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High-capacity cation-exchange column for enhanced resolution of adjacent peaks of cations in ion chromatography

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Abstract

One of the advantages of ion chromatography [Anal Chem. 47 (1975) 1801] as compared to other analytical techniques is that several ions may be analyzed simultaneously. One of the most important contributions of cation-exchange chromatography is its sensitivity to ammonium ion, which is difficult to analyze by other techniques [J. Weiss, in: E.L. Johnson (Ed.), Handbook of Ion Chromatography, Dionex, Sunnyvale, CA, USA]. The determination of low concentrations of ammonium ion in the presence of high concentrations of sodium poses a challenge in cation-exchange chromatography [J. Weiss, Ion Chromatography, VCH, 2nd Edition, Weinheim, 1995], as both cations have similar selectivities for the common stationary phases containing either sulfonate or carboxylate functional groups. The task was to develop a new cation-exchange stationary phase (for diverse concentration ratios of adjacent peaks) to overcome limitations experienced in previous trails. Various cation-exchange capacities and column body formats were investigated to optimize this application and others. The advantages and disadvantages of two carboxylic acid columns of different cation-exchange capacities and different column formats will be discussed.

Keywords: Stationary phases, LC; Inorganic cations

1. Introduction

Over the years, determination of diverse concentration ratio samples has been approached in several ways and with varying degrees of success.

The first effective weak-acid cation-exchanger was introduced by Kolla et al. [1]. It consists of a silica-based polymer-coated cation-exchange material and is intended for single-column (non-suppressed) ion chromatography. Thus, these materials have relatively low cation-exchange capacity. Shortly thereafter, a carboxylic acid stationary phase on macroporous polymeric substrate beads was developed (at the Dionex laboratories), to be used with suppressed conductivity detection.

Methods development using an eluent step change with a polymeric carboxylic acid column initially allowed the determination of ammonium in the presence of sodium at a concentration ratio of 1000:1. Impurities in the eluent concentrated on the column during the weaker eluent step, creating a high blank when the eluent concentration was increased.

Soon, the need to analyze larger concentration ratios with an isocratic eluent prompted the development of a column-switching method between existing column chemistries. Switching between a carboxylic acid and a sulfonic acid functionalized column resulted in sodium-to-ammonium concentration ratios of up to 20 000:1 [2]. Although this

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approach enabled wide-spectrum concentration ratios of ammonium and sodium with a simple isocratic eluent, column switching has been perceived as a complicated and more costly technique (because it requires a column-switching valve and a second column).

In an effort to simplify column switching, new resin chemistry was developed in the IonPac® CS15 column [3,4] that provided very different cation selectivities than with the more typical sulfonated and carboxylated resins. In addition to carboxylic acid functional groups, there are macrocyclic polyether 18-crown-6 groups permanently attached to the polymeric stationary phase. In this resin, sodium is well resolved from ammonium, and potassium is eluted after the divalent cations. The optimized eluent for this column contains organic solvent; thus, the electrolytic suppressor cannot be used in its most convenient ''eluent recycle'' or AutoSuppression mode. There is also an extra cost to dispose of acetonitrile in the eluent.

This paper addresses a fourth approach to diverse concentration determinations. It relies on the stationary phase cation-exchange capacity, and allows a simple acidic isocratic eluent to be used to determine concentrations of up to 1:10 000 ratios of ammonium to sodium.

2. Experimental

2.1. Apparatus

All experiments were carried out with a DX 500 ion chromatographic system (Dionex, Sunnyvale, CA, USA) consisting of a quaternary gradient pump (GP40) with automated membrane eluent degassing, a chromatographic oven (LC 30), and suppressed conductivity detection (CD 20 conductivity detector). Eluent flow-rate, unless otherwise stated, was 1.0 ml/min. All instrument control, data collection and data processing was performed with a PeakNet Chromatography Workstation (Dionex). The output of the conductivity detector is automatically normalized so that a readout of 1 μS is equivalent to 1 μS/cm. The cation self-regenerating suppressor (CSRS-Ultra 4-mm) was used in the AutoSuppression mode.

2.2. Stationary phases

The new IonPac CS16 stationary phase consists of 55% cross-linked polymeric macroporous substrate beads grafted with carboxylic acid groups (Dionex). The raw resin has an average particle size and pore size of 5.5 μm and 150 Å, respectively, and the average surface area of the substrate beads is 450 m^2/g. The dimensions of the analytical column are 250×5 mm (I.D.). Its cation-exchange capacity is approximately 8.4 mequiv./column. The new CS16 will be compared to the IonPac CS12A-5 μm column [5] in a 150×3 mm (I.D.) format, which is also a carboxylic acid-grafted cation-exchanger, but of much lower capacity (approximately 0.9 mequiv./column).

2.3. Chemicals

Deionized water (18 MΩ cm resistivity at room temperature) from a water purification system (Continental Type I, Laboratory Reagent Grade Water System) was used for the preparation of the eluents and standards. Methanesulfonic acid (Fluka) and sulfuric acid (Aldrich) were of analytical reagent grade. Standards were prepared from analytical-reagent grade chemicals.

3. Results and discussion

3.1. High-capacity cation exchange resin

Column capacity essentially refers to the number of cation-exchange functional groups with which the sample analytes interact as they travel through the column. The number of groups can be modified by the column body format and/or by the density of the cation-exchange functional groups in the resin.

Conditions were recently developed in our laboratories to enable grafting of a high number of carboxylic acid groups onto polymeric macroporous resin, yielding carboxylated cation-exchange resins with much higher capacity than previously achieved. Graft conditions were optimized on the 5-μm polymeric beads to maintain a high efficiency of the

analyte peaks, especially the divalents, as its peak efficiency decreases as graft level increases.

This high-capacity carboxylated resin was then packed in three different polyether ether ketone (PEEK) column body dimensions (150×3 mm (I.D.), 250×4 mm (I.D.), and 250×5 mm (I.D.)), and their performance was compared to their ability to determine high-to-low concentration ratios of adjacent peaks. The largest (250×5 mm (I.D.)) column format containing more resin was chosen, since it provided the best sodium/ammonium peak resolution (referred to hereafter as the IonPac CS16 column).

Fig. 1 shows the chromatography obtained with the CS16 column for the six common cations (lithium, sodium, ammonium, potassium, magnesium and calcium). The column in both chromatograms was operated at 40°C and the flow-rate of the methanesulfonic acid eluent was 1 ml/min. Because the eluent contains no organic solvent, the suppressor can be used in the AutoSuppression recycle mode.

The top chromatogram shows the elution of the cations when the column is run isocratically with 30 m*M* methanesulfonic acid as eluent. Compared to the bottom chromatogram, note the larger resolution among all peaks, but also that the total run time is longer. Sulfuric acid can be used as an alternative eluent system to methanesulfonic acid, but in order to have a similar separation of the common six cations at 40°C, the concentration of the sulfuric acid must be 17 m*M* (the same separation requires 30 m*M* methanesulfonic acid).

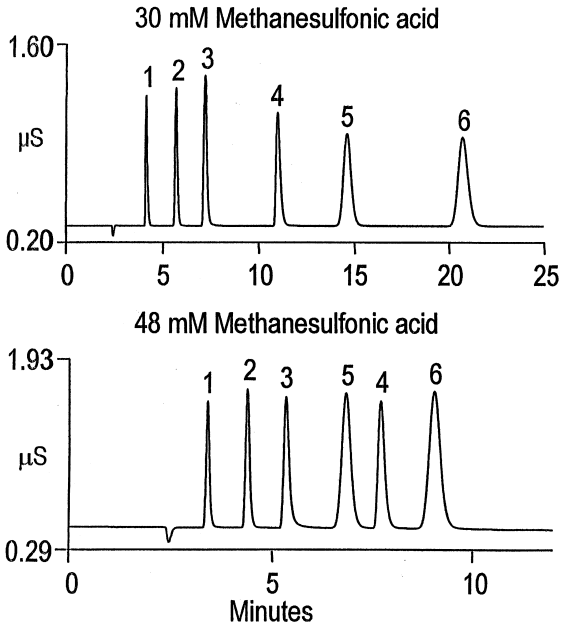

Fig. 1. Separation of common cations with IonPac CS16. Column: IonPac CS16 (250×5 mm (I.D.)); flow-rate, 1.0 ml/min; column temperature, 40°C. Peaks: (1) lithium (0.1 mg/l); (2) sodium (0.4 mg/l); (3) ammonium (0.5 mg/l); (4) potassium (1.0 mg/l); (5) magnesium (0.5 mg/l); (6) calcium (1.0 mg/l).

There is always a trade-off between speed and resolution. There are times when the samples may not contain such disparity in the concentration ratios of adjacent peaks and when sample throughput may be of higher importance. For example, tap water samples may have sodium-to-ammonium concentration ratios in the order of 300:1. In the bottom chromatogram of Fig. 1, the eluent concentration was increased to 48 m*M* methanesulfonic acid to reduce the total run time in half. The separation between sodium and ammonium is smaller, but still adequate for many sample types. Note also that magnesium is now eluted earlier than potassium. This is because with the change in eluent concentration (due to their charge), divalent cations, as opposed to monovalent cations, are affected by the power of two.

3.2. Effects of unbalanced concentration ratios of sodium and ammonium ions on their separations

The greater challenge has always been the quantitation of a low-concentration analyte peak when it is eluted adjacent to a high-concentration analyte peak. Fig. 2 shows the separation of a sample containing a 10 000:1 sodium-to-ammonium concentration ratio. Both chromatograms were obtained with the same column and under the same conditions except for eluent concentration. The bottom chromatogram was obtained under the ''fast run'' conditions. As expected, resolution is not as good as when the eluent is weaker, but the total run time is about half that of a standard run. Under the top chromatogram conditions (30 m*M* methanesulfonic acid eluent), a sample containing 100 mg/l sodium and 10 µg/l ammonium was injected 6 times; it yielded 4% RSD for the peak area of ammonium.

For diverse concentration ratio samples, a cation trap column [Dionex, CTC(4 mm)] may be installed

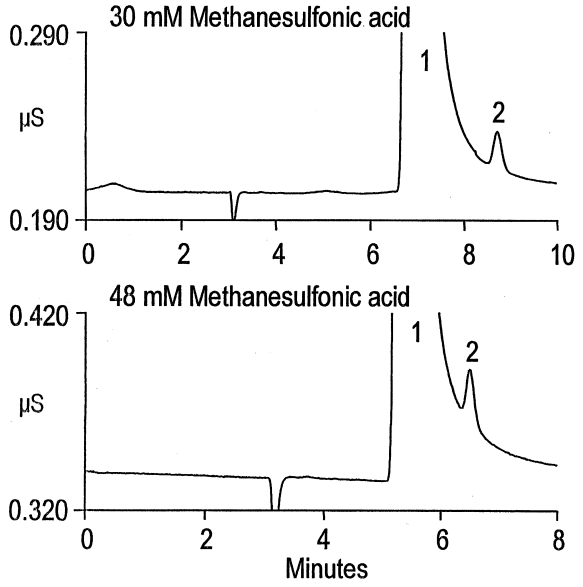

Fig. 2. Determination of dissimilar concentration ratios of sodium-to-ammonium with the IonPac CS16. Column: IonPac CG16 (50×5 mm (I.D.))+CS16 (250×5 mm (I.D.)); flow-rate, 1.0 ml/min; column temperature, 40°C; injection volume, 25 µl. Peaks: (1) sodium (100 mg/l); (2) ammonium (0.01 mg/l).

between the conductivity cell's OUT port and the suppressor's REGENERANT IN port. This trap column contains high-capacity sulfonated resin, and its purpose is to trap the cations in the sample when the suppressor is used in the AutoSuppression (or eluent recycle) mode of operation. Without the trap column, the high-concentration cation peak may take longer to return to baseline levels. However, the trap column is not necessary if the suppressor is used in the external water mode. The high resolution among all the analyte peaks (six common cations) enables the determination of low concentrations of an analyte when an adjacent peak is present in large concentrations.

3.3. Temperature effect on the separation of common cations on the IonPac CS16

Both the top and middle chromatograms in Fig. 3 were run with the high-capacity CS16 with the same methanesulfonic acid eluent concentration, but at different temperatures. Note that analyte elution time

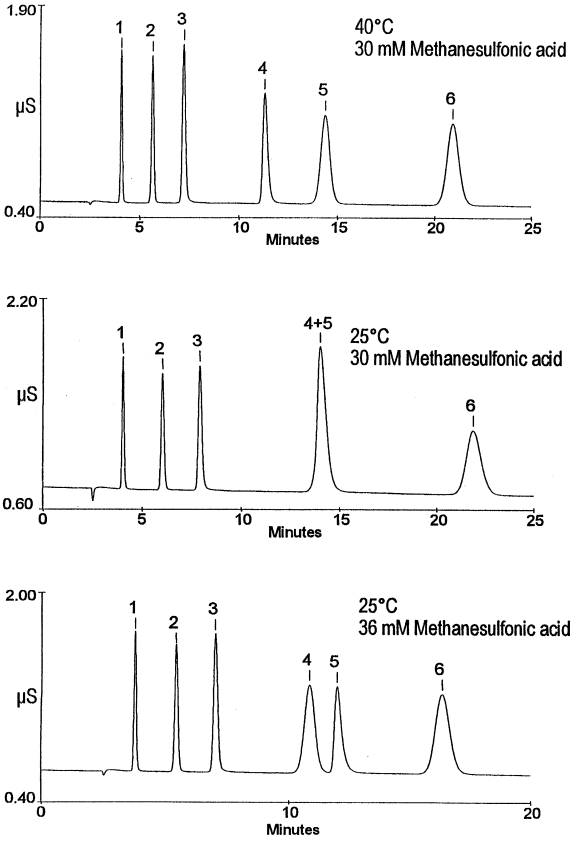

Fig. 3. Temperature effect on the separation of common cations on the IonPac CS16. Column: IonPac CS16; flow-rate, 1.0 ml/min; injection volume, 25 µl. Peaks: (1) lithium (0.1 mg/l); (2) sodium (0.4 mg/l); (3) ammonium (0.5 mg/l); (4) potassium (1.0 mg/l); (5) magnesium (0.5 mg/l); (6) calcium (1.0 mg/l).

is generally shorter at the higher temperature. Potassium elution is the most affected by temperature, whereas magnesium and lithium are least affected. Thus, in order to resolve potassium from magnesium when the column is used at room temperature, the eluent concentration must be increased from 30 to 36 m*M* methanesulfonic acid (see bottom chromatogram in Fig. 3). Note that increasing the eluent concentration has a greater effect on the elution of divalents than monovalents, insofar as magnesium now elutes before potassium. Further increasing the eluent concentration (by 1 or 2 m*M*) will likewise further increase the resolution between magnesium and potassium.

3.4. Separation between amines and common cations

In previous carboxylic acid stationary phases it was difficult to obtain adequate resolution between methylamine and ammonium, and between ethanolamine and ammonium ion.

Fig. 4 shows the isocratic separation of the common cations and three alkylamines (methyl-, dimethyl-, and trimethylamine) plus three of the most commonly used additives in the power industry: ethanolamine, 5-amino-1-pentanol, and morpholine.

The high-capacity carboxylated separator column accomplishes this separation using an isocratic, solvent-free eluent consisting of 26 m*M* methanesulfonic acid. To resolve ammonium from ethanolamine, the column needs to be used at 65°C. The high temperature has the added benefit of improving the peak efficiencies and asymmetries of the analyte peaks, especially for the alkylamines. The electrolytic suppressor should be placed outside the oven when temperatures higher than 40°C are employed.

Fig. 5 shows a sulfuric acid gradient with the column at 70°C (suppressor placed outside the oven) in order to separate the common six cations from ethanolamine, diethanolamine, and triethanolamine. A cation trap column, the CTC-1, was installed between the pump and the injector to reduce the baseline change as the gradient progressed. Besides allowing baseline resolution between ammonium and ethanolamine, the higher temperature also improves efficiencies and peak asymmetries for the alkanolamines.

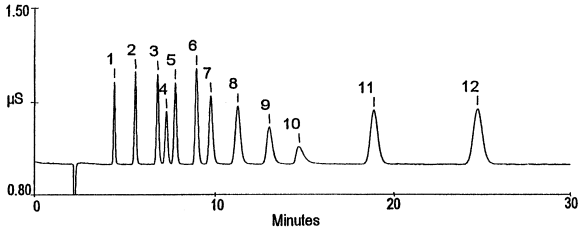

Fig. 4. Separation between amines and common cations. Column: IonPac CS16; eluent, 26 m*M* methanesulfonic acid; flow-rate, 1.0 ml/min; column temperature, 65°C (suppressor placed outside the oven); injection volume, 25 μl. Peaks: (1) lithium (0.05 mg/l); (2) sodium (0.20 mg/l); (3) ammonium (0.25 mg/l); (4) ethanolamine (0.50 mg/l); (5) methylamine (0.50 mg/l); (6) potassium (0.50 mg/l); (7) dimethylamine (1.00 mg/l); (8) 5-amino-1-pentanol (2.00 mg/l); (9) morpholine (2.00 mg/l); (10) trimethylamine (1.50 mg/l); (11) magnesium (0.25 mg/l); (12) calcium (0.50 mg/l).

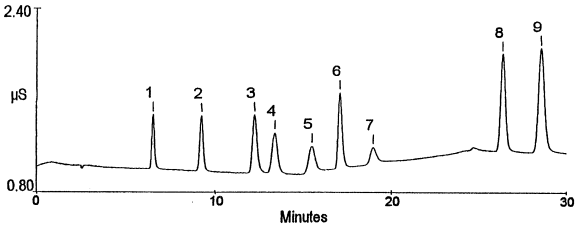

Fig. 5. Gradient elution of alkanolamines and common cations. Column: IonPac CS16; eluent, gradient from 10.5 to 20 min from 6 to 25 m*M* sulfuric acid; flow-rate, 1.0 ml/min; column temperature, 70°C (suppressor placed outside the oven); injection volume, 25 μl. Peaks: (1) lithium (0.1 mg/l); (2) sodium (0.4 mg/l); (3) ammonium (0.5 mg/l); (4) ethanolamine (0.5 mg/l); (5) diethanolamine (1.0 mg/l); (6) potassium (1.0 mg/l); (7) triethanolamine (20 mg/l); (8) magnesium (0.5 mg/l); (9) calcium (1.0 mg/l).

3.5. Influence of sample pH on the IonPac CS16

In the relatively weak carboxylic acid cation-exchange sites, the ionization of the sites is dependent on the eluent pH and on the sample pH. Furthermore, because these cation-exchange sites are hydronium-selective, the sample pH will also impact the elution of the analyte cations from such sites. As the sample pH decreases, so do peak efficiencies and asymmetries.

The IonPac CS12A-5 μm (250×3 mm (I.D.)), with cation-exchange capacity of 0.9 mequiv./column, tolerates about 20 m*M* hydronium ion in the sample (or pH 1.7). Due to its much higher cation-exchange capacity (approximately 8.4 mequiv./column), the IonPac CS16 column can better tolerate low pH samples. Quantification based on peak areas may still be performed for samples with pH 1.0 (or 100 m*M* acid). At pH 0.82 (or 150 m*M* acid), significant peak fronting and loss of peak efficiency occurs, especially for lithium and magnesium. There is no permanent loss of column performance, as the packing is stable even at pH levels below 0.3. Samples containing more than 100 m*M* acid can be pre-treated before injection with an OnGuard II A

cartridge in the hydrogencarbonate form. Anions in the sample are exchanged by the hydrogencarbonate in the resin of the cartridge, and will essentially neutralize the hydronium ion in the sample.

3.6. Linear working range with IonPac CS16

The high cation-exchange capacity of the CS16 stationary phase makes it more difficult to overload with sample concentration. Even though peaks may not have optimum efficiency and asymmetry values at the highest concentration levels, quantification based on peak areas is possible from low μg/l levels to 500 mg/l levels of potassium and calcium. Ammonium has a much shorter linear working range than the other five cations due to its ammonium/ammonia equilibrium. With a 25-μl sample loop, the highest level standard injection contained 50 mg/l lithium, 200 mg/l sodium, 250 mg/l ammonium, 500 mg/l potassium, 250 mg/l magnesium and 500 mg/l calcium. At these concentration levels, asymmetry values are high (i.e., tailing exists) for the final eluting peaks, potassium, magnesium and calcium. Plots of peak areas versus mg/l of analyte nevertheless gave very good correlation coefficients (e.g., $R=0.99995$ for both potassium and calcium), even including this last calibration point.

3.7. Comparison of IonPac CS16 and IonPac CS12A-5 μm

The purpose of Fig. 6 is to show the comparison of two extremes in total separator column cation-exchange capacities and column formats and to demonstrate their advantages and limitations. Both separators were made from macroporous polymeric beads 5 μm in size, grafted with carboxylic acid groups. Each column was run under its own optimized standard conditions, using the same chromatographic system, with the same injection loop and the same standard. To aid in the the discussion, potassium peak efficiency, peak area and peak height will be compared in each case.

The top chromatogram is that of the high-capacity CS16 (250×5 mm (I.D.), 8.4 mequiv./column), which has approximately double the carboxylic acid cation-exchange groups per gram of resin than the CS12A-5 μm, below. The bottom chromatogram is

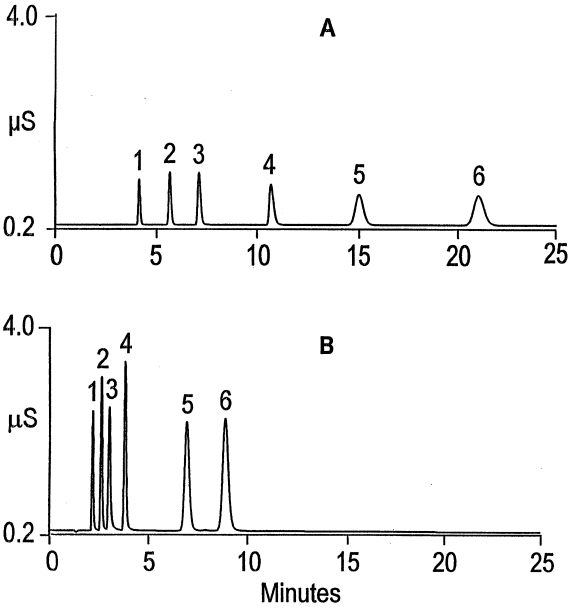

Fig. 6. Comparison of IonPac CS16 and IonPac CS12A-5 μm. Columns: (A) IonPac CS16 (250×5 mm (I.D.)); eluent, 30 m*M* methanesulfonic acid; flow-rate, 1.0 ml/min; column temperature, 40°C. (B) IonPac CS12A-5 μm (150×3 mm (I.D.)); eluent, 20 m*M* methanesulfonic acid; flow-rate, 0.5 ml/min; column temperature, 30°C; injection volume, 25 μl. Peaks: (1) lithium (0.1 mg/l); (2) sodium (0.4 mg/l); (3) ammonium (0.5 mg/l); (4) potassium (1.0 mg/l); (5) magnesium (0.5 mg/l); (6) calcium (1.0 mg/l).

that of the CS12A-5 μm column (150×3 mm (I.D.), 0.9 mequiv./column).

The top chromatogram, obtained with the high-capacity CS16, has approximately twice the peak efficiency (11 282 vs. 5877 plates for potassium) as the bottom chromatogram, primarily due to the difference in length of the two column bodies (250 vs. 150 mm) and the difference in column temperatures employed (40 vs. 30°C).

In comparing the peak areas, note that the top chromatogram (CS16 column) has approximately half the peak area of the bottom chromatogram (106 718 vs. 227 790 for potassium). This is due to the fact that the CS16 column is used at twice the eluent flow-rate than the CS12A-5 μm column. With respect to peak heights, the CS16 column shows only about one-quarter the peak heights of the CS12A-5 μm column (7023 vs. 30 717 for potassium). This is due to the difference in the internal diameter of the

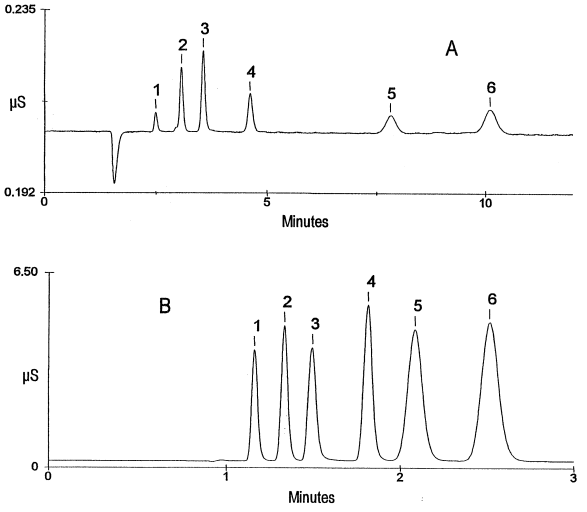

Fig. 7. Advantages of the IonPac CS12A-5 μm. Column: IonPac CS12A-5 μm (150×3 mm (I.D.)). Injection volume: 25 μl. (A) Eluent, 20 m*M* methanesulfonic acid; flow-rate, 0.5 ml/min; column temperature, 25°C. Peaks: (1) lithium (0.25 μg/l); (2) sodium (1 μg/l); (3) ammonium (1.25 μg/l); (4) potassium (2. 5 μg/l); (5) magnesium (1.25 μg/l); (6) calcium (2.5 μg/l). (B) Eluent, 33 m*M* methanesulfonic acid; flow-rate, 0.8 ml/min; column temperature, 30°C. Peaks: (1) lithium (0.1 mg/l); (2) sodium (0.4 mg/l); (3) ammonium (0.5 mg/l); (4) potassium (1.0 mg/l); (5) magnesium (0.5 mg/l); (6) calcium (1.0 mg/l).

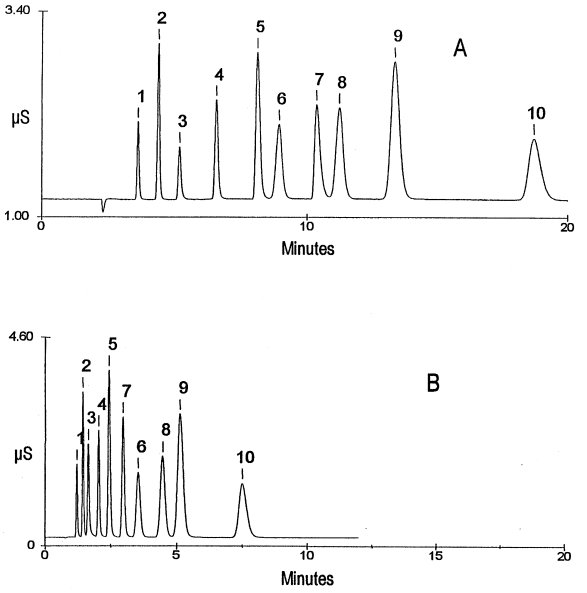

Fig. 8. Group I and Group II cations plus ammonium. (A) Column: IonPac CS16 (250×5 mm (I.D.)); eluent, 40 m*M* methanesulfonic acid; flow-rate, 1.0 ml/min; column temperature, 65°C (suppressor placed outside the oven). Peaks: (1) lithium (0.1 mg/l); (2) sodium (0.4 mg/l); (3) ammonium (0.5 mg/l); (4) potassium (1.0 mg/l); (5) rubidium (5.0 mg/l); (6) magnesium (0.5 mg/l); (7) cesium (5.0 mg/l); (8) calcium (1.0 mg/l); (9) strontium (5.0 mg/l); (10) barium (5.0 mg/l). (B) Column: IonPac CS12A-5 μm (150×3 mm (I.D.)); column temperature, 30°C; eluent, 20 m*M* methanesulfonic acid; flow-rate, 1.0 ml/min. Peaks: (1) lithium; (2) sodium; (3) ammonium; (4) potassium; (5) rubidium; (6) magnesium; (7) cesium; (8) calcium; (9) strontium; (10) barium.

column bodies (5 vs. 3 mm), together with the fact that peaks elute sooner in the CS12A-5 μm column. Chromatogram A in Fig. 7 shows a trace level sample run with the CS12A-5 μm column. Minimum detection levels are directly proportional to the signal-to-noise ratio. Because noise is equivalent for both columns, minimum detection levels are proportional to the peak heights. The CS12A-5 μm column will thus have four times better detection limits than the CS16 column.

Another major difference between these two columns is speed. Chromatogram B in Fig. 7 shows the CS12A-5 μm column optimized for sample throughput. The six common cations are eluted within 3 min with baseline resolution among them.

Group I and Group II cations plus ammonium ion are separated isocratically with the CS16 column at 65°C (suppressor placed outside oven), as shown in Chromatogram A of Fig. 8. Note that in Chromatogram B of Fig. 8, this is similarly accomplished at a lower temperature and in less than half the time with the lower-capacity carboxylated column, the CS12A-5 μm (150×3 mm (I.D.)). In the higher-capacity CS16 column, the monovalent cesium is eluted after the divalent magnesium. The only perceived advantage of the higher-capacity separator for this application is the significantly improved resolution between the pairs sodium and ammonium and calcium and strontium, enabling these analytes to be present at disparate concentration ratios.

4. Conclusions

Without the disadvantages of previous approaches, the high-capacity carboxylated CS16 column allows quantitation of 10 000:1 concentration ratios of sodium to ammonium as well as disparate con-

centration ratios of other pairs of adjacent peaks of cations. It also offers better selectivity of the common cations together with monovalent, small amines. Its high capacity makes this column more tolerant to low sample pH levels while enlarging the linear working range because the column is not as easily overloaded.

For a given sample volume and an overall relatively low concentration sample, minimum detection limits with the high-capacity CS16 column are about four times worse than with the low-capacity CS12A-5 μm column. It should be noted, however, that minimum detection levels are compromised when the peak of a trace level cation rides on the tail of an adjacent peak of a cation with high concentration. Sample dilution, sometimes necessary to prevent overloading the stationary phase, can be detrimental in trace level analysis as contamination of the trace level cation may be introduced.

The low-capacity CS12A-5 μm should be the column of choice when sample throughput and low minimum detection levels are of greatest importance. Run under ''standard'' eluent conditions, the smaller CS12A-5 μm column consumes half the eluent as the high-capacity CS16 column.

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