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Simultaneous determination of common mono- and divalent cations by ion chromatography with an unmodified silica gel column

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Abstract

In order to characterize the cation-exchange properties of a silica gel column in the acidic region, the retention behavior of common mono- and divalent cations (Na^+, NH_4^+, K^+, Mg^{2+} and Ca^{2+}) was investigated. When using 5 m*M* nitric acid (pH 2.3) as an eluent, these cations were retained on a silica gel column (150×4.6 mm I.D.) packed with Develosil 30-5 unmodified silica gel that has a very large surface area (ca. 770 m^2/g), showing that such a stationary phase could be used as a cation-exchanger for ion chromatography with acidic eluents. When using 1.5 m*M* nitric acid and 0.5 m*M* 2,6-pyridinedicarboxylic acid as an eluent, a good separation of these cations was obtained in 12 min using conductimetric detection. This separation was applied successfully to the simultaneous determination of the five cations in various environmental water samples.

Keywords: Water analysis; Silica gel; Cations

1. Introduction

Silica is physically stable, unreactive towards organic solvents and its particle size, pore size, pore volume and surface area can be controlled easily. Furthermore, the silanol group on the surface of silica is easily bonded chemically to various kinds of functional groups. For these reasons, silica is used widely as a packing material for HPLC [1].

In contrast, the silanol group is known to behave as a weak acid with a pK_a of 7.1 [2]. Smith and Pietrzyk [3], Brown and Pietrzyk [4] and Iwachido et al. [5–7] have used silica as a cation-exchange stationary phase for ion chromatography (IC) with conductimetric detection for the separation of common mono- and divalent cations, such as alkali metal, ammonium and alkaline earth metal ions. In each of these studies, lithium ion was used as the competing cation in the eluent (on the basis of its low limiting equivalent ionic conductance) and the eluent pH was approximately neutral. Under these chromatographic conditions, the detection sensitivities of the cations were very low because the differences in equivalent conductance between the solute cations and lithium ion were quite small. Furthermore, the lifetime of the silica stationary phase was expected to be short because of the appreciable solubility of silica at neutral pH [8].

The purpose of the present study was to characterize the cation-exchange properties of unmodified silica in the acidic region and to establish an IC method with conductimetric detection for the

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simultaneous determination of common mono- and divalent cations (Na^+, NH_4^+, K^+, Mg^{2+} and Ca^{2+}).

2. Experimental

2.1. Columns

The silica gel column (150×4.6 mm I.D., stainless steel) was packed with Nomura Chemical (Seto, Japan) Develosil 30-5 porous spherical silica gel. Table 1 shows the details of the silica material used.

A Tosoh (Tokyo, Japan) IC-Cation column (50×4.6 mm I.D.) packed with a lightly sulfonated styrene–divinylbenzene co-polymer resin with a cation-exchange capacity of ca. 12 mequiv./ml and a particle size of ca. 10 μm was also used for the determination of monovalent cations in various environmental waters.

2.2. Ion chromatograph

The ion chromatograph consisted of a Tosoh SC-8020 chromatographic data-processor, a Tosoh CCPM-II pump operated at a flow-rate of 1 ml/min, a Tosoh CO-8020 column oven operated at 35°C, a Tosoh CM-8020 conductimetric detector and a Rheodyne (Cotati, CA, USA) 9125 injector with a 50-μl sample loop.

2.3. Reagents

All reagents were of analytical reagent-grade. Distilled, deionized water was used for the preparation of standard solutions and eluents.

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

Particle size (μm)	5
Pore size (Å)	27
Surface area per weight (m^2 g^{-1})	770
Pore volume per weight (ml g^{-1})	0.53
Packing density (g ml^{-1})	0.76
Column size (mm)	150×4.6
Surface area per column (m^2 $column^{-1}$)	1.43×10^3

3. Results and discussion

3.1. Effect of concentration of nitric acid in the eluent

Cation-exchange on silica is normally performed using weakly acidic or neutral eluents and with conductimetric detection. Under such chromatographic conditions, the detection sensitivities of cations were very low and the lifetime of the stationary phase was short. In order to overcome both of these disadvantages, one possible approach would be to use more strongly acidic eluents. The high equivalent conductance of the hydronium ion (H^+) should lead to sensitive indirect conductimetric detection, whilst the dissolution rate of silica would be reduced with acidic eluents. For these reasons, the cation-exchange properties of silica at acidic pH values were investigated.

Fig. 1 shows the relationship between the concentration of nitric acid as an eluent and the retention volume of five common mono- and divalent cations (Na^+, NH_4^+, K^+, Mg^{2+} and Ca^{2+}). From Fig. 1, it

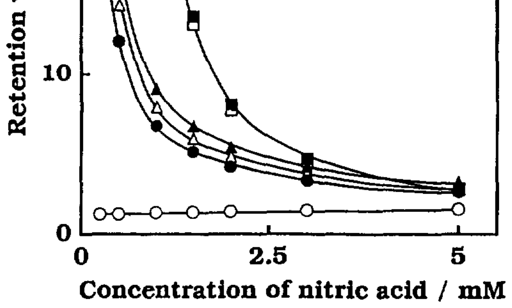

Fig. 1. Effect of the concentration of nitric acid on the retention volumes of common mono- and divalent cations. Conditions: eluent, 0.25–5 m*M* nitric acid; flow-rate, 1 ml/min; column, Develosil 30-5, 150×4.6 mm ID; column temperature, 35°C; injection volume, 50 μl; sample concentration, 0.2 m*M*; (○) water dip, (●) Na^+, (△) NH_4^+, (▲) K^+, (□) Mg^{2+}, (■) Ca^{2+}.

can be seen that the retention volumes of the cations decreased with increasing concentration of nitric acid. However, even when 5 m*M* nitric acid (pH 2.3) was used as the eluent, the five cations were still retained weakly on the silica stationary phase, indicating that the silica still acted as a cation-exchange material in the acidic region. On the other hand, since all of the solute cations were eluted with a relatively low concentration of nitric acid, it was evident that the difference in affinity of monovalent cations and of divalent cations for the ionized silanol cation-exchange sites was very small in the acidic region.

From the above results, it was possible to simultaneously elute the mono- and divalent cations on the silica stationary phase using nitric acid as the eluent. As shown in Fig. 2, the use of 1.5 m*M* nitric acid as the eluent gave a good separation of the monovalent cations without interference from the divalent cations. However, the divalent cations were not resolved from each other.

3.2. Effect of the concentration of 2,6-pyridinedicarboxylic acid in the eluent

Since the simultaneous separation of mono- and divalent cations is very important in the analysis of environmental waters, selective complexation of the divalent cations with 2,6-pyridinedicarboxylic acid (PDCA) was attempted. PDCA has often been used as a complexing agent in the separation of Mg^{2+} and Ca^{2+} in IC because the stability of the Ca^{2+}–PDCA complex is higher than that of the Mg^{2+}–PDCA complex [9]. In order to separate both mono- and divalent cations, eluents containing both PDCA and nitric acid were used.

As shown in Fig. 3, the retention volumes of Ca^{2+} and Mg^{2+} decreased substantially with increasing PDCA concentration, due to complexation effects. The retention volumes of the monovalent cations also decreased slightly with increasing PDCA concentration, due to an increase of the concentration of H^+ as the eluent competing ion and perhaps also because of a reduced cation-exchange capacity of the stationary phase. As a result, the complete separation of the five cations could be achieved in 12 min using 0.5 m*M* PDCA and 1.5 m*M* nitric acid as the eluent, as shown in Fig. 4.

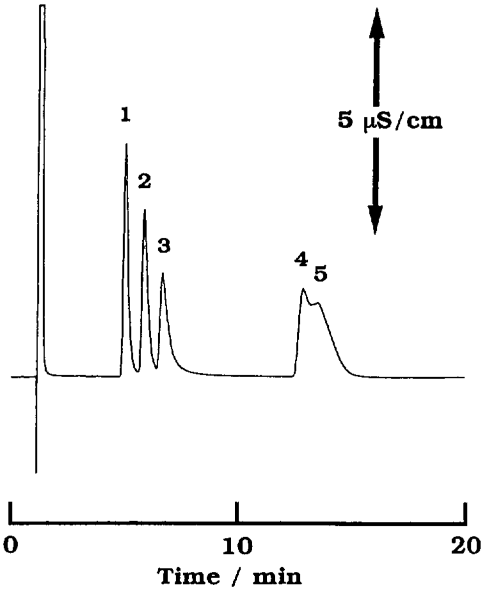

Fig. 2. Chromatogram of common mono- and divalent cations using nitric acid as eluent. Conditions: eluent, 1.5 m*M* nitric acid. Peaks: 1=Na^+, 2=NH_4^+, 3=K^+, 4=Mg^{2+}, 5=Ca^{2+}. Other conditions as for Fig. 1.

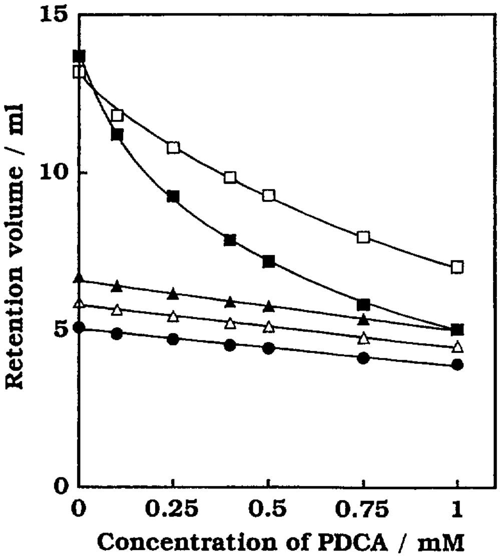

Fig. 3. Effect of the concentration of PDCA in a nitric acid eluent on the retention volumes of common mono- and divalent cations. Conditions: eluent, 1.5 m*M* nitric acid containing 0–1 m*M* PDCA. (●) Na^+, (△) NH_4^+, (▲) K^+, (□) Mg^{2+}, (■) Ca^{2+}. Other conditions as for Fig. 2.

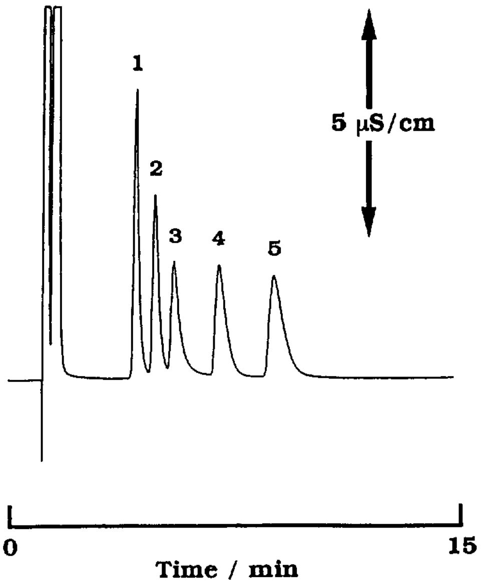

Fig. 4. Chromatogram of common mono- and divalent cations using PDCA–nitric acid as eluent. Conditions: eluent, 1.5 m*M* nitric acid+0.5 m*M* PDCA; flow-rate, 1 ml/min; column, Develosil 30-5, 150×4.6 mm I.D.; column temperature, 35°C; injection volume, 50 µl; sample concentration, 0.2 m*M*. Peaks: 1=Na^+, 2=NH_4^+, 3=K^+, 4=Ca^{2+}, 5=Mg^{2+}.

3.3. Analytical performance parameters

Calibration graphs were obtained by plotting peak area against the concentration of the cations. Linear calibration graphs ($r^2 \geq 0.999$) were obtained in at least the concentration ranges 0.005–1.0 m*M* for the five cations.

The detection limits determined at a signal-to-noise ratio of three were 0.023 m*M* (0.54 ppb) for Na^+, 0.033 m*M* (0.56 ppb) for NH_4^+, 0.053 m*M* (2.1 ppb) for K^+, 0.032 m*M* (0.78 ppb) for Mg^{2+} and 0.029 m*M* (1.2 ppb) for Ca^{2+}. These detection limits compare well with those for non-suppressed IC with conductimetric detection using acidic eluents [10].

The relative standard deviations of the chromatographic peak areas of the five cations under the optimum chromatographic conditions were less than 1.1% ($n=10$).

Interference effects were determined for some common cations. Table 2 shows the retention volumes of various cations under the optimum chromatographic conditions. Most of the di- and trivalent cations tested (except for alkaline earth metal ions and Mn^{2+}) were eluted rapidly because their PDCA complexes are very stable. However, it is evident from Table 2 that the Mn^{2+}–PDCA complex, having a relatively low stability constant [11], was strongly retained and peaks of Mn^{2+} and K^+ overlapped.

Table 2
Retention volume (V_R) of various cations under optimum chromatographic conditions

Cation	V_R (ml)	Cation	V_R (ml)
Li^+	3.8	Co^{2+}	2.0
Na^+	4.3	Cd^{2+}	2.3
NH_4^+	5.0	Fe^{2+}	2.8
K^+	5.6	Mn^{2+}	5.6
Rb^+	6.7		
Cs^+	8.7	Cu^{2+}	N.D.
		Ni^{2+}	N.D.
Mg^{2+}	8.9	Pb^{2+}	N.D.
Ca^{2+}	7.2	Zn^{2+}	N.D.
Sr^{2+}	9.2	Fe^{3+}	N.D.
Ba^{2+}	9.7		

N.D.: not detected.

3.4. Application to the analysis of environmental water samples

The proposed IC method was applied to the simultaneous determination of common mono- and divalent cations in various environmental water samples. Samples were collected close to the city of Nagoya in central Japan and were analyzed after filtration through a 0.45-µm membrane filter.

Fig. 5 shows typical chromatograms for a rain water sample and a river water sample. The resolution between analyte cations in these chromatograms was quite satisfactory. Table 3 lists the analytical results for the common mono- and divalent cations in the sample analyzed, together with values obtained by conventional methods (that is, non-suppressed IC with 2 m*M* nitric acid as eluent and conductimetric detection for monovalent cations and ICP–AES for divalent cations). Agreement between the alternative methods was satisfactory. From these results, it was concluded that the proposed IC method offered a powerful and convenient IC means for the simultaneous determination of common

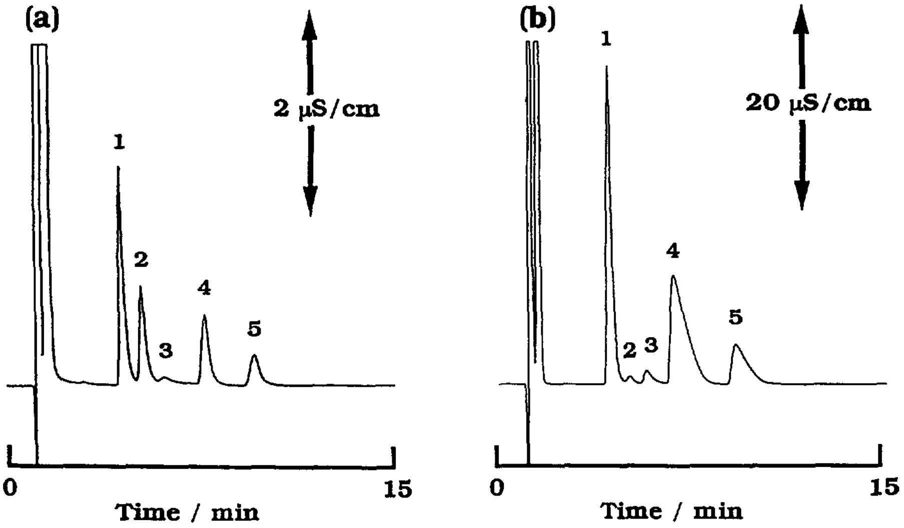

Fig. 5. Chromatograms of rain water and river water samples. (a) Rain water sample. Peaks (concentration/m*M*): 1=Na$^+$ (0.042), 2=NH$_4^-$ (0.035), 3=K$^+$ (0.006), 4=Ca^{2+} (0.012), 5=Mg^{2+} (0.005). (b) River water sample. Peaks (concentration/m*M*): 1=Na$^+$ (0.591), 2=NH$_4^-$ (0.014), 3=K$^+$ (0.046), 4=Ca^{2+} (0.341), 5=Mg^{2+} (0.097). Chromatographic conditions were the same as in Fig. 4.

mono- and divalent cations in various environmental water samples tested.

4. Conclusions

In this work, the cation-exchange properties of unmodified silica (Develosil 30-5) in the acidic region have been investigated and an IC method with conductimetric detection has been established for the simultaneous determination of mono- and divalent cations using a PDCA–nitric acid eluent. The proposed method was applied successfully to the simultaneous determination of major mono- and divalent cations in various environmental water samples. A detailed study of the origin of the cation-exchange properties of the silica under acidic conditions will be the subject of future work.

Acknowledgments

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Table 3
Analytical results for major mono- and divalent cations in various environmental water samples

Samples	Proposed IC method (m*M*)					Conventional IC method (m*M*)			ICP–AES (m*M*)	
	Na$^+$	NH$_4^-$	K$^+$	Mg^{2+}	Ca^{2+}	Na$^+$	NH$_4^+$	K$^+$	Mg^{2+}	Ca^{2+}
Rain water^1	0.042	0.035	0.006	0.005	0.012	0.044	0.034	0.006	0.006	0.012
Rain water^2	0.167	0.033	0.018	0.013	0.005	0.165	0.032	0.020	0.014	0.005
River water^1	0.195	N.D.	0.022	0.033	0.118	0.200	N.D.	0.021	0.034	0.117
River water^2	0.591	0.014	0.046	0.097	0.341	0.591	0.014	0.047	0.100	0.345
Underground water	0.241	N.D.	0.022	0.196	0.272	0.245	N.D.	0.023	0.190	0.270
Soil water	0.202	N.D.	0.037	0.100	0.122	0.200	N.D.	0.035	0.102	0.125

N.D.: not detected. ICP–AES=inductively coupled plasma–atomic emission spectrometry.

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