Available online at www.sciencedirect.com
SCIENCE DIRECT®
Journal of Chromatography A, 1039 (2004) 123–127
JOURNAL OF CHROMATOGRAPHY A
www.elsevier.com/locate/chroma

Alternative approach to enhancing cation selectivity in ion chromatography

Raaidah Saari-Nordhaus*, James M. Anderson, Jr.

Alltech Associates Inc., 2051 Waukegan Road, Deerfield, IL 60015, USA

Available online 17 March 2004

Abstract

A new approach to enhance cation selectivity in ion chromatography (IC) is described. Two packings, one carrying a conventional carboxylate cation exchanger and the other carrying a crown ether (CE) phase are packed into two separate columns and used in series. The resolution between sodium and ammonium and between ammonium and potassium is increased significantly. The two stationary phases may also be mixed and packed into a single column. The selectivity of the cations can be adjusted easily by varying the dimensions of the carboxylate and CE columns (in the two-column configuration), or by changing the ratio of the carboxylate cation exchanger to the CE packing (in the single-column configuration). These new systems separate ammonium and sodium, even when the sodium concentration is 5000 times higher. Amines such as ethanolamine and triethanolamine can also be separated from the alkali and alkaline-earth cations.

Keywords: Selectivity; Inorganic cations

1. Introduction

Ion chromatography (IC) is one of the most widely used techniques for the determination of alkali and alkaline-earth cations, ammonium, and amines. However, samples that contain very different concentration ratios of cations are difficult to quantify by IC, especially if they elute next to each other. Many environmental and industrial samples contain either very low levels of ammonium in the presence of high concentration of sodium or very low levels of sodium in the presence of high concentrations of ammonium. It is difficult to separate these cations on a standard sulfonate or carboxylate-based cation exchangers because they have similar selectivities toward sodium and ammonium.

Several approaches to achieve these separations were previously discussed. One of them was adding crown ethers (CEs) to the mobile phase [1]. This approach resolves sodium and ammonium, however, since crown ethers are toxic, this present hazard to the analysts and the toxic waste is expensive and difficult to dispose. Other approaches incorporated the crown ether onto the stationary phases, producing a trifunctional [2] or bifunctional [3] cation exchanger. A nice separation of sodium and ammonium and some amines can be achieved with these columns.

This paper discusses an alternative approach to enhancing the cation selectivity. Two separate packings, one carrying a conventional cation-exchange phase and the other carrying a crown ether phase are used. This new approach has advantages in controlling cation selectivity compared to previous methods.

2. Experimental

An Alltech (Deerfield, IL, USA) Odyssey ion chromatograph consisting of a model 626 HPLC pump, Model 630 column heater, Model 650 conductivity detector, and Model 570 autosampler was used. All data were recorded using the AllChrom Data Station (Alltech). The Alltech 335 suppressor module was used to run applications in the suppressor-based mode.

Two packing materials were used in this work. The first was a commercially-available cation-exchange material (Alltech Universal Cation) consisting of silica coated with a polybutadiene–maleic acid copolymer. The experimental crown ether (CE) packing was produced by bonding an 18-crown-6 ether chlorosilane to silica.

* Corresponding author. Tel.: +1-847-948-8600; fax: +1-847-948-1078.
E-mail address: rsaarinordhaus@alltechemail.com (R. Saari-Nordhaus).

0021-9673/$ – see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.chroma.2004.02.004

In the two-column configuration, a 100 mm × 4.6 mm Universal Cation column was coupled with either a 100 mm or 250 mm × 4.6 mm CE column. Changing the relative length of the two columns controlled separation selectivity. In the single-column configuration, a 1:2.5 (m/m) mixture of the Universal Cation and CE material was packed into a 250 mm × 4.6 mm column. An Alltech Allsep A-2 anion column, 100 mm × 4.6 mm i.d. was used to analyze anions in the bulk mobile phase and the system peak fraction.

Cations and amines standards were prepared by diluting the 1000 ppm certified IC standards from Alltech. Mobile phase were prepared using the Alltech EZ-LUTE buffer concentrates. Deionized water was used for preparing all solutions.

3. Results and discussion

A typical chromatogram for the alkali and alkaline-earth cations obtained using only a carboxylate cation-exchange column (Alltech Universal Cation) is shown in Fig. 1. Methanesulfonic acid (MSA) was used as the mobile phase. Since the acid mobile phase is very conductive, the cations are detected in the non-suppressed IC mode with indirect conductivity detection. Other acids such as sulfuric acid, oxalic acid, tartaric acid, and hydrochloric acids can also be used [4,5]. This column is ideal for the separation of monovalent and divalent cations if their concentration levels in the samples are within the same range. If one of the cation is present at much higher concentration than the others, especially in the case of sodium and ammonium, it is difficult to separate them. It is also difficult to separate amines from the monovalent cations on this column as shown in Fig. 2.

In a previous study, we used a bifunctional crown ether/carboxylate stationary phase to increase the resolution between sodium and ammonium [3]. In this study, instead of incorporating the CE and cation-exchange functions on a single stationary phase, two discrete packing materials were used—one containing solely CE functional groups and another containing solely carboxylate functional groups. Columns were packed with the CE material only, the carboxylate material only, and with a mixture containing both materials.

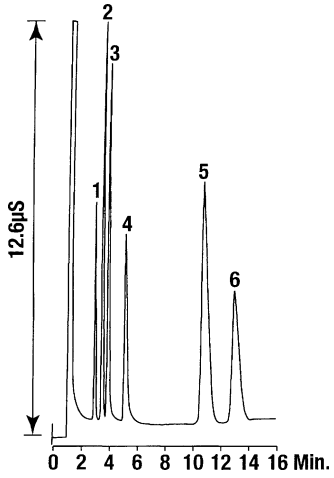

Fig. 1. Alkali and alkaline-earth cations separated on the carboxylate cation-exchange column. Peak identification: (1) lithium (0.2 mg/l), (2) sodium (1.5 mg/l), (3) ammonium (1.5 mg/l), (4) potassium (2.5 mg/l), (5) magnesium (2.0 mg/l) and (6) calcium (2.0 mg/l). Column: Alltech Universal Cation, 100 mm × 4.6 mm; mobile phase, 3 mM methanesulfonic acid; flowrate, 1.0 ml/min; detection, conductivity; injection volume, 100 μl.

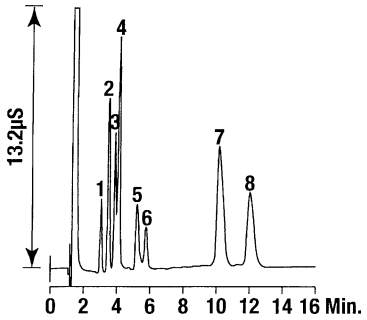

Fig. 2. Six inorganic cations and amines separated on the carboxylate cation-exchange column. Peak identification: (1) lithium, (2) sodium, (3) ammonium, (4) ethanolamine, (5) potassium, (6) triethanolamine, (7) magnesium and (8) calcium. Column: Alltech Universal Cation, 100 mm × 4.6 mm; mobile phase, 3 mM methanesulfonic acid; flowrate, 1.0 ml/min; detection, conductivity; injection volume, 100 μl.

When only the CE column is used for the separation, only sodium, ammonium and potassium are retained and separated as shown in Fig. 3. The highest retention was for potassium, followed by ammonium and then sodium (only slightly retained). This elution order is as expected since the 18-crown-6 forms the strongest complexes with potassium [6]. Lithium, magnesium and calcium eluted in the void.

When the CE column is used in series with the carboxylate cation exchanger, the separation reflects both ion-exchange and complexation retention mechanisms. Fig. 4 shows the chromatogram obtained when the CE column is placed be-

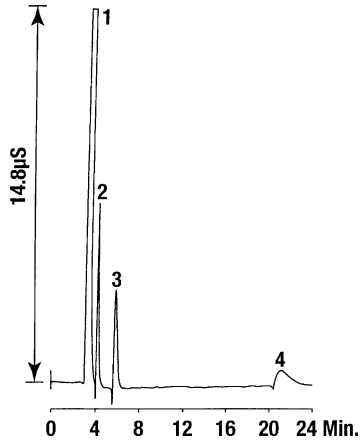

Fig. 3. Alkali and alkaline-earth cations separated on the crown ether column. Peak identification: (1) lithium, magnesium, calcium, (2) sodium, (3) ammonium and (4) potassium. Column: experimental crown ether column, 250 mm × 4.6 mm; mobile phase, 3 mM methanesulfonic acid; flowrate, 1.0 ml/min; detection, conductivity; injection volume, 100 μl.

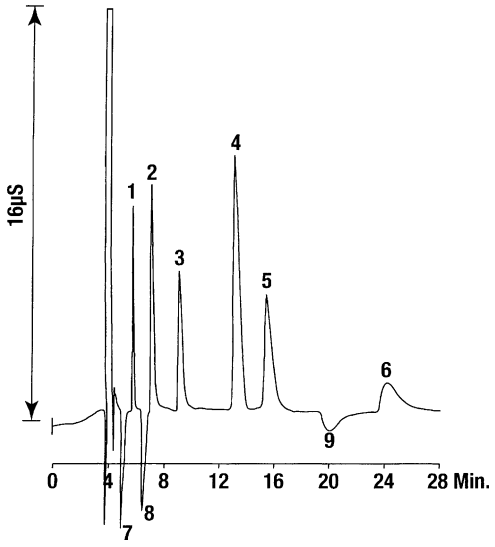

Fig. 4. Alkali and alkaline-earth cations separated on the crown ether and carboxylate cation-exchange columns connected in series (the CE column is placed before the Universal Cation). Peak identification: (1) lithium (0.2 mg/l), (2) sodium (1.5 mg/l), (3) ammonium (1.5 mg/l), (4) magnesium (2.0 mg/l), (5) calcium (2.0 mg/l), (6) potassium (2.5 mg/l), (7) sodium system peak, (8) ammonium system peak and (9) potassium system peak. Column: experimental crown ether, 250 mm × 4.6 mm, and Alltech Universal Cation, 100 mm × 4.6 mm; mobile phase, 3 mM methanesulfonic acid; flowrate, 1.0 ml/min; detection, conductivity; injection volume, 100 μl.

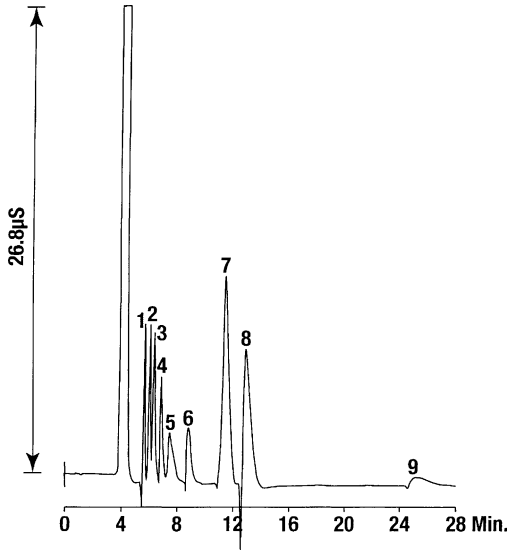

Fig. 5. Alkali and alkaline-earth cations separated on the carboxylate cation-exchange and crown ether columns connected in series (the CE column is placed after the Universal Cation). Peak identification: (1) lithium (0.2 mg/l), (2) sodium system peak, (3) ammonium system peak, (4) sodium (1.5 mg/l), (5) potassium system peak, (6) ammonium (1.5 mg/l), (7) magnesium (2.0 mg/l), (8) calcium (2.0 mg/l) and (9) potassium (2.5 mg/l). Column: Alltech Universal Cation, 100 mm × 4.6 mm, and experimental crown ether, 250 mm × 4.6 mm; mobile phase, 3 mM methanesulfonic acid; flowrate, 1.0 ml/min; detection, conductivity; injection volume, 100 μl.

fore the carboxylate column. Compared to using the carboxylate column alone as shown in Fig. 1, the retention of sodium, ammonium and potassium increases significantly, as does the resolution between sodium and ammonium and between ammonium and potassium. This selectivity matches that achieved using a bifunctional stationary phase or by adding 18-crown-6 ether to the mobile phase. As seen in Fig. 4, three negative system peaks are observed on the chromatogram. These system peaks are associated with sodium, ammonium, and potassium peaks, respectively. Cations that do not form complexes with the CE stationary phase do not produce any system peak.

In an effort to explain the system peaks phenomenon, the system peak fraction associated with ammonium was collected and analyzed for anions by IC. The methanesulfonic acid mobile phase was also injected as blank. The methanesulfonate concentration in the system peak fraction was higher than in the bulk mobile phase, thus producing the negative peak (increase in conductivity with indirect detection). This may be explained by the nature of the complexation retention mechanism where metal ions are retained on the CE stationary phases along with the associated anions [6]. Because the complexation process does not involve ion exchange, the sodium, ammonium and potassium are retained with an equivalent amount of MSA to maintain electrical neutrality. The sodium, ammonium and potassium therefore exit the CE column with an equivalent amount of MSA. The sample band thus contains the cation and an increased concentration of MSA relative to the bulk mobile phase. The analyte ion and the MSA counterion hit the top of the carboxylate cation-exchange column simultaneously. The cation is retained on the column while the MSA is not. They exit the column at different times (MSA first, cation second). Two discrete peaks are therefore produced for each cation that forms a complex in the CE column—one positive peak for the analyte ion and one negative peak for its MSA counterion. A single peak is produced for cations that do not form complexes with the CE stationary phase.

A similar phenomenon is observed when the CE column is placed after the carboxylate column as shown in Fig. 5. Two positive peaks appear for each cation that forms a complex on the CE column. In this case the cations leave the carboxylate column, but because they were separated on the caboxylate column by ion exchange, the MSA concentration in the bulk mobile phase and the cation-containing band is identical. When the sodium, ammonium and potassium are retained on the CE column, they take an equivalent amount of MSA counterion out of the mobile phase. This produces a band with lower MSA concentration than the bulk mobile phase. This band travels through the CE column unretained, reaching the detector as a positive peak (reduce in conductivity), followed by the retained cation band. Two discrete peaks are therefore produced for each cation that forms a complex in the CE column. First a positive peak from the unretained MSA-depleted zone followed by the analyte peak.

This theory is supported by the fact that when the two-column system is used with a suppressor, the system

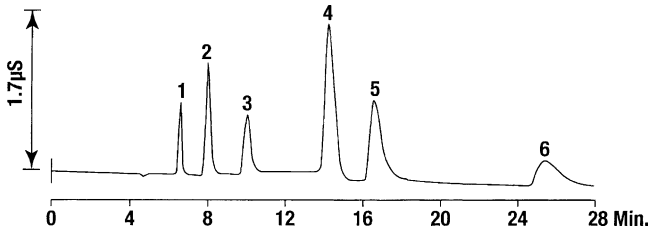

Fig. 6. Alkali and alkaline-earth cations separated on the crown ether and carboxylate cation-exchange columns connected in series (the CE column is placed before the Universal Cation), detected by suppressed conductivity detection. Peak identification: (1) lithium (0.2 mg/l), (2) sodium (1.5 mg/l), (3) ammonium (1.5 mg/l), (4) magnesium (2.0 mg/l), (5) calcium (2.0 mg/l) and (6) potassium (2.5 mg/l). Chromatographic conditions as in Fig. 4 except that the detection is by suppressed conductivity.

peaks disappear as shown in Fig. 6. The suppressor converts the MSA to water, removing the MSA-related peaks before detection. Fig. 7 shows the chromatogram obtained using a column packed with a mixture of the CE stationary phase and the carboxylate cation exchanger. Only the cations peaks are observed on the chromatogram. Since the ion-exchange and complexation mechanisms occur simultaneously and continuously as the analyte travels through the column, system peaks do not appear. The same mechanisms probably occur during separations on bifunctional packing or with a CE mobile phase additive. The multiple peaks only appear when the two mechanisms occur separately and sequentially. The configurations used in Figs. 6 and 7 are probably the best configurations for this approach since no system peak is observed.

When the CE column is placed before the Universal Cation column, the system peaks do not interfere with the analyte peaks. Fig. 8 shows a separation of 5000:1 concentration ratio of sodium to ammonium using this configuration. Ammonium is fully resolved from sodium and easily quantified. This separation is impossible with just the

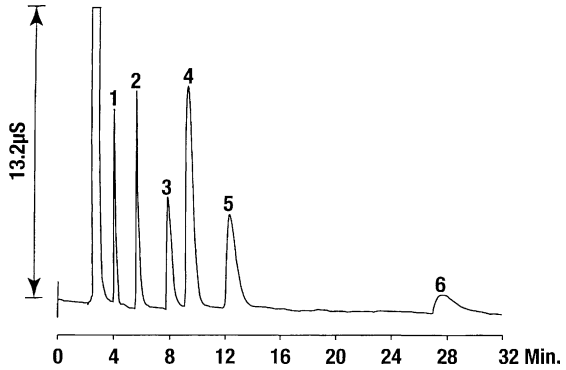

Fig. 7. Alkali and alkaline-earth cations separated on a column packed with a mixture of the CE phase and the carboxylate cation exchanger. Peak identification: (1) lithium (0.2 mg/l), (2) sodium (1.5 mg/l), (3) ammonium (1.5 mg/l), (4) magnesium (2.0 mg/l), (5) calcium (2.0 mg/l) and (6) potassium (2.5 mg/l). Column: mixed bed crown ether and Alltech Universal Cation (2.5:1 ratio), 250 mm × 4.6 mm; mobile phase, 3 mM methane sulfonic acid; flowrate, 1.0 ml/min; detection, conductivity; injection volume, 100 µl.

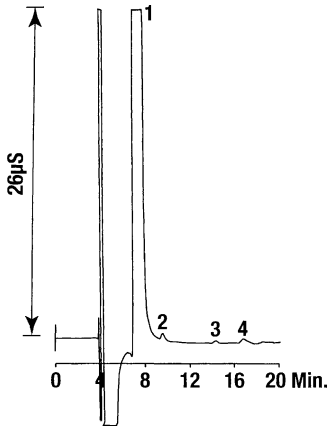

Fig. 8. Separation of 5000:1 ratio of sodium to ammonium. Peak identification: (1) sodium (100 mg/l), (2) ammonium (0.02 mg/l), (3) magnesium (0.02 mg/l) and (4) calcium (0.09 mg/l). Chromatographic conditions and column configuration as in Fig. 4. Column: experimental crown ether, 250 mm × 4.6 mm, and Alltech Universal Cation, 100 mm × 4.6 mm; mobile phase, 3 mM methanesulfonic acid; flowrate, 1.0 ml/min; detection, conductivity; injection volume, 100 µl.

Universal Cation column by itself. This column configuration is also ideal for samples containing low sodium and high levels of ammonium. Also, since potassium is strongly retained and elutes after the divalent cations, this configuration is useful for samples that contain high potassium concentrations relative to other analytes.

Fig. 9 shows a separation of amines and the alkali and alkaline-earth cations. As shown earlier in Fig. 2, this separation could not be achieved using the Universal Cation column alone.

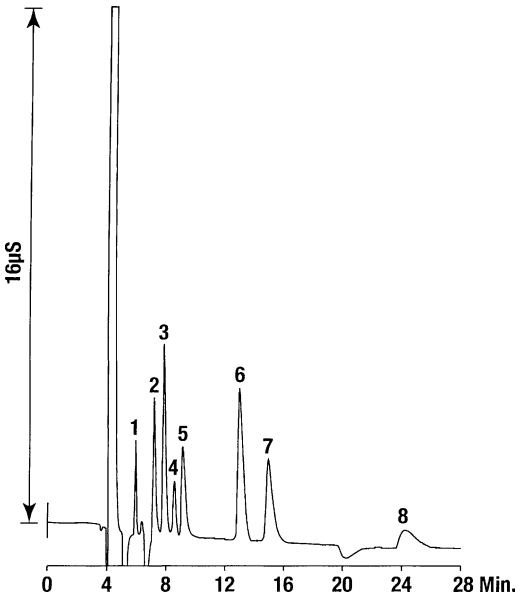

Fig. 9. Inorganic cations and amines. Peak identification: (1) lithium, (2) sodium, (3) ethanolamine, (4) triethanolamine, (5) ammonium, (6) magnesium, (7) calcium and (8) potassium. Chromatographic conditions and column configuration as in Fig. 8.

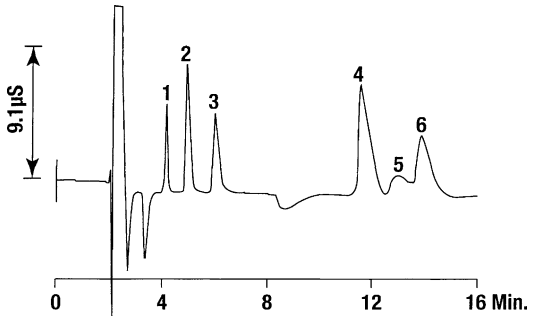

Fig. 10. Alkali and alkaline-earth cations separated on the crown ether and carboxylate cation-exchange columns connected in series (the CE column is placed before the Universal Cation and both columns are of the same dimension). Peak identification: (1) lithium (0.2 mg/l), (2) sodium (1.5 mg/l), (3) ammonium (1.5 mg/l), (4) magnesium (2.0 mg/l), (5) potassium (2.5 mg/l) and (6) calcium (2.0 mg/l). Column: experimental crown ether, 100 mm × 4.6 mm, and Alltech Universal Cation, 100 mm × 4.6 mm; mobile phase, 3 mM methanesulfonic acid; flowrate, 1.0 ml/min; detection, conductivity; injection volume, 100 μl.

This approach of using two separate packings, one carrying a conventional cation-exchange phase and the other carrying a CE phase offers several advantages. One is the ability to switch between two operating modes by adding or removing the CE column from the system. The former configuration is only required for analysis of low levels of ammonium in the presence of excess sodium, or vice versa. The configuration is also useful for samples containing excess potassium or certain amines. The latter configuration is appropriate in all other situations, yielding a faster analysis time and better potassium peak shape. The two-packing configuration also allows independent control of the cation-exchange and CE contributions to selectivity and retention. Changing the relative size of the CE and cation-exchange columns (two-column configuration) or changing the ratio of the CE to cation-exchange packing (single-column method) accomplishes this goal. As an example, Fig. 10 shows the separation of six cations using CE and Universal Cation columns with equivalent dimensions (1:1 ratio). Unlike the chromatogram in Fig. 4 where the CE column ratio to the Universal Cation was 2.5:1 and potassium elutes last, potassium elutes between magnesium and calcium under this configuration. This can be an advantage when analyzing lithium, sodium or ammonium in the presence of high levels of potassium. The resolution between ammonium and potassium is still sufficient and the total analysis time is reduced by 10 min.

4. Conclusion

Independent carboxylate cation-exchange and 18-crown-6 ether packings enhance cation selectivity in ion chromatography. Columns packed with each material may be used in series, or the packings may be combined in one column. Both systems improve the resolution between sodium and ammonium and allow the separation of amines from alkali and alkaline-earth cations. This system eliminates the need for toxic crown ether mobile phase additives. The ability to independently control the cation-exchange and complexation contributions to resolution and retention is more flexible than fixed-ratio bifunctional media and column. In the two-column configuration, system peaks are present for cations that are retained on the CE column. The system peaks generally do not interfere with the analysis, and are eliminated when a suppressor is used.

References

[1] M.W. Laubli, B. Kampus, J. Chromatogr. A 706 (1995) 103.
[2] M.A. Rey, C.A. Pohl, J.J. Jagodzinski, E.Q. Kaiser, J.M. Riviello, J. Chromatogr. A 804 (1998) 201.
[3] R. Saari-Nordhaus, H. Pham, J.M. Anderson Jr., in: Presented at the Pittsburg Conference 1999, paper 2292P.
[4] L.M. Nair, R. Saari-Nordhaus, J.M. Anderson Jr., J. Chromatogr. 640 (1993) 41.
[5] L.M. Nair, R. Saari-Nordhaus, J.M. Anderson Jr., J. Chromatogr. A 671 (1994) 43.
[6] P.R. Haddad, P.E. Jackson, Ion Chromatography (Journal of Chromatography Library 46), Elsevier, Amsterdam, 1990, p. 233.