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Ion chromatography on chelating stationary phases: separation of alkali metals

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Abstract

Analytical 250×4.6 mm I.D. columns packed with iminodiacetic acid (IDA) derivatised silica were used to separate alkali metal ions and the ammonium ion in combination with non-suppressed conductivity detection. The addition of 2.5–10 mmol/l of the macrocyclic crown ether 18-crown-6 to the nitric acid eluent resulted in a change in the elution order and a significant improvement in the resolution between potassium and ammonium because of selective complexation of potassium. However, the admixture of 15-crown-5 did not improve the resolution of lithium and sodium, although 15-crown-5 is a selective complexing agent for sodium. Retention and resolution of lithium, sodium, ammonium, cesium, rubidium and potassium ions increased at lower temperatures down to 1°C. The simultaneous separation of alkali and transition metals under isocratic conditions was achieved with an eluent comprising 10 mmol/l 18-crown-6, 1.5 mmol/l dipicolinic acid, and 1.9 mmol/l nitric acid. The chromatographic system enabled the quantitation of alkali metal ions with detection limits in the low ppb range and excellent linearity. Finally, the applicability of the method was approved by quantitation of sodium, ammonium and potassium in different water samples. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Stationary phases, LC; Chelating stationary phases; Complexation; Alkali metals

1. Introduction

Besides its widespread application to the quantitative analysis of inorganic and organic anions, ion chromatography (IC) has emerged as one of the most important analytical methods for the determination of mono- and polyvalent cations. Compared to spectrophotometric methods, IC holds several advantages such as detection limits in the ppb range, the

feasibility of simultaneous determination of multiple analytes in one single run, and very small sample requirements. Moreover, the analysis of ammonium ion and monovalent amines has gained great importance due to the lack of sensitive spectrophotometric methods for their determination.

While the first IC methods for the separation of alkali metal ions and ammonium ion used sulfonated cation-exchange resins along with dilute solutions of inorganic acids, cation exchangers based on micropellicular support materials coated with cation-exchange latex particles exhibited a significantly better chromatographic efficiency resulting in better

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peak shapes and higher resolution [1]. On these stationary phases, the separation of alkali and alkaline earth metals was achieved in a single run under isocratic conditions. A further improvement in separation capability was offered with the introduction of a silica-based polybutadiene-maleic acid (PBDMA) stationary phase [2] which allowed the separation of alkali and alkaline earth metal ions under isocratic conditions in one single run in a much shorter analysis time. The mobile phase applied for elution of the analytes comprised chelating organic acids such as citric acid, tartaric acid or pyridine-2,6-dicarboxylic acid. The same stationary phase allowed the simultaneous isocratic separation of alkali, alkaline earth and transition metals using complexing eluents (oxalic acid, tartaric acid or citric acid) and non-suppressed conductivity detection [3].

An alternative method for separating alkali and alkaline earth metals used the selective complexing abilities of crown ethers and cryptands. These macrocyclic compounds were immobilised onto suitable support materials either by covalent attachment [4], impregnation [5], or dynamic coating [6]. Complexation of cations largely depended on the size of the hydrophilic cavity of the complexing ligand in relation to the ionic radius of the analytes. Recently, commercially available columns containing carboxylic acid functions combined with crown ether groups [7] and carboxylic acid functions combined with crown ether groups as well as phosphonate functions [8] became available for the simultaneous separation of alkali and alkaline earth metal ions with sulfuric acid eluents. Good resolution between sodium, ammonium and potassium was achieved even for samples containing highly differing amounts of these analytes [8].

Iminodiacetic acid silica (IDA-silica) stationary phases have been successfully applied to the on-line trace enrichment of alkaline earth and transition metals with subsequent analysis on a conventional sulfonic acid cation exchanger [9,10]. Moreover, IDA stationary phases have been used for direct chromatographic separation of alkaline earth metals, transition metals, and lanthanides [11–13]. Although IDA-based stationary phases show ion-exchange properties in addition to the strong chelating abilities, only few reports discuss the use of IDA-derivatised stationary phases as weak cation exchangers [14].

Consequently, in this report we investigate the separation of alkali metal ions and ammonium ion on IDA-silica. The major motivation of this work was to enlarge the field of applications for this type of stationary phase in IC. The effect of combined application of two orthogonal separation mechanisms, namely ion exchange involving the carboxylic functions of IDA and complexation upon adsorption of 18-crown-6, on selectivity is systematically explored. Finally, the applicability to the quantitation of metal ions present at highly differing concentrations is demonstrated by the trace-analysis of alkali metal ions and ammonium ion in different water samples.

2. Experimental

2.1. Apparatus

All experiments were performed with an IC system comprising a high-performance liquid chromatography (HPLC) pump (Model 480 G, Gynkoteck, Germering, Germany), a vacuum degasser (Model ERC-3522, Erma, Tokyo, Japan), a column oven (Model CTO-2A, Shimadzu, Kyoto, Japan), an injection valve (Model 8125, Rheodyne, Cotati, CA, USA) equipped with 20- and 100- μ l sample loops, respectively, a conductivity detector (Model 690 Ion Chromatograph, Metrohm, Herisau, Switzerland) and a personal computer-based data system (Gynkosoft, Ver. 5.32, Germering, Germany). The conductivity cell was thermostated to $35 \pm 0.01^\circ\text{C}$. For chromatographic experiments below ambient temperature the column was chilled in a water-ice bath with an immersion thermostat (Lauda, Type B, Lauda-Königshofen, Germany).

2.2. Stationary phase

The stationary phase was 5 μm silica-based material with an average pore-size of 50 Å (Nucleosil 50-5, Macherey & Nagel, Düren, Germany). The silica material was derivatised according to a procedure by Larsson et al. [15]. After surface activation the silica was derivatised with γ -glycidopropyltrimethoxysilane (Aldrich, Steinheim, Germany). In a second step, IDA (Merck, Darmstadt,

Germany) was covalently bound to the activated silica surface. The stationary phase was suspended in cyclohexanol–toluene (56:44, v/v) and slurry-packed at 20 MPa into a 250×4.6 mm stainless steel column with the help of an air-driven high-pressure packing pump (Knauer, Berlin, Germany).

2.3. Chemicals

All analytes were analytical-reagent grade and purchased as chlorides from different manufacturers (Sigma, St. Louis, MO, USA; Fluka, Buchs, Switzerland). Stock solutions (1000 ppm) were prepared by dissolving the salts in high-purity water from a NANOpure unit (Epure, Barnstead, Newton, MA, USA) and stabilised with 0.1% nitric acid. Nitric acid (suprapure), 15-crown-5 (synthesis grade) and acetonitrile (HPLC gradient grade) were purchased from Merck, 18-crown-6 (>99%), ethylenediamine (analytical reagent grade) were from Fluka, dipicolinic acid was from Riedel-de Haën (Seelze, Germany). The eluents were prepared from high-purity water. Prior to use, all eluents were filtered through a 0.45- μ m filter (Sartrolon, Sartorius, Göttingen, Germany) and degassed for 5 min under vacuum.

3. Results and discussion

3.1. Ion-exchange chromatography with non-complexing and complexing mobile phase additives

Alkali metal ions form no or only weak complexes with most complexing agents. Therefore, the mechanism of separation for these metal ions on a weakly acidic cation exchanger with chelating functionalities, such as immobilised IDA, is determined pre-

dominantly by ion exchange. According to theory, a double logarithmic plot of capacity factors versus proton concentration should give straight lines with a slope of -1 for monovalent ions, if pure ion exchange is responsible for retention. This has been verified on a 250×4.6 mm Nucleosil 50-5 IDA-derivatised column with nitric acid as eluent in a pH range of 2.5 to 3.25 for all alkali metal ions and ammonium ion. The slope of the regression curves at 30°C was -1.12 for all analytes, which is in good agreement with the theoretical value of -1 . Moreover, the elution order of $\text{Li}^+ < \text{Na}^+ < \text{NH}_4^+ < \text{K}^+ < \text{Rb}^+ < \text{Cs}^+$ is identical to that obtained on a sulfonic acid ion exchanger. However, due to only small differences in retention time, resolution between the monovalent analytes was only poor. With increasing pH of the mobile phase an increase in selectivity was observed, but the resolution remained practically unchanged because of more pronounced peak broadening.

The addition of citric acid or dipicolinic acid as complexing agents to the eluent did not result in improved resolution because of the poor stability of most alkali metal complexes. Crown ethers, on the other hand, were expected to influence retention and selectivity because of their different behaviour in forming complexes with alkali metal ions. The stability of the crown ether alkali metal complex depends on the size of the hydrophilic cavity of the macrocyclic ligand and the diameter of the ion (Table 1). It is higher the more there is accordance between the cavity size of the macrocyclic ligand and the diameter of the metal ion. The stability constants of different monovalent ions with 18-crown-6 are given in Table 2. Despite a quite similar ionic diameter of ammonium and potassium it is interesting to note that there is a significant difference in complex stability with 18-crown-6. Due to

Table 1
The ionic diameter of the alkali metals and ammonium in comparison with the cavity size of different crown ethers

Cation	Ionic diameter (pm)	Crown ether	Cavity size (pm)	Ref.
Li^+	152	14-Crown-4	120–150	[21]
Na^+	204	15-Crown-5	170–220	[21]
K^+	276	18-Crown-6	260–320	[21]
NH_4^+	286			[22]
Rb^+	304	21-Crown-7	340–430	[21]
Cs^+	334			[21]

Table 2
Stability constants of different monovalent ions with 18-crown-6

	Cation						
	H ₃ O ⁺ a	Li ⁺ b	Na ⁺ b	NH ₄ ⁺ b	K ⁺ b	Rb ⁺ b	Cs ⁺ b
Log <i>K</i>	6.4	~0	0.8	1.23	2.03	1.56	0.99

^a Measured in acetonitrile at 25°C.

^b Measured in water at 25°C [23].

this effect the order of complex stability, namely potassium>rubidium>ammonium>cesium>sodium>>lithium, is quite different in comparison to other complex forming agents like organic acids. As can be seen in Table 2, there is also an interaction between hydronium ion and 18-crown-6. The high complex stability of hydronium ion is based upon ion–dipole interactions and additional hydrogen bonds to the oxygen atoms of the crown ether.

Fig. 1 illustrates in detail the effect of 18-crown-6 on the separation of alkali metal ions and ammonium ion on IDA-silica at 18-crown-6 concentrations between 0 and 10 mmol/l and a constant concentration of 1.9 mmol/l nitric acid. Because of complexation of hydronium ion, there was an almost linear increase of the pH from 2.75 to 2.95 with

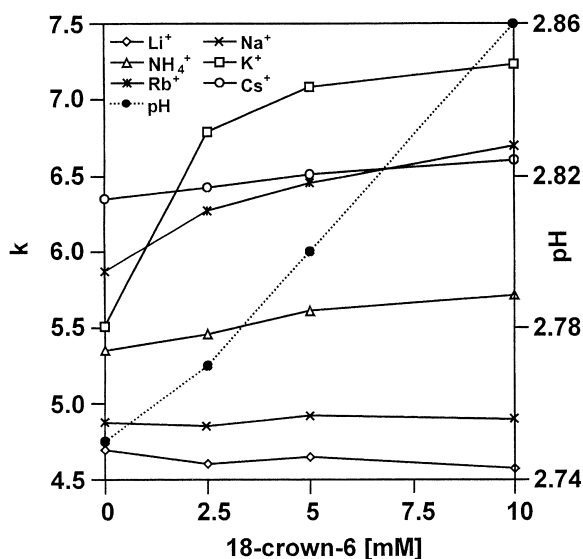


Fig. 1. Effect of 18-crown-6 on the retention of the alkali metals with uncorrected pH (change of pH on secondary axis). Column, 250×4.6 mm, Nucleosil 50-5 IDA derivatised; flow-rate, 1 ml/min; temperature, 30°C; detection, indirect conductivity, 35°C; injection volume, 20 μl.

increasing crown ether concentration. As shown in Fig. 1, the addition of 18-crown-6 had only little influence on the retention of lithium, sodium, ammonium and cesium, but a small increase in resolution between lithium and sodium is observed. Potassium and rubidium ions, on the other hand, exhibited a strong increase in retention time due to their high affinity to 18-crown-6.

In a second experiment, nitric acid was added to compensate for the increase in pH due to complexation of hydronium ion by 18-crown-6 in order to keep the pH constant. The increase in ionic strength of the eluent resulted in a decrease in retention of all analytes with increasing crown ether concentration (Fig. 2). Again, because of complexation with the dynamically adsorbed crown ether, potassium and, to a lesser extent, rubidium are most strongly retained on the column, resulting in the elution order lithium<sodium<ammonium<cesium<rubidium<potassium at 18-crown-6 concentrations of 10.0 and 20.0 mmol/l. The same elution pattern is achieved when the macrocyclic ligand is covalently bound to the stationary phase [4]. The dynamic coating is most probably based on the interaction of the crown ether with the spacer group [(2-hydroxypropyl)propyl ether] and/or the polar interaction between the silanol groups at the surface with the hydrophilic cavity of the crown ether. A significant increase in resolution between lithium and sodium was observed with increasing crown ether concentration whereas the resolution between rubidium and cesium decreased because of the inversion of their elution order. The best separation was achieved with 10.0 mmol/l 18-crown-6, where five out of six ions were completely separated, and only cesium and rubidium coeluted (Fig. 2d). For all further separations a crown ether concentration of 10 mmol/l and a pH of 2.75 were chosen, because satisfactory resolution between lithium/sodium and rubidium/potassium was obtained. Nevertheless, separation of rubidium and cesium was not possible under these conditions.

The influence of proton concentration on the capacity factors was examined at a constant crown ether concentration of 10 mmol/l. A linear decrease in retention time was obtained for all analytes in a pH range from 2.5 to 3.0 with slopes ranging from –1.24 to –1.30 in the double logarithmic plots. The

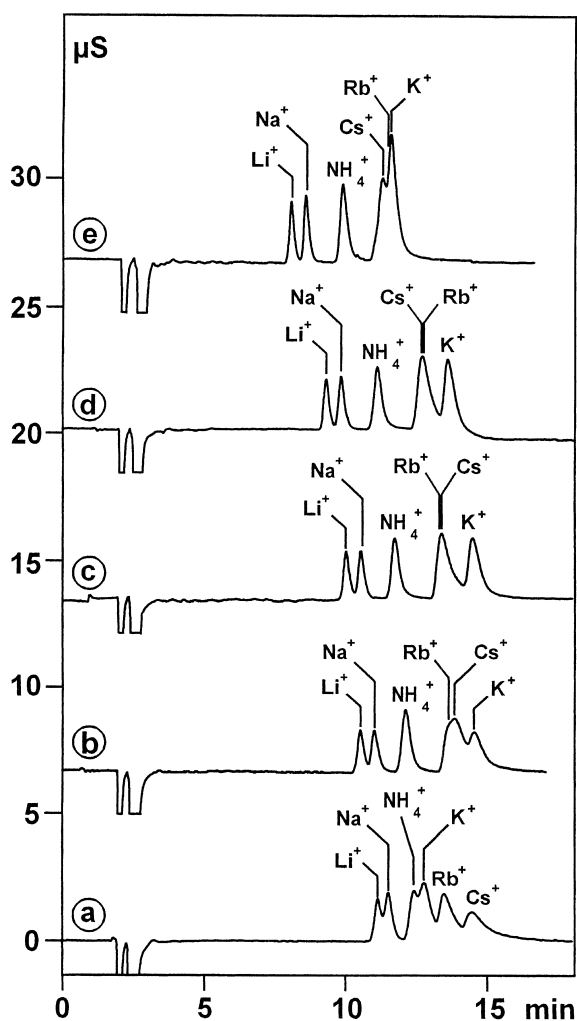


Fig. 2. Effect of 18-crown-6 on the separation of the alkali metals at pH 2.75. Column, 250×4.6 mm, Nucleosil 50-5 IDA derivatised; mobile phase, (a) HNO₃, pH 2.75, (b) 2.5 mmol/l 18-crown-6, HNO₃, pH 2.75, (c) 5.0 mmol/l 18-crown-6, HNO₃, pH 2.75, (d) 10.0 mmol/l 18-crown-6, HNO₃, pH 2.75, (e) 20.0 mmol/l 18-crown-6, HNO₃, pH 2.75, flow-rate, 1 ml/min; temperature, 30°C; detection, indirect conductivity, 35°C; injection volume, 20 µl; sample, Li⁺ (1 mg/l), Na⁺ (3 mg/l), NH₄⁺ (4 mg/l), K⁺ (10 mg/l), Rb⁺ (25 mg/l), Cs⁺ (30 mg/l).

deviation from the theoretical value of -1 can be explained by the different separation mechanism involved in the presence of the crown ether. Using a nitric acid eluent, solely ion exchange is responsible for separation on the weakly acidic carboxyl functions of the IDA groups. In this context it should be

mentioned that underivatized silanols of the silica support material act as ion-exchange functionalities and might influence the selectivity of separation [14]. Nevertheless, in our separation system it is difficult to distinguish between retention due to ion exchange with the carboxylic acid functions and silanol groups. Upon addition of crown ether to the eluent, however, additional complexation and adsorption equilibria take influence on the separation. Therefore, the greatest deviations in slope were observed for potassium and rubidium, which are most significantly affected by complex formation with 18-crown-6.

In an attempt to improve the resolution between lithium and sodium at low pH, the influence of 15-crown-5 on the separation of the alkali metals was examined. As listed in Table 1 there is a good accordance between the cavity size of 15-crown-5 and the diameter of the sodium ion, whereas the ionic diameter of lithium is smaller than the cavity. This is also reflected in complex stability constants of 0 and 0.79, respectively, for lithium and sodium in water [23]. Nevertheless, no increase in resolution between lithium and sodium was observed in a concentration range from 5 to 20 mmol/l 15-crown-5 at a pH of 2.5. However, the retention of potassium and rubidium decreased significantly at higher 15-crown-5 concentrations. This effect can be explained by a competition of the two crown ether species for adsorption sites on the stationary phase. Moreover, only a slight improvement in the resolution between lithium and sodium was observed even in the absence of 18-crown-6.

The next step in optimisation of the chromatographic conditions involved the addition of ethylenediamine (EDA), which is commonly used in IC of cations as a strong eluting agent. EDA is doubly protonated under acidic conditions and, therefore, competes with the analytes for the ion-exchange sites on the stationary phase. The addition of EDA to an eluent containing 10 mmol/l of 18-crown-6, pH 2.75, caused a linear decrease in the capacity factors of all analytes with increasing EDA concentration in the double logarithmic plot. All analytes, even those with a strong interaction with 18-crown-6, showed the same decrease in the capacity factors. The selectivity coefficients of all analytes remained constant over the examined range from 0 to 1 mmol/l

EDA. Therefore, it can be concluded that EDA influences the dynamic coating of the stationary phase without major effect on the selectivity of separation.

3.2. Influence of organic modifier on resolution of monovalent cations

The development of solvent-compatible stationary phases allowed the use of organic modifiers to improve the separation in IC [16]. In some applications pure organic solvents have been utilised for the separation of alkali metal ions [17] or protonated amines [18]. Organic solvents have influence on the formation of complexes due to the change in the hydration sphere of the metal ions. The addition of solvents also changes the dielectric constant of the eluent which directly influences the ionisation constant of the carboxylic acid functions on the stationary phase. Thus, inversions in elution order, a sharpening in peak shape, or an increase in resolution is sometimes possible upon the addition of organic solvents to the eluent. However, in our separation system the addition of 10% (v/v) acetonitrile to the eluent completely suppressed the interaction of the crown ether with the stationary phase and the retaining effect of 18-crown-6 on potassium and rubidium was completely suppressed. We assume that the addition of acetonitrile prevents the formation of a dynamic coating of 18-crown-6 on the stationary phase as it is described for stationary phases dynamically coated or impregnated with crown ethers [13]. The elution order of the alkali metal ions in the presence of acetonitrile and 18-crown-6 corresponds to that using a nitric acid eluent of the same pH value indicating pure ion exchange as the separation mechanism.

3.3. Influence of the column temperature

In most IC applications, the optimal column temperature is found at ambient temperature. However, the ion exchange process can be exothermic or endothermic depending on the nature of the analyte and the column temperature [19]. Exothermic interaction will result in decreased retention at higher temperatures. In contrast to the ion exchange process, complex formation is always exothermic [20].

Thus, an increase in temperature will cause faster elution from complexing stationary phases. Since in our separation system both ion exchange and complex formation may be responsible for chromatographic retention, a more complex temperature dependence of retention can be expected.

The influence of column temperature on retention was investigated in the range from 1 to 75°C. As shown in the Van 't Hoff plots in Fig. 3, the dependence of $\ln k$ on $1/T$ can be adequately approximated by second-order polynomials. This behaviour corresponds well with that observed by Kolpachnikova et al. for alkali metal ions on an IDA-silica stationary phase [14]. The reason for the parabolic dependence of $\ln k$ on $1/T$ is a dependence of the adsorption enthalpy on temperature. An exceptional behaviour of the Van 't Hoff curves was observed for potassium and rubidium ion. Due to complexation with adsorbed crown ether, the retention of these two ions is significantly higher compared to the other alkali ions and ammonium ion

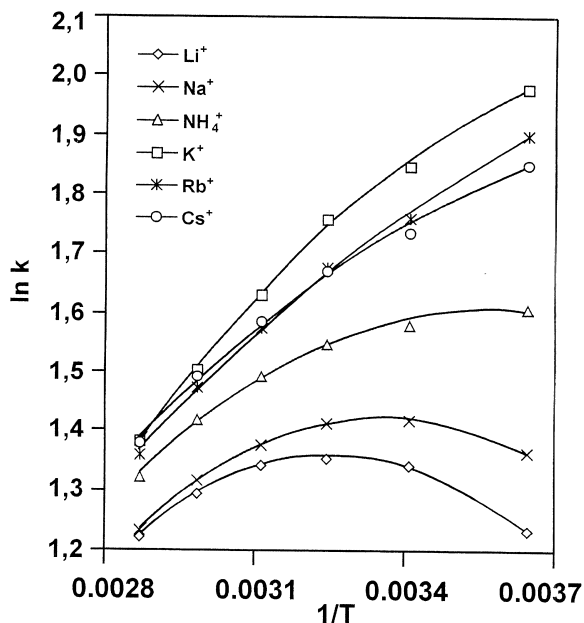


Fig. 3. Dependence of capacity factors of the alkali metals on temperature. Column, 250×4.6 mm, Nucleosil 50-5 IDA derivatised; mobile phase, 10.0 mmol/l 18-crown-6, HNO₃, pH 2.75, flow-rate, 1 ml/min; temperature, 274, 293, 307, 321, 335, 348 K respectively; detection, indirect conductivity, 35°C. Solid lines represent second-order polynomial regression.

which were only retained by ion exchange. A similar correlation between retention and column temperature of potassium and rubidium was observed using stationary phases impregnated with crown ether [5]. The comparatively strong decrease in retention of potassium and rubidium ion at elevated temperature can be explained by a combination of the effects of exothermic complexation as well as exothermic adsorption of 18-crown-6 onto the stationary phase. This observation may serve as another proof for the mixed retention mechanism with ions that can be complexed by 18-crown-6. The adsorption enthalpies calculated from the Van 't Hoff plots for the different ions at 1 and 75°C were as follows: Li^+ , 5.48 and -5.57 kJ/mol; Na^+ , 3.62 and -6.25 kJ/mol; K^+ , -3.03 and -9.67 kJ/mol, NH_4^+ , 0.69 and -6.51 kJ/mol; Rb^+ , -3.64 and -7.68 kJ/mol, Cs^+ , -2.42 and -7.28 kJ/mol. As can be deduced from Fig. 3, resolution between all analytes was highest at 1°C. This temperature can be used for the baseline separation of lithium, sodium, and ammonium at 1°C, whereas cesium, rubidium, and potassium are still only partially resolved (Fig. 4).

3.4. Simultaneous separation of alkali and transition metals

Advantage of the multimodal mechanism of retention with 18-crown-6 coated IDA-silica can be taken to achieve a separation of both mono- and polyvalent ions under isocratic separation conditions with unsuppressed conductivity detection. Fig. 5 depicts the separation of alkali metals and transition metals in a single isocratic run on IDA-derivatised silica in combination with an eluent containing 10 mmol/l 18-crown-6, 1.5 mmol/l dipicolinic acid (DPA), and 1.9 mmol/l nitric acid. The three mechanisms responsible for retention of the different analytes are: (1) cation exchange utilising the carboxylic acid functions of IDA-silica, which determines the retention of lithium, sodium, ammonium, and cesium; (2) complex formation with the dynamically adsorbed 18-crown-6, which determines the retention of potassium; and (3) competing complex formation between covalently bound IDA on the stationary phase and DPA in the mobile phase, which determines the retention of the transition metals cobalt, cadmium and iron(II). Alkali metals were

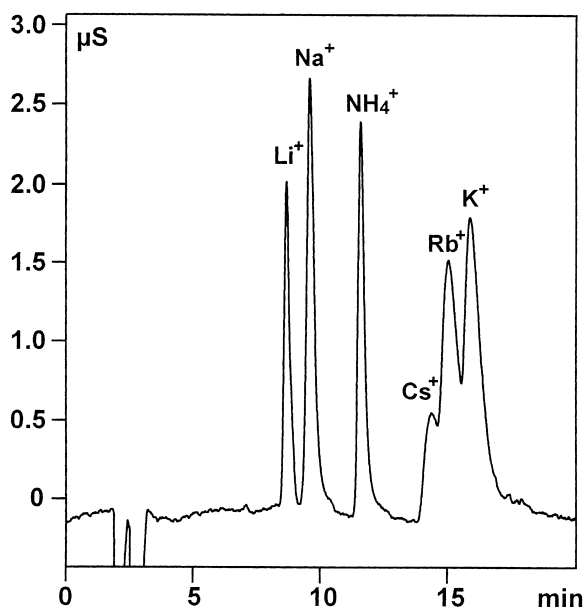


Fig. 4. Separation of the alkali metals at 1°C. Column, 250×4.6 mm, Nucleosil 50-5 IDA derivatised; mobile phase, 10 mmol/l 18-crown-6, HNO_3 , pH 2.75; flow-rate, 1 ml/min; temperature, 1°C; detection, indirect conductivity, 35°C; injection volume, 20 μl ; sample, Li^+ (1 mg/l), Na^+ (3 mg/l), NH_4^+ (4 mg/l), K^+ (10 mg/l), Rb^+ (25 mg/l), Cs^+ (30 mg/l).

unaffected in their retention by the addition of DPA to the eluent because of their poor tendency to form DPA complexes. The transition metal ions eluted before the alkali metal ions due to the high complex stability of the DPA complexes in comparison to the corresponding IDA complexes under the given conditions. In this separation system, mercury, lead, and zinc eluted as one peak immediately after the injection peak. It was also attempted to separate alkaline earth metals with this chromatographic phase system. However, since DPA forms only weak complexes with alkaline earth metals their retention was too long to enable elution within reasonable time under the given conditions.

3.5. Examples of application

Because of insufficient separation selectivity, the analysis of very small amounts of ammonium in natural and industrial samples in the presence of high levels of sodium and potassium is challenging with many commercial stationary phases. Nevertheless,

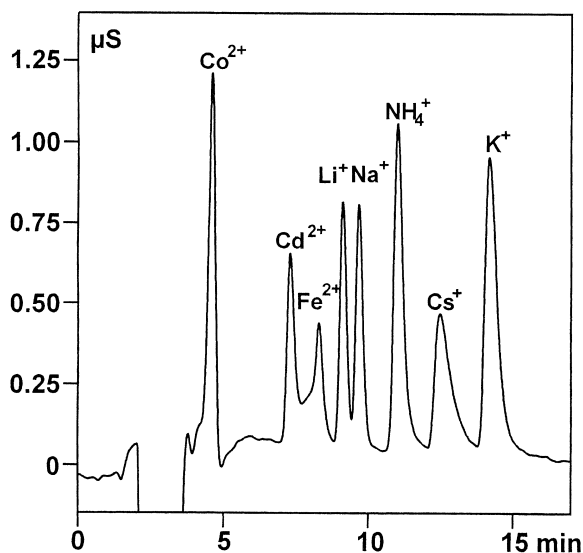


Fig. 5. Isocratic separation of alkali and transition metals on IDA-silica. Column, 250×4.6 mm, Nucleosil 50-5 IDA derivatised; mobile phase, 10 mmol/l 18-crown-6, 1.5 mmol/l DPA, HNO₃, pH 2.75; flow-rate, 1 ml/min; temperature, 30°C; detection, indirect conductivity, 35°C; injection volume, 100 µl; sample, Li⁺ (0.1 mg/l), Na⁺ (0.3 mg/l), NH₄⁺ (0.4 mg/l), K⁺ (1 mg/l), Rb⁺ (2.5 mg/l), Cs⁺ (3.0 mg/l), Co²⁺ (2.5 mg/l), Cd²⁺ (2.5 mg/l), Fe²⁺ (3 mg/l).

IDA-silica as stationary phase in combination with an eluent containing 18-crown-6 and nitric acid allows the quantitation of low levels of one in the presence of high amounts of the others. Fig. 6 shows the separation of 0.5 mg/l ammonium in the presence of 100 mg/l sodium and potassium. To obtain a maximal resolution the separation was performed at 1°C.

To test the suitability of the system for quantitative analysis of sodium, ammonium and potassium, reproducibility of retention times and peak areas as well as limits of detection (LODs) were determined. Retention time and peak area reproducibility data from 10 replicate runs are summarised in Table 3. The small relative standard deviations (RSDs) in retention times and peak areas prove the suitability of the chromatographic method for the qualitative and quantitative determination of the investigated ions. The LODs (calculated at a signal-to-noise ratio of 3; noise determined as peak-to-peak envelope of the baseline based on 100 µl injection volume) were in good accordance with the data published in

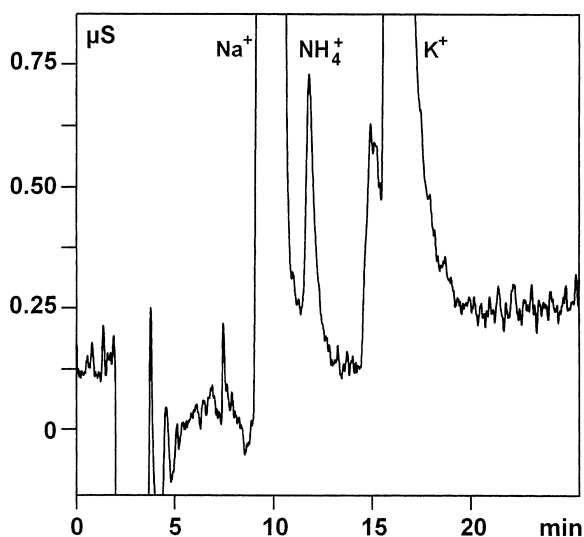


Fig. 6. Determination of 0.5 mg/l ammonium in presence of 100 mg/l sodium and potassium at 1°C. Column, 250×4.6 mm, Nucleosil 50-5 IDA derivatised; mobile phase, 10 mmol/l 18-crown-6, HNO₃, pH 2.75; flow-rate, 1 ml/min; temperature, 1°C; detection, indirect conductivity, 35°C; injection volume, 20 µl; sample, Na⁺ (100 mg/l), NH₄⁺ (0.5 mg/l), K⁺ (100 mg/l).

literature for single column IC with conductivity detection (Table 4). The calibration plots were linear over 2 to 2.5 orders of magnitude with an excellent linearity as indicated by the correlation coefficient.

Three different water samples, namely drinking water, river water, and rain water, were examined for their content of sodium, ammonium and potassium. Prior to injection all samples were filtered through a 0.45-µm syringe filter. No further sample pretreatment was performed before injection. The chromatograms of the three samples are depicted in Fig. 7. After four 20-min runs there was a disturbance of the baseline by the eluting alkaline earth metals. By injection of 100 µl of diluted nitric acid, pH 1.75 into to the chromatographic system the alkaline earth metals were eluted within 10 min and after a re-

Table 3

Reproducibility of retention time (*t*) and peak area (*A_p*) by the given concentration (chromatographic conditions as in Fig. 7)

Cation	Concentration (µg/l)	RSD (%) (<i>t</i>)	RSD (%) (<i>A_p</i>)
Na ⁺	50	0.35	1.71
NH ₄ ⁺	100	0.36	0.96
K ⁺	100	0.18	2.27

Table 4

Limit of detection (LOD), LOD values from literature [24] and correlation coefficients of the calibration curves (measured at 0.5, 1.0, 5.0, 10.0, 50.0, 100.0 ng) (injection volume 100 μ l; other chromatographic conditions as in Fig. 7)

Cation	LOD (ng)	Literature (ng)	Linear range (ng)	Correlation coefficient
Li ⁺	0.25	0.10	n.d.	n.d.
Na ⁺	0.50	0.20	0.5–100.0	0.99995
NH ₄ ⁺	0.50	0.30	0.5–100.0	0.99998
K ⁺	1.00	0.80	1.0–100.0	0.99998
Rb ⁺	5.00	–	n.d.	n.d.
Cs ⁺	50.00	–	n.d.	n.d.

n.d., Not determined.

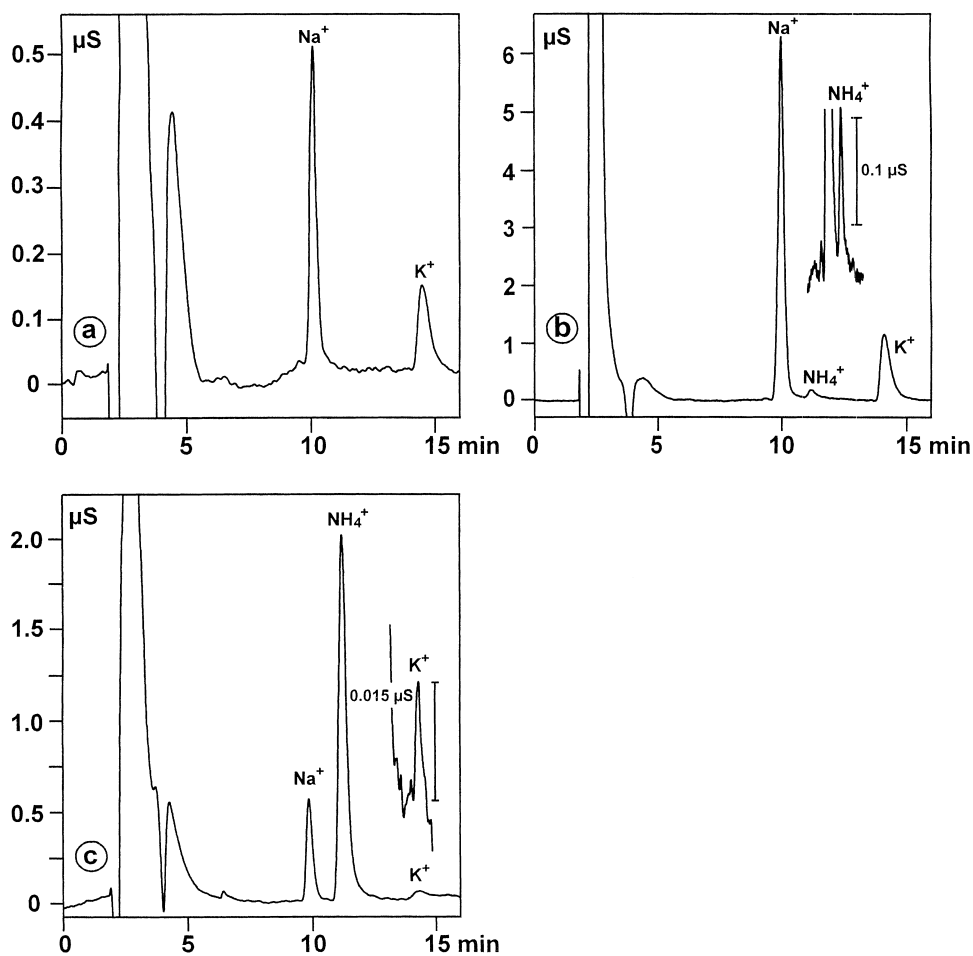


Fig. 7. Chromatographic analysis of sodium, ammonium and potassium in different water samples. Column, 250×4.6 mm, Nucleosil 50-5 IDA derivatised; mobile phase, 10 mmol/l 18-crown-6, HNO₃, pH 2.75; flow-rate, 1 ml/min; temperature, 30°C; detection, indirect conductivity, 35°C; injection volume, 100 μ l; (a) drinking water, (b) river water, (c) rain water.

Table 5
Quantitation of sodium, ammonium and potassium in different water samples (*n*, number of injections)

Sample	Cation	<i>n</i>	Content ($\mu\text{g/l} \pm s_d$)	RSD (%)
Drinking water	Na ⁺	5	51.6 \pm 2.6	5.0
	K ⁺	4	118.3 \pm 7.1	6.0
River water	Na ⁺	6	564.1 \pm 6.0	1.1
	NH ₄ ⁺	6	26.9 \pm 2.6	9.7
	K ⁺	4	858.6 \pm 10.8	1.3
Rain water	Na ⁺	7	59.9 \pm 1.8	3.0
	NH ₄ ⁺	6	618.4 \pm 18.2	2.9
	K ⁺	5	18.8 \pm 2.1	11.1

equilibration time of 15 min the system was ready for a new injection. The three samples show a very different pattern of concentrations of the analytes. As expected, only sodium and potassium were detected in the drinking water sample (Fig. 7a). While relatively small amounts of ammonium were found in the presence of high levels of sodium and potassium in the sample of river water (Fig. 7b), the rain water sample showed a high level of ammonium with trace amounts of potassium and sodium (Fig. 7c). The results of quantitative analysis are summarised in Table 5.

4. Conclusions

Addition of the macrocyclic crown ether 18-crown-6 to a nitric acid eluent enables the separation of alkali metals on an IDA-silica stationary phase. Potassium and rubidium are retained longer in the chromatographic system due to their interaction with the dynamically adsorbed macrocyclic ligand. Upon addition of dipicolinic acid to the eluent, the simultaneous separation of alkali metals and transition metals is possible in a single isocratic run with conductivity detection. The practicability of this new method is approved by separation and quantitation of

sodium, ammonium and potassium in different water samples.

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