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Macrocycle-based column for the separation of inorganic cations by ion chromatography

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Abstract

A tetradecyl-18-crown-6 (TD18C6) column previously used exclusively for anion separations, has been successfully applied to the separation of mono- and divalent cations. The separation is dependent on the selectivity of the macrocycle for inorganic cations. Because of the unusual selectivity exhibited by TD18C6, this macrocycle-based stationary phase is suitable for the simultaneous separation of three alkaline earth metal cations, five alkali metal cations and the ammonium ion. Due to the similar selectivity of TD18C6 for Mg^{2+} and Ca^{2+}, these ions coelute. The affinity of this column for the hydronium ion is great enough that the cations of interest can be eluted by mildly acidic eluents which are amenable to chemical suppression. The innovations of the macrocycle-based cation chromatographic separation system described herein are fourfold. First, due to the high capacity of the columns, an acidic eluent is employed resulting in a different selectivity than previously seen. The selectivity is unique among macrocycle-based columns because there is no variability in retention times resulting from different counter-anions associated with the analytes. Second, the stationary phase is composed of macrocycle adsorbed onto a non-polar polymer resin, rather than to a silica-based column. This allows for the use of basic eluents for the separation of anions without fear of destroying the polymeric substrate. Third, tetradecyl-substituted 18-crown-6 has not been used in other reported separation schemes of this type. Fourth, this system allows for a greater sensitivity for Cs^+ because it elutes early in the analysis without coelution. Gradient separations employing organic modifiers, temperature, and pH provided improvements in separation over isocratic analyses.

1. Introduction

Macrocyclic ligands have been used as effective components of both the stationary and mobile phases in ion chromatography (IC) as described in a recent review [1] and in other publications [2–6]. These ligands provide novel IC separations due to the unusual specificity with which they selectively bind cations of various sizes to create charged complexes on the column [1]. This selectivity can be exploited to manipulate the separations of an assortment of analytes.

With its long hydrocarbon tail, the tetradecyl-18-crown-6 macrocycle utilized in this study is sufficiently hydrophobic to adsorb strongly onto a non-polar polystyrene–divinylbenzene substrate. When such adsorbed resins are packed into separatory columns and used with aqueous eluents, the macrocycle remains adsorbed to the resin. In the past, macrocycle-based columns using silica gel substrates have been employed as a separation system for the alkali and alkaline earth metal cations [7–11]. However, the TD18C6 column used in this work has a distinct advantage over its predecessors in that the polymer substrate is stable to basic eluent systems.

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This stability makes it possible to use the same column for separating both inorganic cations and inorganic anions [1,3]. The separation mechanism for both types of analyses is based on the selectivity of the macrocycle among cations. Cation separations result from complexation of sample cations by the column macrocycle, while anion separations result from an interaction between the sample anions and the positively charged macrocycle–cation complex exchange sites.

Macrocycle-based ion chromatographic cation separations result from the formation of complexes between analytes and stationary phase macrocyclic ligands. Much research has been directed at obtaining thermodynamic binding constants and related selectivities of macrocycle–metal cation complexes. Table 1 shows log K values for the interaction between inorganic cations and 18-crown-6 in water [12,13].

The cryptands decyl-2.2.1 (D221) and decyl-2.2.2 (D222), which were suitable for chromatographic anion separations [1–6], are not adapted to the separation of cations as they are easily protonated in acidic environments. Consequently, when acidic eluent is used, cryptands are unable to bind metal cations due to competition from hydronium ion. Unlike the cryptands, crown ethers interact only weakly with H_3O^+. Therefore, the resulting competition for macrocyclic binding sites by the H_3O^+ is just sufficient to provide eluent strength. All cation separations reported herein were performed at low pH, using the hydronium ion as eluent.

The log K values in Table 1 predicted that the elution order of the cations on a TD18C6 column would be Li^+, Na^+, Cs^+, NH_4^+, Rb^+, and K^+ among the monovalent cations and Ca^{2+}, Sr^{2+}, and Ba^{2+} among the alkaline earth cations. This selectivity is attributed to the different cationic sizes and their related hydration energies. For example, the size of K^+ corresponds more closely to that of the TD18C6 cavity than for any of the other alkali metal ions. Therefore, the binding constant is significantly higher for K^+ than for the other alkali metal cations.

2. Experimental

2.1. Materials

All columns used in this work were prepared in our laboratory by the following method: the macrocycle-based resin used in packing columns was prepared by dissolving ~0.8 g of TD18C6 in methanol. The dissolved ligand was added to a slurry of ~2.5 g of underivatized MPIC resin (Dionex Corp., Sunnyvale, CA, USA) in methanol–water (60:40) and the resulting mixture was evaporated to dryness. The resin-macrocycle mixture was subsequently resuspended in NaOH and a small amount of methanol and packed into a 28 cm × 4 mm I.D. column using a Dionex column packing system.

The TD18C6 was synthesized specifically for this research by Dr. Jacek Jagodzinsky (Dionex Corporation) using a procedure reported by Ikeda et al. [14]. The 10-μm MPIC resin was also supplied by Dionex and it is an ethylvinyl benzene particle crosslinked with 55% divinylbenzene. Reagent-grade compounds were used in making all standards and eluents. Water used in making eluents and standards was purified to 18 MΩ resistivity with a Milli-Q water purification system (Millipore) and all eluents were degassed by sparging with helium.

Table 1
Log K^a binding for monovalent and divalent cations to 18-crown-6 in water at 25°C

Cation	Li^+	Na^+	Cs^+	NH_4^+	Rb^+	K^+	Ca^{2+}	Sr^{2+}	Ba^{2+}
Log K	0	0.8	0.99	1.23	1.56	2.03	1.26	2.72	3.87

[a] Refs. [12,13].

2.2. Instrumentation

A Dionex 4000i series ion chromatograph with conductivity detection was used for all chromatography. A Dionex cation micromembrane suppressor (CSRS-I) was employed in all separations–using the autosuppression mode for all separations not involving organic additives to the eluent, and the external water mode of suppression when an organic species was added. Column temperature was controlled as needed by a Dionex column heater. The instrument was controlled by a personal computer and data collected using Dionex AI-450 software.

3. Results and discussion

3.1. Isocratic separations–the effect of eluent concentration

The separation of five alkali metal cations and NH_4^+ was accomplished using a single TD18C6-MPIC column. A typical chromatogram of the separation using a methanesulfonic acid (MSA) eluent is presented in Fig. 1B. As predicted from thermodynamic data in Table 1, the monovalent cations eluted in the order $Li^+ < Na^+ < Cs^+ < NH_4^+ < Rb^+ < K^+$.

Experiments were designed to determine the effect of eluent concentration on the macrocycle-based separation of these cations. The acid concentration was varied from 0.1 m*M* MSA to 5.0 m*M* MSA in a series of isocratic analyses (Fig. 1A–D). As the pH of the eluent was lowered, sample cations eluted more rapidly due to the increased H_3O^+ concentration. More rapid elution resulted in poor resolution of Li^+ and Na^+ as well as Cs^+ and NH_4^+, with resolution between these analytes almost completely disappearing when 5.0 m*M* MSA eluent was used (Fig. 1D). This loss of resolution was accompanied by a large decrease in overall analysis time, with retention times for both Rb^+ and K^+ reduced by a factor of ten. The two alkali metal ions with the greatest affinities for TD18C6, Rb^+ and K^+, eluted in under six min

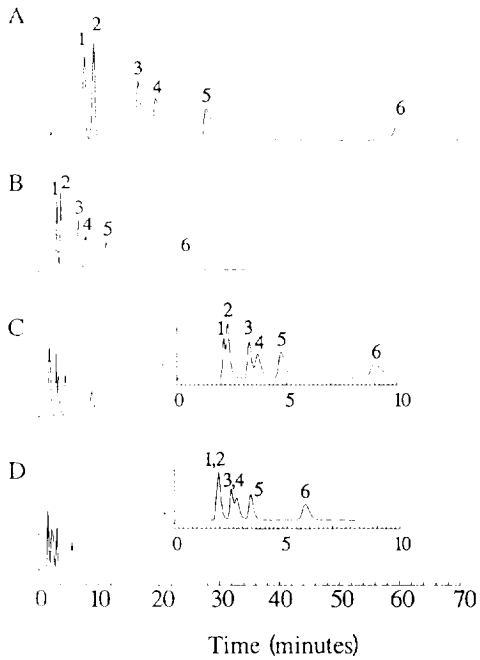

Fig. 1. Isocratic separation of 5 alkali metal cations and NH_4^+ on a TD18C6 column. The eluent concentrations are (A) 0.1 m*M* MSA (methanesulfonic acid); (B) 0.25 m*M* MSA; (C) 1.0 m*M* MSA; and (D) 5.0 m*M* MSA. The injection volume is 50 μl and all analyte concentrations are 0.1 m*M*. The peak identities are as follows: 1 = Li^+, 2 = Na^+, 3 = Cs^+, 4 = NH_4^+, 5 = Rb^+, 6 = K^+. Suppressed conductimetric detection was used.

with the increased H_3O^+ concentration (Fig. 1C,D).

The effect of eluent strength on the alkaline earth metals was similar to that seen with the alkali metals. As eluent strength increased, the increased H_3O^+ concentration resulted in a dramatic change in elution times. Fig. 2 exhibits the relationship between eluent concentration and retention time for all nine cations examined in this study. A dramatic change in retention time was observed as eluent concentrations approached 1.0 m*M* MSA. However, after the 1.0 m*M* MSA concentration was reached, little further change occurred. This trend is made even more obvious by comparing the alkaline earth separations under acidic conditions from 0.25

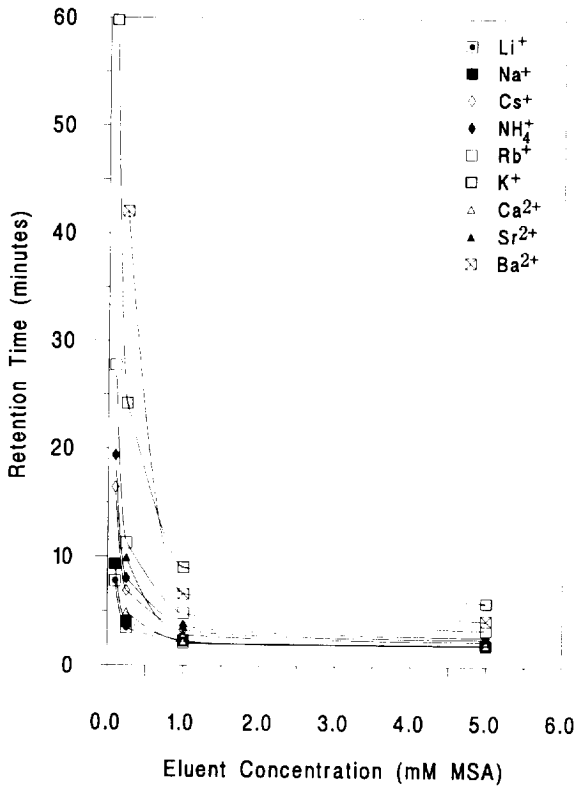

Fig. 2. Plot of eluent concentration vs. retention time for the 9 cations explored in this study.

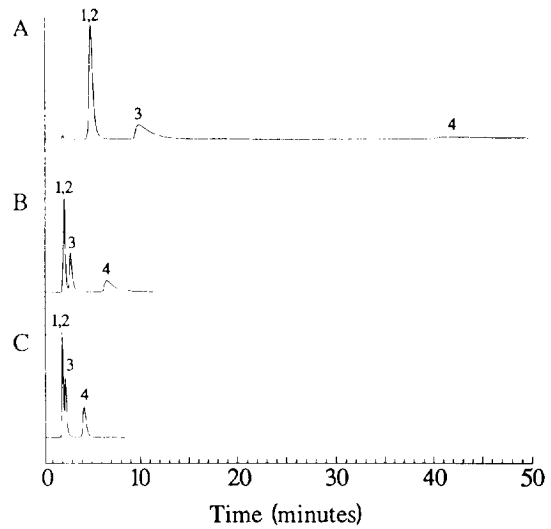

Fig. 3. Chromatograms showing the separation of 4 alkaline earth metal cations on a TD18C6/MPIC column. The eluent concentrations are (A) 0.25 m*M* MSA; (B) 1.0 m*M* MSA; and (C) 5.0 m*M* MSA. The injection volume is 50 μl and all analyte concentrations are 0.1 m*M*. The peak identities are as follows: 1, 2 = Ca^{2+} and Mg^{2+}, 3 = Sr^{2+}, 4 = Ba^{2+}. Suppressed conductimetric detection was used.

m*M* to 5.0 m*M* MSA (Fig. 3). The analysis times are more than halved as the mobile phase is changed to more acidic eluents.

A drawback to alkaline earth cation separations using the TD18C6 column results from the lack of selectivity of TD18C6 between Mg^{2+} and Ca^{2+}. This is evidenced by their coelution at all eluent concentrations in Fig. 3A-C.

A composite standard of the nine alkali, alkaline earth, and NH_4^+ cations was prepared and chromatographed. Isocratic separation conditions were used at eluent concentrations ranging from 0.1 m*M* MSA to 5.0 m*M* MSA. The separations are illustrated in Fig. 4. The best isocratic separations achieved were at low H_3O^+ concentrations (0.1, 0.25 m*M*), where the early eluting peaks were resolved (Fig. 4A,B). However, the total analysis time on such a separations was ~2 h. Nine peaks were observed when an eluent of 0.5 m*M* MSA was used but a number of peaks were unresolved (Fig. 4C).

The most noteworthy result of this experiment is the greater effect of eluent pH on divalent cations than on monovalent ions. This is likely due to the distribution coefficients for divalent cations. In an ion-exchange system the K_D, and therefore k', is inversely proportional to the square of the hydronium activity for divalent cations. For monovalent cations, a simple inverse relationship applies. Therefore, the change in retention of divalent species decreases more rapidly than for monovalent species [15]. While the system we used is not a sulfonated stationary phase, this inverse relationship for divalent cations clearly applies. As the divalent species partitions between the mobile and stationary phases a charge balance is maintained resulting in this relationship. Although the alkali metals retain the same elution order among themselves at all eluent concentrations, the retention relationship between the alkali and alkaline earth

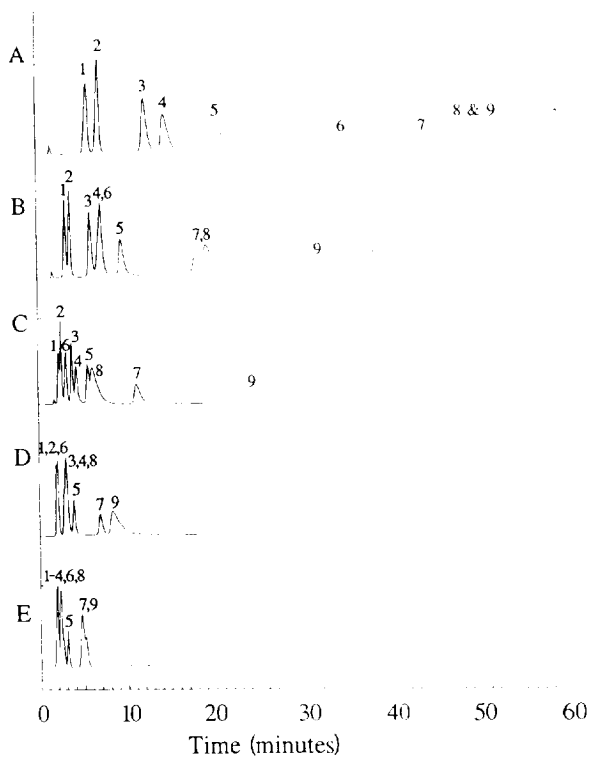

Fig. 4. Chromatograms showing the effect of eluent concentration on the 9 cations explored in this study. All separations were performed on a TD18C6/MPIC column. The eluent concentrations are (A) 0.1 m*M* MSA; (B) 0.25 m*M* MSA; (C) 0.5 m*M* MSA; (D) 1.0 m*M* MSA; and (E) 5.0 m*M* MSA. The injection volume is 50 μl and all analyte concentrations are 0.1 m*M*. The peak identities are as follows: 1 = Li^+, 2 = Na^+, 3 = Cs^+, 4 = NH_4^+, 5 = Rb^+, 6 = Ca^{2+}, 7 = K^+, 8 = Sr^{2+} and 9 = Ba^{2+}. Suppressed conductimetric detection was used.

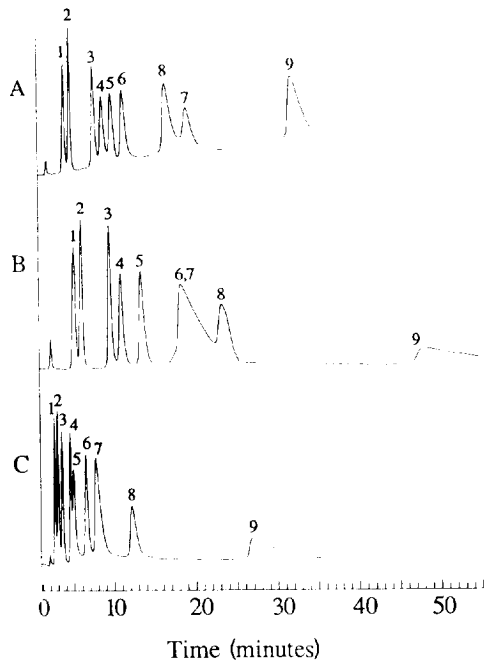

Fig. 5. Three chromatograms showing three different gradient separations of the 9 cations explored in this study. The injection volume is 50 μl, all separations are performed on a TD18C6/MPIC column and all analyte concentrations are 0.1 m*M*. The gradients were as follows: (A) Linear concentration gradient of 0.2 m*M* MSA eluent to 0.5 m*M* MSA from 0 to 15 min followed by a second gradient of 0.5 m*M* MSA to 1.0 m*M* MSA from 15–20 min. The peak identities are as follows: 1 = Li^+, 2 = Na^+, 3 = Cs^+, 4 = NH_4^+, 5 = Ca^{2+}, 6 = Rb^+, 7 = Sr^{2+}, 8 = K^+ and 9 = Ba^{2+}. (B) Temperature gradient from 25°C to 99°C at the time of injection. The eluent was 0.15 m*M* MSA and the peak identities are as follows: 1 = Li^+, 2 = Na^+, 3 = Cs^+, 4 = NH_4^+, 5 = Rb^+, 6 = Ca^{2+}, 7 = K^+, 8 = Sr^{2+} and 9 = Ba^{2+}. (C) Organic modifier gradient from 0.5 m*M* MSA + 5% methanol to 0.5 m*M* MSA at the time of injection. The peak identities are as follows: 1 = Li^+, 2 = Na^+, 3 = Ca^{2+}, 4 = Cs^+, 5 = NH_4^+, 6 = Rb^+, 7 = Sr^{2+}, 8 = K^+ and 9 = Ba^{2+}. Suppressed conductimetric detection was used.

metals changed dramatically. The higher H_3O^+ concentration altered the overall elution order and resulted in poor resolution between the alkaline earth metals and some of the alkali metal ions (Fig. 4D,E).

3.2. Gradient separations–the effect of eluent concentration

Gradients are commonly used in chromatographic separations to decrease the overall analysis time, as well as to enhance the efficiency of later eluting peaks, while retaining resolution between early peaks. Due to the poor affinity of the TD18C6 column for Li^+ and Na^+, it was necessary to keep eluent [H_3O^+] low until after the elution of these two peaks. A variety of step gradients were studied. However, step gradients were always accompanied by a corresponding baseline shift, a result of the suppressor's inability to immediately adjust to large changes in

$[H_3O^+]$. It was therefore necessary to attempt linear gradients involving more gradual changes in $[H_3O^+]$. A linear gradient was performed in which the eluent was changed from 0.2 m*M* MSA to 0.5 m*M* MSA over a 15-min period, then from 0.5 m*M* MSA to 1.0 m*M* MSA over a 5-min period. This gradient produced the best separation of nine cations in terms of total analysis time (Fig. 5. Not only were all peaks resolved, but the efficiency improved from that of an isocratic run in which the eluent was 0.2 m*M* MSA. As expected, the efficiencies of later eluting peaks were improved considerably using the linear gradient over the isocratic run, as indicated in Table 2. While there was a gradual rise in baseline accompanying this separation, the abrupt shifts in the baseline seen with step gradients were not evident.

3.3. Isocratic separations–the effect of temperature

In the past, chromatographic separations involving the use of macrocyclic ligands at variable temperatures were effective in removing longer-retained anionic species from macrocycle-based columns [2]. The binding of ions to macrocyclic ligands is an exothermic process; therefore, at higher temperatures binding decreases. This concept was exploited in our cation separations system by raising the eluent temperature in an effort to decrease overall analysis time via reduced binding of K^+, Sr^{2+}, and Ba^{2+}. Fig. 6 shows a plot of the retention times for all nine cations as isocratic temperature analyses were performed at intervals from 25°C to 80°C. With the exception of Ca^{2+}, the increased temperature resulted in the decrease in retention times as thermodynamically predicted. As can be seen by the slope of the lines, the general trend was a greater change in retention time for longer retained species.

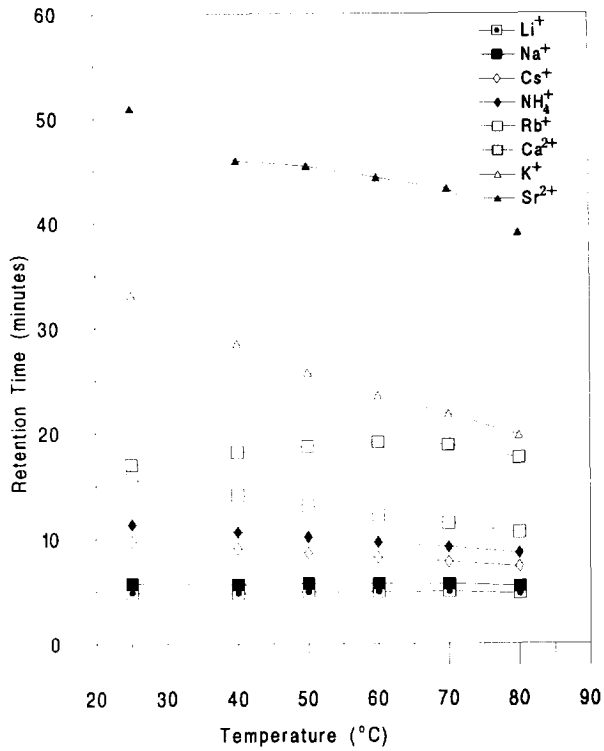

Fig. 6. Plot of temperature vs. retention time for each of the 9 cations studied.

The chromatograms illustrating the irregular behavior of Ca^{2+}, as well as the effect of tem-

Table 2
Efficiency: linear gradient vs. isocratic separation

Analysis	Li^+	Na^+	Cs^+	NH_4^+	Rb^+	Ca^{2+}	Sr^{2+}	K^+	Ba^{2+}
Isocratic[a]	1086	1711	1726	1594	836	1757	1498	1662	not eluted
Linear[a]	1105	1755	2280	2094	2122	2259	1507	2429	1918

[a] Theoretical plates.

Conditions: Separations were performed on a TD18C6/MPIC column, the injection volume was 50 μl and all analyte concentrations were 0.1 m*M*; 0.2 m*M* MSA eluent was used for the isocratic analysis and a changing eluent of 0.2 m*M* MSA eluent to 0.5 m*M* MSA from 0 to 15 min followed by 0.5 m*M* MSA to 1.0 m*M* MSA from 15 to 20 min was employed for the linear gradient. Suppressed conductimetric detection was used for both types of analyses.

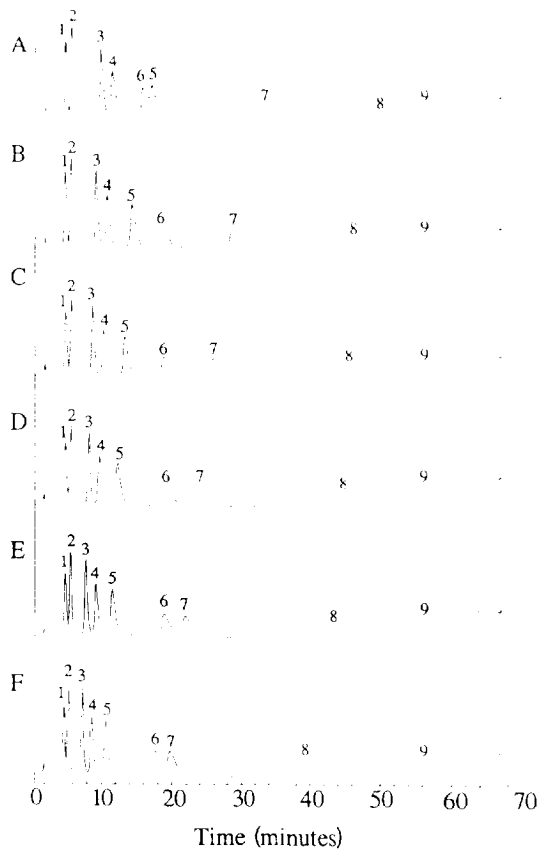

Fig. 7. Chromatograms showing the effect of increasing temperature on the 9 cations explored in this study. All separations were performed on a TD18C6/MPIC column. The eluent concentration was 0.15 m*M* MSA and the temperatures were (A) 25°C; (B) 40°C; (C) 50°C; (D) 60°C; (E) 70°C and (F) 80°C. The injection volume is 50 μl and all analyte concentrations are 0.1 m*M*. The peak identities are as follows: 1 = Li^+, 2 = Na^+, 3 = Cs^+, 4 = NH_4^+, 5 = Rb^+, 6 = Ca^{2+}, 7 = K^+, 8 = Sr^{2+} and 9 = Ba^{2+}. Suppressed conductimetric detection was used.

perature on resolution, are shown in Fig. 7. Initially, Ca^{2+} and Rb^+ are unresolved. However, as temperature increases, the retention of Ca^{2+} increases, then decreases. At the upper end of the temperature scale (80°C), the retention time of Ca^{2+} is still relatively unchanged, causing it to coelute with K^+. This may be due to its small ΔH value of complexation (Table 3) [12]. The ΔH values shown in Table 3 are for reactions in a homogeneous solution. Indeed, the ΔH values for the extraction reaction may be endothermic. The alkaline earth metal ions exhibit strong retention even at higher temperatures, for example at the highest temperatures, Ba^{2+} is retained longer than 70 min.

As separations were performed at higher temperatures, the ions Li^+ and Na^+ as well as Cs^+ and Rb^+ began to lose resolution. The resolution between these analytes can be seen in Table 4. However, the minor effect of the increase in temperature on resolution is a distinct advantage over experiments in which concentration gradients are used. With differences in concentration, the resolution between early eluting species disappears (Fig. 1), whereas the loss of resolution between these early peaks is minor when temperature is increased.

3.4. Gradient separations–the effect of temperature

Temperature gradients were attempted as a means to avoid the baseline shift which generally accompanies concentration gradient separations. Fig. 5B shows a chromatogram which employed a step gradient from 25°C to 99°C at the time of

Table 3
ΔH Values for complexation–homogeneous solution

Analyte	Li^+	Na^+	K^+	Rb^+	Cs^+	NH_4^+	Ca^{2+}	Sr^{2+}	Ba^{2+}
ΔH Values (kJ/mol)	–	−9.41	26.0	−16.0	−15.85	−9.79	−2.91	−15.1	−31.7

Conditions: ΔH values were obtained from the literature [12,13].

Table 4
The effect of temperature on resolution

Analytes	25°C	40°C	50°C	60°C	70°C	80°C
Li^+/Na^+ resolution	1.52	1.44	1.37	1.37	1.32	1.29
Cs^+/NH_4^+ resolution	1.62	1.72	1.83	1.84	1.83	1.84

Conditions: Separations were performed on a TD18C6/MPIC column and all analyte concentrations were 0.1 m*M*. The eluent concentration was 0.15 m*M* MSA and suppressed conductimetric detection was used.

injection. This procedure dramatically improved the overall analysis time, as eight of the nine cations eluted in under 25 min with only one coelution. In addition, there was no baseline rise like that seen in the concentration gradient separation in Fig. 5A. This enhanced baseline stability is due to the nature of the separation. Instead of an increase in eluting power of the eluent, the ability of the stationary phase to bind cations is decreased and column capacity decreases. Therefore the inability of the suppressor to compensate for an increase in eluent concentration is not a factor in temperature gradient separations. In addition, the heated mobile phase is cooled by the regenerant in the suppressor before being detected. This eliminates any increase in conductivity due to the increase in temperature.

3.5. Isocratic separations–the effect of adding an organic modifier to the eluent

To aid in the simultaneous separation of all cations, addition of an organic modifier to the eluent was tested. It was anticipated that by adding an organic solvent, such as methanol, the effective capacity of the column would increase. Methanol increases the binding constants of cations with macrocyclic ligands by reducing competition of solvent molecules for the cations. Thus, when methanol is present in the eluent, the cations are retained longer on the column than when an aqueous eluent is used. This would allow use of higher eluent concentrations, resulting in a more rapid analysis. In previous studies, it was shown that high percentages of organic solvent strip the macrocycle from the column [1]. Fig. 8A shows a separation without methanol in the eluent. It is compared to eluents containing 1% (Fig. 8B), 5% (Fig. 8C) and 10% (Fig. 8D) methanol. As expected, the increasing percentage of organic modifier in the eluent increased retention times and thus yielded better resolution for the early eluting Li^+ and Na^+ peaks (see Table 5).

3.6. Gradient separations–the effect of adding an organic modifier to the eluent

It was desirable to develop a gradient system that not only eliminated baseline shifts (e.g. temperature gradient Fig. 5B) but also resulted in short analysis times (e.g. concentration gradient Fig. 5A). One experiment aimed at achieving this goal was a gradient which switched, at the time of injection, from a 0.5 m*M* MSA eluent that contained methanol to an eluent without methanol. The switch allowed residual methanol to aid in the resolution of early eluting peaks, while the acidic eluent decreased the analysis time. Fig. 5C shows the effect of such a methanol gradient on a 9 cation separation. As predicted, the first peaks were better resolved with the gradient than with an isocratic separation using 0.5 m*M* MSA (Fig. 4C), and the overall analysis time was decreased from analyses in which methanol was ever present in the eluent (Fig. 8B–D). In addition, altering the concentration of methanol had no significant effect on the performance of the suppressor, and therefore, baseline shifts did not occur.

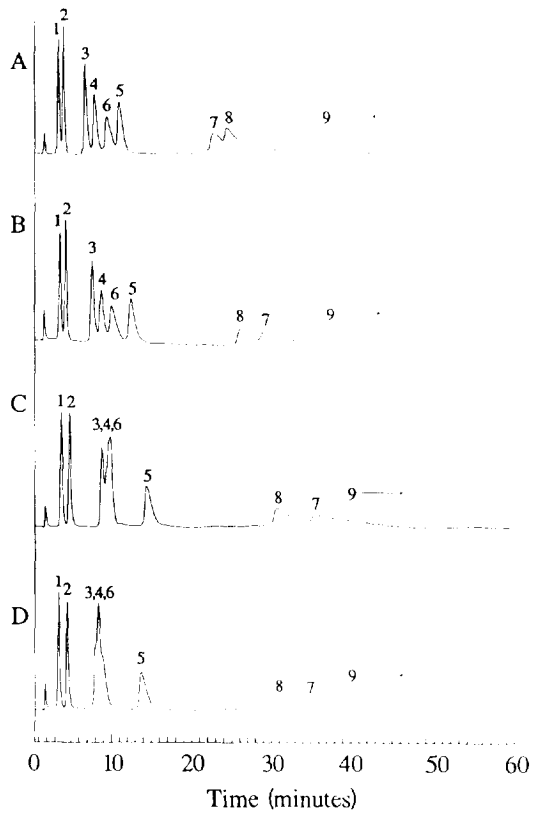

Fig. 8. Chromatograms showing the effect of the addition of an organic modifier on the 9 cations explored in this study. All separations were performed on a TD18C6/MPIC column. The eluent concentration was 0.2 m*M* MSA and the % methanol was (A) 0%; (B) 1%; (C) 5%; and (D) 10%. The injection volume is 50 μl and all analyte concentrations are 0.1 m*M*. The peak identities are as follows: 1 = Li^+, 2 = Na^+, 3 = Cs^+, 4 = NH_4^+, 5 = Rb^+, 6 = Ca^{2+}, 7 = K^+, 8 = Sr^{2+} and 9 = Ba^{2+}. Suppressed conductimetric detection was used.

3.7. Quantitative aspects

Linearity of calibration curves

Calibration curves were generated for each species studied and detection limits were determined at 3σ baseline noise. The correlation coefficients for each sample's calibration curve as well as detection limits can be seen in Table 6. In generating the calibration curves, each concentration was measured three times and a standard deviation calculated. As the retention time increased, band broadening occurred and detection limits decreased. NH_4^+ was the only exception to this trend. Its detection limit was as low as that of Li^+. This result may be due to the higher conductivity of the NH_4^+ ion over the other cations examined in this study.

It is significant to note that the detection limit for Cs^+ is 100 ppb using this macrocycle-based IC system. Other analytical methods such as inductively coupled plasma (ICP) [16], exhibits a poor sensitivity for Cs^+. In addition, other methods of analysis by IC elute Cs^+ very late, and only then after changing eluent strength considerably. Consequently, loss of efficiency, band broadening, and decreased detection occur.

While the correlation coefficients indicate linearity for all analytes over a wide range of concentrations, there were a few unusual results. For instance, at concentrations greater than 10 ppm, NH_4^+ exhibited a significant flattening in the calibration curve. This may be due to the equilibrium expression NH_4^+&rjhar2;NH_3 and H^+. Indeed, all cations show deviations from linearity at high concentrations.

Another oddity we noticed concerned K^+ and column capacity. The column capacity was determined to be 1670 μmol assuming 100% adsorption of the macrocycle. At concentrations greater than 100 ppm, results for K^+ were not reproducible. Perhaps the concentration of K^+ had exceeded the capacity of the column and therefore behaved unpredictably. Other species would likely behave similarly at high concentrations, however this behavior was seen by K^+ at this relatively low concentration because it binds TD18C6 to a greater degree.

3.8. Effect of the counter-anion

Experiments were performed to determine whether the presence of a sample counter-anion played any significant role in the separation and detection of alkali metal cations. Individual samples of various K^+ and Na^+ salts were separated on a TD18C6 column to determine the average retention time of these alkali metal cations with different counter-anions. Specifically, four analyses of potassium acetate, dichromate, bromate, thiocyanate, fluoride, nitrate, nitrite, and iodide were performed. The overall

Table 5
The effect of methanol on the resolution of Li^+ and Na^+

Analyte	No (0%) Methanol	1.0% Methanol	5.0% Methanol	10.0% Methanol
Li^+/Na^+	1.50	1.69	2.08	2.39

Conditions: Separations were performed on a TD18C6/MPIC column and all analyte concentrations were 0.1 m*M*. The eluent concentration was 0.2 m*M* MSA and HPLC grade methanol was used in all analyses. Suppressed conductimetric detection was used.

Table 6
Quantitative results

Analyte	Li^+	Na^+	K^+	Rb^+	Cs^+	NH_4^+	Ca^{2+}	Sr^{2+}	Ba^{2+}
Detection limit	10 ppb	50 ppb	500 ppb	100 ppb	100 ppb	100 ppb	10 ppb	100 ppb	1 ppm
Correlation coefficient	0.9985	0.9993	0.9989	0.9999	0.9999	0.9971	0.9993	0.9999	0.9999

Conditions: Analyses were performed on a TD18C6/MPIC column with varying analyte concentrations. The eluent concentration was 1.0 m*M* MSA and suppressed conductimetric detection was used.

Table 7
Counter-anion effect

Analyte	Number of runs	Deviation (%)
KCH_3COOH	4	0.6
$K_2Cr_2O_7$	4	0.3
KBr	4	0.8
KSCN	4	0.8
KF	4	0.5
KNO_3	4	0.7
KNO_2	4	1.7
KI	4	0.1
$NaNO_3$	3	0.2
NaI	3	0.3
NaH_2PO_4	3	0.2
Na_2CO_3	3	0.3
NaBr	3	1.0
NaCl	2	0.3
Na_2SO_4	3	0.3
NaF	3	1.0
$NaCH_3COOH$	3	0.3
All K-salts	32	3.4
All Na-salts	26	1.2

Conditions: All experiments were performed on a TD18C6/MPIC column and all analyte concentrations were 10 ppm. Dilute concentrations of MSA were used in analyzing both sodium salts and potassium salts. For the potassium analysis, the eluent pH 1.6, and for the sodium analysis, the eluent pH 3.6. Suppressed conductimetric detection was used.

retention time for these runs was 6.20 ± 0.21 when eluted at pH 1.6. In addition, 3 runs each of sodium nitrite, iodide, biphosphate, carbonate, bromide, chloride, sulfate, fluoride, and acetate were performed and the overall retention time for these runs was 3.11 ± 0.04 when eluted at a pH 3.6. Table 7 shows the relative standard deviation of each potassium and sodium salt elution. It is important to note that the larger overall standard deviations for each set of alkali salts is due to a baseline drift which occurs throughout each day, possibly due to environmental temperature changes.

It is noteworthy that the different counter-anions play no significant role in the retention of the alkali metals when an acidic eluent is employed. This is because unlike H_2O–methanol systems studied in the past [7,8,10,11], the acidic eluent system allows the sample counter-anions to be uniformly replaced by the eluent counter-anion, methylsulfonate. The literature demonstrates that when pure water is used as the eluent, the counter-ions associated with the sample cations are not displaced and therefore a different retention time is observed for each cation-anion pair [8–11]. In contrast, we observe no effect of sample counter-anions on cation

retention in the presence of an acidic mobile phase.

4. Conclusions

The TD18C6-based IC system reliably separates and quantitates both anions and cations. The shifting retention times due to matrix anions or analyte concentration seen previously using water eluents is effectively eliminated by the use of acidic eluents. In addition, the polymer stationary phase substrate makes it possible to use this column with basic eluents for the separation of anions.

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