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Journal of Chromatography A, 850 (1999) 239–245

JOURNAL OF CHROMATOGRAPHY A

Determination of sodium and ammonium ions in disproportionate concentration ratios by ion chromatography

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Abstract

In ion chromatography, samples of very different ammonium-to-sodium concentration ratios are difficult to quantify since these two cations have similar selectivities for stationary phases containing commonly used sulfonate or carboxylate cation-exchange functional groups. The IonPac CS15 cation-exchange column, with carboxylate and phosphonate functional groups as well as a crown ether group, was developed to address this limitation. Selectivity for the common inorganic cations on this column is different from that of conventional cation-exchange columns in that the separation between sodium and ammonium ions has been greatly increased, allowing for determinations of low levels of one in the presence of high levels of the other with an isocratic eluent. For larger than 4000:1 sodium-to-ammonium concentration ratios, an eluent step change or gradient elution is needed. For moderate ratios, combinations of this column with a carboxylate column, containing no crown ether group, can be used at room temperature with an isocratic eluent containing no organic solvent.

Keywords: Sodium; Ammonium; Inorganic cations

1. Introduction

Ion chromatography (IC) is ideal for the determination of alkali and alkaline-earth cations, ammonium and amines. Applications where low levels of ammonium need to be determined in the presence of high concentrations of sodium pose a challenge in IC, since traditional cation-exchange columns offer similar selectivities for these two ions [1].

Crown ethers are macrocyclic ligands that form stable complexes by coordinating metal cations within their cavities [2,3]. The IonPac CS15 column, in addition to carboxylate and phosphonate functional groups, has an 18-crown-6 ether moiety that is responsible for the much higher selectivity of the stationary phase for ammonium and potassium ions [4]. The interaction between the crown ether moiety and potassium ion is especially strong. Since kinetics are slow, solvent and temperature are required to improve potassium peak shape.

This paper shows how to optimize the use of the CS15 crown ether stationary phase to improve cation determinations with very diverse concentration ratios. Also, a simplified method for use with moderate concentration ratios will be demonstrated.

2. Experimental

2.1. Apparatus

A DX-500 IC system (Dionex, Sunnyvale, CA, USA) consisting of a quaternary gradient pump

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0021-9673/99/$ – see front matter
PII: S0021-9673(99)00002-3

(GP40) with automated membrane eluent degassing, a chromatographic oven (LC 30), and suppressed conductivity detection (CD20 conductivity detector) was used. The output of the conductivity detector is automatically normalized so that a readout of 1 μS is equivalent to 1 μS/cm. The eluent was electrolytically suppressed with a Cation Self-Regenerating Suppressor (CSRS-ULTRA). The sample loop was 25 μL.

2.2. Chemicals

Deionized water (18 MΩ cm resistivity at room temperature) from a water purification system (Barnstead, NANOpure system) was used for the preparation of the eluents and standards. Sulfuric acid (J.T. Baker, NJ, USA) was Baker Instra-Analyzed reagent grade. Methanesulfonic acid (MSA) (Fluka, NY, USA), was >99% (w/w). Acetonitrile and methyl ethyl ketone (MEK) were HPLC grade (Burdick & Jackson, MI, USA).

2.3. Stationary phases

The packings for all the columns used in this study consist of solvent-compatible particles of ethylvinylbenzene cross-linked with 55% divinylbenzene. On the surface of this inert substrate are attached a variety of functional groups, where the cation-exchange process takes place. The IonPac CS12A column has both carboxylate and phosphonate functionalities [5,6]. The IonPac CS15 has carboxylate, phosphonate and crown ether functional groups [4]. The analytical separators used in this study were packed in 250×4 mm format; the respective guard columns in 50×4 mm. Fig. 1 shows the typical running conditions and chromatography for each stationary phase.

The IonPac CTC-1 trap column contains a high capacity resin with sulfonic acid functional groups. The column strips trace contaminants from the eluent and prevents them from reaching the guard and analytical columns.

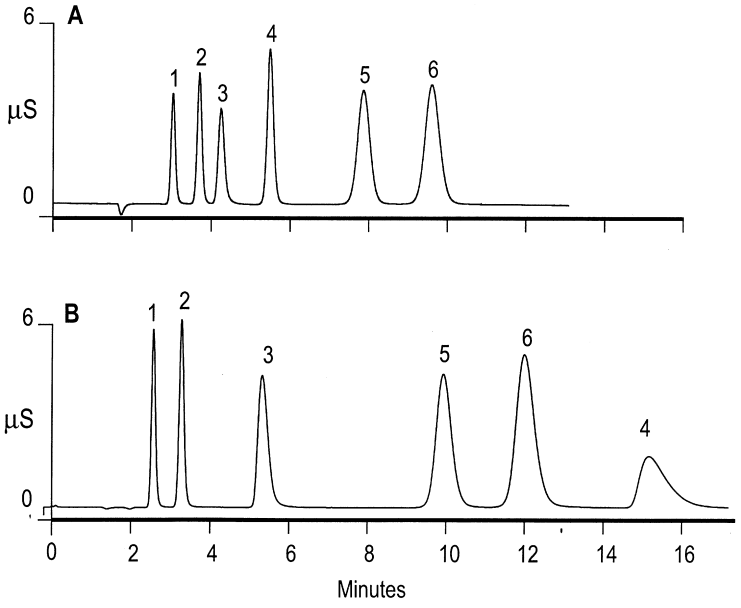

Fig. 1. Comparison of the IonPac CS12A and the CS15. Column A: IonPac CS12A. Eluent A: 11 m*M* sulfuric acid. Flow-rate A: 1.0 ml/min. Temperature A: 25°C. Suppressor A: recycle mode. Peaks A: 1=Lithium (0.5 mg/l); 2=sodium (2.0 mg/l); 3=ammonium (2.5 mg/l); 4=potassium (5.0 mg/l); 5=magnesium (2.5 mg/l); 6=calcium (5.0 mg/l). Column B: IonPac CS15. Eluent B: 5 m*M* sulfuric acid+9% acetonitrile. Flow-rate B: 1.2 ml/min. Temperature B: 40°C. Suppressor B: external water mode. Peaks B: 1=Lithium (1.0 mg/l); 2=sodium (4.0 mg/l); 3=ammonium (10.0 mg/l); 4=potassium (10.0 mg/l); 5=magnesium (5.0 mg/l); 6=calcium (10.0 mg/l).

3. Results and discussion

3.1. Sample matrices with high sodium-to-low ammonium concentrations

The 18-crown-6 ether in the CS15 stationary phase is responsible for the high resolution between sodium and ammonium ions, allowing determination of low levels of one in the presence of high levels of the other. Fig. 2 shows a 4000:1 concentration ratio of sodium-to-ammonium. The eluent is isocratic and column temperature is maintained at 40°C. The suppressor is used in the external water mode since the eluent contains acetonitrile.

3.2. Alternate eluent

It is necessary to use the suppressor in the external water mode when acetonitrile is present in the eluent. MEK was used as an alternate eluent component to acetonitrile. An advantage of this solvent over acetonitrile is that it may be practical to use the suppressor in the eluent recycle mode. MEK is currently being investigated to determine its long-term chromatography system compatibility. Fig. 3 shows the elution of the common inorganic cations and ammonium on the IonPac CS15 using this eluent system, both at room temperature and at elevated temperature. Increasing the temperature has a larger effect on potassium ion, followed by ammonium. These two are retained both by cation-exchange as well as by complexation within the 18-crown-6 ether groups.

3.3. Eluent step change for larger sodium-to-ammonium concentration ratios

Quantification of even more diverse concentration ratios of sodium and ammonium ions can be accomplished by using a more dilute eluent at the beginning of the run. This effectively increases the resolution between the sodium and ammonium ions, allowing determinations of low ppb levels of ammonium in 100 ppm sodium. In order to speed the chromatographic run, the eluent concentration is increased by an eluent step during the run. A trap column, the CTC-1, is placed between the eluent pump and the injection valve. The CTC-1 traps contaminants in the eluent, thus minimizing the baseline shift when the concentration of the eluent is changed. Fig. 4 shows the chromatograms for an eluent step change of a standard sample and of a sample containing a sodium-to-ammonium concentration ratio of 10 000:1. Sulfuric acid can be used as substitute for MSA and acetonitrile as substitute for MEK. Minor adjustments for the change of either

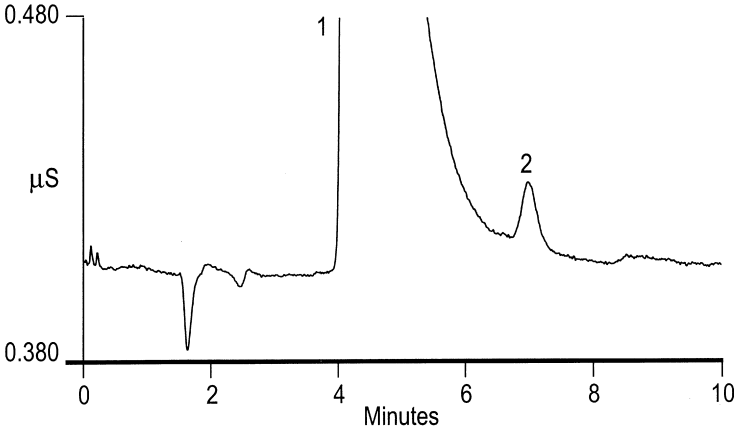

Fig. 2. Isocratic determination of a 4000:1 concentration ratio of sodium-to-ammonium with the IonPac CS15. Column: IonPac CG15 and CS15. Eluent: 5 m*M* sulfuric acid+9% acetonitrile. Flow-rate: 1.2 ml/min. Temperature: 40°C. Suppressor: external water mode. Peaks: 1=Sodium (100 mg/l); 2=ammonium (0.025 mg/l).

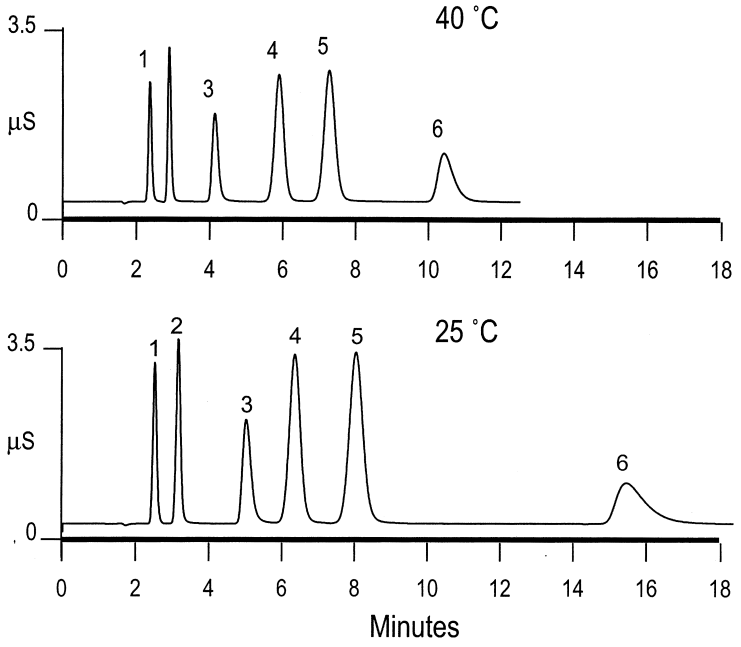

Fig. 3. IonPac CS15 with MEK in the eluent. Column: IonPac CS15 (no guard). Eluent: 15 m*M* MSA+5% MEK. Flow-rate: 1.2 ml/min. Suppressor: recycle mode. Peaks: 1=Lithium (0.5 mg/l); 2=sodium (2.0 m/l); 3=ammonium (2.5 mg/l); 4=magnesium (2.5 mg/l); 5=calcium (5.0 mg/l); 6=potassium (5.0 mg/l).

eluent component should provide comparable chromatographic results.

3.4. Combining stationary phases for less stringent sodium-to-ammonium concentration ratios

For sodium-to-ammonium concentration ratios of up to 1000:1, a simplified method using combined stationary phases can be used to achieve adequate resolution of these two cations. This method uses a CG12A, CS12A and CG15 column in series.

The IonPac CG15 guard column is one-fifth the length of the CS15 separator column, and therefore has one-fifth the capacity. By combining the IonPac CG12A and CS12A columns (no crown ether in the stationary phase) with the smaller CG15 (with crown ether in the stationary phase), the sodium/ammonium peak resolution is sufficient for less demanding applications. The advantage of combining these columns is that elevated temperature and organic solvent are not required. Fig. 5A shows the typical separation between sodium and ammonium ions in a CG12A/CS12A with MSA in the eluent. Fig. 5B shows much improved resolution between sodium and ammonium ions when a CG15 guard is added in series. Fig. 6 shows a 1000:1 sodium-to-ammonium concentration ratio with the column combination approach. Quantitation of trace levels of ammonium in the presence of high levels of sodium is made easier by the improved resolution between the two peaks when the CG15 is added in series (Fig. 6B).

3.5. Power industry amines and the common inorganic cations

Separation of the common inorganic cations and commonly used corrosion inhibitor additives to power industry waters is shown in Fig. 7. This separation is possible by further increasing the resolution between sodium and ammonium ions with a dual gradient of both MSA and MEK. The chromatography was run at room temperature and the suppressor was used in the recycle mode.

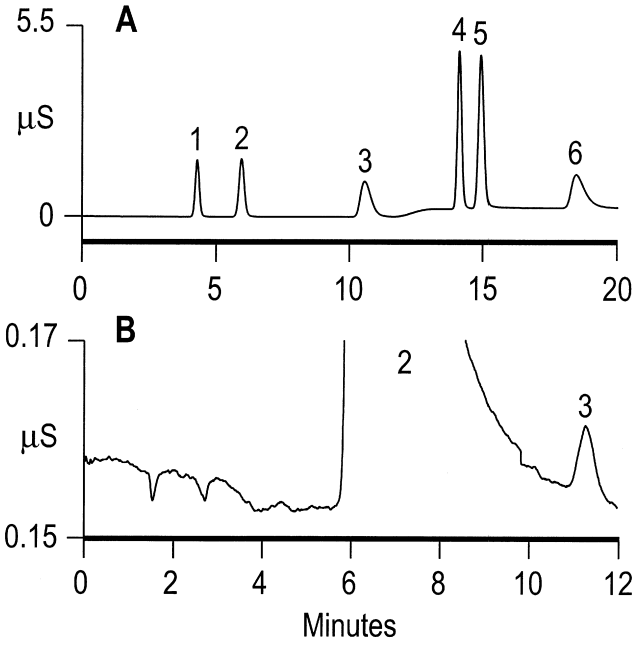

Fig. 4. 10 000:1 Sodium-to-ammonium concentration ratio with IonPac CS15. Column: IonPac CG15 and CS15. Trap column: CTC-1. Eluent: 6 m*M* MSA+5% MEK, step at 9.6 min to 20 m*M* MSA+5% MEK. Flow-rate: 1.2 ml/min. Suppressor: recycle mode. Temperature: 25°C. Peaks A: 1=Lithium (0.5 mg/l); 2=sodium (2.0 mg/l); 3=ammonium (2.5 mg/l); 4=magnesium (2.5 mg/l); 5=calcium (5.0 mg/l); 6=potassium (5.0 mg/l). Peaks B: 2=Sodium (100 mg/l); 3=ammonium (0.010 mg/l).

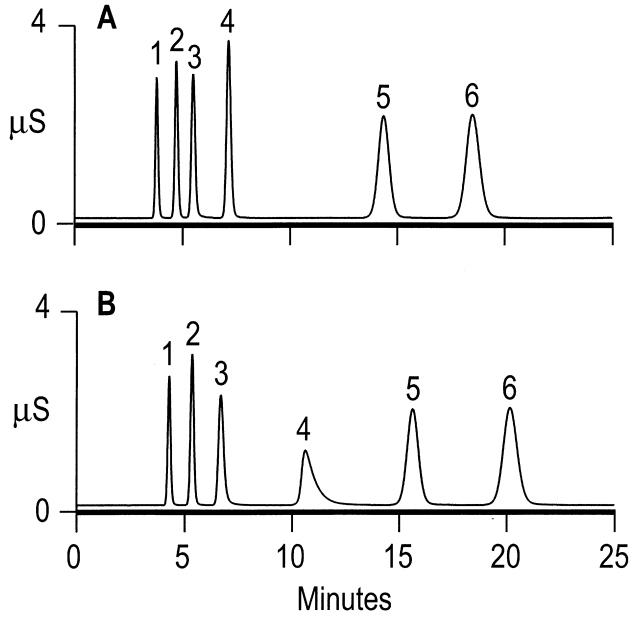

Fig. 5. Column combination for less stringent sodium-to-ammonium concentration ratios. Column A: IonPac CG12A and CS12A. Column B: IonPac CG12A, CS12A and CG15 in series. Eluent: 16 m*M* MSA. Flow-rate: 1.0 ml/min. Suppressor: recycle mode. Temperature: 25°C. Peaks: 1=Lithium (0.5 mg/l); 2=sodium (2.0 mg/l); 3=ammonium (2.5 mg/l); 4=potassium (5.0 mg/l); 5=magnesium (2.5 mg/l); 6=calcium (5.0 mg/l).

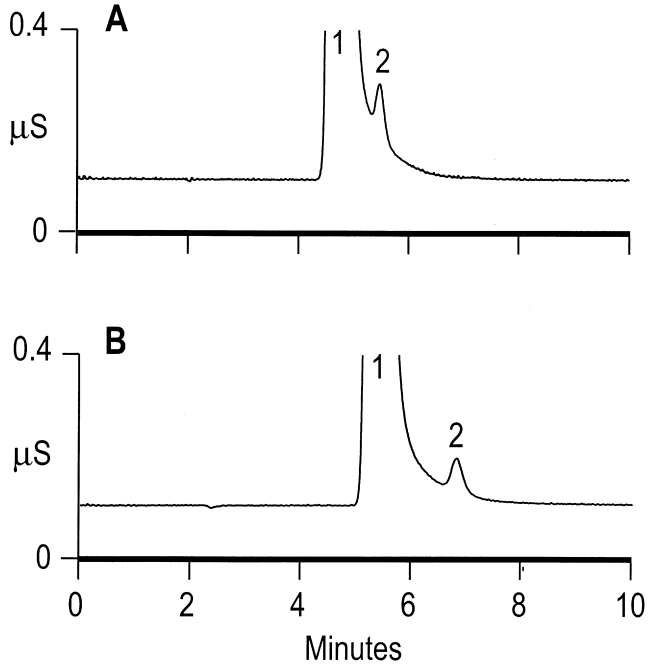

Fig. 6. 1000:1 Sodium-to-ammonium concentration ratio with column combination. Column A: IonPac CG12A and CS12A. Column B: IonPac CG12A, CS12A and CG15 in series. Eluent: 16 m*M* MSA. Flow-rate: 1.0 ml/min. Suppressor: recycle mode. Temperature: 25°C. Peaks: 1=Sodium (50 mg/l); 2=ammonium (0.050 mg/l).

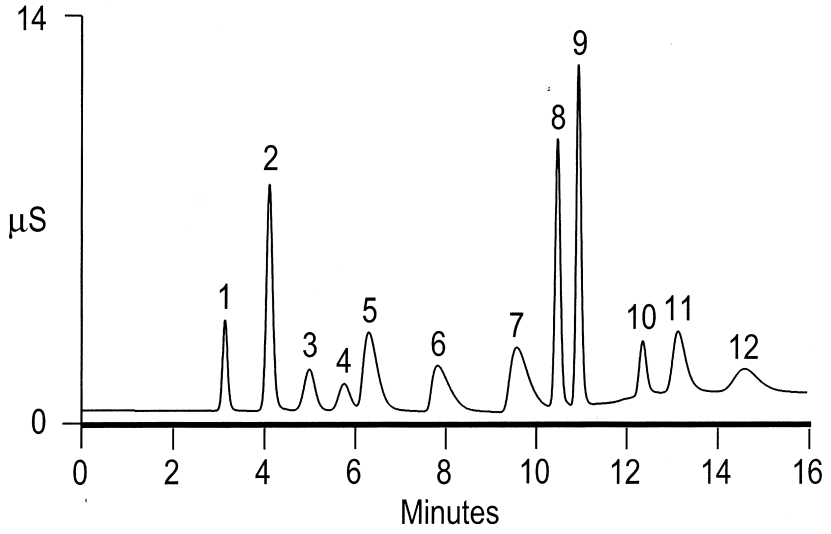

Fig. 7. Power industry amine additives and the common inorganic cations with the IonPac CS15. Column: IonPac CS15 (no guard). Eluent: 9 m*M* MSA+0.7% MEK, gradient from 6 to 9 min to 27 m*M* MSA–10% MEK. Flow-rate: 1.0 ml/min. Temperature: 25°C. Suppressor: recycle mode. Peaks: 1=Lithium (0.5 mg/l); 2=sodium (2.0 mg/l); 3=2-diethylaminoethanol (10.0 mg/l); 4=morpholine (10.0 mg/l); 5=ethanolamine (10.0 mg/l); 6=ammonium (2.5 mg/l); 7=5-amino-1-pentanol (20.0 mg/l); 8=magnesium (2.5 mg/l); 9=calcium (5.0 mg/l); 10=3-dimethylaminopropylamine (10.0 mg/l); 11=potassium (5.0 mg/l); 12=cyclohexylamine (15.0 mg/l).

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