calcining at 600°C for 5 h. The effect of the concentration of nitric acid in the eluent on the retention behaviour of mono- and divalent cations was investigated.

As shown in Fig. 5, the retention volumes of these cations drastically decreased with increasing concentration of nitric acid. This is due to an increase in the concentration of H^+ as the competing ion and perhaps due to a reduced cation-exchange capacity of the stationary phase. When using 10 mM nitric acid eluent, the retention volumes of these cations were

Table 1
Effect of calcining temperature on physical properties of aluminium-adsorbing silica gels

Gel	Drying or calcining (°C)	Surface area (m ² g ⁻¹)	Pore volume (ml g ⁻¹)
Silica gel (untreated)	130	512	0.85
Aluminium-adsorbing silica gel (450 µg Al g ⁻¹ silica)	200	518	0.85
	400	499	0.85
	600	487	0.84
	800	388	0.73

larger than that of the water dip (V_0). This indicated that the aluminium-adsorbing silica gel still acted as a cation-exchanger under such strongly acidic eluent conditions (pH 2). As shown in Fig. 6, a reasonable separation of monovalent cations was achieved using 2 mM nitric acid as the eluent, in 15 min. However, incomplete separation of divalent cations (Mg^{2+} and

Ca^{2+}) was obtained under the same eluent conditions. Therefore, in order to separate simultaneously common mono- and divalent cations, the effect of the addition of 2,6-pyridinedicarboxylic acid (PDCA) to 2 mM nitric acid eluent was investigated. PDCA is commonly employed as a selective complexation agent for the separation of Mg^{2+} and Ca^{2+} under strongly acidic eluent conditions [10].

As shown in Fig. 7, the retention volumes of

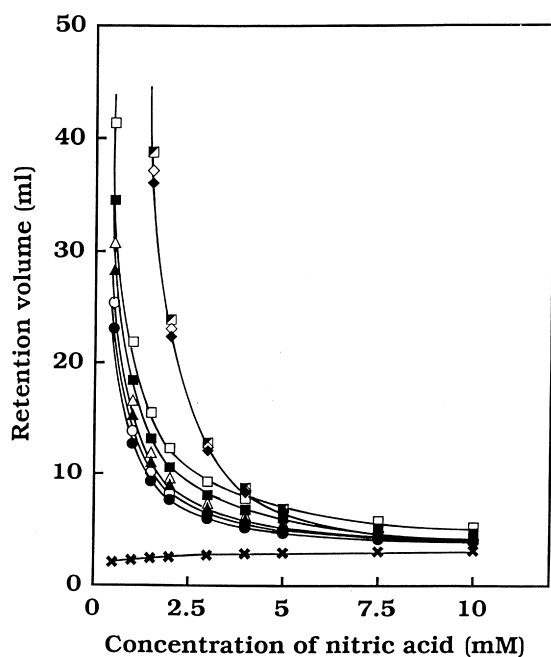


Fig. 5. Effect of concentration of nitric acid in the eluent on retention volumes of common mono- and divalent cations. Column: aluminium-adsorbing silica gel (450 µg aluminium g⁻¹ silica gel) calcined at 600°C for 5 h; eluent: 1 to 10 mM HNO₃; symbols: ×=water dip, ●=Li⁺, ○=Na⁺, ▲=NH₄⁺, △=K⁺, ■=Rb⁺, □=Cs⁺, ◆=Mg²⁺, ◇=Ca²⁺, ▣=Ba²⁺. Other chromatographic conditions as for Fig. 3.

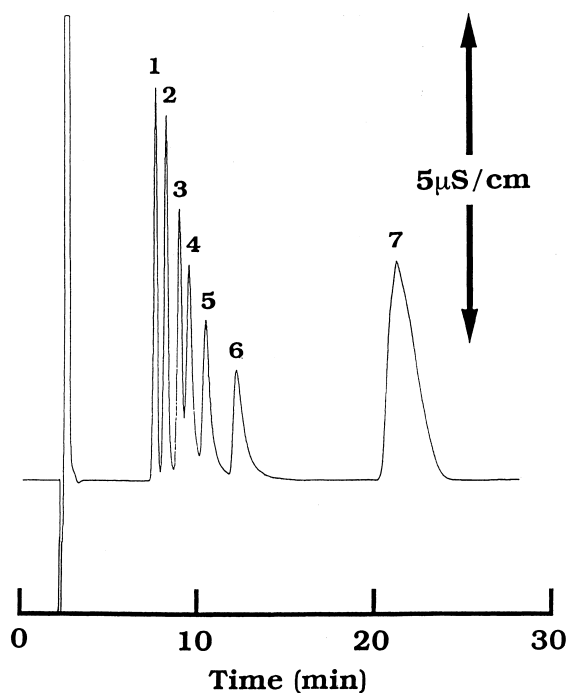


Fig. 6. Chromatogram of common mono- and divalent cations using nitric acid eluent. Eluent: 2 mM HNO₃; peaks: 1=Li⁺, 2=Na⁺, 3=NH₄⁺, 4=K⁺, 5=Rb⁺, 6=Cs⁺, 7=Mg²⁺+Ca²⁺. Other chromatographic conditions as for Fig. 3.

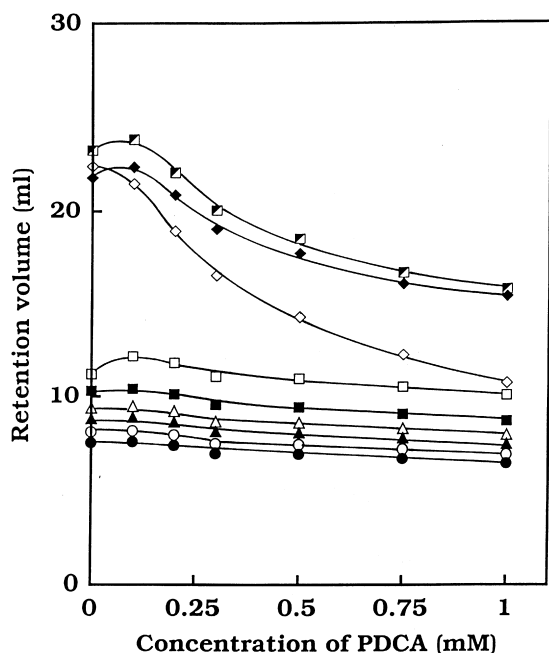


Fig. 7. Effect of concentration of PDCA in nitric acid eluent on retention volumes of mono- and divalent cations. Eluent: 0 to 1 mM PDCA in 2 mM nitric acid; other chromatographic conditions and symbols as for Fig. 3.

mono- and divalent cations decreased with increasing concentration of PDCA. The slight decrease of the retention volumes for monovalent cations was mainly due to an increase in the concentration of H^+ as the competing ion and perhaps due to a reduction in the cation-exchange capacity of the stationary phase. The decrease of the retention volumes for divalent cations was mainly due to the complexation effect. The degree of decrease of retention volumes for Ca^{2+} was larger than those for other divalent cations. This is because the Ca^{2+} -PDCA complex is more stable when compared with other divalent cations-PDCA complexes. As shown in Fig. 8, when using 2 mM nitric acid-0.5 mM PDCA eluent, a good separation of common mono- and divalent cations (Li^+ , Na^+ , NH_4^+ , K^+ , Rb^+ , Cs^+ , Mg^{2+} and Ca^{2+}) was achieved in ca. 20 min.

As shown in Table 2, since the retention behaviour of alkali, alkaline earth and transition metal cations on the aluminium-adsorbing silica gel was similar to that on the Develosil 30-5 silica gel [8], the modi-

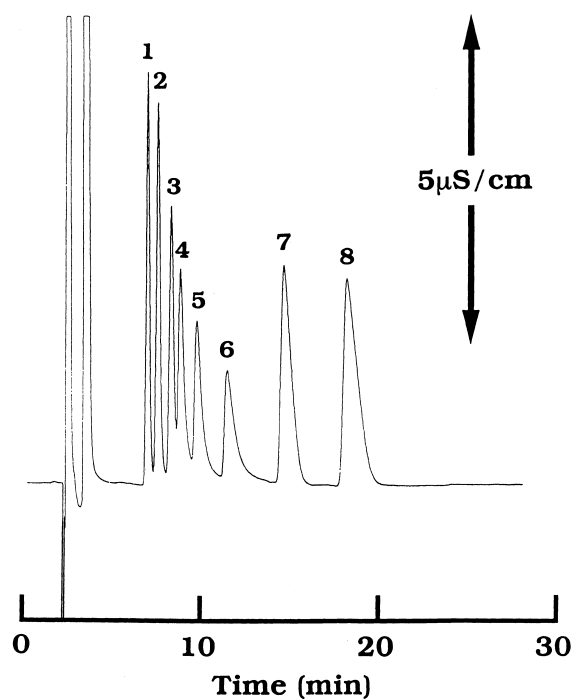


Fig. 8. Chromatogram of common mono- and divalent cations using nitric acid-PDCA eluent. Eluent: 2 mM HNO_3 +0.5 mM PDCA; peaks: 1= Li^+ , 2= Na^+ , 3= NH_4^+ , 4= K^+ , 5= Rb^+ , 6= Cs^+ , 7= Ca^{2+} , 8= Mg^{2+} . Other chromatographic conditions as for Fig. 3.

Table 2
Retention volumes (V_R) of alkali, alkaline earth and transition metal cations

Cation	V_R (ml)	Cation	V_R (ml)
Li^+	7.0	Cd^{2+}	4.5
Na^+	7.9	Fe^{2+}	5.7
NH_4^+	8.2	Mn^{2+}	11.7
K^+	8.8		
Rb^+	9.7	Co^{2+}	N.D. ^a
Cs^+	11.4	Cu^{2+}	N.D.
		Ni^{2+}	N.D.
Mg^{2+}	18.1	Pb^{2+}	N.D.
Ca^{2+}	14.6	Zn^{2+}	N.D.
Si^{2+}	18.2	Fe^{3+}	N.D.
Ba^{2+}	19.0		

^a Not detected.

Chromatographic conditions as for Fig. 8.

fication was strongly recognized to be useful for the preparation of cation-exchanger for IC.

4. Conclusion

In this work, the simple modification of silica gel by a coating method with aluminium was carried out for the preparation of silica-based cation-exchanger for IC under strongly acidic eluent conditions. The aluminium-adsorbing silica gel prepared in this study was found to be very useful for the cation-exchange separation of common mono- and divalent cations (Li^+ , Na^+ , NH_4^+ , K^+ , Rb^+ , Cs^+ , Mg^{2+} and Ca^{2+}) using nitric acid–PDCA eluent. However, the separation of divalent cations (Mg^{2+} , Sr^{2+} and Ba^{2+}) on aluminium-adsorbing silica gel column was not satisfactory. Both the complete separation of these divalent cations and the practical application of aluminium-adsorbing silica gel to various environmental waters will be subject of future work.

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