Separation and detection of common mono- and divalent cations by ion chromatography with an ODS column and conductivity/UV detection

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Abstract

The retention and detection behavior of common mono- and divalent cations (M^+, alkali metal (Li^+, Na^+, K^+, Rb^+, Cs^+) and ammonium ions (NH_4^+); M^{2+}, alkaline earth metal ions (Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}) was examined using an ODS column (150×4.6 mm I.D.) and conductivity (CD)/UV detection. The results obtained were as follows: (1) for M^+, the mobile phase, 0.1 mM sodium dodecyl sulphate (SDS)+10 mM HNO_3 and indirect CD detection were effective. (2) Addition of Ce(III) in the mobile phase accelerated the elution of both M^+ and M^{2+}. The separation of above 10 cations on an ODS column was achieved for the first time without any coelution of cations and disturbance by system peak. Addition of higher SDS resulted in good separation of M^+ and M^{2+} with longer retention times. CD detection was possible for M^+ and M^{2+} and UV detection for M^{2+}. (3) For M^{2+}, the mobile phase, 0.8 mM Ce(III)+0.1 mM SDS+1 mM HNO_3 and indirect UV detection were effective. The IC methods were applied to real samples. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Mobile phase composition; Inorganic cations; Alkali metals; Alkaline earth metals; Ammonium

1. Introduction

Reversed-phase columns such as the octadecyl-bonded silica (ODS) column have been examined as separation columns for ion chromatography (IC) [1–3]. The main reason is due to its high flexibility to both cation and anion separations by simple pretreatments or optimization of mobile phases. Other points are due to their greater chromatographic efficiencies and low price and no need for special equipments.

Two methods have been examined for the sepa-

ration of title cations. One method is attained by permanent or dynamic coating of cation-exchange groups by using anionic surfactants and micellar taurine-conjugated bile salts [4–7]. The other is that analyte cations are separated due to the difference in selectivity between cations and neutral ligands such as crown compounds immobilized on the surface of columns [8–12]. For three ODS columns (each 250×4.6 mm I.D.) with 5 mM n-heptylsulfonate [$CH_3(CH_2)_6SO_3^-$] (pH 2, 2 ml/min) as mobile phase, the order of retention times was Li^+~Na^+< K^+<NH_4^+~Rb^+ (in the range of 9–12 min)<Ca^{2+} (32 min) [4]. For ODS column (250×4 mm I.D.) with 2 mM n-hexylsuccinic acid+1 mM oxalic acid

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(pH 2.92, 1 ml/min), the order of retention times was $Li^+ < Na^+ < K^+$ (in the range of 8–10 min) and $Mg^{2+} < Ca^{2+} < Sr^{2+}$ (33–37 min) [5]. Conductivity (CD) detection was used for these IC systems. For microcolumns of ODS coated with micellar taurine-conjugated bile salts, the retention times by 0.5 mM Ce(III) (indirect UV detection) were in the range of 3–4.5 min for $Na^+ < K^+ < Cs^+$ and of 13–17 min for $Mg^{2+} < Ca^{2+} < Ba^{2+}$ [6].

For the latter, the separation of M^+ [Li^+, Na^+, K^+, Rb^+ and Cs^+ (NH_4^+ was not shown)] and of M^{2+} (Mg^{2+}, Ca^{2+}, Sr^{2+} and Ba^{2+}) was possible for the system of silica column modified with poly- or bis(benzo-18-crown-6) (300 or 150 mm×4 mm I.D.) and mobile phases of water–methanol mixtures (flow-rate, 1 ml/min) [8]. However, mutual separation of M^+ and M^{2+} was difficult because their retention times are in the similar range (3–15 min). Similar trends were obtained for silica column modified with poly- and bis(benzo-15-crown-5) and an ODS column modified with dodecyl-18-crown-6 [10]. The separation of M^+ and M^{2+} was also not good for the systems of silica gel and polymer matrices modified with benzo-15-crown-5, benzo-18-crown-6 and benzo-21-crown-7 [11]. Further, the retention times of the cations changed with counter-anions [8–11]. Lamb et al. recently showed the good separation by using the IC system of a non-polar polymer resin coated with tetradecyl-18-crown-6 (TD18C6) (280 mm×4 mm I.D.) and methanesulfonic acid as mobile phase [12]. The advantage of TD18C6 is that the separation of M^+ and M^{2+} is possible and that the retention times of the cations do not change by counter-anions associated with the analytes. The effects of gradient separations employing organic modifiers, temperature and pH were precisely addressed. However, Mg^{2+} and Ca^{2+} co-eluted due to the similar selectivity of TD18C6 for these ions. Thus, to our knowledge, up to date, the complete separation and detection of all mono- and divalent cations [M^+, alkali metal (Li^+, Na^+, K^+, Rb^+, Cs^+) and ammonium ions (NH_4^+); M^{2+}, alkaline earth metal ions (Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+})] by reversed-phase columns have not been performed yet.

In this study, the separation behavior of common mono- and divalent cations [M^+, alkali metal (Li^+, Na^+, K^+, Rb^+, Cs^+) and ammonium ions (NH_4^+);

M^{2+}, alkaline earth metal ions (Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+})] on an ODS column was examined using mobile phases containing three components, SDS [$CH_3(CH_2)_{11}OSO_3Na$], nitric acid (HNO_3) and cerium(III) chloride (Ce(III)Cl$_3$). The detection behavior was examined using indirect CD and UV detection due to the use of HNO_3 and the light absorbing ion, Ce(III) in mobile phases. In a previous study [7], we indicated the separation and detection of six monovalent cations M^+, alkali metal (Li^+, Na^+, K^+, Rb^+, Cs^+) and ammonium ions (NH_4^+) are possible by the IC system of an ODS column, 0.1 mM SDS+10 mM HNO_3 mobile phase, and indirect CD detection. However, the elution of alkaline earth metal ions was difficult due to weak eluting power of HNO_3. Thus, the effect of Ce(III) with strong eluting power in this study was examined.

2. Experimental

2.1. Ion chromatographic system

The IC system used in this study was composed of a computer-controlled pump (CCPM: Tosoh, Tokyo, Japan), a Rheodyne 7125 injector equipped with a 100-μl sample loop (Cotati, CA, USA), a conductivity detector (CM-8010: Tosoh), a UV–Vis detector (L-4200: Hitachi, Tokyo, Japan), and a chromato-processor (SC-8010: Tosoh).

The ODS column employed was Capcellpak C_{18} (AG120) (150 mm×4.6 mm I.D.; Shiseido, Tokyo, Japan). The packing materials were 5-μm spherical particles of ODS coated with silicone polymer. The flow-rate of mobile phases was 1 ml/min.

2.2. Standard cationic solution and mobile phase preparation

All solutions of common mono- and divalent cations [M^+, alkali metal (Li^+, Na^+, K^+, Rb^+, Cs^+) and ammonium ions (NH_4^+); M^{2+}, alkaline earth metal ions (Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+})] were prepared from their chloride salts of reagent grade (Wako Chemicals, Tokyo, Japan or Katayama Chemicals, Osaka, Japan). Standard cationic solutions were

prepared by mixing and diluting the stock solutions of each cation (10–100 mM).

Cerium(III) chloride heptahydrates [Ce(III)Cl$_3$·7H$_2$O] and SDS of reagent grade and nitric acid (HNO$_3$) for heavy metal analysis (Katayama Chemicals) were used for the preparation of each stock solution of 10 mM Ce(III), 10 mM SDS, and 1 M nitric acid. Mobile phases prepared by mixing and

diluting the stock solutions were filtered through a membrane filter (pore size, 0.45 μm) before use. When preparing mobile phases, 10 mM Ce(III) was added after 10 mM SDS and 1 M HNO$_3$ were mixed and diluted to almost desired concentrations. Because it took long time to dissolve Ce(III) precipitates with dodecyl sulfate ion, when the precipitates are formed. Mobile phases prepared were stirred
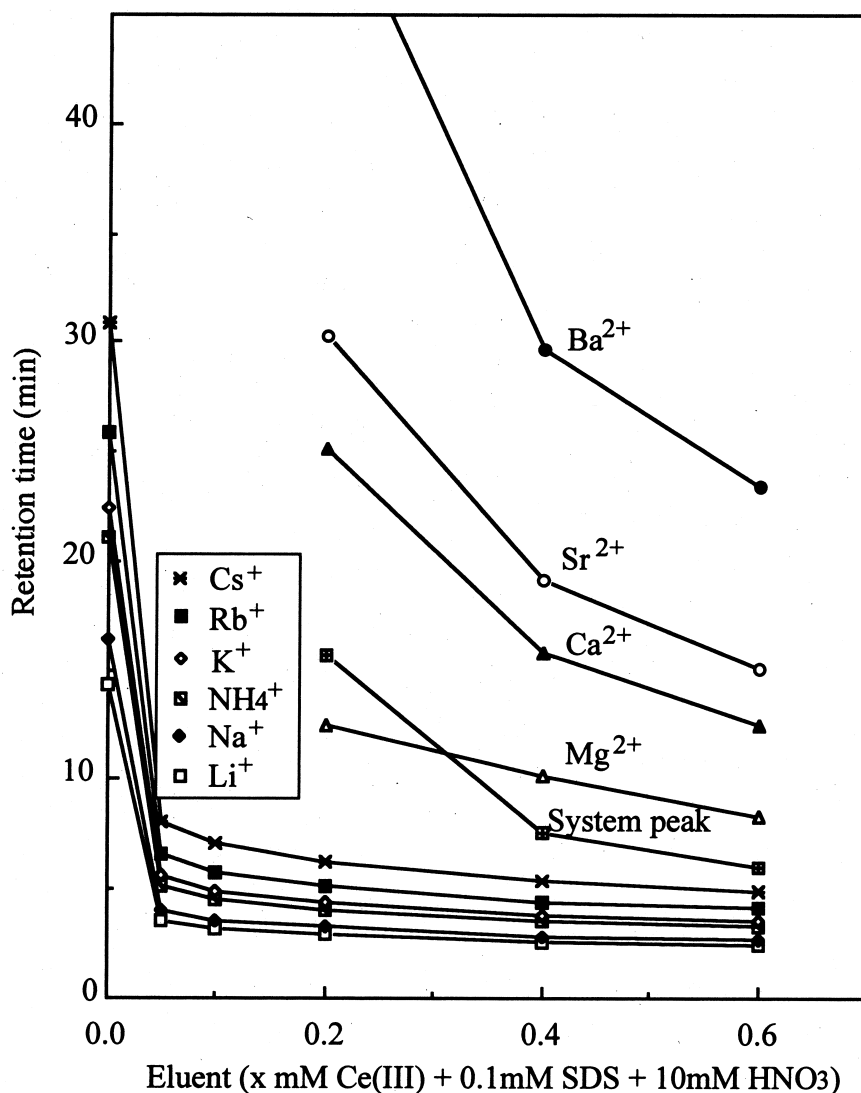

Fig. 1. Effect of the concentration of Ce(III) in 0.1 mM SDS+10 mM HNO$_3$ mobile phase on the retention time of common mono- and divalent cations. Conditions: column, Capcellpak C$_{18}$ (AG 120) (150×4.6 mm I.D.); mobile phase, x mM Ce(III)+0.1 mM SDS+10 mM HNO$_3$; flow-rate, 1 ml/min; injection volume, 100 μl; sample concentration, mono- (0.4 mM, each) and divalent cations (0.2 mM, each).

vigorously for at least 5 h, usually overnight. Distilled–deionized water was used for the preparation of all standard solutions and mobile phases.

2.3. Dynamic coating of ODS column with SDS

For dynamic coating of an ODS column with dodesyl sulfate ion, mobile phases prepared were pumped to an ODS column at a flow-rate of 1.0 ml/min until the adsorption equilibrium between mobile and solid phases was accomplished. The period to obtain the equilibrium was usually longer more than 10 h, depending on the mobile phases used. The lower the concentration of Ce(III) and SDS in mobile phases, the longer the time for equilibrium was required. The judgement was based on constant retention times of M^+ and M^{2+} and also

constant conductivity and UV absorbance of mobile phases.

3. Results and discussion

3.1. Effect of Ce(III) in mobile phase

The separation of mono- and divalent cations depends on the concentration of SDS, HNO_3, and Ce(III) in mobile phases. Fig. 1 shows the effect of concentration of Ce(III) in 0.1 mM SDS+10 mM HNO_3 mobile phase on the retention time of common mono- and divalent cations. The separation of monovalent cations [M^+, alkali metal (Li^+, Na^+, K^+, Rb^+, Cs^+) and ammonium ions ($NH4^+$)] was obtained for 0.1 mM SDS+10 mM HNO_3 mobile phase without Ce(III) (Figs. 1 and 2a) [7]. The
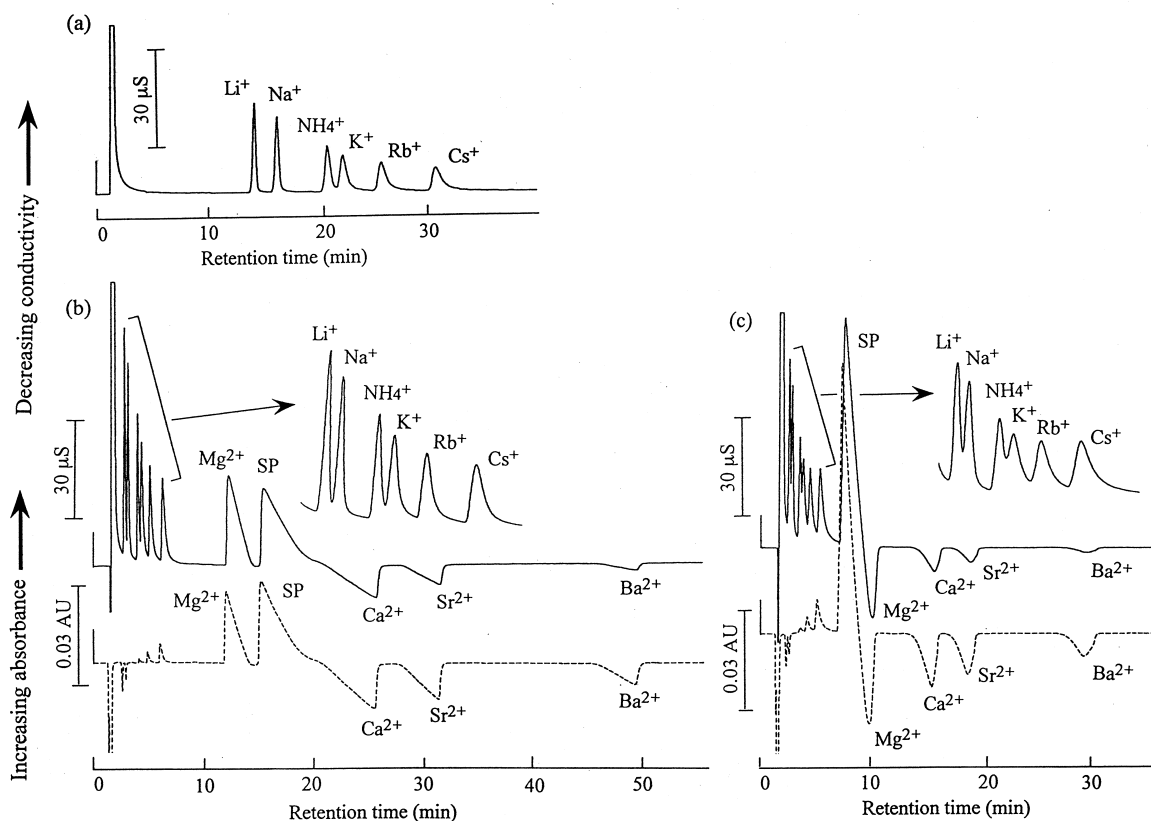

Fig. 2. Ion chromatograms of common mono- (0.4 mM, each) and divalent cations (0.2 mM, each). Conditions: mobile phase, (a) 0.1 mM SDS+10 mM HNO_3, (b) 0.2 mM Ce(III)+0.1 mM SDS+10 mM HNO_3, (c) 0.4 mM Ce(III)+0.1 mM SDS+10 mM HNO_3; detection, solid line=conductivity detection, dashed line=UV (253 nm) detection. Other conditions as for Fig. 1.

retention time of system peak was ca. 540 min. However, elution of divalent cations [M^{2+}, alkaline earth metal ions (Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+})] was difficult due to lower eluting power of HNO_3. Thus, lower SDS mobile phases were at first examined for faster elution of divalent cations in this study. For example, the retention times of Mg^{2+} and Ca^{2+} were 135 and 164 min, respectively, for 0.01 mM SDS + 10 mM HNO_3, but those of M^+ were in the range of

5–10 min where NH_4^+ and K^+ coeluted without separation and the separation of other monovalent cations was not good. These results suggest that the use of lower SDS in mobile phase is not effective for separation of both M^+ and M^{2+}.

The addition of Ce(III) in the mobile phases led to the rapid decrease in retention times of both mono- and divalent cations (Fig. 1). The retention time of system peak also decreased rapidly. Fig. 2 shows the
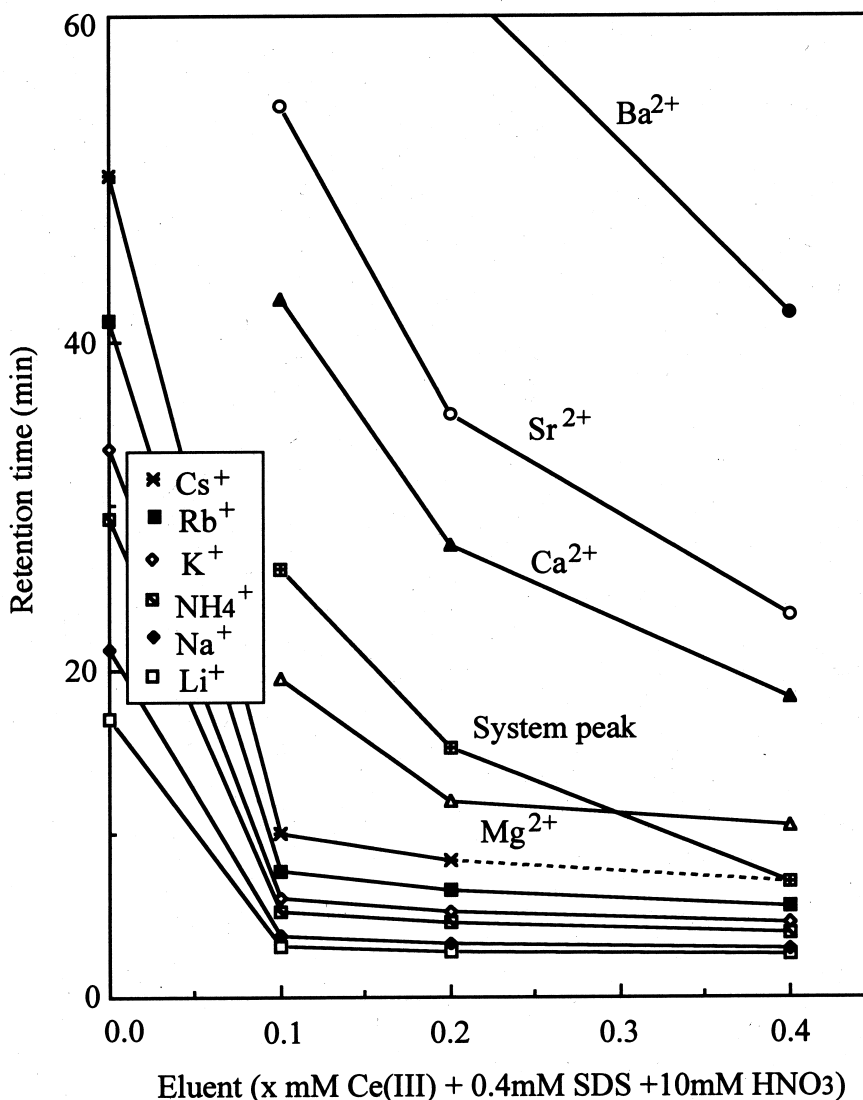

Fig. 3. Effect of the concentration of Ce(III) in 0.4 mM SDS + 10 mM HNO_3 mobile phase on the retention time of common mono- and divalent cations. Other conditions as for Fig. 1.

separation and detection behavior of common mono- and divalent cations for the mobile phases containing 0, 0.2, and 0.4 mM Ce(III). For the mobile phase containing 0.2 mM Ce(III), the separation of both M^+ and M^{2+} was possible in spite of larger decrease in their retention times of M^+ (Fig. 2b). The order of retention times $(Li^+ < Na^+ < NH_4^+ < K^+ < Rb^+ < Cs^+ << Mg^{2+} < Ca^{2+} < Sr^{2+} < Ba^{2+})$ was same as those by the columns with "fixed" cation-exchange sites [2].

As the mobile phases in this study contain higher HNO_3 and UV absorbing ion, Ce(III), indirect CD and UV detection is basically possible. However, the sensitivity of indirect UV detection at 253 nm was poor for M^+ and was good for M^{2+}. This might be due to that both HNO_3 and Ce(III) were effective for elution of M^+ but higher HNO_3 might be more effective compared to Ce(III), leading to poor indirect UV detection. It is noted that the direction of each peak changes before and after a big system peak. Especially, the Mg^{2+} peak is different between Figs. 2b and c. These phenomena are well known that the analytes eluting after the system peak give the reverse peaks providing the visualization agents is transferred from the stationary phase to the mobile phase [13,14]. Similar results were obtained for conductivity detection.

3.2. Effect of SDS in mobile phase

The effect of increased SDS (from 0.1 to 0.4 mM) in mobile phases was examined. Fig. 3 shows the effect of concentration of Ce(III) in 0.4 mM SDS+ 10 mM HNO_3 mobile phase on the retention time of common mono- (M^+) and divalent (M^{2+}) cations. For a mobile phase without Ce(III), the increase in SDS led to the longer retention times of M^+ compared to those of Fig. 1. Similar results were obtained for the mobile phases containing Ce(III). The order of separation of M^+ and M^{2+} was same as
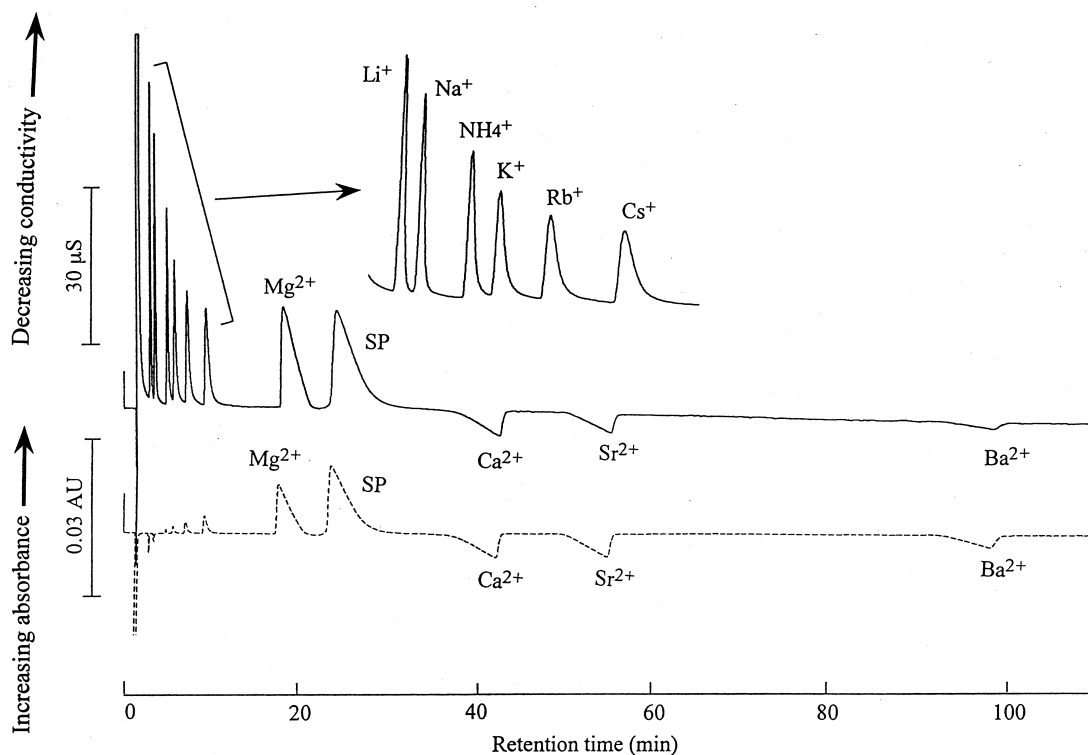

Fig. 4. Ion chromatograms of common mono- (0.4 mM, each) and divalent cations (0.2 mM, each). Conditions: mobile phase, 0.4 mM Ce(III)+0.1 mM SDS+10 mM HNO_3; detection, solid line=conductivity detection, dashed line=UV (253 nm) detection. Other conditions as for Fig. 1.

that by mobile phases containing 0.1 mM SDS (Fig. 1). Fig. 4 shows the ion chromatograms of M$^+$ and M^{2+} using 0.1 mM Ce(III)+0.4 mM SDS+10 mM HNO$_3$ mobile phase. The baseline separation of M$^+$ was obtained but the retention times of divalent cations increased due to lower Ce(III). The stability of the baselines for the mobile phases containing 0.4 mM SDS was less compared to those containing 0.1 mM SDS. Although no conclusive reason for this behavior was found, it is possible that the fluctuation

of equilibrium of SDS between mobile and solid phases is a little large for the mobile phases containing higher SDS (0.4 mM SDS).

3.3. Effect of nitric acid in mobile phase

The effect of concentration of HNO$_3$ in mobile phase was examined for the faster elution of divalent cations. It was not easy to separate Mg^{2+} and system peak for the mobile phases containing 10 mM HNO$_3$
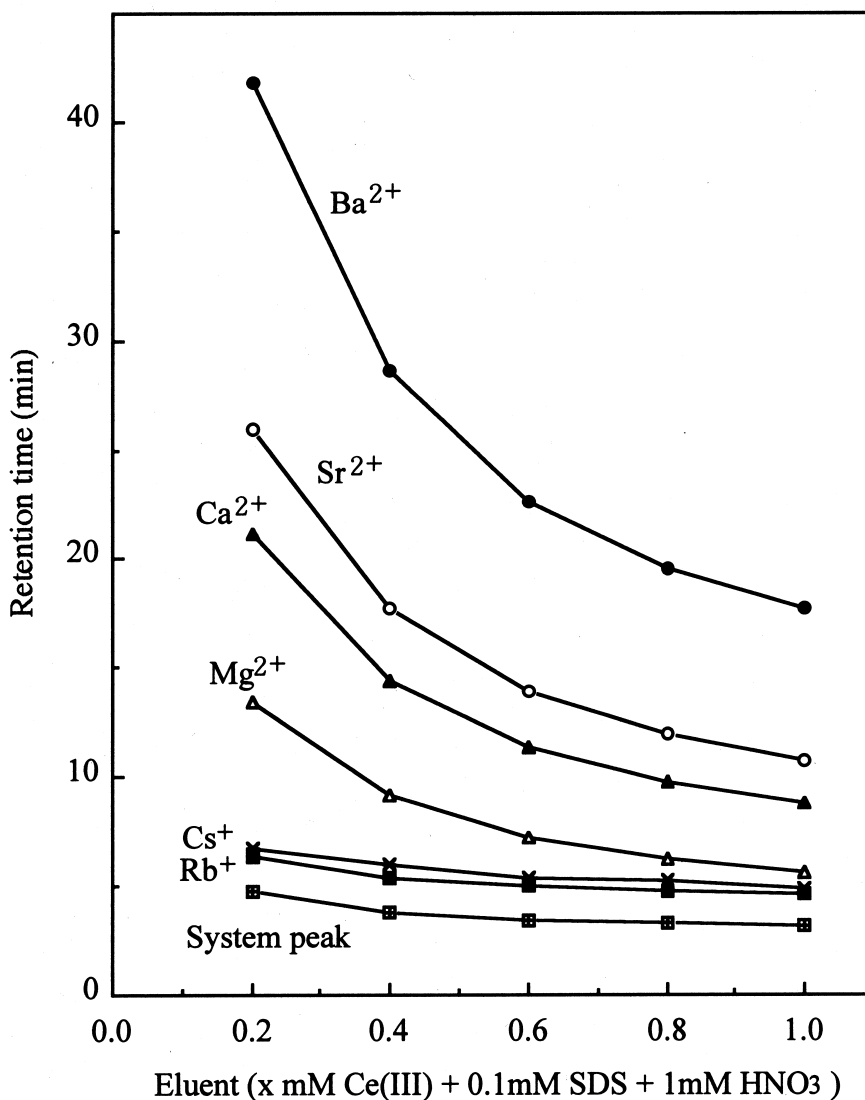

Fig. 5. Effect of the concentration of Ce(III) in 0.1 mM SDS+1 mM HNO$_3$ mobile phase on the retention time of common mono- and divalent cations. Other conditions as for Fig. 1.

and higher Ce(III) (Figs. 2c and 3). The decrease of HNO_3 in mobile phases from 10 mM (pH 2.2) to 1 mM (pH 3.0) resulted in the faster appearance of system peaks although the retention times of M^{2+} were similar to those of mobile phases containing 10

mM HNO_3. Fig. 5 shows the effect of concentration of Ce(III) on the separation of M^+ and M^{2+} under the condition of 1 mM HNO_3. Fig. 6 shows the separation of M^+ and M^{2+} by 0.8 mM Ce(III)+0.1 mM SDS+1 mM HNO_3 mobile phase. Baseline of
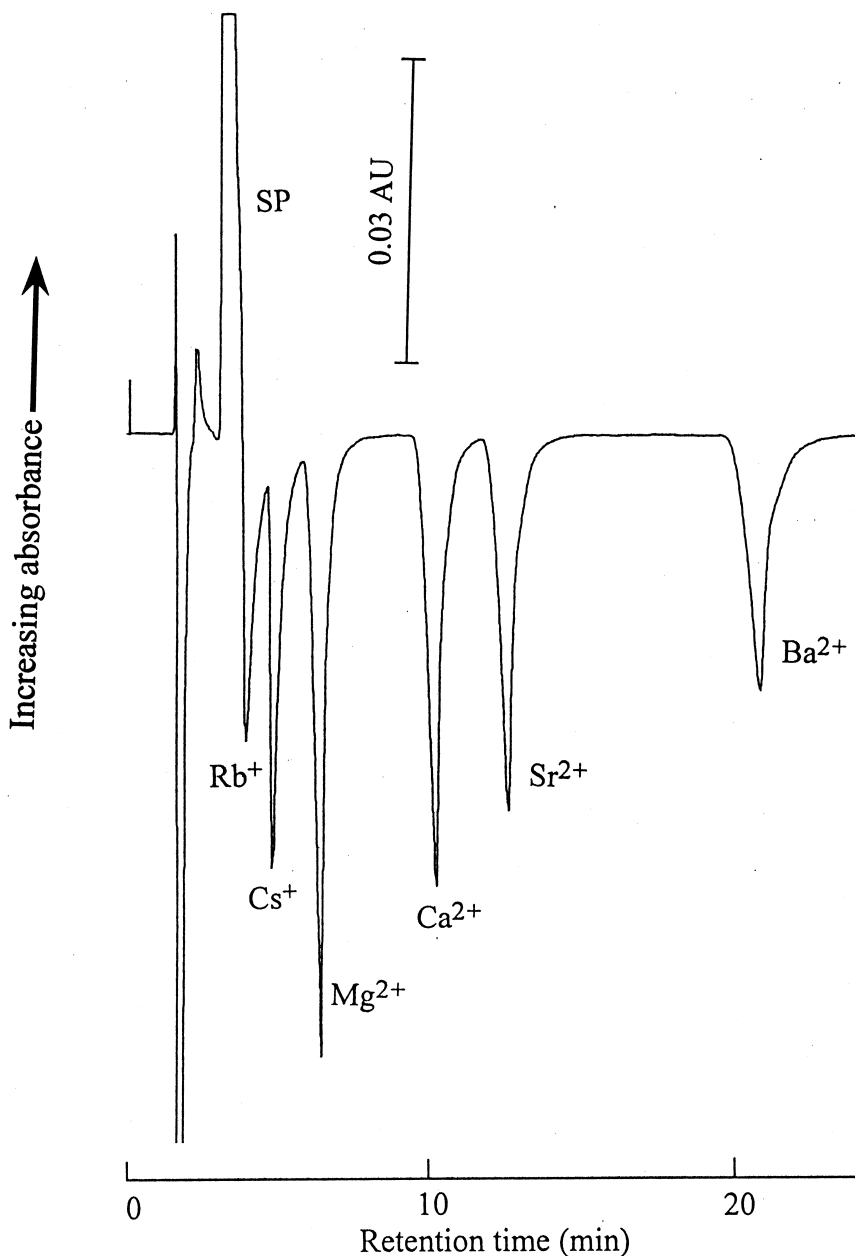

Fig. 6. Ion chromatograms of common mono- (0.4 mM, each) and divalent cations (0.2 mM, each). Conditions: mobile phase, 0.8 mM Ce(III)+0.1 mM SDS+1 mM HNO_3; UV (253 nm) detection. Other conditions as for Fig. 1.

UV absorbance (0.53 AU at 253 nm) for this mobile phase was stable in spite of higher Ce(III). This indicates that complete separation of Mg^{2+} and system peak and high sensitivity is possible, which is different from the results by mobile phases con- taining higher HNO_3 (Fig. 2c). The response of CD detection was complicated and was not good due to lower HNO_3 and higher Ce(III). No addition of HNO_3 was also effective for the separation of divalent cations.
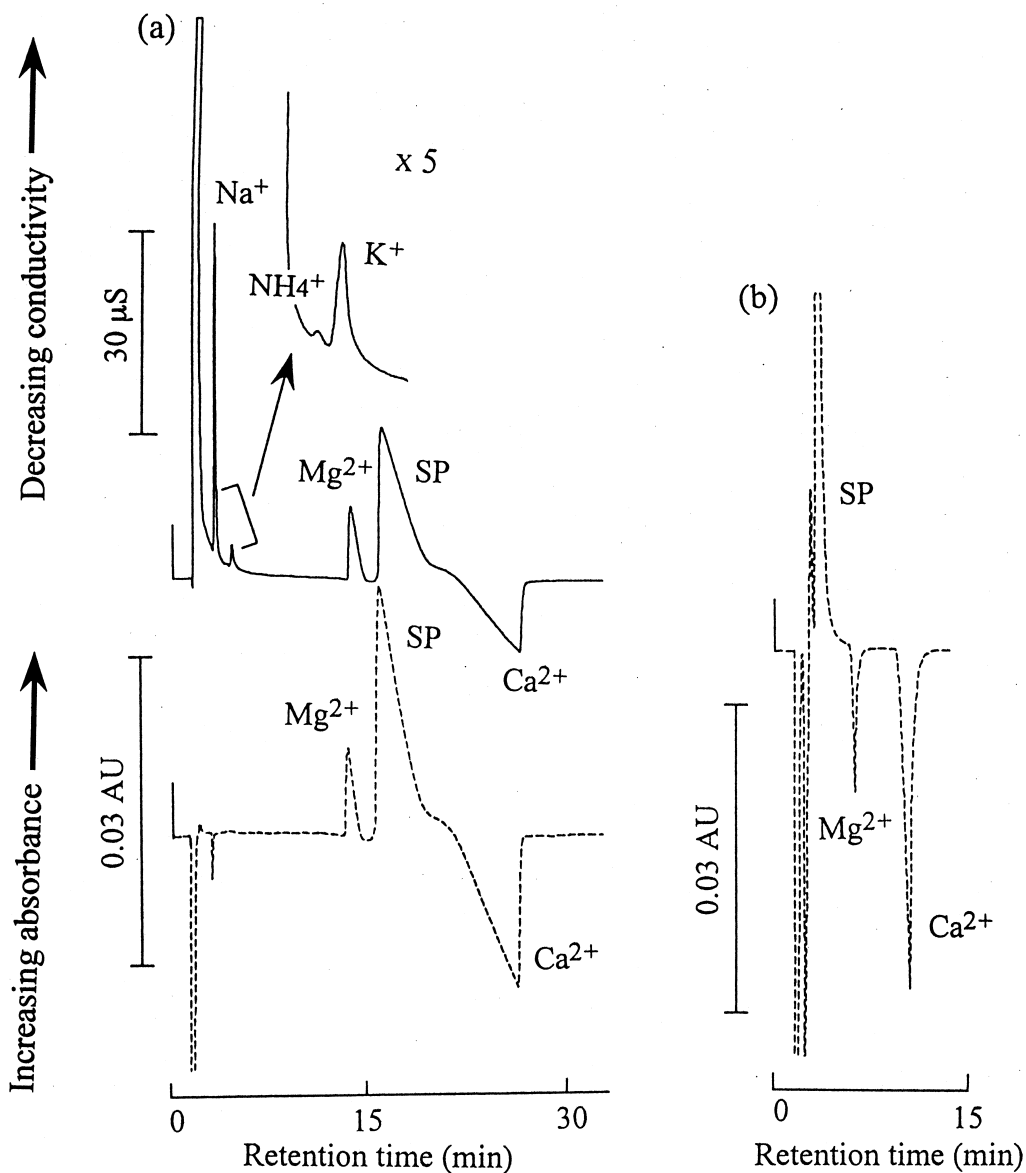

Fig. 7. Ion chromatograms of river water [(a) 2-fold dilution, (b) no dilution]. Conditions: mobile phase, (a) 0.2 mM Ce(III)+0.1 mM SDS+10 mM HMO_3, (b) 0.8 mM Ce(III)+0.1 mM SDS+1 mM HNO_3; detection, solid line=conductivity detection, dashed line=UV (253 nm) detection. Other conditions as for Fig. 1. The concentration in river water, Na^+ (0.62 mM), NH_4^+ (0.003 mM), K^+ (0.067 mM), Mg^{2+} (0.088 mM), Ca^{2+} (0.41 mM).

3.4. Application to real samples

The present IC systems were applied to the determination of common mono- and divalent cations contained in river and tap waters. The samples were directly injected after filtration by a 0.45-μm membrane filter. Fig. 7 demonstrates the separation and detection of the cations by using two mobile phases and conductivity/UV detection. Good chromatograms were obtained for both systems. For mobile phase containing 1 mM HNO_3 (Fig. 7b), however indirect UV detection was only possible. Determination was carried out by calibration curves by peak area which were linear up to 0.4 mM examined for both eluent systems. Table 1 shows detection limits of the cations for two mobile phases. Reproducible chromatograms for both Figs. 2b and 6 were obtained during repeated chromatographic run.

In conclusion, it was found that the mutual separation of M^+ (alkali metal and ammonium ions) and M^{2+} (alkaline earth metal ions) on an ODS column without any coelution and disturbance by system peak was possible under the condition of mobile phases containing SDS, HNO_3, and Ce(III). Conductivity detection was effective for M^+ and M^{2+} and indirect UV detection for M^{2+}. However, for the optimization of mobile phase composition, it is important to ensure the separation between the analytes and system peak.

Table 1
Detection limits of common mono- and divalent cations

Cation	Detection limit (μM)[a]		
	Conductivity[b]	UV (253 nm)[b]	UV (253 nm)[c]
Na^+	1.3	–	–
NH_4^+	1.0	–	–
K^+	1.2	–	–
Mg^{2+}	1.4	1.5	0.9
Ca^{2+}	1.7	1.9	1.2

[a] Signal-to-noise ratio=3.
[b] Mobile phase; 0.2 mM Ce(III)+0.1 mM SDS+10 mM HNO_3.
[c] Mobile phase; 0.8 mM Ce(III)+0.1 mM SDS+1 mM HNO_3.

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