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Journal of Chromatography A, 997 (2003) 199–206
JOURNAL OF CHROMATOGRAPHY A
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Novel cation-exchange column for the separation of hydrophobic and/or polyvalent amines

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Abstract

The term amines encompasses a wide variety of compounds: monovalent or polyvalent amines, hydrophobic or hydrophilic amines, and combinations of all of these. Due to their charge, polyvalent amines such as the biogenic amines have very strong cation-exchange interaction with the cation-exchange groups in the stationary phase. Very high acid concentrations are required to elute them effectively from a high-capacity, carboxylated cation-exchange column. The eluent must contain a divalent ion to elute them from a sulfonated cation-exchange column due to its selectivity. Chromatography for these amines with a new ''tailored'' amine column of moderate capacity using a simple acidic eluent is described. The hydrophobic nature of other amines, such as long-carbon-chained amines, results in partitioning into the polymeric substrate of previous carboxylated stationary phases, so that organic solvent is required to elute them effectively. The substrate resin of this new ''tailored'' amine column is first coated so that, when it is functionalized in a subsequent step, this type of interaction is minimized. Examples are given. Methods that require eluent gradients and/or step changes of eluent concentration are especially well suited to this column because the background conductivity remains almost unchanged under gradient conditions.

Keywords: Gradient elution; Cation exchangers; Amines; Biogenic amines

1. Introduction

The first effective weak-acid cation exchanger for use in ion chromatography 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. Later on, a carboxylic acid stationary phase on macroporous polymeric substrate beads was developed (at Dionex's laboratories), to be used with suppressed conductivity detection [2]. Several other carboxylic acid-based cation exchangers were subsequently developed. Some of these differed mainly in the graft conditions to obtain more efficient peaks for the Group I and II cations [3]. In a more unique case, crown ether groups and carboxylic acid groups were covalently attached to the polymeric substrate beads in an effort to quantify disparate concentration ratios of sodium and ammonium [4,5]. Other stationary phases differed in either the acidity of the carboxylic acid group, the co-monomer used during polymerization, or the cation-exchange capacity [6]. Most of these phases were geared towards the determination of Group I and II cations.

In this paper a new cation-exchange polymeric phase is introduced. In contrast to the others, it has been designed for the separation of amines, especially polyvalent and/or hydrophobic amines.

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0021-9673/03/$ – see front matter
doi:10.1016/S0021-9673(03)00113-4

Advances in hardware, such as the EG40 Eluent Generator [7], which through programmed current values can generate methanesulfonic acid in predetermined concentrations, simplifies the use of gradient chromatography. Only deionized water needs to be supplied by the user, conductivity backgrounds are low, and gradients are more reproducible, human error or potential problems with the proportioning valve in the eluent pump not being factors.

One of the drawbacks in using gradient elution was an increase in background conductivity as the eluent concentration increased, which made peak quantitation more difficult. The combination of a very clean eluent provided by the EG40 Eluent Generator, a cation trap column to trap impurities in the deionized water used to supply the EG40, and an analytical column which is clean, results in almost flat baselines with either eluent step changes or eluent gradients. Furthermore, a gradient mixer is no longer required when the Eluent Generator is used, thus minimizing the column's equilibration time.

In conductivity detection, it is always more desirable to work with eluents which do not contain organic solvent, as the electrolytic suppressor can then be used in its most convenient ''eluent recycle'' or AutoSuppression mode [8]. This also avoids the extra cost to dispose of the solvent containing eluent. This new stationary phase allows for more applications to be run without the need for organic solvent. It is however compatible with organic solvents such as acetonitrile, acetone, and alcohol, therefore analytes that are not water-soluble can also be separated using this column.

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), suppressed conductivity detection (CD 20 conductivity detector), an EG40 Eluent Generator with an EluGen EGC-MSA Cartridge, and a CSRS-ULTRA 2-mm Cation Self-Regenerating Suppressor or Cation Atlas Electrolytic Suppressor used in the AutoSuppression mode.

Controlled by the Method Program in the PeakNet Chromatography Workstation software, the Eluent Generator automatically converts deionized water into the method-specified methanesulfonic acid eluent concentration. All instrument control, data collection and data processing was performed with the 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 background conductivity in all cases was below 0.2 μS, and typical noise levels were about 0.2 nS.

2.2. Stationary phase

An IonPac CTC-1 cation trap column, containing high-capacity, sulfonated cation-exchange resin in hydrogen form, is placed between the GP40 pump and the EG40 Eluent Generator. Cationic impurities in the deionized water are removed by this trap column before they reach the EG40, thus ensuring that clean methanesulfonic acid reaches the column.

The new guard and separator columns—the IonPac CG17 and CS17, respectively—are packed with solvent-compatible particles of ethylvinylbenzene crosslinked with 55% divinylbenzene. The surface of the beads are coated with a non-functional monomer, followed by functionalization through grafting. The resulting weak carboxylic acid functionalized surface, which has very high selectivity for hydronium ions, provides the stationary phase with moderate cation-exchange capacity. This tailors the IonPac CS17 column (Dionex) for the analysis of polyvalent amines. The underlying non-functional monomer reduces the interaction of hydrophobic analytes with the substrate, which in many cases permits the use of simple acidic eluents containing no organic solvent. Thus, the IonPac CS17 column is also tailored for the analysis of hydrophobic amines.

The raw resin has an average particle size and pore size of 7.0 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 either 250 mm×4 mm I.D., or 250 mm×2 mm I.D. The cation-exchange capacity for the 250×4 mm column is approximately 1.45 mequiv./column, and

its capacity for the 250×2 mm column is 0.36 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. Eluent preparation consisted of simply filling an eluent bottle with deionized water, as the Eluent Generator automatically converts deionized water into the method-specified methanesulfonic acid eluent concentration. Standards were prepared from analytical reagent grade chemicals. Lithium, sodium, potassium, magnesium, and calcium standards were purchased from the US National Institute of Standards and Technology (NIST, Gaithersburg, MD, USA). Ammonium standard was purchased from VGH Labs. (NH, USA), and amine standards from Aldrich (MO, USA).

3. Results and discussion

3.1. The power of gradient or step-change elution

Fig. 1 illustrates the improvement in resolution of close-eluting peaks by using gradient or step-change elution instead of isocratic elution. Notice the improved resolution (chromatogram B) among the first five peaks, the four monovalent cations, and dimethylamine. These cations are eluted with the isocratic portion of eluent B and their method detection levels (MDLs) will be higher because the peaks are shorter. These peaks are shorter than in chromatogram A because a weaker eluent concentration is used to elute them. On the other hand, when a peak is eluted with an eluent step change or gradient, its peak efficiency is higher. This means a taller peak and therefore a lower MDL for that specific peak. Under the step-change conditions employed (eluent B), this can be seen for the last three eluting peaks.

By using the EG40 Eluent Generator, a cation trap column (CTC), and the IonPac CS17 column, the baseline change is minimal when stepping from a low to a high acid concentration. Quantification is simple because peaks are integrated over a flat background.

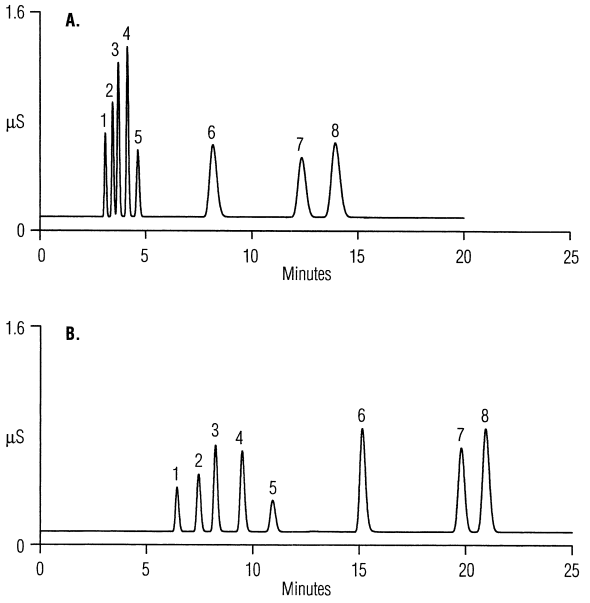

Fig. 1. The power of gradient or step-change elution. Column, IonPac CS17 (250 mm×4 mm I.D.); sample volume, 25 μL; flow-rate, 1.0 mL/min; column temperature, 30 °C; suppressor, Cation Atlas Electrolytic Suppressor in AutoSuppression Recycle Mode, 24 mA. Eluent A, 6 m*M* methanesulfonic acid (MSA); eluent B, 2 m*M* MSA isocratic to 11.0 min; step change to 7 m*M* MSA at 11.1 min; isocratic to 22 min; step change back to 2 m*M* MSA at 22.1 min; equilibration time 2 min. 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=dimethylamine (1.0 mg/L), 6=triethylamine (7.0 mg/L), 7=magnesium (0.5 mg/L), 8=calcium (1.0 mg/L).

Triethylamine, a moderately hydrophobic amine, can be eluted efficiently on this stationary phase without addition of organic solvent to the eluent. Because the eluent contains no organic solvent, the suppressor can be used in the more convenient AutoSuppression recycle mode.

3.2. Gradient elution of Group I and II cations and ammonium, plus the biogenic amines

Lithium, sodium, ammonium, potassium, magnesium, and calcium, plus histamine and the biogenic amines putrescine, cadaverine, spermine, and spermidine can all be separated with an aqueous eluent containing no organic solvent, as Fig. 2 shows. The

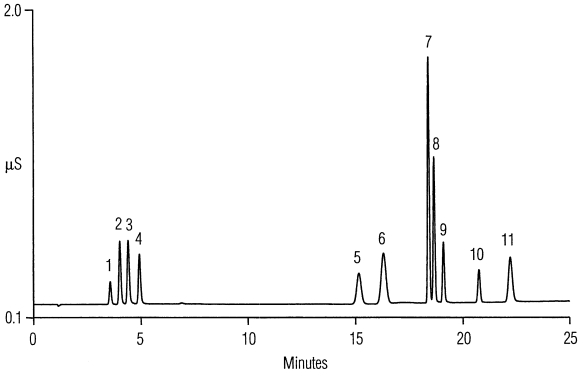

Fig. 2. Gradient elution of Group I and II cations and ammonium, plus the biogenic amines. Column, IonPac CG17 (50 mm×2 mm I.D.) plus CS17 (250 mm×2 mm I.D.); sample volume, 25 μL; flow-rate, 0.40 mL/min; column temperature, 40 °C; suppressor, CSRS-ULTRA 2-mm Cation Self-Regenerating Suppressor, AutoSuppression Recycle Mode, 100 mA. Eluent, 3 m*M* MSA isocratic to 3.5 min; gradient to 6 m*M* MSA at 12 min; isocratic to 15 min; gradient to 40 m*M* MSA at 20 min; isocratic to 24 min; step change back to 3 m*M* MSA at 24.1 min; equilibration time 2 min. Peaks: 1=lithium (10 μg/L), 2=sodium (40 μg/L), 3=ammonium (50 μg/L), 4=potassium (100 μg/L), 5=magnesium (50 μg/L), 6=calcium (100 μg/L), 7=putrescine (1000 μg/L), 8=cadaverine (600 μg/L), 9=histamine (600 μg/L), 10=spermidine (200 μg/L), 11=spermine (400 μg/L).

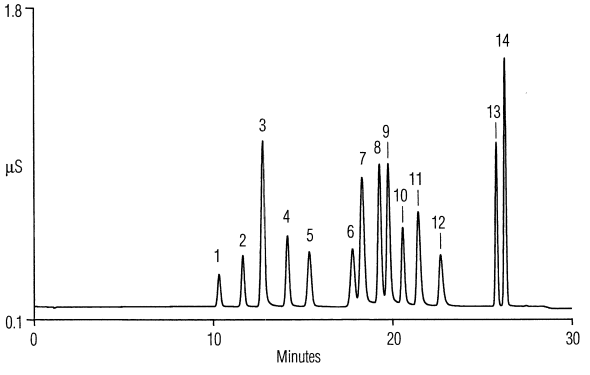

Fig. 3. Gradient elution of Group I and II cations, ammonium and alkylamines. Column, IonPac CG17 (50 mm×2 mm I.D.) plus CS17 (250 mm×2 mm I.D.); sample volume, 25 μL; flow-rate, 0.40 mL/min; column temperature, 40 °C; suppressor, Cation Atlas Electrolytic Suppressor in AutoSuppression Recycle Mode, 13 mA. Eluent, 0.5 to 1.1 m*M* MSA gradient at 12 min; gradient to 1.3 m*M* MSA at 16 min; gradient to 10 m*M* MSA at 25 min; isocratic to 27 min; step change back to 0.5 m*M* MSA at 27.1 min; equilibration time 2 min. Peaks: 1=lithium (0.03 mg/L), 2=sodium (0.10 mg/L), 3=ammonium (0.34 mg/L), 4=potassium (0.25 mg/L), 5=ethylamine (0.50 mg/L), 6=propylamine (0.75 mg/L), 7=*tert*.-butylamine (1.25 mg/L), 8=*sec*.-butylamine (1.25 mg/L), 9=isobutylamine (1.25 mg/L), 10=*n*-butylamine (3.75 mg/L), 11=1,2-dimethylpropylamine (1.00 mg/L), 12=di-*n*-propylamine (1.00 mg/L), 13=magnesium (0.14 mg/L), 14=calcium (0.34 mg/L).

biogenic amines elute with good peak efficiencies and peak symmetries when the column is run with a simple acidic gradient at elevated temperature.

Even though the gradient ranges from 3 to 40 m*M* methanesulfonic acid (MSA), the baseline change is almost imperceptible. The EG40 Eluent Generator with a methanesulfonic acid cartridge was used for optimum low-conductivity background and minimum change in conductivity signal when performing the gradient. A CTC-1 cation trap column was placed between the GP40 Gradient Pump and the EG40 Eluent Generator to trap any impurities that may be present in the deionized water pumped into the EG40. Due to the column's selectivity, moderate capacity, and hydrophilic nature, these polyvalent amines are eluted easily with 40 m*M* MSA.

3.3. Gradient elution of Group I and II cations, ammonium and alkylamines

Fig. 3 shows the elution of lithium, sodium, ammonium, potassium, magnesium, calcium, and eight alkylamines with an organic solvent-free eluent. The alkylamines elute with good peak efficiencies and symmetries when the CS17 column is run with a simple acidic gradient at elevated temperature. The baseline change with a gradient from 0.5 to 10 m*M* MSA is almost unnoticeable.

3.4. Gradient elution of Group I and II cations, ammonium and diamines

Lithium, sodium, ammonium, potassium, magnesium, calcium, six alkyl diamines, and four other diamines can be eluted and separated with an organic solvent-free eluent. As Fig. 4 shows, the diamines elute after the six common cations with good peak efficiencies and symmetries when the column is run with a simple acidic gradient at elevated temperature. Selectivity for the diamines is very good. Despite the gradient change from 3 to 40 m*M* methanesulfonic acid, baseline change is unnoticeable.

Alkyl diamines longer than 1,10-decanediamine

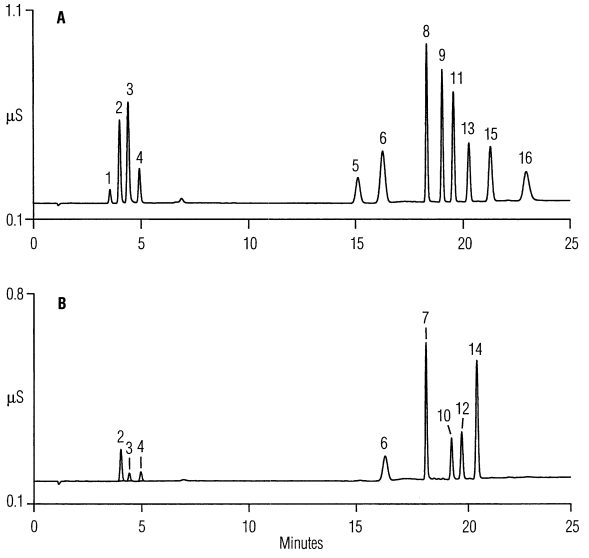

Fig. 4. Gradient elution of Group I and II cations, ammonium and diamines. Column, IonPac CG17 (50 mm×2 mm I.D.) plus CS17 (250 mm×2 mm I.D.); sample volume, 25 μL; flow-rate, 0.40 mL/min; column temperature, 40 °C; suppressor, CSRS-ULTRA 2-mm Cation Self-Regenerating Suppressor, AutoSuppression Recycle Mode, 100 mA. Eluent, 3 m*M* MSA isocratic to 3.5 min; 3 to 6 m*M* MSA gradient at 12 min; isocratic to 15 min; gradient to 40 m*M* MSA at 20 min; isocratic to 24 min; step change back to 3 m*M* MSA at 24.1 min; equilibration time 2 min. Peaks in (A): 1=lithium (5 μg/L), 2=sodium (65 μg/L), 3=ammonium (89 μg/L), 4=potassium (47 μg/L), 5=magnesium (24 μg/L), 6=calcium (56 μg/L), 8=1,2-propanediamine (500 μg/L), 9=1,6-hexanediamine (250 μg/L), 11=1,7-heptanediamine (125 μg/L), 13=1,8-octanediamine (250 μg/L), 15=1,9-nonanediamine (375 μg/L), 16=1,10-decanediamine (375 μg/L). Peaks in (B): 2=sodium (16 μg/L), 3=ammonium (4 μg/L), 4=potassium (8 μg/L), 6=calcium (18 μg/L), 7=ethylenediamine (200 μg/L), 10=*N*,*N*-diethylenediamine (200 μg/L), 12=*N*,*N*,*N*,*N*-tetramethylethylenediamine (200 μg/L), 14=3,3-diaminopropylamine (200 μg/L).

are not appreciably soluble in aqueous solutions and therefore organic solvent should be added to the eluent when they are present in the sample.

3.5. Influence of sample pH on the IonPac CS17

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 symmetries.

When quantification is based on peak areas and a 6.25 μL sample loop is used, the IonPac CS17 (250 mm×2 mm I.D.), with a cation-exchange capacity of 0.36 mequiv./column, tolerates up to about 20 m*M* hydronium ion in the sample (or pH 1.7). If, however, the sample loop used is larger (e.g. 25 μL), chromatography will be compromised at a sample pH higher than that, as Fig. 5 shows. Higher capacity carboxylated stationary phases, or phases with lower pK_a carboxylic acid groups, are able to handle more acidic samples better [6].

There is no permanent loss of column performance, as the packing is stable even at pH levels below 0.3. Samples containing more than 20 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. Gradient elution of Group I and II cations, ammonium and ethylamines

As shown in Fig. 6, lithium, sodium, ammonium, potassium, magnesium and calcium, plus ethylamine, diethylamine, and triethylamine can be separated on the IonPac CS17 column with an organic solvent-free eluent. The amines elute with good peak efficiencies and good peak symmetries when the column is run with a simple acidic gradient at 30 °C.

Notice that a 0.35 mL/min eluent flow-rate is used instead of 0.4 mL/min as in the previous chromatograms run at 40 °C. This is because, at the lower 30 °C column oven temperature, the total system pressure approaches the 3000 p.s.i. (1 p.s.i.=6894.76 Pa) maximum limit for the proper operation of the EG40 eluent generator [7]. At 0.35 mL/min, total system pressure is about 2600 p.s.i.

3.7. Gradient elution of Group I and II cations, ammonium and ethanolamines

Ethanolamines are hydrophilic amines, but they still can be separated from lithium, sodium, ammonium, potassium, magnesium, and calcium on the

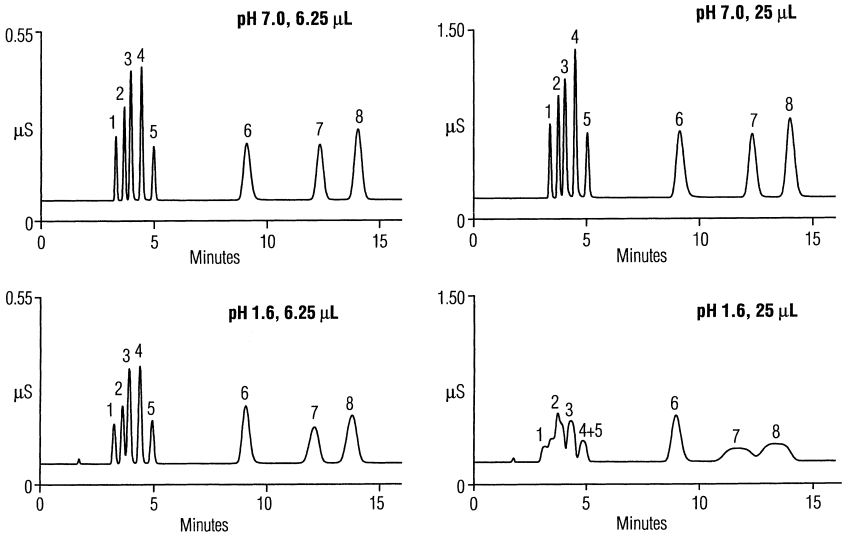

Fig. 5. Influence of sample pH on the IonPac CS17. Column, IonPac CS17 (250 mm×2 mm I.D.); sample volume, 25 or 6.25 μL; flow-rate, 0.25 mL/min; column temperature, 30 °C; suppressor, Cation Atlas Electrolytic Suppressor in AutoSuppression Recycle Mode, 6 mA. Eluent, 6 m*M* methanesulfonic acid. Peaks: 1=lithium (25 μg/L), 2=sodium (100 μg/L), 3=ammonium (125 μg/L), 4=potassium (250 μg/L), 5=dimethylamine (250 μg/L), 6=triethylamine (1750 μg/L), 7=magnesium (125 μg/L), 8=calcium (250 μg/L).

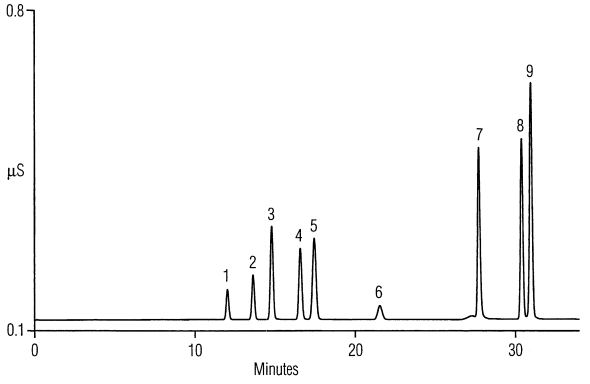

Fig. 6. Gradient elution of Group I and II cations, ammonium and ethylamines. Column, IonPac CG17 (50 mm×2 mm I.D.) plus CS17 (250 mm×2 mm I.D.); sample volume, 25 μL; flow-rate, 0.35 mL/min; column temperature, 30 °C; suppressor, Cation Atlas Electrolytic Suppressor in AutoSuppression Recycle Mode, 13 mA. Eluent, 0.5 to 2.0 m*M* MSA gradient at 25 min; step change to 10 m*M* MSA at 25.1 min; isocratic to 32 min; step change back to 0.5 m*M* MSA at 32.1 min; equilibration time 2 min. Peaks: 1=lithium (10 μg/L), 2=sodium (40 μg/L), 3=ammonium (50 μg/L), 4=potassium (100 μg/L), 5=ethylamine (250 μg/L), 6=diethylamine (100 μg/L), 7=triethylamine (300 μg/L), 8=magnesium (50 μg/L), 9=calcium (100 μg/L).

IonPac CS17 column, as Fig. 7 shows. Monoethanolamine is well separated from ammonium and elutes closer to potassium. The resolution of monoethanolamine and potassium decreases as the temperature increases.

3.8. Gradient elution of boiler water amine additives

The cations of lithium, sodium, potassium, magnesium, calcium, ammonium, and seven of the most commonly used amine additives in the power industry can be separated with an organic solvent-free eluent (Fig. 8). The amines elute with good peak efficiencies and good peak symmetries when the column is run with a simple acidic gradient at 30 °C. Due to the column's selectivity, moderate cation-exchange capacity and hydrophilic nature, cyclohexylamine (peak 11) is eluted easily from the column without the need for organic solvent in the eluent.

4. Conclusions

The new CS17 polymeric carboxylated cation-

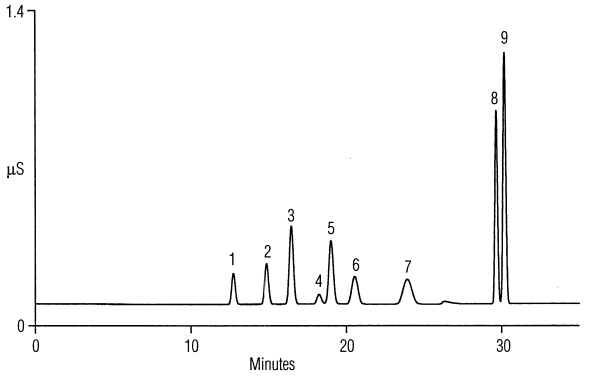

Fig. 7. Gradient elution of Group I and II cations, ammonium and ethanolamines. Column, IonPac CS17 (250 mm×4 mm I.D.); sample volume, 25 µL; flow-rate, 1.4 mL/min; column temperature, 30 °C; suppressor, Cation Atlas Electrolytic Suppressor in AutoSuppression Recycle Mode, 43 mA. Eluent, 0.5 to 0.8 m*M* MSA gradient at 25 min; step change to 9 m*M* MSA at 25.1 min; isocratic to 35 min; step change back to 0.5 m*M* MSA at 35.1 min; equilibration time 2 min. 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=potassium (1.0 mg/L), 6=diethanolamine (1.0 mg/L), 7=triethanolamine (18.0 mg/L), 8=magnesium (0.5 mg/L), 9=calcium (1.0 mg/L).

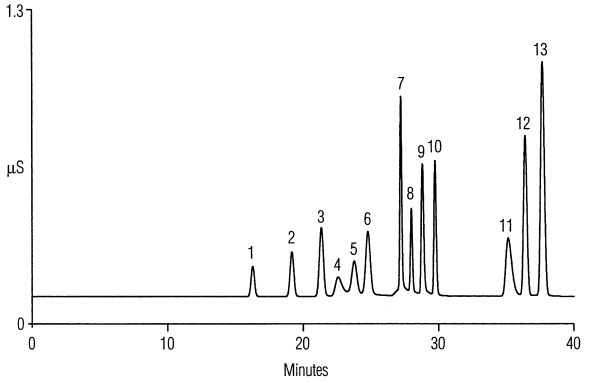

Fig. 8. Gradient elution of boiler water amine additives. Column, IonPac CG17 (50 mm×2 mm I.D.) plus CS17 (250 mm×2 mm I.D.); sample volume, 25 µL; flow-rate, 0.35 mL/min; column temperature, 30 °C; suppressor, Cation Atlas Electrolytic Suppressor in AutoSuppression Recycle Mode, 8 mA. Eluent, 0.5 to 0.7 m*M* MSA gradient at 25 min; step change to 4 m*M* MSA at 25.1 min; isocratic to 27 min; step change to 6.5 m*M* MSA at 27.1 min; isocratic to 37 min; step change back to 0.5 m*M* MSA at 37.1 min; equilibration time 2 min. Peaks: 1=lithium (25 µg/L), 2=sodium (100 µg/L), 3=ammonium (125 µg/L), 4=hydrazine (1000 µg/L), 5=ethanolamine (250 µg/L), 6=potassium (250 µg/L), 7=2-(2-aminoethoxy) ethanol (1000 µg/L), 8=5-amino-1-pentanol (500 µg/L), 9=morpholine (1000 µg/L), 10=2-diethylamino ethanol (1000 µg/L), 11=cyclohexylamine (1000 µg/L), 12=magnesium (125 µg/L), 13=calcium (250 µg/L).

exchange stationary phase for the separation and determination of amines is a hydronium-selective column. This means that a simple acidic eluent is sufficient for effective analyte elution, even for divalent cations.

Due to its hydronium-selective cation-exchange sites, the incorporation of a spacer monomer during the functionalization step, and its moderate cation-exchange capacity, only a modest acid concentration is required for elution of polyvalent cations.

The polymeric beads' coating, together with the spacer monomer used during the functionalization step, gives this stationary phase its hydrophilic nature, which permits use of organic solvent-free eluents for many applications.

For all of the above-mentioned reasons, this results in optimized selectivity for polyvalent and/or hydrophobic amines.

Very low background changes when used with gradients makes the CS17 the optimum column for gradient work. This versatility on eluent concentration with minimum baseline disturbance allows the phase to be effective in the separation of hydrophilic amines, such as the alkanolamines.

The CS17, consisting of 55% crosslinked polymeric beads, is also compatible with organic solvents, including alcohols.

Gradient elution is powerful, and can now be simple and user-friendly. Powerful, as more applications can be performed with one column because it improves the resolution of adjacent peaks and shortens total run times. It can also improve minimum detection levels. Simple, as only deionized water is required for the eluent when the EG40 Eluent Generator with a methanesulfonic acid cartridge is used. User-friendly, as peak integration is easy due to a very low conductivity background change when performing gradients or eluent step changes with the CS17 column.

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