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Interference of some matrix ions in cation-exchange chromatography ☆

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Abstract

Ion chromatographic analysis of ions in samples containing complex matrix composition strongly depends on the on-column co-processes caused by sample matrix components. In the present publication studies of different separation phenomena in cation-exchange chromatography are described. The studies were performed at 'non-linear' chromatographic conditions, when the concentration of matrix (interfering) ions significantly exceeded the concentration of the eluent ions. During the research work, the processes already identified in anion-exchange chromatography, i.e. self-elution, on-column change of the eluent and sample-induced micro-gradient elution were used to explain the chromatographic behavior of alkaline and earth-alkaline cations when samples with high matrix cation concentration were analyzed. When present at higher concentrations, the ammonium cation was found to cause self-elution (NH_4^+ fraction) as well as on-column eluent neutralization due to its ability to diffuse into/back from the porous core of the stationary phase (NH_3 fraction). Co-elution of a matrix component and analytes of interest caused spectroscopic interferences that additionally influenced the peak shape of each individual analyte.

Keywords: Matrix effects; Gradient elution, sample-induced; Alkaline metals; Alkaline earth metals; Inorganic cations

1. Introduction

In ion chromatography (IC), samples of very dissimilar analyte concentrations are difficult to quantify, especially when the analytes have very similar selectivities for the applied stationary phase. This statement holds true also for the cation exchange, where alkali metals, earth-alkaline metals, and ammonium are the cations of interest. In recent years a requirement for IC quantification of difficult samples, such as environmental samples or industrial waste, has been frequently encountered. In the majority of cases, high sodium-to-ammonium [1–4] or high ammonium-to-sodium ratios [1,2] must be dealt with, while high concentrations of some other cations may also influence the separation and detection of cations [2,5–7].

Some problems associated with very dissimilar concentrations of analyte cations have been over-

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come in different ways in the past. In order to determine magnesium and calcium in 30% NaCl, Laikhtman et al. applied an on-line matrix elimination procedure, which involved concentration of magnesium and calcium on a metal-chelating resin, rinsing of the excess sodium and elution of magnesium and calcium from the mentioned column on a cation-exchange column [5]. High sodium-to-ammonium ratios (and vice versa) were addressed by Rey et al. using two different approaches [1,2]. In the first, a column switching technique for changing the order of a carboxylated and a sulfonated stationary phase column was used, thus allowing the determination of trace concentrations of lithium, sodium, potassium, magnesium, calcium and ammonium in the presence of large concentrations of either sodium or ammonium ions [1]. The drawbacks of this approach are the use of two columns instead of one and a need for a column-switching valve. The second approach for the improvement of difficult cation separations was directed toward the development of a new stationary phase with mixed carboxylic and phosphonate groups and an improvement of this stationary phase with permanently attached 18-crown-6 ether groups [2]. Both stationary phases were especially developed to enable sodium-to-ammonium quantitation at very diverse concentration ratios of these two cations. Additionally, the stationary phase with 18-crown-6 ether groups allowed determination of cations in sample matrices with high potassium concentration due to its high selectivity for potassium [2]. The determination of selected earth-alkaline metals in the presence of matrix components can be performed by using chelation ion chromatography, which is a technique that offers differing selectivities and increased sensitivity compared to simple ion-exchange chromatography [7–11]. In some cases, problems encountered in the analysis of brine samples could be reduced by preparation of matrix matched calibration standard solutions to obtain accurate results [4].

Although considerable effort was put in to obtaining adequate solutions for the IC analysis of cations in difficult samples, no reports on the influence of the sample matrix cations on the retention behavior of other cations, such as in anion-exchange chromatography [12–14], can be found. Hence, experiments showing matrix effects were expanded upon using the Dionex IonPac CS12A analytical column, which offers the possibility of separating the alkaline, earth-alkaline cations and ammonium using sulfuric acid (H_2SO_4) as an eluent. The scope of this work was to show that on-column processes, such as self-elution, on-column change of the eluent, sample-induced micro-gradient elution, and matrix composition had an influence on the detection response, presented and explained and detailed in our previous publications [12–14] can also be predicted in cation-exchange chromatography.

2. Experimental

2.1. Reagents and standard solutions

All reagents used in this study (unless otherwise stated) were of analytical-reagent grade (Merck, Darmstadt, Germany). Stock solutions of lithium, sodium, potassium, cesium and calcium (1.000 g/l), were prepared by dissolving 610.7 mg of LiCl, 308.9 mg of Na_2SO_4, 222.9 mg of K_2SO_4, 126.7 mg of CsCl and 276.9 mg of $CaCl_2$ in 100 ml of water, respectively. Concentrated standard solutions of Li^+ (8.0 g/l), Na^+ (20.0 g/l), and Ca^{2+} (10.0 g/l), were prepared by dissolving 4.89 g LiCl, 6.18 g Na_2SO_4, and 2.77 g $CaCl_2$ in 100 ml of water, respectively. Working solutions of selected alkaline and earth-alkaline metals in different lithium, sodium and calcium matrixes were prepared by an appropriate dilution of the standard stock solutions and addition of an appropriate amount of the concentrated standard solution of a selected matrix cation. Milli-Q water (Millipore, Bedford, MA, USA) was used in all dilutions.

The alkaline and earth-alkaline metals were separated using 15 m*M* H_2SO_4 as an eluent; 15 m*M* H_2SO_4 was prepared by diluting 1.50 g of 98% H_2SO_4 (ρ=1.835 g/l) with Milli-Q water to 1 l.

2.2. Chromatographic conditions

A Hewlett-Packard (HP) 1100 liquid chromatography module (Waldbronn, Germany) equipped with a Dionex (Sunnyvale, CA, USA) IonPac CG12A (4×50 mm) guard column and IonPac CS12A (4×250 mm) separation column was used [15]. Some

further details: particle diameter 8.5 μm, substrate cross-linking 55%, functional groups carboxylic–phosphonic acids, hydrophobicity medium-low, column capacity 2.8 mEq./column (CG12A-0.56 mEq./column), column void volume 1.75 ml. The samples were injected using an HP1100 autosampler equipped with a 100-μl injection loop. The eluent flow rate was 1.0 ml/min. The outlet of the separation column was directly connected with a 70-cm polyether–ether–ketone (PEEK) tube (I.D.= 0.13 mm) to the Babington nebulizer of a HP4500 inductively coupled plasma (ICP) MS instrument (Hewlett- Packard), which served as an element-specific detector. The data were evaluated using HP chromatographic software and with Microcal Origin (Microcal Software, USA) software package.

2.3. ICP-MS system

The ICP-MS detector was equipped with a Babington type nebulizer. The tuning was done according to the HP operator's manual [16] with a Li, Y, Ce and Tl solution (10 μg/l each). The ICP-MS operating conditions, adjusted by monitoring signals at $m/z=7$ (^{7}Li), 89 (^{89}Y), 140 (^{140}Ce) and 205 (^{205}Tl) with the integration time of 0.1 s for each monitored mass-to-charge ratio, were: radio frequency (RF) power 1350 W, reflected power <2 W, plasma gas 14.8 l/min, auxiliary gas 0.93 l/min, carrier gas 1.05 l/min, cooling temperature 2 °C. The $^{140}Ce^{16}O^{+}/^{140}Ce^{+}$ oxide ion ratio and the $^{70}Ce^{2+}/^{140}Ce^{+}$ doubly charged ion ratio at the applied operating ICP-MS conditions were both below 0.4%. The alkaline and earth-alkaline metals were monitored at $m/z=7$ for Li, 23 for Na, 39 for K, 133 for Cs and 44 for Ca.

3. Results and discussion

When analyzing samples containing high concentrations of matrix cations with ion chromatography, matrix-induced effects, such as peak broadening, prolongation of the retention times and co-elution, prevent or even hinder the correct interpretation of the chromatograms obtained. To overcome or eliminate the problems caused by matrix effect(s), it is necessary either to use a selective post-column derivatization of the selected analyte or a selective detector. One of the most suitable choices for element-selective detection available today is ICP-MS, due to its high linear response range and exclusive element specificity. Additionally, when analytes are present in minute quantities, ICP-MS is advantageous due to its low detection limits.

An example of the applicability of ICP-MS detection system mentioned is shown in Fig. 1, which illustrates chromatograms obtained for low concentrations of the cations of interest (Na^{+}, 5.0 mg/l) in the presence of a large amount of interfering cation (Li^{+}, 2500 mg/l). As expected, the detection of low concentrations of the cations of interest in the presence of a large amount of interfering cation was enabled by the use of the ICP-MS detection system.

One can also observe several additional features in Fig. 1. The first important feature is a significantly lower peak area for Na^{+} co-eluting with Li^{+} [trace ^{23}Na(Li), Fig. 1] compared to the pure sodium peak area (trace ^{23}Na, Fig. 1). Upon comparing both peak areas (integration time interval 2 min and 4.2 min) it was found that the peak area for sodium co-eluting with lithium was diminished by approx. 20%. This phenomenon arises from the application of ICP-MS

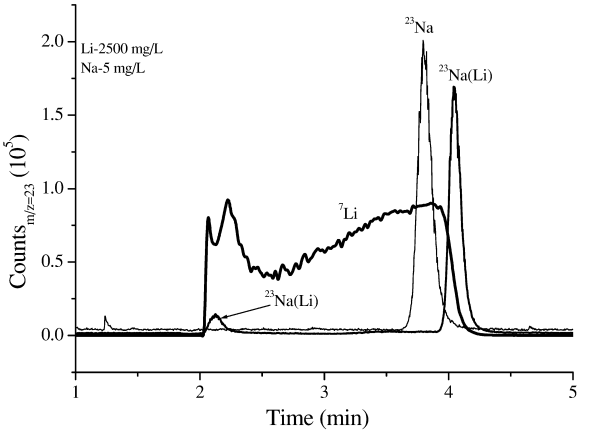

Fig. 1. Element-specific detection of cations in ion chromatographic separation. Peaks ^{23}Na and ^{23}Na(Li) mean ICP-MS signals for sodium (5 mg/l) and for sodium (5 mg/l) in the presence of a matrix cation (Li, 2500 mg/l). Detector signal for ^{7}Li is marked with a thicker black line. Analytical column: Dionex IonPac CS12A; eluent: 15 m*M* H_2SO_4; eluent flow rate: 1 ml/min; injection volume: 100 μl; detection: ICP-MS; monitored ions: ^{23}Na ($m/z=23$) and ^{7}Li ($m/z=7$).

as the element-specific detection method; the diminution of ^{23}Na peak area is namely a consequence of spectroscopic interferences occurring in the plasma source. Since the study of spectroscopic interferences was not the aim of this work, no further investigations in this area were carried out within the present work.

A closer look at Fig. 1 reveals two other interesting features; the prolongation of the retention time for sodium in the presence of Li matrix and sodium peak splitting (a part of Na^+ was eluted within the system void volume at approx. 2 min). It was shown in recent publications that the retention behavior of analyte anions in samples with high matrix anion concentrations strongly depended on the relative affinity of the matrix anion in comparison to the affinities of the analyte and eluent anions, as well as on the matrix anion concentration [12,14]. Since Na^+ possess slightly stronger affinity to the CS12A stationary phase than Li^+, and Li^+ cations are present in the sample as the matrix, the prolongation of the retention time could be the consequence of the so-called on-column change of the eluent composition from H_3O^+ form to Li^+ form in the elution step, when the H_3O^+-based eluent enters the column after the sample plug. Until Na^+ cations retained at the column entrance are under the influence of Li^+-based eluent (weak elution capacity), they move along the analytical column more slowly than they do under the influence of a H_3O^+-based eluent. Reduced elution dynamics is restored to normal when Li^+ cations are separated from Na^+ cations retained on the stationary phase, and the eluent composition is converted back to its H_3O^+ form. Using the proposed mechanism, it is possible to explain the prolongation of the retention time for the main part of the $^{23}Na(Li)$ peak, but not its splitting into two fully separated sub-peaks, the lesser peak eluting at the system void volume (2.1 min) and the main peak eluting at 4.1 min. An appropriate explanation for sodium peak splitting was found after a separated experiment was performed in which the influence of the retention behavior of Na^+ cations on the concentration of H_3O^+ cations in the sample plug was measured (sample-induced micro gradient elution). It was found that increased H_3O^+ concentration significantly decreases the Na^+ separation efficiency. Intensive peak broadening was observed after H_3O^+ concentration in the sample was increased above 100 m*M*. At a H_3O^+ concentration of 500 m*M*, most of Na^+ cations were eluted within the system void volume. In the experiment shown in Fig. 1, a high concentration of H_3O^+ cations was released into the sample plug after Li^+ (0.36 *M*) was retained by the H_3O^+-form stationary phase, which finally resulted in the elution of part of the Na^+ cations within the system void volume.

In order to check the universal validity of the effects found in anion-exchange chromatography [12,14] in providing an explanation for some matrix effects found in cation-exchange chromatography, two sets of experiments were performed with Na^+ as the analyte cation and selected matrix cations. The key for the selection of matrix cations was their relative affinities, which also corresponded to the elution order of cations separated on CS12A column using 15 m*M* H_2SO_4 as an eluent. Accordingly, the first eluted cation, Li^+ and the last one, Ca^{2+} were selected as matrix cations. Chromatograms of model solutions containing 5.0 mg/l of Na^+ in a calcium or lithium matrix with increasing matrix cation concentrations are presented in Fig. 2A,B.

In order to explain the phenomena observed in Fig. 2A, one should bear in mind that Na^+ exhibits a similar affinity to the applied stationary phase (CS12A) as H_3O^+, but a significantly lower affinity than Ca^{2+}. Consequently, when the sample plug rich in Ca^{2+} enters the column, the stationary phase retains Ca^{2+} ions while simultaneously releasing an equivalent amount of H_3O^+, which subsequently causes a micro-gradient elution of Na^+. Micro-gradient elution starts to occur significantly below a Ca^{2+} concentration of 500 mg/l and can be observed in chromatograms as broadening of the analyte (Na^+) chromatographic peak (Fig. 2A). By measuring the analyte peak areas it was observed that with increasing Ca^{2+} concentration (0.0–0.7 g/l) sodium peak area decreased by approximately 50% (integration time interval between 2.0 and 4.2 min). The only reason for the observed phenomena can be a spectroscopic interference caused by the presence of Ca^{2+} in the sample. In Fig. 3 the retention behavior of Ca^{2+} (1 g/l) at the same chromatographic conditions (Fig. 2A) is presented. It can be seen that at the given concentration, the calcium peak is already quite broadened, heaving two maxima at a retention

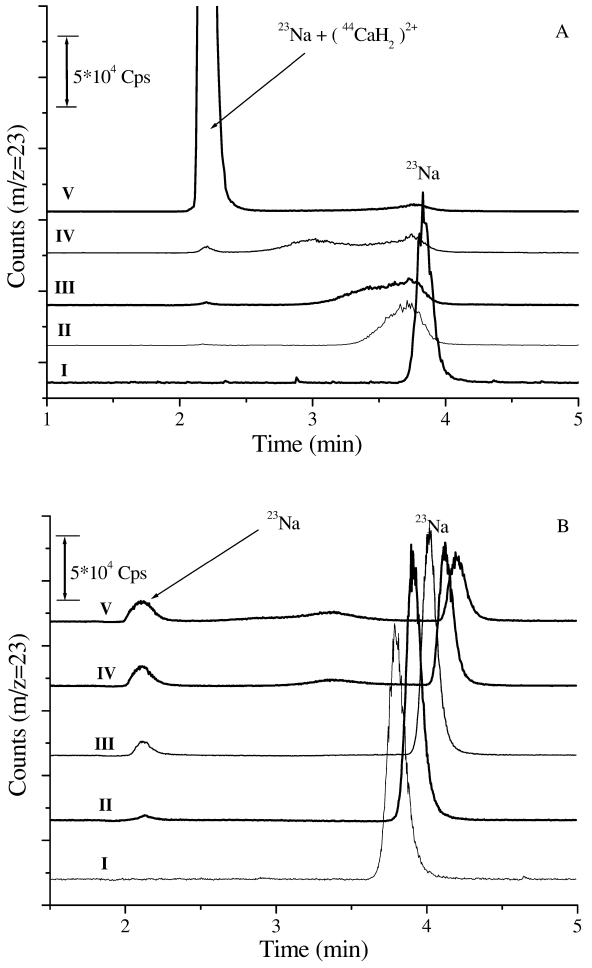

Fig. 2. Chromatograms of model solutions containing 5.0 mg l^{-1} of Na^+ in: (A) calcium matrix (I, 0.0; II, 0.5; III, 0.7; IV, 1.0; and V, 5.0 g l^{-1} Ca^{2+}); and (B) lithium matrix (I, 0.0; II, 1.0; III, 2.0; IV, 5.0; and V, 10.0 g l^{-1} Li^+). Analytical column: Dionex IonPac CS12A; eluent: 15 m*M* H_2SO_4; eluent flow rate: 1 ml min^{-1}; injection volume: 100 μl; detection, ICP-MS; monitored ion, ^{23}Na ($m/z=23$).

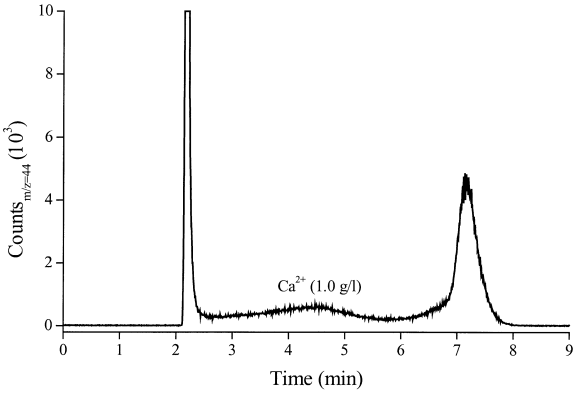

Fig. 3. Chromatograms of a model solution containing 1.0 g/l of Ca^{2+}. Monitored ion, ^{44}Ca ($m/z=44$), other experimental conditions as in Fig. 2.

time 7.2 min and at the system void volume (2.2 min). Between those two maxima, Ca^{2+} was eluted as a broad peak masking the Na^+ peak at 3.8 min. Na^+ co-elution with Ca^{2+} most probably caused some spectroscopic interferences resulting in the diminution of Na^+ peak intensity. At very high calcium concentrations, an increase of the peak eluting within the system void volume, was observed (curve V, Fig. 2A). As there was no compound other than Ca^{2+} and Na^+ in the sample, the only reason for the appearance of the mentioned peak can be spectroscopic interferences, which result in ions with a mass-to-charge ratio $m/z=23$ equal to sodium, such as $^{46}Ca^{2+}$ or $(^{44}CaH_2)^{2+}$, for example. An interfering compound $(^{44}CaH_2)^{2+}$ is extremely likely because at Ca^{2+} concentrations above 1 g/l, a significant part of Ca^{2+} starts to co-elute within the system void volume (Fig. 3), coinciding with an increased concentration of H_3O^+, which appears due to the H_3O^+ displacement from the stationary phase when the matrix-enriched sample plug enters the column.

On the contrary, different chromatographic behavior is expected when the affinity of the matrix cation is much smaller than that of the analyte cation, which holds true in the case of Li^+ and Na^+ as matrix and analyte cations, respectively (see Fig. 2B). In this case, a portion of the analyte cations is eluted at longer retention times with an increase in matrix cation concentration, while the other part is eluted within the system void volume due to the reasons mentioned above (sample-induced microgradient elution). The prolongation of the retention time was found to be dependent on the concentration of matrix component. This situation strongly resembles the on-column change of the eluent composition, observed and described in anion-exchange chromatography [12]. During the passage of the sample plug through the separation column, the stationary phase is converted to its Li^+ form (excess of Li^+ ions) and analyte-cations are displaced deeper

into the column due to the self-elution effect of Li^+. When column back-conversion starts, the increased concentration of Li^+ in the mobile phase reduces its elution effectiveness for Na^+, which results in the prolongation of the retention time for Na^+. A small sodium peak observed on chromatograms IV and V in Fig. 2B (retention time approx. 3.4 min) could originate from the formation of a Li^+ peak profile, which was observed to be quite asymmetric at Li^+ concentrations of 5.0 g/l (chromatogram IV) and 10.0 g/l (chromatogram V).

In order to prove that exchanging some H_3O^+ with Li^+ causes the reduction of the elution strength of H_3O^+-based eluent, a series of experiments was conducted in which part of the H_3O^+ cations were systematically replaced by Li^+ cations in such a way that the final molar concentration of both cations present in the eluent remained constant (30 m*M*). The results of such an experiment demonstrated the expected phenomena. The increase of Li^+ concentration in the mobile phase increased the retention times for Na^+, thereby confirming the proposed mechanism for the prolongation of retention time for Na^+ in case when Li^+ is present as the sample matrix component. At the same time, the Na^+ peak area decreases with an increase of Li_2SO_4 in the eluent. This observation is in good agreement with the data shown in Fig. 1, where Na^+ peak area decreased when sodium co-eluted with Li^+. The addition of Li_2SO_4 to the eluent equally causes a change in the plasma conditions, which influences the ionisation of the elements and leads to the decrease of the ICP-MS signal.

In addition, micro-gradient elution caused by H_3O^+ was also cross-checked with another set of experiments where samples containing different cations in matrices composed of an increased concentration of sulfuric acid, were chromatographed. The results are shown in Fig. 4.

By comparing Fig. 4A,B it is obvious that micro-gradient elution influences the retention of Li^+ and Ca^{2+} apparently more intensively than the retention of K^+ and Cs^+ [which was found to be slightly affected only at elevated concentrations of sulfuric acid (200 m*M*)]. Comparable results for the matrix cations under study were obtained for their self-elution effect. The most pronounced consequences of the self-elution effect were observed for Na^+, Li^+, Ca^{2+}, and Mg^{2+}, in contrast to the self-elution effect of Rb^+, Cs^+, and K^+, which was found to be of limited intensity only. During the present study, no further investigation was carried out in order to find the appropriate explanation for these phenomena.

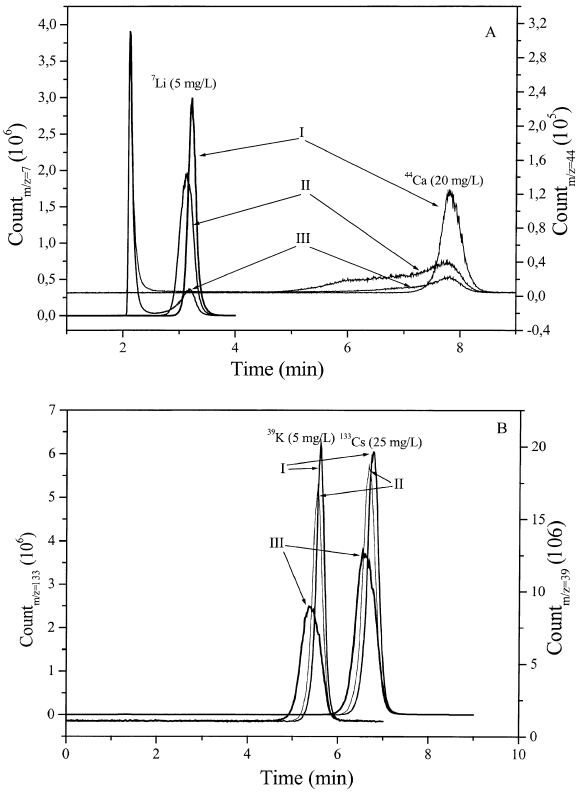

Fig. 4. Chromatograms of solutions containing 5 mg/l of Li^+ and 20 mg/l of Ca^{2+} (A) and 5 mg/l of K^+ and 25 mg/l of Cs^+ (B) in eluent (H_2SO_4)-enriched samples (I, 0.0 m*M*; II, 50 m*M* and III, 200 m*M*). Analytical column, Dionex IonPac CS12A; flow rate, 1 ml/min; sample volume, 100 μl; detection, ICP-MS. Monitored ions were ^{7}Li ($m/z=7$), ^{44}Ca ($m/z=44$), ^{39}K ($m/z=39$) and ^{133}Cs ($m/z=133$).

Due to the frequent requirement for analysis of samples with high sodium-to-ammonium or high ammonium-to-sodium ratio, the influence of Na^+ on NH_4^+ (and vice versa) was also checked. Because it is not possible to monitor NH_4^+ with ICP-MS, only the influence of NH_4^+ on the retention behavior of Na^+ is presented (Fig. 5).

Ammonium cations present in the sample influenced sodium peak in such a way that with increased

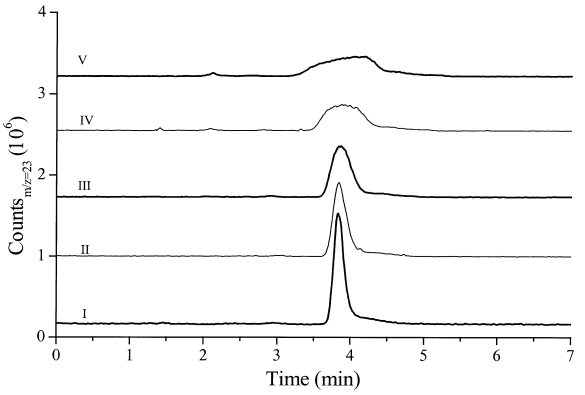

Fig. 5. Chromatograms of standard solutions of 5 mg/l Na^+ containing different concentrations of NH_4^+ (I, 0; II, 0.5; III, 1.0; IV, 2.0; and V, 5.0 g/l). Separation column: Dionex IonPac CS12A; eluent: 15 m*M* H_2SO_4; eluent flow rate: 1 ml/min; injection volume, 100 μl; detection: ICP-MS; monitored ions, ^{23}Na ($m/z=23$).

ammonium concentration the sodium peaks became broadened. Opposite to expectations, the peaks broadened towards shorter as well as towards longer retention times, which was found to be a new phenomenon in matrix effects observed in cation separation. Broadening could be explained by self-elution of sodium by ammonium cations, accompanied by micro-gradient elution, which appears due to the release of higher concentrations of H_3O^+ cations during the retention of ammonium cations by the H_3O^+-form stationary phase. However, if these two phenomena alone would occur, the peaks did not broaden towards longer retention times, which is what can be clearly observed in chromatograms IV and V (Fig. 5). Therefore, an additional mechanism which caused intensive, but time-limited decrease in the elution strength of the eluent was sought. One of the most likely mechanisms was found to have its origin in the fact that ammonium present in the sample is partly in NH_3 form, which can diffuse into the pores of the stationary phase. Later, NH_3 diffuses back into the eluent causing its neutralization and consequently weakening its eluent strength. The higher the concentration of ammonium in the sample, the higher the amount of NH_3 that can diffuse into the stationary phase, and consequently more intensive is eluent neutralization and peak broadening toward longer retention times.

4. Conclusions

In the present paper, matrix cation concentrations on the retention behavior of selected alkaline and earth-alkaline cations was studied. Similarly to the phenomena observed in anion chromatography, a strong influence of matrix cations on analyte retention behavior was also observed in cation-exchange chromatography. The types of matrix effects found in cation chromatography could be classified into similar groups, i.e. self-elution, on-column change of the eluent and sample-induced micro-gradient elution. Some differences in the intensity of the observed phenomena most probably originate in increased capacity of CS12A stationary phase compared to that of AS4A-SC. Regarding individual cations, K^+ and Cs^+ were found to be less influenced by a matrix component than Li^+, Na^+, Ca^{2+} and Mg^{2+}. The reasons for this are still under investigation. Alkaline analytes, which can diffuse into the pores of the stationary phase were found to cause the prolongation of the retention times due to their neutralization effect when they were back-diffused into the bulk of the acidic eluent.

Based on the above conclusions it can be said that the explanations obtained in previous works [12,14] can also be applied in cation-exchange chromatography. In routine work, all of the stated effects must be considered in order to obtain correct data from IC analysis of alkaline and earth-alkaline cations in real samples, even when an element-specific detector is applied for selective detection of co-eluting cations.

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