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Retention behavior of alkali, alkaline earth and transition metal cations in ion chromatography with an unmodified silica gel column

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Abstract

An unmodified silica gel (Develosil 30-5) column (150×4.6 mm I.D.) has been applied to the ion chromatographic separation of alkali, alkaline earth and transition metal cations. The retention behavior of the above cations on the bare substrate was investigated using a number of weak inorganic and organic acid eluents. During this investigation, several separations were achieved and the most suitable eluent conditions were identified. It was concluded that: (a) 1.5 mM HNO₃–0.5 mM pyridine-2,6-dicarboxylic acid eluent was the most effective for the simultaneous separation of common alkali and alkaline earth metal cations, (b) 1.5 mM oxalic acid eluent resulted in the best separation of alkali, alkaline earth, and transition metal cations, (c) 0.5 mM CuSO₄ eluent could be used for the separation of alkali metal cations alone and (d) 0.5 mM ethylenediamine–oxalic acid eluent at pH 5.5 resulted in the most efficient separation of both alkaline earth and transition metal cations.

Keywords: Mobile phase composition; Metal cations

1. Introduction

Ion chromatography (IC), developed by Small et al. [1], is recognized as being a useful technique for the determination of various inorganic and organic anions and cations. In the IC separation of cations, separation columns packed with either sulfonated styrene–divinylbenzene co-polymer resins, or sulfonated or carboxylated silicas, are commonly used [2]. Unmodified silica gel can also be used as a weakly acidic cation exchanger because of the silanol group on the surface of silica [3,4]. On the basis of the cation-exchange characteristics, Smith and Pietrzyk [5], Brown and Pietrzyk [6] and Iwachido et al. [7–9] have all applied unmodified silica gel

columns to the IC separation of alkali, alkaline earth and transition metal cations. In the above studies, lithium ion was used as the competing cation to achieve the separation of alkali and alkaline earth metal cations, and the eluent pH was kept approximately neutral. Under these chromatographic conditions, the conductimetric detection sensitivities of these cations were very low and the lifetime of the silica stationary phase was considerably shortened [10].

The use of acidic eluents removes the above disadvantages. In a previous study [11], we demonstrated that a commercially available unmodified silica gel (Develosil 30-5) acts as a cation exchanger under acidic conditions. On the basis of the characteristics of the Develosil 30-5 silica gel, we have established a useful IC method for the simultaneous

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determination of common alkali and alkaline earth metal cations (Na^+ , NH_4^+ , K^+ , Mg^{2+} and Ca^{2+}) using HNO_3 –pyridine-2,6-dicarboxylic acid (PDCA) as an eluent. However, in the above study, the detailed cation-exchange characteristics of the Develosil 30-5 column were not investigated fully.

The purpose of the present study was to evaluate the cation-exchange characteristics of the Develosil 30-5 column under acidic–neutral conditions and to demonstrate the application of the Develosil 30-5 column to the IC separation of alkali, alkaline earth and transition metal cations.

2. Experimental

2.1. Instrumentation

The ion chromatograph consisted of a Tosoh (Tokyo, Japan) SC-8020 chromatographic data-processor, a Tosoh CCPM-II pump operated at 1 ml/min, a Tosoh SD-8023 on-line degasser, a Tosoh CO-8020 column oven that was set at 35°C, a Tosoh CM-8020 conductimetric detector, a Shimadzu (Kyoto, Japan) SPD-10AV UV–Vis spectrophotometric detector and a Rheodyne (Cotati, CA, USA) 9125 injector with a 50- μl sample loop.

2.2. Silica gel column

The stainless steel column (150 \times 4.6 mm I.D.) was packed with a Nomura Chemical (Seto, Japan) Develosil 30-5 porous spherical unmodified silica gel and was equilibrated thoroughly with eluent before each chromatographic run. The specific details of the Develosil 30-5 substrate are shown in Table 1.

Table 1
Properties of the Develosil 30-5 unmodified silica gel used in this study

Particle size (μm)	5
Pore size (\AA)	27
Surface area per weight (m^2/g)	770
Pore volume per weight (ml/g)	0.53
Packing density (g/ml)	0.76
Column size (mm)	150 \times 4.6 I.D.
Surface area per column (m^2/column)	$1.43 \cdot 10^3$

2.3. Reagents

All reagents were of analytical reagent-grade and were purchased from Wako (Osaka, Japan) and Tokyo Kasei (Tokyo, Japan). Distilled deionized water was used for the preparation of standard solutions and eluents. The pH of the eluent was measured using a Toa Denpa (Tokyo, Japan) IM-40S ion meter with a glass electrode.

3. Results and discussion

3.1. Retention behavior of cations using various inorganic and organic acid eluents

In order to evaluate the cation-exchange characteristics of the Develosil 30-5 column under acidic conditions, the retention behavior of alkali, alkaline earth and transition metal cations was investigated using various inorganic and organic acids as the eluent. The retention volumes (V_R) of each cation, using each of the eluents investigated, are shown in Table 2. The pH of the eluent was adjusted to between 2.7 and 2.8 by controlling the concentration of each acid in the eluent.

First, the retention behavior of alkali metal cations (Li^+ , Na^+ , K^+ , Rb^+ and Cs^+), including ammonium ion (NH_4^+), was studied. As shown in Table 2, when using any of the acid eluents studied, the separation of alkali metal cations could be achieved. The V_R values of alkali metal cations were practically the same using each acid eluent, provided that the pH of the eluents were the same. These results indicated that the pH of the eluent, that is, the concentration of hydronium ion (H^+) in the eluent was a dominant factor for deciding the V_R values of alkali metal cations. However, it was also found that the indirect conductimetric detector response of alkali metal cations decreased when using weak acids as eluents. This is due mainly to interaction between H^+ and weak acid [12].

Next, the retention behavior of alkaline earth metal cations (Mg^{2+} , Ca^{2+} , Sr^{2+} and Ba^{2+}) was studied. As shown in Table 2, when using 2 mM oxalic acid, 2 mM PDCA, or 1.5 mM HNO_3 –0.5 mM PDCA as the eluent, the separation of alkaline earth metal cations could be achieved. The role of oxalic acid was to retard the elution of alkaline earth

Table 2
Retention volumes of alkali, alkaline earth and transition metal cations using various inorganic and organic acid eluents

Eluent, pH	Retention volume (ml)																		
	Li ⁺	Na ⁺	NH ₄ ⁺	K ⁺	Rb ⁺	Cs ⁺	Mg ²⁺	Ca ²⁺	Sr ²⁺	Ba ²⁺	Cd ²⁺	Co ²⁺	Cu ²⁺	Fe ²⁺	Mn ²⁺	Ni ²⁺	Pb ²⁺	Zn ²⁺	Fe ³⁺
2 mM Nitric acid, 2.72	3.9	4.6	5.4	6.2	7.5	9.9	9.5	10.0	10.3	10.7	9.2	9.5	9.63	9.4	9.3	9.5	10.6	9.4	SR
2 mM Oxalic acid, 2.74	4.3	5.0	5.9	6.9	8.3	11.2	11.2	12.4	13.5	14.0	9.2	5.0	ND	7.3	9.4	3.3	3.0	9.2	ND
4 mM Malonic acid, 2.73	4.2	4.9	5.7	6.6	8.0	10.7	11.1	11.7	12.2	12.6	10.5	10.9	6.2	10.9	10.8	10.9	11.6	10.9	8.1
5 mM Tartaric acid, 2.74	4.1	4.7	5.6	6.5	7.9	10.4	10.6	10.8	11.4	11.8	9.8	9.9	7.1	10.2	10.2	9.6	8.2	10.2	26.3
5 mM Citric acid, 2.79	4.4	5.2	6.1	7.1	8.6	11.5	12.9	13.4	14.0	14.5	12.0	11.8	7.9	12.4	12.5	10.7	10.0	12.4	2.9
7.5 mM Malic acid, 2.80	4.6	5.3	6.3	7.4	8.9	12.0	13.9	14.4	15.2	15.7	12.9	13.0	9.5	13.4	13.3	12.5	11.7	13.4	36.3
30 mM Succinic acid, 2.83	4.9	5.8	6.9	8.1	9.8	13.1	17.1	18.0	18.7	19.4	16.0	16.7	15.4	16.7	16.6	16.9	15.3	16.7	SR
2 mM PDCA, 2.79	4.7	5.5	6.5	7.5	9.1	12.2	14.4	6.1	12.0	13.8	ND	ND	ND	ND	4.0	ND	ND	ND	ND
1.5 mM Nitric acid + 0.5 mM PDCA, 2.72	4.2	4.8	5.7	6.5	7.8	10.4	10.7	8.3	10.9	13.3	2.4	2.1	ND	3.0	6.2	ND	ND	3.0	ND
5 mM IDA, 2.71	3.6	4.2	4.9	5.6	6.6	8.8	7.59	8.0	8.4	8.5	7.2	7.4	ND	7.5	7.4	7.6	7.6	7.3	ND
1.5 mM NTA, 2.75	3.9	4.5	5.2	6.0	7.2	9.5	9.00	9.3	9.7	10.0	3.53	2.61	ND	7.2	8.5	ND	ND	2.0	ND
1 mM EDTA, 2.93	5.3	6.2	7.4	8.6	10.4	14.0	19.9	20.4	21.1	21.3	ND	ND	ND	ND	4.5	ND	ND	ND	ND

PDCA = pyridine-2,6-dicarboxylic acid, IDA = iminodiacetic acid, NTA = nitrilotriacetic acid, NTA = nitrilotriacetic acid, EDTA = ethylenediaminetetraacetic acid.
ND = not detected, SR = strongly retained.

metal cations and thus the separation of three alkaline earth metal cations (a) Mg^{2+} , Ca^{2+} and Ba^{2+} , or (b) Mg^{2+} , Sr^{2+} and Ba^{2+} was possible. In contrast, PDCA could be used to selectively accelerate the elution of Ca^{2+} and thus the separation of three alkaline earth metal cations (a) Mg^{2+} , Ca^{2+} and Ba^{2+} , or (b) Ca^{2+} , Sr^{2+} and Ba^{2+} could be achieved when using 1.5 mM HNO_3 –0.5 mM PDCA as the eluent. It is well known that nitrilotriacetic acid (NTA) and ethylenediaminetetraacetic acid (EDTA) form stable complexes with alkaline earth metal cations under basic conditions. However, when using 1.5 mM NTA or 1.0 mM EDTA as the eluent, the separation of alkaline earth metal cations was not possible. This was because the complexes were too unstable under the acidic conditions used. The remainder of the eluents shown in Table 2 were also not suitable for the separation of alkaline earth metal cations.

From the above results, it was concluded that 1.5 mM HNO_3 –0.5 mM PDCA and 2 mM oxalic acid were the most useful eluents studied for the separation of alkaline earth metal cations on the Develosil 30-5 column. An additional advantage with the use of 1.5 mM HNO_3 –0.5 mM PDCA and 2 mM oxalic acid eluents, as shown in Table 2, was the ability to simultaneously separate common alkali and alkaline earth metal cations (Li^+ , Na^+ , NH_4^+ , K^+ , Mg^{2+} and Ca^{2+}). A typical chromatogram of the above cations, using 1.5 mM HNO_3 –0.5 mM PDCA eluent is shown in Fig. 1.

Following the above studies into the retention behavior of alkali and alkaline earth metal cations, the retention behavior of transition metal cations (Co^{2+} , Cd^{2+} , Cu^{2+} , Fe^{2+} , Mn^{2+} , Ni^{2+} , Pb^{2+} , Zn^{2+} and Fe^{3+}) was studied. As shown in Table 2, when using either 2 mM oxalic acid, 5 mM tartaric acid, 5 mM citric or 3 mM NTA as the eluent, the separation of a number of transition metal cations was possible. When using 2 mM oxalic acid as the eluent, although the separation of six transition metal cations [Pb^{2+} , Ni^{2+} , Zn^{2+} , Co^{2+} , Fe^{2+} and Mn^{2+} (Cd^{2+})] was achieved, Cu^{2+} and Fe^{3+} were not detected because the Cu^{2+} - and Fe^{3+} -oxalic acid complexes formed were very stable and passed through the column unretained. When using either 5 mM tartaric acid or 5 mM citric acid eluents, the separation of four transition metal cations (Cu^{2+} , Pb^{2+} , Zn^{2+} and Mn^{2+}) was possible. When using 1.5 mM NTA

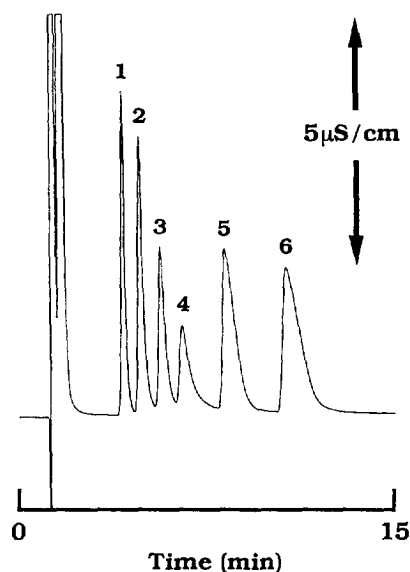


Fig. 1. Chromatogram of common alkali and alkaline earth metal cations using HNO_3 –pyridine-2,6-dicarboxylic acid as the eluent. Conditions: Eluent, 5 mM HNO_3 –0.5 mM pyridine-2,6-dicarboxylic acid; flow-rate, 1 ml/min; Column, Develosil 30-5, 150×4.6 mm I.D.; Column temperature, 35°C; Detection, indirect conductivity; Injection volume, 50 μl ; Sample concentration, 0.1 mM. Peaks: 1= Li^+ , 2= Na^+ , 3= NH_4^+ , 4= K^+ , 5= Ca^{2+} and 6= Mg^{2+} .

eluent, the separation of five transition metal cations (Zn^{2+} , Co^{2+} , Cd^{2+} , Fe^{2+} and Mn^{2+}) was possible. In contrast, when using either 1.5 mM HNO_3 –0.5 mM PDCA, 2 mM PDCA, or 1 mM EDTA as the eluent, almost no transition metal cations could be separated. This was because the PDCA- and EDTA-transition metal cation complexes formed were too stable and were unretained. The remainder of the acid eluents investigated also failed to produce a separation of the transition metal cations.

From the above results, it was concluded that the 2 mM oxalic acid eluent was the most suitable for the separation of transition metal cations. As shown in Table 2, the advantage of using 2 mM oxalic acid eluent was that the simultaneous separation of transition and alkaline earth metal cations was also possible. This was due to the transition metal cations being eluted prior to the alkaline earth metal cations. In contrast, when using 5 mM tartaric acid, 5 mM citric acid, or 1.5 mM NTA as the eluent, the simultaneous separation could be not achieved due to the transition and alkaline earth metal cations being co-eluted.

3.2. Retention behavior of cations using oxalic acid eluent

As described above, the oxalic acid eluent proved to be the most suitable eluent for the simultaneous separation of (a) alkali, and alkaline earth metal cations, and (b) transition and alkaline earth metal

cations. Therefore, the retention behavior of alkali, alkaline earth and transition metal cations using an oxalic acid eluent was investigated in more detail. The relationship between the concentration of oxalic acid in the eluent and the V_R values of each cation is shown in Fig. 2. The V_R values decreased with increasing concentrations of oxalic acid in the eluent.

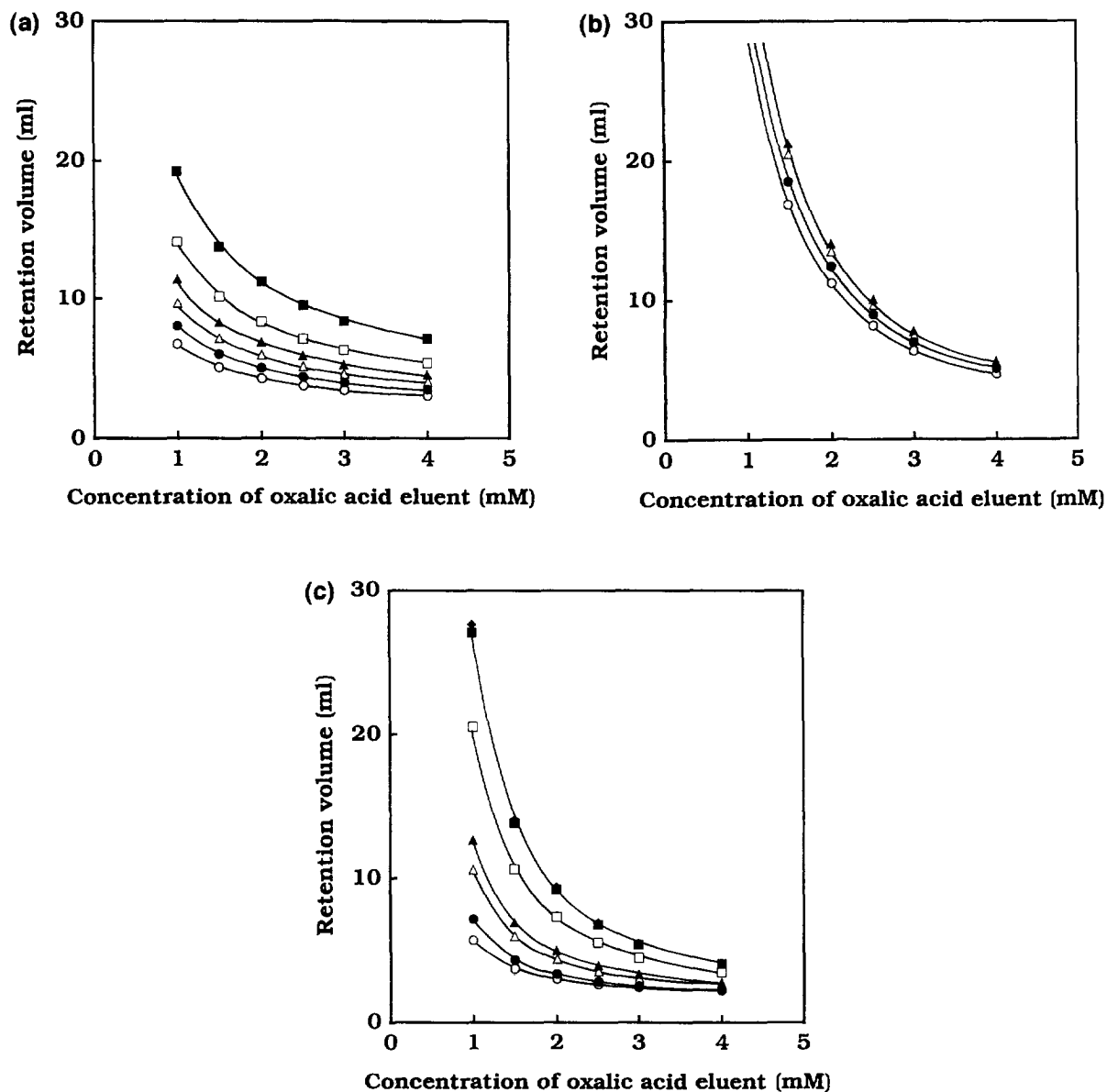


Fig. 2. Effect of the concentration of oxalic acid in the eluent on the retention volumes of (a) alkali, (b) alkaline earth and (c) transition metal cations. Conditions: Eluent, 1–4 mM oxalic acid. Symbols: (a) \circ = Li⁺, \bullet = Na⁺, \triangle = NH₄⁺, \blacktriangle = K⁺, \square = Rb⁺ and \blacksquare = Cs⁺; (b) \circ = Mg²⁺, \bullet = Ca²⁺, \triangle = Sr²⁺ and \blacktriangle = Ba²⁺; (c) \circ = Pb²⁺, \bullet = Ni²⁺, \triangle = Zn²⁺, \blacktriangle = Co²⁺, \square = Fe²⁺, \blacksquare = Cd²⁺ and \blacklozenge = Mn²⁺. Other conditions as for Fig. 1.

The rate of decrease in the V_R values of transition and alkaline earth metal cations was larger than that of alkali metal cations. As a result, when using 1.5 mM oxalic acid as an eluent, good separations of (a) alkali and alkaline earth metal cations, and (b) transition and alkaline earth metal cations were achieved in a reasonable separation time. Typical chromatograms of alkali and alkaline earth metal cations, and transition metal cations under the optimum chromatographic conditions are shown in Fig. 3a and b, respectively.

3.3. Retention behavior of cations using CuSO_4 eluent

Copper(II) ion may be used as a competing cation for the determination of cations by IC with indirect UV–photometric detection [13]. Miyazaki et al. [14] have demonstrated the effectiveness of CuSO_4 eluents for the simultaneous determination of alkali and alkaline earth metal cations. Therefore, in order to evaluate the cation-exchange characteristics of the Develosil 30-5 column, the retention behavior of alkali, alkaline earth, and transition metal cations was investigated using CuSO_4 as an eluent. The V_R values of each cation using 0.5 mM CuSO_4 eluent are shown in Table 3. Although the separation of alkali metal cations was achieved, the separation of alkaline earth metal and transition metal cations was not possible. Thus, for the separation of alkaline earth and transition metal cations, the effect of the concentration of CuSO_4 in the eluent was also investigated, but the separation of these species could not be achieved using any of the tested concentrations of CuSO_4 . However, as shown in Fig. 4, when using 0.5 mM CuSO_4 as the eluent, the separation of common alkali metal cations (Li^+ , Na^+ , NH_4^+ and K^+) from alkaline earth and transition metal cations was achieved in 10 min.

3.4. Retention behavior of cations using ethylenediamine–oxalic acid eluent

Ethylenediamine (EDA) eluents are commonly used for the IC separation of alkaline earth and transition metal cations [15]. Organic acids, such as oxalic, tartaric and citric acids, have been used to adjust the pH of EDA eluents, improving the separation of alkaline earth and transition metal cations

[16]. Therefore, the retention behavior of alkali, alkaline earth, and transition metal cations using 0.5 mM EDA eluent was investigated in detail. The pH

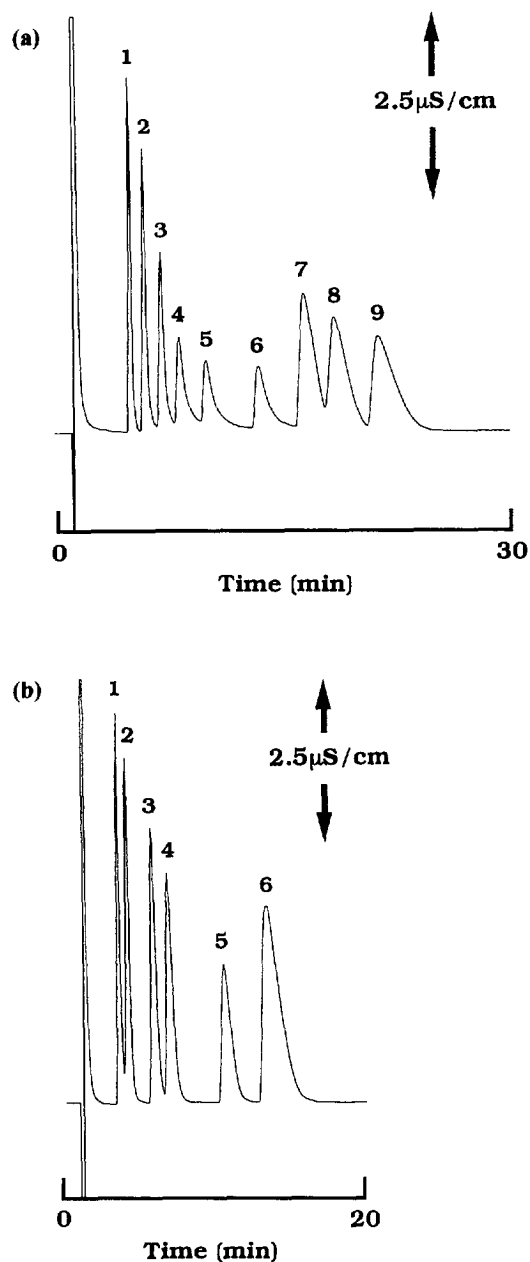


Fig. 3. Chromatograms of (a) alkali and alkaline earth metal cations and (b) transition metal cations using 1.5 mM oxalic acid as the eluent. Conditions: Eluent, 1.5 mM oxalic acid. Peaks: (a) 1 = Li^+ , 2 = Na^+ , 3 = NH_4^+ , 4 = K^+ , 5 = Rb^+ , 6 = Cs^+ , 7 = Mg^{2+} , 8 = Ca^{2+} and 9 = Ba^{2+} ; (b) 1 = Pb^{2+} , 2 = Ni^{2+} , 3 = Zn^{2+} , 4 = Co^{2+} , 5 = Fe^{2+} and 6 = $\text{Cd}^{2+} + \text{Mn}^{2+}$. Other conditions as for Fig. 2.

Table 3
Retention volumes of alkali, alkaline earth and transition metal cations using 0.5 mM CuSO₄ as the eluent (pH 4.30)

Cation	Retention volume (ml)
Li ⁺	3.8
Na ⁺	4.5
NH ₄ ⁺	5.3
K ⁺	6.1
Rb ⁺	7.3
Cs ⁺	9.8
Mg ²⁺	8.8
Ca ²⁺	9.1
Sr ²⁺	9.5
Ba ²⁺	9.8
Cd ²⁺	8.4
Co ²⁺	8.7
Fe ²⁺	8.8
Mn ²⁺	8.6
Ni ²⁺	8.7
Pb ²⁺	11.0
Zn ²⁺	8.8
Fe ³⁺	26.4

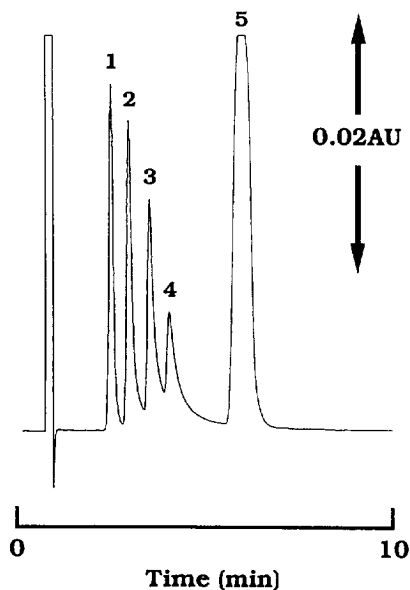


Fig. 4. Chromatograms of common alkali and alkaline earth metal cations using 0.5 mM CuSO₄ as the eluent. Conditions: Eluent, 0.5 mM CuSO₄; Detection, indirect UV at 210 nm; Sample concentration, 0.2 mM. Peaks: 1=Li⁺, 2=Na⁺, 3=NH₄⁺, 4=K⁺ and 5=Mg²⁺+Ca²⁺. Other conditions as for Fig. 3.

of the EDA eluent was adjusted by the addition of various concentrations of oxalic acid. The relationship between the pH of the EDA eluent and the V_R values of each cation is shown in Fig. 5, which indicates that the V_R values of the cations increased with increasing pH of the eluent. In particular, the V_R values of alkaline earth and transition metal cations increased drastically at an eluent pH>6. The reasons are because (a) the cation-exchange capacity of the Develosil 30-5 column increased drastically at an eluent pH>6 due to the dissociation of the silanol group (pK_a of ca. 7.1 [3]) and (b) the eluent strength decreased due to suppression of the dissociation of EDA (pK_{a1} of 6.8). A system peak appeared at an eluent pH<4.5 and interfered with the determination of cations. In addition, the lifetime of the Develosil 30-5 column was very short at an eluent pH of 6.7 because the solubility of silica under neutral conditions is much larger than that under acidic conditions [10]. As a result, the optimum eluent conditions were concluded to be 0.5 mM EDA at pH 5.5. Typical chromatograms of alkali metal cations, and transition and alkaline earth metal cations are shown in Fig. 6A–B, respectively. The conductimetric detector response to NH₄⁺, K⁺, Rb⁺ and Cs⁺ was very small because the equivalent conductivities of these cations are close to that of the EDA ion. The chromatogram indicated that the IC method was not suitable for the determination of alkali metal cations, especially NH₄⁺, K⁺, Rb⁺ and Cs⁺. In contrast, the simultaneous separation of some transition and alkaline earth metal cations (Ni²⁺, Co²⁺, Fe²⁺, Mn²⁺, Mg²⁺, Ca²⁺, Sr²⁺ and Ba²⁺) was achieved in 15 min with a reasonable detection sensitivity. From the above results, it was concluded that the IC method developed was suitable for the simultaneous determination of transition and alkaline earth metal cations.

4. Conclusion

For the determination of the cation-exchange characteristics of the Develosil 30-5 unmodified silica gel column, the retention behavior of alkali, alkaline earth, and transition metal cations was investigated using various kinds of inorganic and organic acid eluents. As a result, it was found that (a)

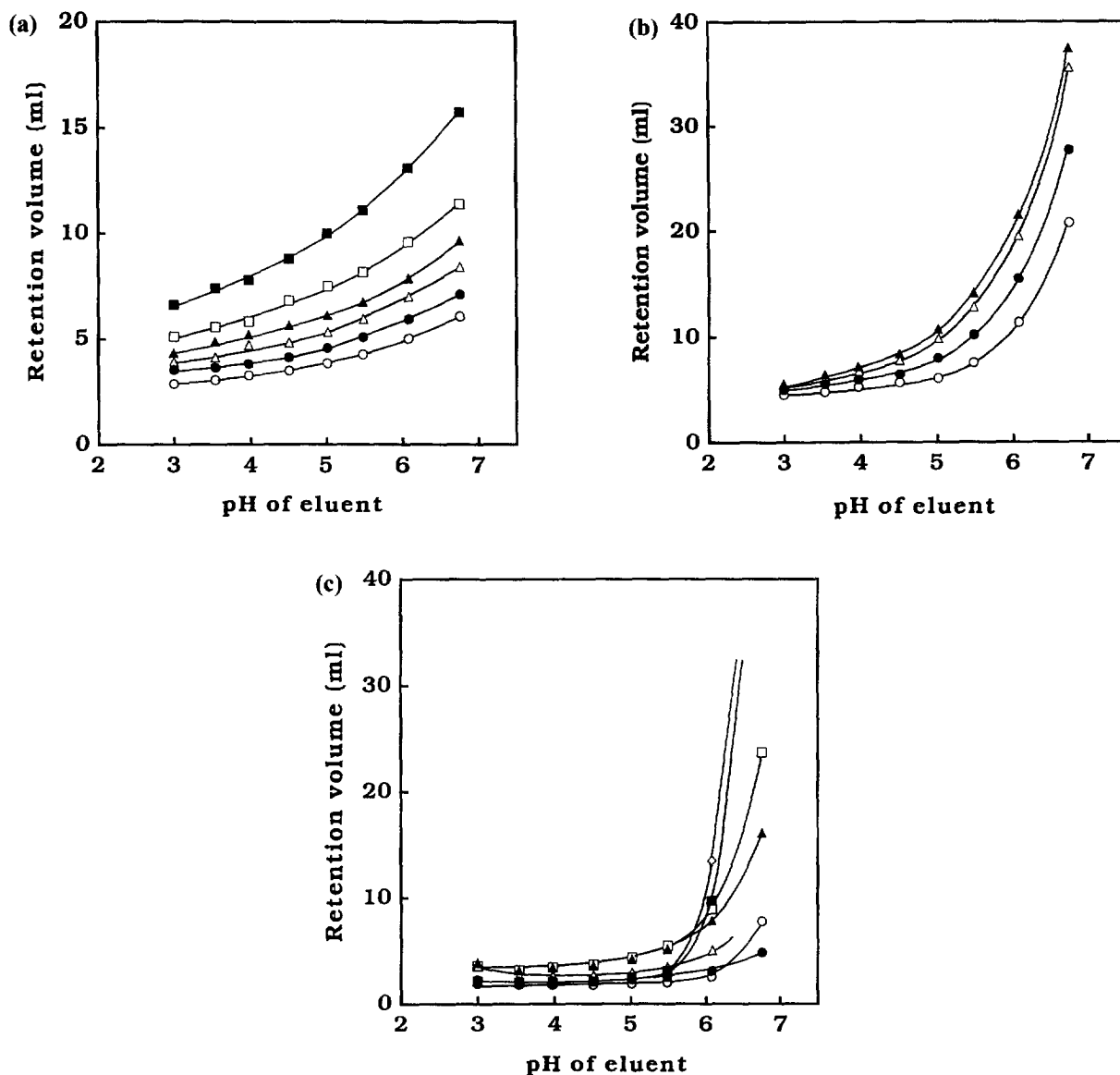


Fig. 5. Effect of the pH of ethylenediamine eluent on the retention volumes of (a) alkali, (b) alkaline earth and (c) transition metal cations. Conditions: Eluent, 0.5 mM ethylenediamine at pH values of 3–6.7. The pH was adjusted using oxalic acid. Detection, indirect conductivity. Symbols: (a) \circ = Li^+ , \bullet = Na^+ , \triangle = NH_4^+ , \blacktriangle = K^+ , \square = Rb^+ and \blacksquare = Cs^+ ; (b) \circ = Mg^{2+} , \bullet = Ca^{2+} , \triangle = Sr^{2+} and \blacktriangle = Ba^{2+} ; (c) \circ = Ni^{2+} , \bullet = Co^{2+} , \triangle = Fe^{2+} , \blacktriangle = Mn^{2+} , \square = Cd^{2+} , \blacksquare = Pb^{2+} and \diamond = Zn^{2+} . Other conditions as for Fig. 4.

1.5 mM HNO_3 –0.5 mM PDCA eluent was the most suitable for the simultaneous separation of alkali and alkali earth metal cations (Li^+ , Na^+ , NH_4^+ , K^+ , Mg^{2+} and Ca^{2+}), (b) 1.5 mM oxalic acid eluent produced the best separation of the following alkali and alkaline earth metal cations, Li^+ , Na^+ , NH_4^+ ,

K^+ , Rb^+ , Cs^+ , Mg^{2+} , Ca^{2+} (Sr^{2+}) and Ba^{2+} , and the simultaneous separation of alkaline earth and transition metal cations (Mg^{2+} , Ca^{2+} (Sr^{2+}), Ba^{2+} , Pb^{2+} , Ni^{2+} , Zn^{2+} , Co^{2+} , Fe^{2+} and Mn^{2+} (Cd^{2+})), (c) 0.5 mM CuSO_4 eluent could be used for the separation of alkali metal cations alone and (d) 0.5

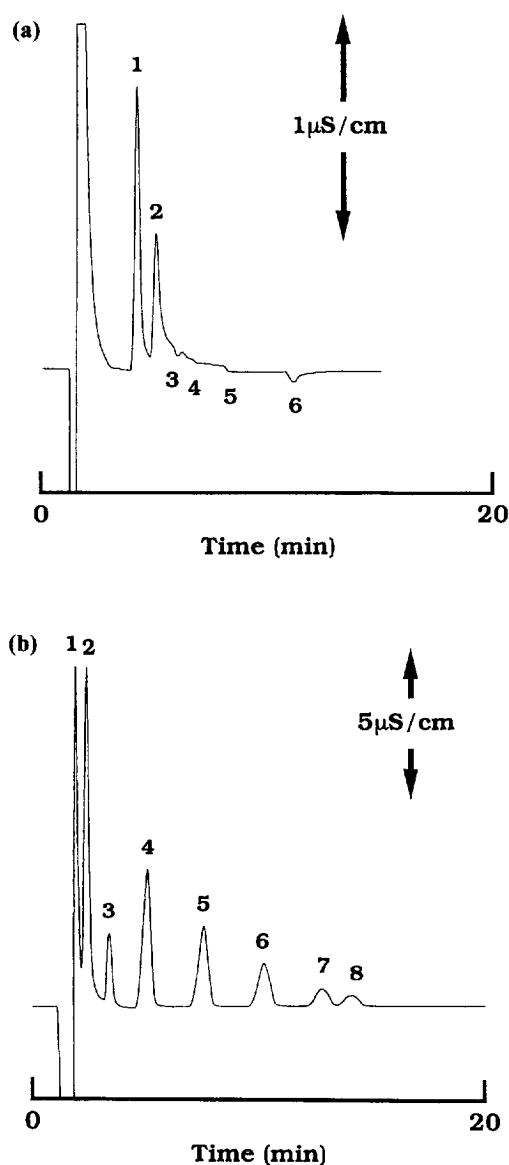


Fig. 6. Chromatogram of (a) alkali metal and (b) alkaline earth and transition metal cations using 0.5 mM ethylenediamine at pH 5.5 as the eluent. Conditions: Eluent, 0.5 mM ethylenediamine at pH 5.5. Peaks: (a) 1=Li⁺, 2=Na⁺, 3=NH₄⁺, 4=K⁺, 5=Rb⁺ and 6=Cs⁺; (b) 1=Ni²⁺, 2=Co²⁺, 3=Fe²⁺, 4=Mn²⁺, 5=Mg²⁺, 6=Ca²⁺, 7=Sr²⁺ and 8=Ba²⁺. Other conditions as for Fig. 5.

mM EDA–oxalic acid eluent at pH 5.5 was suitable for the simultaneous separation of alkaline earth and certain transition metal cations (Mg²⁺, Ca²⁺, Sr²⁺,

Ba²⁺, Ni²⁺, Co²⁺, Fe²⁺ and Mn²⁺). These results indicated that the Develosil 30-5 column could produce efficient IC separation of alkali, alkaline earth, and transition metal cations. The origin of the cation-exchange characteristics of the Develosil 30-5 unmodified silica gel under acidic conditions and the application of this method to environmental water samples are the subject of future work.

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