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Column switching for difficult cation separations

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Abstract

In ion chromatography, samples of very different concentration ratios of ammonium-to-sodium are difficult to quantify since these two cations have similar selectivities for stationary phases containing commonly used sulfonate or carboxylate cation-exchange functional groups. These cations, therefore, elute in close proximity, making quantification of the ion of lower concentration difficult. For example, in the power generation industry, ammonium is often used as a corrosion inhibitor in cooling waters, and determination of low concentrations of sodium in the presence of high concentrations of ammonium is required. Conversely, in environmental samples, it is necessary to determine low levels of ammonium in matrices with high concentrations of sodium. An isocratic column-switching method using two cation exchange columns of different functionalities allows either of these determinations in concentration ratios greater than 10 000:1. © 1997 Elsevier Science B.V.

Keywords: Column switching; Ammonium; Sodium

1. Introduction

The determination of alkali metals, alkaline earth cations and ammonium ions typically involves a cation-exchange separation followed by suppressed conductimetric detection. The purpose of this work was to enable quantitation of sodium and ammonium ions when present in samples with very different concentration ratios. One way to achieve this is to have a large retention time difference between the cations of interest. Samples containing these two cations often also contain the other four common inorganic cations, i.e., lithium, potassium, magnesium and calcium. Column-switching between a carboxylated (IonPac CS12A) and a sulfonated column (IonPac CS10) provides the needed selectivity.

Sulfonated columns are normally used with an acidic eluent that also contains a divalent eluent component, 2,3-diaminopropionic acid monohydrochloride (DAP·HCl), needed to effectively elute the divalent analytes [1]. On the other hand, carboxylated columns are hydronium-selective, and elution of both monovalent and divalent cations is accomplished with a simple acidic eluent [2]. The sulfonated column, when used with a simple, dilute acidic eluent, allows for greater separation between sodium and ammonium ions. With this eluent, however, divalent cations would be retained in this column for a very long time, as DAP·HCl is not present. By appropriately switching the two columns, divalent cations in the sample by-pass the sulfonated column and are chromatographed in the carboxylated column only. Another advantage of this approach is that, because the eluent does not contain DAP·HCl, the electrolytic suppressor (cation self-regenerating suppressor or CSRS-1) can be used in the eluent recycle mode, greatly simplifying its use.

Ethanolammonium and ammonium ions, often found together in a sample, have similar selectivities for carboxylated or sulfonated cation-exchange col-

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umns. Their separation by cation-exchange chromatography has often required eluent gradients or weak eluents, leading to long retention times and inadequate baseline separation of these two cations. Column-switching between a carboxylated and a sulfonated column enhances the resolution of this pair.

Another example of a difficult separation is in the cosmetic and chemical industries, where ethanolamine, diethanolamine and triethanolamine need to be separated from ammonium, the alkali metals and alkaline earth cations. The effect of temperature to aid this separation is discussed.

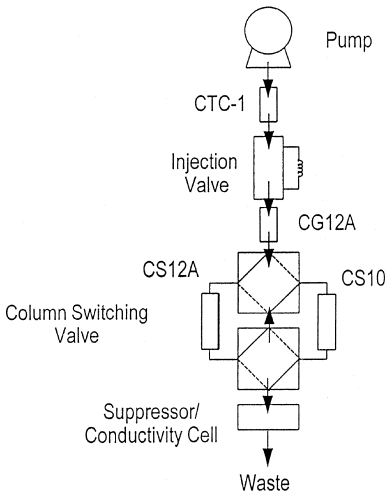

Fig. 1. Schematic diagram of the components of the system.

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 with automated membrane eluent degassing, a chromatographic oven (LC 30) and a conductivity detector (CD 20). All instrument control, data collection and data processing was performed with the PeakNet Chromatography Workstation (Dionex). Conductivity detection was carried out in the recycle mode using a cation self-regenerating suppressor (CSRS-1). Column-switching between 4 mm I.D. columns was done in a high pressure, eight-port, four-way slider PEEK valve (BF-2). This valve is pneumatically activated and was controlled by the gradient pump. Similarly, to switch between 2 mm I.D. columns and minimize the analytes' band dispersion, a 9126 Rheodyne valve modified to do column-switching (Dionex kit P/N 45595) was used. A CTC-1 cation trap column was installed in the eluent line prior to the injection valve, to trap impurities in the eluent (see Fig. 1). A 25-μl sample loop and a 1.0-ml/min eluent flow-rate were used with the 4 mm I.D. columns, while a 2.5-μl sample loop and a 0.25 ml/min eluent flow-rate were used for the narrow-bore 2 mm I.D. columns. Preconcentration can be accomplished by replacing the sample loop with a carboxylate trace cation concentrator low pressure column, the TCC-LP1. This concentrator column has a low enough back-pressure to allow manual preconcentration. A 3-ml injection of sample into the TCC-LP1 using a disposable 3 ml syringe takes approximately 3 min.

2.2. Stationary phases

In the case of the 4 mm system, a polymeric 50×4 mm guard column, packed with a resin containing a combination of carboxylate and phosphonate functional groups, IonPac CG12A (Dionex), was installed between the injection valve and the column-switching valve (see Fig. 1). Two 250×4 mm analytical columns, the IonPac CS12A (packed with the same resin as the CG12A) and the IonPac CS10 (Dionex), packed with a sulfonated polymeric material, are installed on either side of the column-switching valve (see Fig. 2). The CS10 columns are shipped in

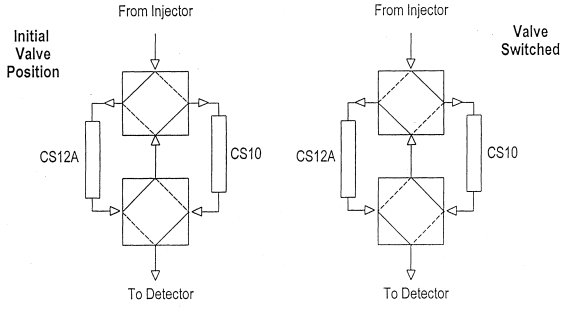

Fig. 2. Plumbing of the column-switching valve.

HCl and DAP·HCl storage solution. The column should be washed (effluent by-passing the suppressor and going directly to waste) with 24 m*M* methanesulfonic acid for at least 1 h, so that, before turning the power on to the CSRS-1, there is no residual chloride in the sulfonated CS10 column, as it would oxidize to chlorine and damage the suppressor.

In the case of the 2 mm systems, a 50×2 mm CG12A-2mm, a 250×2 mm CS12A-2mm and a 250×2 mm CS11 (2-mm equivalent of the CS10) are installed in a similar situation, but using the modified 9126 Rheodyne valve to minimize peak broadening.

The two columns are actually in series, eluent flowing always in the same direction. The column-switching valve (see Fig. 2) essentially changes the order of the two columns. Initially, eluent flows first through the carboxylated (CS12A) column and into the sulfonated CS10 column. When the valve is activated, eluent goes first into the sulfonated column and then into the carboxylated 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) was of analytical reagent grade. Standards were prepared from analytical-reagent grade chemicals, and all standard solutions were stored in polyethylene containers.

3. Results and discussion

3.1. Pictorial elution of cations

Fig. 3 shows what happens to the monovalent and divalent cations during this column-switching application. After the sample is injected, monovalent and divalent cations travel quickly through the CG12A carboxylated guard column. At this point, the column switching valve has not been activated and the CS12A column is first in the series, followed by the sulfonated CS10 column. Monovalent cations move

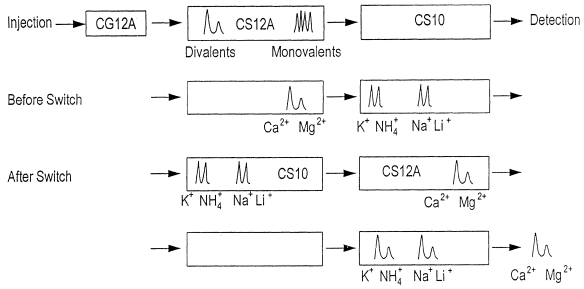

Fig. 3. Pictorial elution of cations.

through this column much faster than divalent cations, as they have lower selectivity for the stationary phase. Monovalent cations then enter the CS10 column, while divalent cations are still in the CS12A column. At this point, the column-switching valve is activated, so that the column order is reversed, and now the CS10 column is first in the series followed by the CS12A column. The reason to switch the columns at this point is to prevent the divalent cations from going into the sulfonated CS10 column, as the eluent is too weak to elute these in a reasonable time and with good efficiency. Magnesium and calcium therefore exit the CS12A column, are detected, and go to waste. The monovalent cations exit the CS10 column to be once again chromatographed in the CS12A column.

3.2. Independent column selectivity

Fig. 4 shows what happens to the analytes when they go through each individual column. In all cases, the eluent contained 24 m*M* methanesulfonic acid. The first chromatogram shows the carboxylated guard column, the CG12A. This column has the same packing material as the analytical CS12A column, but only a fifth of its length and, therefore, only 20% of its capacity; this is the reason why the analytes elute so early and are poorly resolved. This column is used as a guard column for the other two columns.

The second chromatogram was obtained with the CS12A separator column. All peaks show good efficiencies, symmetries, and are well resolved. The total run time is about 8 min.

The last chromatogram shows the sulfonated CS10 column. It is also used as an analytical column in the

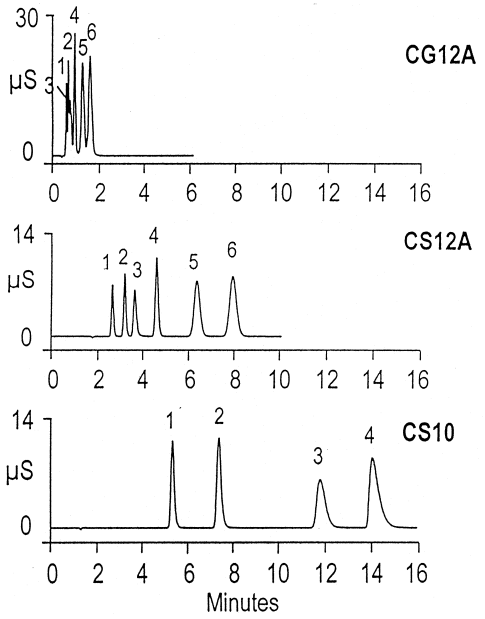

Fig. 4. Independent column selectivity. Columns' I.D., 4 mm; eluent, 24 m*M* methanesulfonic acid. Peaks: 1=lithium (0.5 mg/l); 2=sodium (2.0 mg/l); 3=ammonium (2.5 mg/l); 4=potassium (5.0 mg/l); 5=magnesium (2.5 mg/l) and 6=calcium (5.0 mg/l).

column-switching valve. The simple acidic eluent used with this column (which is not hydronium-selective) allows for an increased retention time difference between sodium and ammonium ions. Notice also that the divalent cations are not shown. In this column, without DAP·HCl in the eluent, they elute very late and with poor peak efficiencies.

3.3. Step-by-step chromatographic separation of inorganic cations

Fig. 5 shows the actual chromatograms of what was described in the pictorial elution of cations (Fig. 3). The top chromatogram shows all of the analytes after they have been chromatographed in the CG12A and CS12A carboxylated columns. The second chromatogram shows the monovalent cations only after they have gone through the CG12A, CS12A and the sulfonated CS10 columns. Note the larger separation among the monovalent cations after they have been chromatographed in the CS10 column.

The last and final chromatogram was obtained

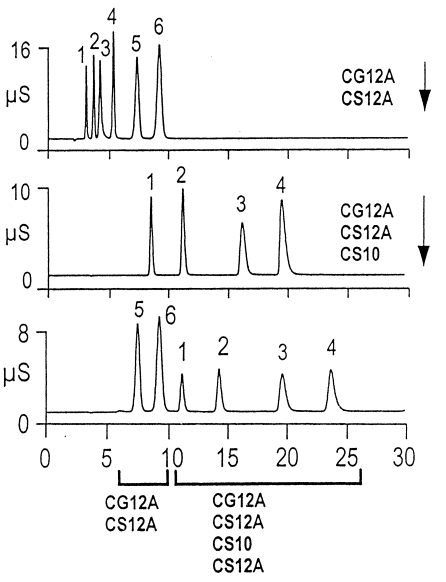

Fig. 5. Step-by-step chromatographic separation of inorganic cations. Columns' I.D., 4 mm. Columns switch at 6 min. Eluent, 24 m*M* methanesulfonic acid. Peaks: 1=lithium (0.5 mg/l); 2=sodium (2.0 mg/l); 3=ammonium (2.5 mg/l); 4=potassium (5.0 mg/l); 5=magnesium (2.5 mg/l) and 6=calcium (5.0 mg/l).

after column-switching at 6 min; the monovalent cations went through the CS12A column one more time. Note that the divalent cations (peaks 5 and 6) only went through the CG12A and the CS12A columns and, therefore, show the same retention time as in the top chromatogram.

3.4. Chromatographic separation of inorganic cations via column-switching

In order to get the chromatographic separation shown in Fig. 6, it is very important to activate the column-switching valve before magnesium starts eluting from the CS12A separator column. The optimum column-switching time depends on the cation-exchange capacities of the columns involved. Failure to switch at the appropriate time window would result in divalent cations getting chromatographed in the sulfonated CS10 column and, due to the simple and weak eluent involved (for this column), they would be retained for far too long. Divalent cation quantitation would be impaired. Furthermore, baseline upsets would be observed as the divalent cations from previous injections finally

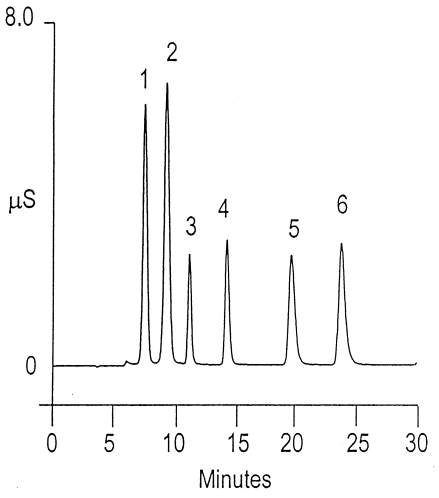

Fig. 6. Chromatographic separation of inorganic cations via column-switching. Columns' I.D., 4 mm. Columns switch at 6 min. Eluent, 24 m*M* methanesulfonic acid. Peaks: 1=magnesium (2.5 mg/l); 2=calcium (5.0 mg/l); 3=lithium (0.5 mg/l); 4=sodium (2.0 mg/l); 5=ammonium (2.5 mg/l) and 6=potassium (5.0 mg/l).

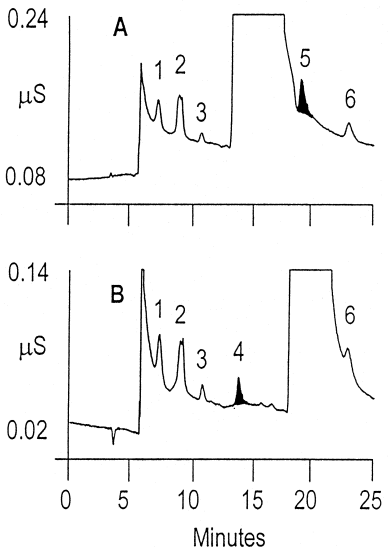

Fig. 7. Determination of very different ratios of sodium-to-ammonium via column-switching. Columns' I.D., 4 mm. Columns switch at 6 min. Eluent, 24 m*M* methanesulfonic acid. Peaks in (A): 1=magnesium (12.5 μg/l); 2=calcium (25.0 μg/l); 3=lithium (2.5 μg/l); 4=sodium (500 000 μg/l); 5=ammonium (12.5 μg/l) and 6=potassium (25.0 μg/l). Peaks in (B): 1=magnesium (12.5 μg/l); 2=calcium (25.0 μg/l); 3=lithium (2.5 μg/l); 4=sodium (10.0 μg/l); 5=ammonium (200 000 μg/l) and 6=potassium (25.0 μg/l).

eluted, potentially compromising the quantitation of monovalent cations.

Column-switching allows the quantitation of low concentrations of either sodium or ammonium in the presence of high concentrations of the other, as Fig. 7 shows.

The same eluent conditions and column-switching set-up can be used to determine low levels of ammonium ion in the presence of high levels of ethanolamine, as shown in Fig. 8. This is a typical application in the power industry, where ethanolamine is sometimes added as a corrosion inhibitor, and quantitation of sodium and ammonium is required.

3.5. Determination of ethanolamine and the common inorganic cations by a 2-mm column-switching operation

The IonPac CS11 column is the 2 mm version of the sulfonated CS10 analytical column, but with a 1.75-fold higher cation-exchange capacity. It is due to this capacity difference that slight adjustments are needed to be done to the eluent and to the column-switching time, compared to the 4 mm column formats. The chromatogram in Fig. 9 shows superior resolution among ethanolamine and the common six inorganic cations, but it also increases the analysis time by about 10 min.

3.6. Temperature effect on the separation of ethanolamines and the common inorganic cations by column-switching

The two chromatograms in Fig. 10 show the separation of mono-, di- and triethanolamine from the common six inorganic cations. At room temperature, potassium and diethanolamine partially coelute. By raising the temperature to 40°C, diethanolamine can be resolved from potassium, but now ethanolamine coelutes with potassium. In either case, triethanolamine is well resolved from the other analytes.

To optimize this separation, as shown in Fig. 11, the eluent strength was decreased, the chromato-

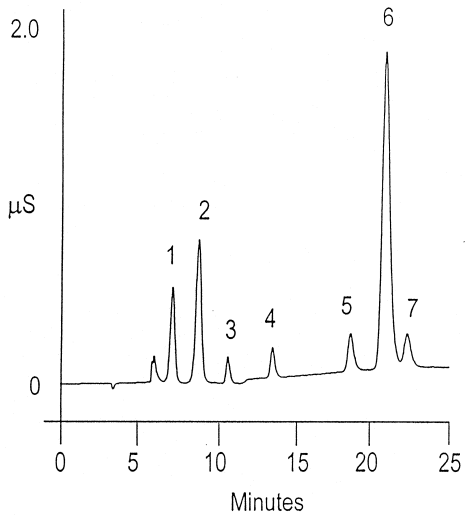

Fig. 8. Determination of low levels of ammonium in the presence of high levels of ethanolamine via column-switching. Columns' I.D., 4 mm. Columns switch at 6 min. Eluent, 24 m*M* methanesulfonic acid. Peaks: 1=magnesium (0.25 mg/l); 2=calcium (0.5 mg/l); 3=lithium (0.05 mg/l); 4=sodium (0.2 mg/l); 5=ammonium (0.25 mg/l); 6=ethanolamine (10.0 mg/l) and 7=potassium (0.5 mg/l).

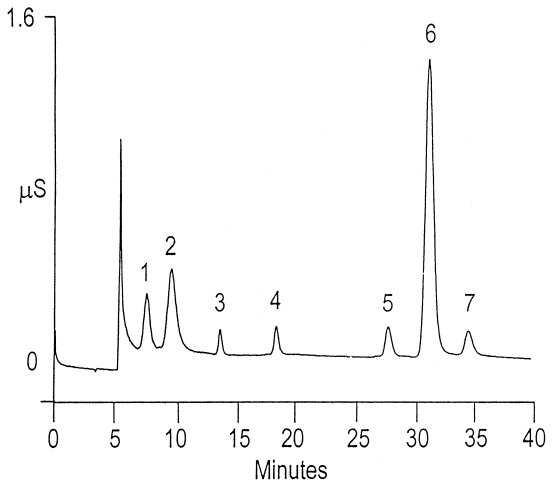

Fig. 9. Determination of ethanolamine and the common inorganic cations by a 2-mm column-switching operation. Columns' I.D., 2 mm. Columns switch at 5.5 min. Eluent, 23 m*M* methanesulfonic acid. Peaks: 1=magnesium (0.25 mg/l); 2=calcium (0.5 mg/l); 3=lithium (0.05 mg/l); 4=sodium (0.2 mg/l); 5=ammonium (0.25 mg/l); 6=ethanolamine (10.0 mg/l) and 7=potassium (0.5 mg/l).

graphic oven was heated to 30°C and the column-switching time was adjusted.

3.7. Retention time reproducibility

Retention time reproducibility depends on the eluent concentration and flow-rate and on the capacities of the columns involved. A decrease in column capacity due to column contamination would result in a shorter retention time for the analytes of interest. For example, sample matrices that contain hydrophobic, polyvalent cations other than the six common inorganic cations could ''take up'' cation-exchange sites in the sulfonated column, and they would remain there for a very long time with the relatively weak eluent system involved. Shorter retention times could also result from a decrease in the eluent flow-rate or the eluent concentration. Retention time reproducibility for the six common cations was less than 1%. Only standards and simulated samples were used in the reproducibility measurements.

3.8. Minimum detection limits

Minimum detection limits, in a similar manner to that of to one-column (either CS10 or CS12A) systems, will depend on the background noise and the peak signal. The background noise should be similar to a one-column system, and for suppressed conductivity with the eluent systems mentioned here, it is normally around 2 nS. The peak signal will depend on how much sample is injected or pre-concentrated. Peak area reproducibility (R.S.D.) is similar to that found when using one-column, and this is typically below 2% at high-ppb levels.

Sodium-to-ammonium concentration ratios of up to 20 000:1 can be determined, and expected R.S.D. values at these ratios should be between 5 and 10%. For example, 1 ppb of ammonium can be determined in a matrix containing 20 ppm of sodium by using a 250-μl sample loop (direct) injection. Fig. 7 shows an even larger concentration ratio than this for sodium-to-ammonium, but this larger ratio would obviously have much higher R.S.D. values.

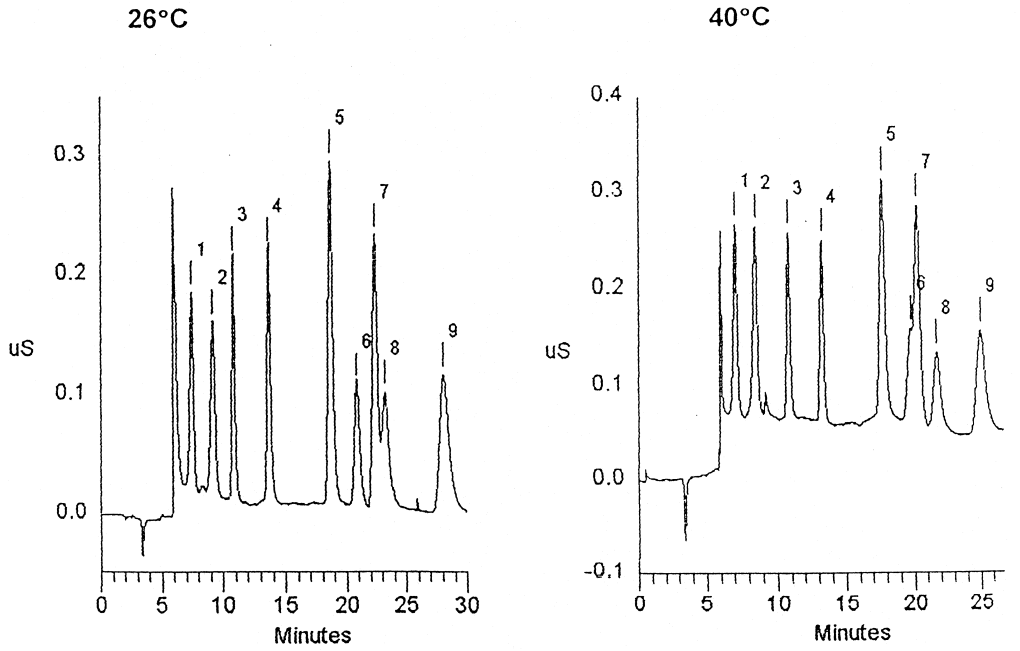

Fig. 10. Temperature effect on the separation of ethanolamines and the common inorganic cations by column switching. Columns' I.D., 4 mm. Columns switch at 6 min. Eluent, 24 m*M* methanesulfonic acid. Peaks: 1=magnesium (0.1 mg/l); 2=calcium (0.15 mg/l); 3=lithium (0.05 mg/l); 4=sodium (0.2 mg/l); 5=ammonium (0.25 mg/l); 6=ethanolamine (0.5 mg/l); 7=potassium (0.5 mg/l); 8=diethanolamine (1.0 mg/l) and 9=triethanolamine (10.0 mg/l).

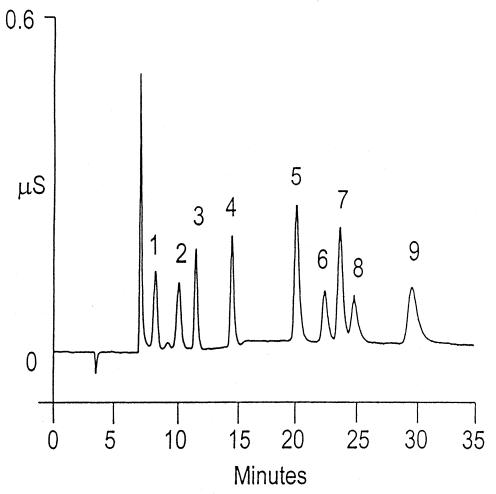

Fig. 11. Determination of ethanolamines and the common inorganic cations by column-switching. Columns' I.D., 4 mm. Columns switch at 7 min. Eluent: 22 m*M* methanesulfonic acid. Peaks: 1=magnesium (0.1 mg/l); 2=calcium (0.15 mg/l); 3=lithium (0.05 mg/l); 4=sodium (0.2 mg/l); 5=ammonium (0.25 mg/l); 6=ethanolamine (0.5 mg/l); 7=potassium (0.5 mg/l); 8=diethanolamine (1.0 mg/l) and 9=triethanolamine (10.0 mg/l).

4. Conclusions

Column-switching to change the order of a carboxylated and a sulfonated stationary phase column allows the determination of trace concentrations of the common inorganic cations (lithium, sodium potassium, magnesium and calcium) and ammonium in the presence of large concentrations of either sodium or ammonium ions. It also helps resolve ethanolammonium from ammonium ion. It only requires a simple, isocratic acidic eluent, and the cation self-regenerating suppressor can be used in the eluent recycle mode. Drawbacks to this approach are the use of two analytical columns (instead of one, as is normal) and the need for a column-switching valve.

References

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[2] M. Rey, C. Pohl, J. Chromatogr. A 739 (1996) 87–97.