Novel cation-exchange stationary phase for the separation of amines and of six common inorganic cations

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Abstract

Currently available polymeric cation-exchange phases tend to be best suited to the separation of either amines as a class or the inorganic cations as a class. In this paper we will describe a new cation-exchange phase based on a polymeric, highly crosslinked macroporous substrate to which two different monomers, one with carboxylate and the other with phosphonate functional groups, have been covalently grafted. Due to the type of monomers used and the conditions under which the resin is grafted, it offers good selectivity for both inorganic cations and amines, and is more hydrophilic than its predecessor, IonPac CS12 (Dionex). It is possible to chromatograph the more hydrophilic amines without the use of solvent, and for the more hydrophobic amines solvent can be added to the eluent, as the resin is solvent-compatible. Applications in which temperature is used on the column to affect chromatography will be shown.

Keywords: Stationary phases, IC; Amines; Inorganic cations

1. Introduction

In the years immediately following the introduction of ion chromatography in 1975 [1], column packings for cation determinations consisted of surface-sulfonated 25-μm beads of polystyrene crosslinked with 2% divinylbenzene, and they were used with a packed bed suppressor. At the eluent concentrations commonly used in ion chromatography, these ion-exchange resins had much higher selectivity for divalent than for monovalent cations [2]. HCl was needed to elute the monovalent cations, while the stronger divalent eluent component *meta*-phenylenediamine was used to elute the divalents. This latter eluent had the disadvantage of slowly poisoning the column due to contaminants in the reagent. Column equilibration time between the two eluent systems was so long that it essentially re-

quired one column to be dedicated for the alkali metals plus ammonium, and another column for the alkaline earth cations. Total run times were very long and peak efficiencies were very poor.

In 1985 a major breakthrough occurred in cation analysis with the development of the first latexed column (IonPac CS3). A layer of micro-anion-exchange latex, functionalized with a tertiary amine to generate positively charged sites, was attached to a surface-sulfonated polystyrene–divinylbenzene substrate bead. A layer of sulfonated cation-exchange latex particles was then electrostatically attached to the positively charged, latexed surface (see Fig. 1). Due to the new ion-exchange nature of the column packing and to the fact that smaller size substrate beads could be made (providing a shorter mean free path for the analytes), peak efficiencies for the cationic analytes were greatly improved.

The development of the latexed column together with the replacement of *meta*-phenylenediamine by
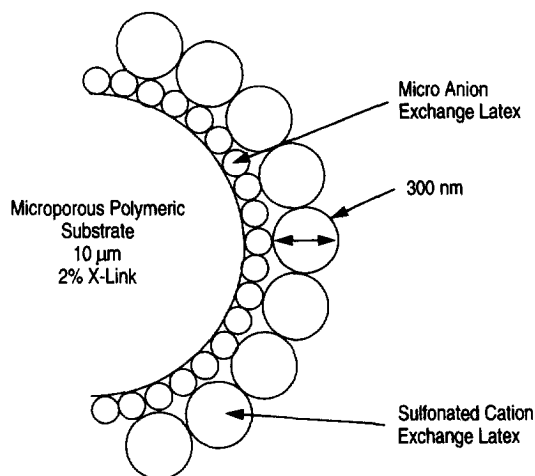
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Fig. 1. Schematic of the IonPac CS3, a latex-coated pellicular strong acid cation exchanger.

the zwitterion 2,3-diaminopropionic acid mono-hydrochloride (DAP·HCl) made it possible to simultaneously analyze both the Group I and Group II cations plus ammonium in one column. The cation micro membrane suppressor, or the CMMS, was introduced the same year making easier the use of suppressed conductivity, as it is continuously regenerated with tetrabutylammonium hydroxide as regenerant. The separation could be done isocratically, but total run time was long: calcium would elute in about 28 min. Furthermore, monovalent peaks were not baseline resolved. Eluent step changes or gradients were then used to better resolve the monovalent cations as well as to shorten the total run time. However, impurities in the weaker eluent concentrated in the column and were later eluted by the stronger eluent causing high blanks. Column equilibration time added to the total analysis time.

In 1988, a technique using column switching between two latexed columns of very different capacity but with the same cation-exchange functionality (IonPac Fast Cation I and II) was introduced to determine monovalent and divalent cations simultaneously and isocratically in about 8 min. Limitations of this approach are that divalent cations have poorer peak efficiencies and contamination of the low capacity column is rapidly manifested as decreasing retention times, compromising the resolution.

In 1990, a sulfonated cation-exchange column (IonPac CS10) with decreased cation-exchange site density was developed by adding a monomer that is sulfonation deactivated to the latex polymerization mixture. The effect of this was to reduce the retention of both the monovalent and the divalent cations. The decreased retention of the divalents was much more pronounced due to a significant reduction in their interaction with the stationary phase [3]. The common six inorganic cations could be eluted from the column, isocratically, in about 15 min. The substrate of this column packing was 50% cross-linked instead of 4% as with previous materials, allowing for solvent compatibility. This enabled the columns not only to be used with solvent-containing eluents, but also to be washed with solvent to remove hydrophobic or water-insoluble contaminants.

All of these cation-exchange columns have sulfonic acid functionalities, which have relatively low selectivity for hydronium ion. In order to efficiently elute divalent cations, a divalent eluent component such as DAP·HCl is added to the eluent.

Kolla et al. [4] developed a silica-based polymer-coated stationary phase containing carboxylate cation-exchange functional groups. It was developed for non-suppressed ion chromatography, utilizing an isocratic eluent consisting of mildly acidic complexing agents. Elution of the monovalent and divalent cations was possible within a reasonable time. The retention-elution mechanism uses the unique selectivity of the carboxylate site along with a mild chelating agent in the eluent that competes with the ion-exchange sites for divalent ion retention only. This competition causes even shorter than expected retention for divalent cations. Due to the silica substrate of these columns, they can only be used with mobile phase pH values from 2 to 8.

A few years later, in 1992, a polymer-based cation-exchange column (IonPac CS12) with carboxylate functional groups was introduced [5]. This column has a high selectivity for hydronium ion. A simple acidic isocratic eluent is used for the separation and elution of the group 1 and group 2 cations (plus ammonium ion) in about 8 min. A divalent eluent component is no longer required to elute divalent cations. Shortly after the introduction of the IonPac CS12, the cation self regenerating suppressor

(CSRS) was introduced [6]. This membrane-based electrolytic suppressor cannot be used in the electrolytic mode with chloride-containing eluents such as DAP·HCl, since the chloride ion can oxidize to form hypochlorite which could damage the ion-exchange membrane [7]. Thus, this new polymeric carboxylate column facilitated the use of suppressed conductivity for cations without the need for base regenerant. The water from the eluent itself is reduced electrolytically to provide the hydroxide ions needed for the neutralization reaction.

The CS12 introduction was followed by the development of the CS14 [8] and the CS12A [9], this last one having been introduced in 1995. These are all carboxylic acid functionalized cation-exchange columns. The unique feature of the CS12A when compared to all of its predecessors, is that this is the first ion chromatography stationary phase that uses a combination of carboxylic acid and phosphonic acid monomers. This combination allows the separation of a wide variety of amines as well as inorganic cations, as will be shown later.

Because carboxylic acid phases are used in a weakly ionized form, that is to say they are used in the protonated form, only a small fraction of the available ion-exchange sites are actually available for retention of cations. Because of this, a large increase in overall functional capacity must be accomplished in order to get sufficient retention of inorganic cations and amines with commonly useful eluent systems. In order to accomplish this, it was necessary to abandon the latex-based system, which provides high efficiency in a very thin film design, and pursue a much higher surface area strategy. To accomplish this higher capacity, we switched from a microporous substrate bead to a highly crosslinked, macroporous, high-surface-area sphere. In this case, the substrate particle consists of 55% crosslinked ethylvinylbenzene–divinylbenzene core with a surface area in the range of 450 m^2/g. Over this entire surface a thin film is applied in the range of about 5–10 nm in thickness of polymer containing three carboxylic acid groups, or in the case of the CS12A, a mixture of carboxylic acid and phosphonic acid groups.

Fig. 2 shows schematically this situation. In this figure, the linear structure of the attached polymeric phase can be seen. Do not be misled, however, into
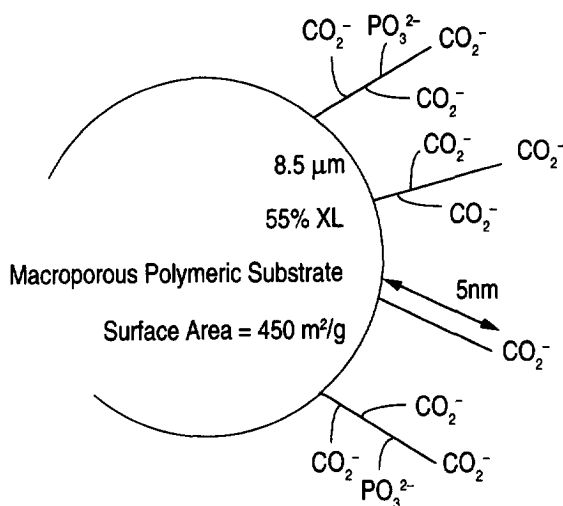

Fig. 2. Schematic of the IonPac CS12A, a weak acid cation exchanger.

thinking that the attached phase is only on the exterior surface. Actually, close to 99% of the available surface is in the interior, and there would simply not be enough capacity if this attached phase were limited solely to the exterior of the support particle.

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), a conductivity detector (CD 20), and a UV detector (AD 20). Eluent flow-rate was 1.0 ml/min, and injection volume was 25 μl. All instrument control, data collection and data processing was performed with the PeakNet chromatography workstation (Dionex). When solvents were not used in the eluent, the cation self-regenerating suppressor (CSRS-1) was used in the recycle mode; when solvent was used as an eluent component, the suppressor was used in the external water mode. When the temperature of the LC 30 oven was set above 30°C, the suppressor was placed outside the oven and external water mode was used.

2.2. Stationary phase

All the columns used in this work were packed with carboxylate-functionalized polymeric cation-exchange resin (Dionex). The IonPac CS12A column is the one mainly used throughout this work. This column has a combination of carboxylate and phosphonate functional groups. Its average particle size and pore size are 8.5 μm and 150 Å, respectively. The average surface area of the substrate beads is 450 m^2/g. Dimensions of all of the columns were 250×4 mm.

2.3. Chemicals

Deionized water (18 MΩ-cm resistivity at room temperature) from a water purification system (Continental type 1, laboratory reagent-grade water system) was used for the preparation of the eluents and standards. Methanesulfonic acid (Fluka, Ronkonkoma, NY, USA) and sulfuric acid (Aldrich, Milwaukee, WI, USA) were of analytical reagent grade. Standards were prepared from analytical reagent grade chemicals.

3. Results and discussion

3.1. Optimization of monomer composition for manganese selectivity

During the development of a stationary phase many experiments are necessary to achieve the desired product, and for the new product to meet the required specifications. Fig. 3 shows a comparison of three different resins produced with different ratios of a carboxylate and a phosphonate monomer attached simultaneously to the polymer support particle. From the chromatograms it can be seen that increasing the amount of phosphonate in the resin causes manganese to elute later than the other common inorganic cations. The middle chromatogram in the figure shows a separation where the ratio of monomers is 1:1. While this may appear on the surface to be quite satisfactory, there were two problems with this particular copolymer. First, the monovalent cations elute too close to one another
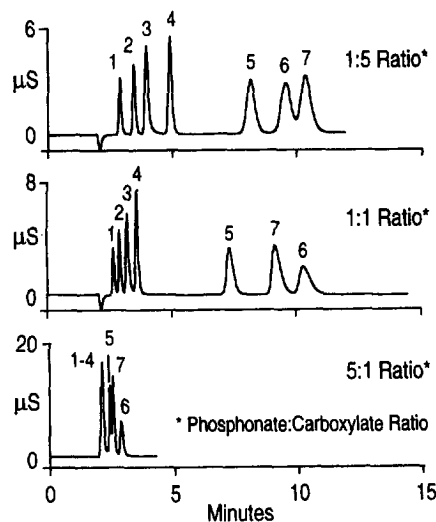

Fig. 3. Optimization of monomer composition for manganese selectivity during the development of the CS12A. The monomer ratio of phosphonate–carboxylate was increased. Eluent: 20 mM methanesulfonic acid. Detection: suppressed conductivity. Peaks: 1=lithium; 2=sodium; 3=ammonium; 4=potassium; 5=magnesium; 6=manganese; 7=calcium.

with that copolymer, compromising their resolution. Secondly, even though not shown here, while manganese is resolved from calcium, strontium and calcium coelute with this particular phase. Obviously that makes this resin impractical since significant amounts of strontium are commonly found in ground water.

The bottom chromatogram, obtained using a copolymer with high levels of phosphonate has quite low capacity primarily because this monomer does not graft efficiently to the support particle.

The top chromatogram was obtained using a mixture containing a small amount of phosphonate; it gives a separation which is incomplete in terms of resolution of calcium and manganese, but it is possible by reducing further the amount of phosphonate added to have manganese be baseline resolved from and elute between magnesium and calcium. The final product in the CS12A actually contains a slightly lower amount of phosphonate than shown in the upper chromatogram of Fig. 3.

To perform this application with the predecessors to this column, we had to add pyrophosphoric acid to the eluent. The problem with this approach was the poor reproducibility of the method due to the vari-

able purity and stability of the reagent. This application was the starting point for the development of the CS12A column: it was decided that the phosphonate group should be added not to the eluent but to the stationary phase.

Fig. 4 shows a comparison of sulfuric acid and methanesulfonic acid as an eluent system when analyzing manganese along with the other common cations. The eluent concentrations in each case were adjusted to keep the total run time the same. There is baseline resolution among magnesium, manganese and calcium when methanesulfonic acid is used as eluent. The separation is incomplete, however, when sulfuric acid is used as eluent, due to a weak complex which sulfate forms with calcium, magnesium and manganese. The result is a decrease in retention time for these three, manganese showing the largest reduction in retention, probably because it forms the more stable complex.

3.2. Comparison of two carboxylated columns

Fig. 5 shows a direct comparison of the CS12A with its predecessor, the CS12. In both cases, the eluent used was the same, 11 mM sulfuric acid.
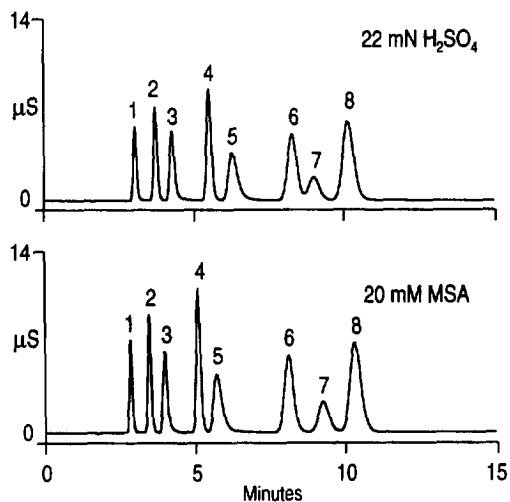

Fig. 4. Determination of manganese, diethylamine, alkali and alkaline earth metals with the IonPac CS12A. Detection: suppressed conductivity. Peaks: 1=lithium (0.5 mg/l); 2=sodium (2 mg/l); 3=ammonium (2.5 mg/l); 4=potassium (5 mg/l); 5= diethylamine (10 mg/l); 6=magnesium (2.5 mg/l); 7=manganese (2.5 mg/l); 8=calcium (10 mg/l). MSA=methanesulfonic acid. 22 mN H$_2$SO$_4$=11 mM H$_2$SO$_4$.
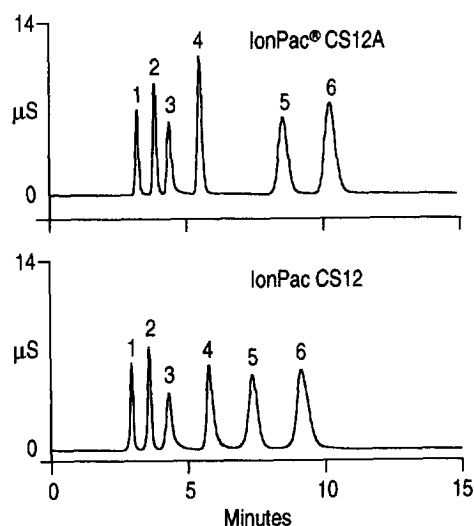

Fig. 5. Comparison of IonPac CS12A and CS12. Eluent: 11 mM sulfuric acid. Detection: suppressed conductivity. Peaks: 1= lithium (0.5 mg/l); 2=sodium (2 mg/l); 3=ammonium (2.5 mg/l); 4=potassium (5 mg/l); 5=magnesium (2.5 mg/l); 6= calcium (5 mg/l).

Adding phosphonate as a co-monomer in the stationary phase for the CS12A resulted in selectivity improvements over the CS12. Substantial changes were also made in the way the phase is attached so as to avoid any inner core penetration of the polymer stationary phase into the support particle. Peak symmetries and peak efficiencies were improved as a result.

3.3. Fast separation of alkali and alkaline earth metals

Due to the higher peak efficiencies and to the larger separation between monovalent and divalent cations in the CS12A as compared to the CS12 (see Fig. 5), it is possible to increase the eluent concentration from 11 to 15.5 mM sulfuric acid and not have the divalents run into the monovalents, as would be the case with the CS12 (see Fig. 6).

Fig. 7 shows the results when the eluent concentration is increased further, from 15.5 to 20 mM sulfuric acid. Because changing the eluent strength has a larger effect (power of 2) on divalent cations than on monovalents, at room temperature magnesium and potassium coelute. By increasing the
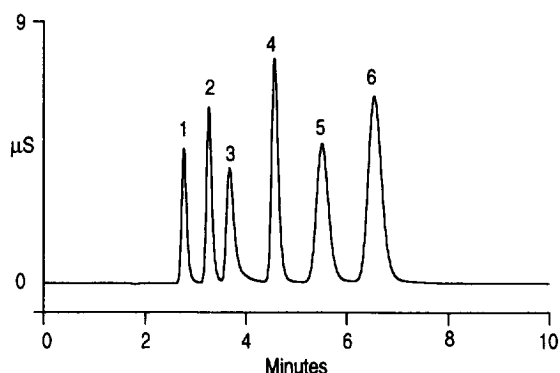
Fig. 6. Fast separation of alkali and alkaline earth metals and ammonium with the CS12A. Eluent: 15.5 mM sulfuric acid. Detection: suppressed conductivity. Peaks: 1=lithium (0.5 mg/l); 2=sodium (2 mg/l); 3=ammonium (2.5 mg/l); 4=potassium (5 mg/l); 5=magnesium (2.5 mg/l); 6= calcium (5 mg/l).

temperature to 40°C, it is possible to resolve the six cations due to higher peak efficiencies and a change in divalent/monovalent selectivity. The total analysis time for the six common inorganic cations is thus reduced to less than 5 min. At room temperature divalent cations form a weak complex with the sulfate ion, so that their retention in the stationary phase is slightly reduced. At higher temperatures it is speculated that the complex is not as stable and thus the divalents are actually retained a little longer in

the resin; at the same time, monovalents are eluted sooner, so that the total effect is the resolution of potassium and magnesium. Temperature also affects the extent of ionization of the weak carboxylic acid groups and the phosphonic acid groups in the resin, as well as the ionization of the sulfuric acid in the eluent. To different extents, all these factors are probably responsible for the chromatographic results.

3.4. Temperature effect on peak efficiencies of the inorganic cations and ammonium

Fig. 8 shows the temperature effect when the CS12A is used with 18 mM methanesulfonic acid eluent, and Table 1 shows the tabulated changes in peak efficiencies and capacity factors. Column peak efficiency N was calculated from $N=5.54[t/w]^2$, where t is the analyte's net retention time (i.e. total gross retention time−column dead time), and w is the peak width at half the peak height. Efficiency for all cations is significantly increased by raising the temperature to 50°C, as temperature affects the stationary phase mass transport. Increasing the temperature decreased the capacity factors and hence the retention of all cations in the stationary phase, with the decrease being more pronounced as the ionic hydrated radii of the analytes gets smaller within a
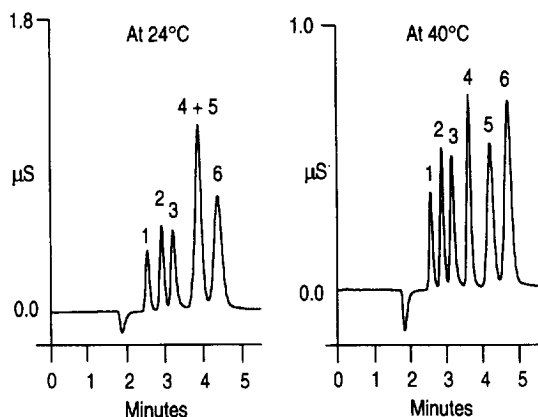

Fig. 7. Fast separation of alkali and alkaline earth metals and ammonium with the CS12A and temperature. Eluent: 20 mM sulfuric acid. Detection: suppressed conductivity. Peaks: 1 = lithium (0.05 mg/l); 2=sodium (0.2 mg/l); 3=ammonium (0.25 mg/l); 4=potassium (0.5 mg/l); 5=magnesium (0.25 mg/l); 6=calcium (0.5 mg/l).
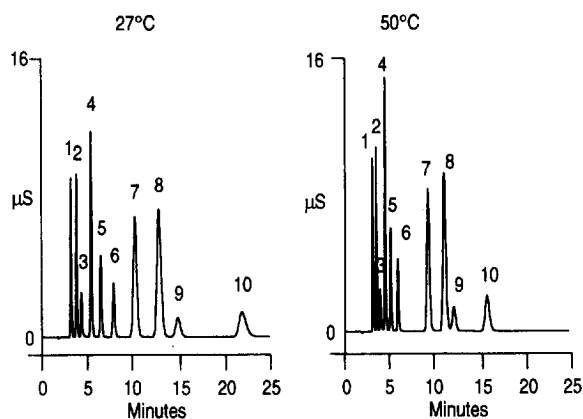

Fig. 8. Temperature effect on peak efficiencies of the inorganic cations and ammonium with the CS12A. Eluent: 18 mM methanesulfonic acid. Detection: suppressed conductivity. Peaks: 1=lithium (1 mg/l); 2=sodium (4 mg/l); 3=ammonium (5 mg/l); 4=potassium (10 mg/l); 5=rubidium (10 mg/l); 6= cesium (10 mg/l); 7=magnesium (5 mg/l); 8=calcium (10 mg/l); 9=strontium (10 mg/l); 10=barium (10 mg/l).

Table 1
Temperature effect on peak efficiencies and retention times for inorganic cations when using the CS12A

Ion	Increase of efficiency at 50°C (%)	Decrease of capacity factor at 50°C (%)
Lithium	26	10
Sodium	31	20
Ammonium	10	22
Potassium	23	36
Rubidium	24	43
Cesium	24	49
Magnesium	41	13
Calcium	34	19
Strontium	32	28
Barium	35	44

group. At the higher temperature, the carboxylic acid groups of the resin are less ionized and therefore its cation-exchange capacity is effectively "lowered". Temperature has also an effect in column selectivity: the separation between monovalent and divalent cations, as a class, is more pronounced. This is probably the result of a combination of factors, like the changes in ionization with temperature for the different acid groups involved: the methanesulfonic acid in the eluent, and both the carboxylate and the phosphonate functional groups.

3.5. Separation of morpholine from the common inorganic cations

Morpholine is used in the power industry as a corrosion inhibitor, and it is important to monitor its concentration as well as that of sodium, ammonium, potassium, magnesium and calcium. In order to get the morpholine peak efficiency and peak symmetry shown in Fig. 9 with the predecessors (CS12 and CS14) of the CS12A column, solvent had to be added to the eluent. Through improvements in the nature of the stationary phase, morpholine can be separated from the common inorganic cations with an entirely aqueous–acid eluent system, reducing both the cost of the eluent and of waste disposal.

3.6. Temperature as a separation aid

In many applications involving amines, due to either solubility of the analyte or because the amine is hydrophobic and therefore can strongly interact by
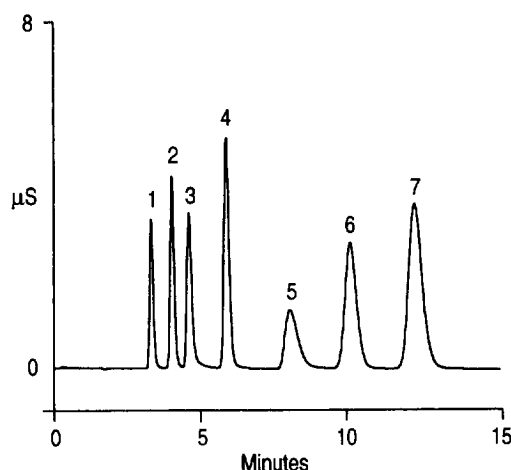
Fig. 9. Isocratic separation of morpholine, alkali and alkaline earth metals on the CS12A. Eluent: 10 mM sulfuric acid. Detection: suppressed conductivity. Peaks: 1 = lithium (0.5 mg/l); 2 = sodium (2 mg/l); 3 = ammonium (2.5 mg/l); 4 = potassium (5 mg/l); 5 = morpholine (25 mg/l); 6 = magnesium (2.5 mg/l); 7 = calcium (5 mg/l).

adsorption with the polymeric stationary phase, it is necessary to add solvent to the eluent. In many applications of this nature with the CS12A, it is possible to use the column under elevated temperature conditions in lieu of having to add solvent to the eluent.

Fig. 10 shows the separation of morpholine, 2-diethylaminoethanol and cyclohexylamine from the common inorganic cations. These volatile amines are added to water as vapor phase inhibitors to reduce corrosion in steam-generating and other boiler applications [10]. It is necessary to monitor the concentration of these amines so that optimum levels can be properly maintained. In order to separate these from the inorganic cations and to elute the more hydrophobic cyclohexylamine off the CS12A column, the eluent needs to contain solvent when the column is at room temperature. At 60°C, however, it is possible to use a solvent-free eluent.

The separation of methylamines, alkali and alkaline earth metals requires that the CS12A be used at elevated temperature. At ambient temperature conditions, methylamine and ammonia coelute on the CS12A (see Fig. 11). By elevating the temperature to 60°C, the effect is both substantial improvements in the analytes' peak efficiencies, which aid in their
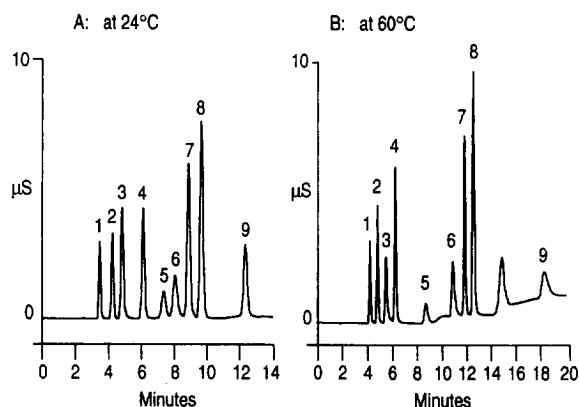
Fig. 10. Determination of volatile amines on the CS12A. (A) Step gradient at 4.1 min from 8 mM sulfuric acid–2% acetonitrile to 14 mM sulfuric acid–8% acetonitrile, step gradient at 8.1 min to 25 mM sulfuric acid–15% acetonitrile; (B) step gradient at 6.1 min from 10 mM methanesulfonic acid to 26 mM methanesulfonic acid, step gradient at 11.1 min to 110 mM methanesulfonic acid. Detection: suppressed conductivity. Peaks: 1=lithium (0.5 mg/l); 2=sodium (2 mg/l); 3=ammonium (2.5 mg/l); 4=potassium (5 mg/l); 5=morpholine (10 mg/l); 6=2-diethylaminoethanol (10 mg/l); 7=magnesium (2.5 mg/l); 8=calcium (5 mg/l); 9= cyclohexylamine (15 mg/l).

resolution, and more importantly in this case, changes in selectivity, which allow for the pair methylamine and ammonia to be resolved.
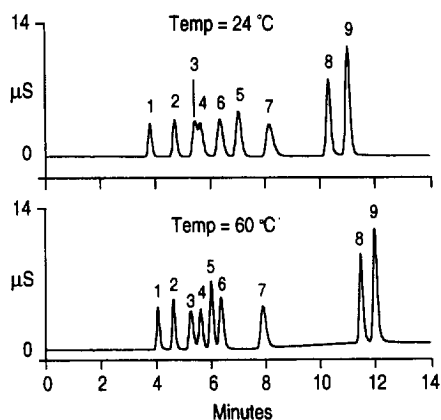

Fig. 11. Separation of methylamines, alkali and alkaline earth metals on the CS12A. Eluent: 8 mM sulfuric acid for 4 min; gradient to 20 mM sulfuric acid from 4.1 to 8 min. Detection: suppressed conductivity. Peaks: 1=lithium (0.5 mg/l); 2=sodium (2 mg/l); 3=ammonium (2.5 mg/l); 4=methylamine (5 mg/l); 5=potassium (5 mg/l); 6=dimethylamine (10 mg/l); 7= trimethylamine (15 mg/l); 8=magnesium (2.5 mg/l); 9=calcium (5 mg/l).
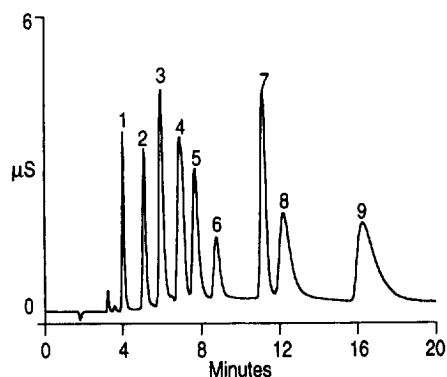

Fig. 12. Solvent-free gradient separation of aliphatic amines on the CS12A at elevated temperature. Eluent: 15.5 mM to 25 mM sulfuric acid in a 10-min gradient. Detection: suppressed conductivity. Column temperature: 60°C. Peaks: 1=ethylamine (5 mg/l); 2=propylamine (7.5 mg/l); 3=$tert$.-butylamine (12.5 mg/l); 4=sec-butylamine (12.5 mg/l); 5=isobutylamine (12.5 mg/l); 6=n-butylamine (20 mg/l); 7=1,2-propanediamine (20 mg/l); 8=1,2-dimethylpropylamine (20 mg/l); 9=di-n-propylamine (40 mg/l).

Fig. 12 further reinforces the point of improved chromatography of this stationary phase for amines. A variety of aliphatic amines can be separated using a simple aqueous–acid eluent gradient system when the column is operated at 60°C. While several of the late eluting amines would clearly benefit from a modest addition of acetonitrile to the eluent, the point is that relatively hydrophobic amines, which are only slightly soluble in water, can be separated with respectable efficiencies in an entirely aqueous eluent system with the help of temperature.

3.7. Solvent-compatibility

In the case when the analytes require solvent to keep them in solution, or when they are more hydrophobic, the high crosslinking of the substrate polymeric bead allows the column to be used with an eluent containing solvent.

Fig. 13 shows the separation of the common inorganic cations along with a range of diamines. Separation of the highly retained aliphatic diamines was accomplished by raising the temperature to 40°C and using a sulfuric acid–acetonitrile gradient. The longer the carbon chain length of the diamine, the more hydrophobic it is, and the longer it is retained
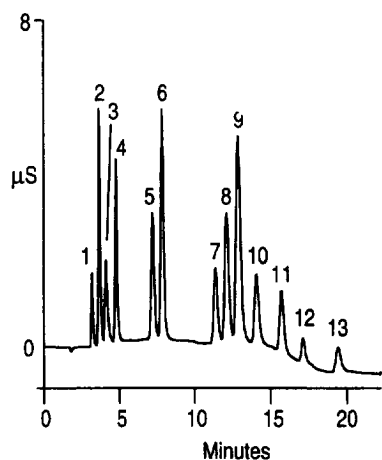
Fig. 13. Gradient elution of diamines on the CS12A. Eluent: 11 mM sulfuric acid–2% acetonitrile to 22 mM sulfuric acid–15.6% acetonitrile in 10 min, to 25 mM sulfuric acid–30% acetonitrile in 14 min. Detection: suppressed conductivity. Column temperature: 40°C. Peaks: 1=lithium (0.2 mg/l); 2=sodium (0.8 mg/l); 3= ammonium (1 mg/l); 4=potassium (2 mg/l); 5=magnesium (1 mg/l); 6=calcium (2 mg/l); 7=1,2-propanediamine (8 mg/l); 8=1,6-hexanediamine (8 mg/l); 9=1,7-heptanediamine (8 mg/l); 10=1,8-octanediamine (8 mg/l); 11=1,9-nonanediamine (8 mg/l); 12=1,10-decanediamine (8 mg/l); 13=1,12-dodecanediamine (8 mg/l).

Fig. 14. Gradient elution of quaternary ammonium ions on the CS12A. Eluent: 11 mM sulfuric acid–10% acetonitrile to 11 mM sulfuric acid–80% acetonitrile in 15 min. Detection: suppressed conductivity. Peaks: 1=sodium (0.3 mg/l); 2=ammonium (2 mg/l); 3=potassium (5 mg/l); 4=tetramethylammonium (5 mg/l); 5=calcium (8 mg/l); 6=tetraethylammonium (20 mg/l); 7= tetrapropylammonium (25 mg/l); 8=tributylmethylammonium (50 mg/l); 9=heptyltriethylammonium; 10=tetrabutylammonium; 11=decyltrimethylammonium (50 mg/l); 12=tetrapentyl-ammonium (50 mg/l); 13=dodecyltrimethylammonium (100 mg/l); 14=tetrahexylammonium (100 mg/l); 15=tetraheptyl-ammonium (100 mg/l); 16=hexadecyltrimethylammonium (100 mg/l).

in the column substrate through reversed-phase adsorption.

Fig. 14 shows the separation of a variety of quaternary ammonium compounds on the CS12A column. The common inorganic cations shown were actually impurities in the standards of the quaternary ammonium compounds. The column was used at room temperature, and the eluent consisted of an acetonitrile gradient with a constant amount of sulfuric acid. These monovalent compounds are being separated on the column through differences in hydrophobicity.

3.8. Separation of amines on the CS12A and detection by UV

Cation-exchange columns are not limited to be used with conductivity detection, other detectors can also be used. Due to the macroporous nature of the CS12A column's substrate, hydrophobic analytes can interact with it through reversed-phase adsorption. Many of these "organic" analytes either have
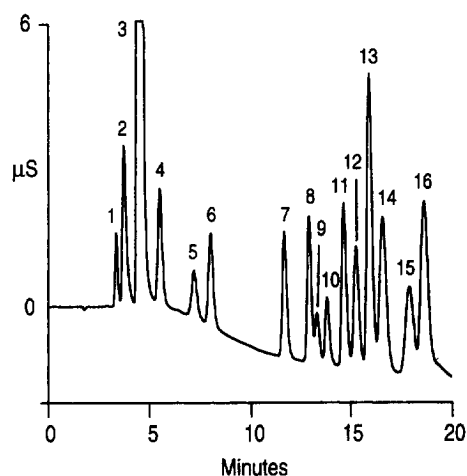
chromophores and absorb in the visible range, or more commonly, will absorb in the UV.

Fig. 15 shows the separation of a series of anilines and detection by UV at 210 nm. These analytes are chromatographed in the CS12A column through a combination of cation-exchange and reversed-phase interaction. The eluent consisted of a fixed amount of sulfuric acid and a gradient of acetonitrile. Peak efficiencies were improved, especially for the late-eluting amines, when the temperature was raised to 40°C.

Fig. 16 shows the separation of pyridines using a combined sulfuric acid–acetonitrile gradient on the CS12A. Detection was by UV at 254 nm. As in the case described above, separation was achieved through a combination of cation-exchange and reversed-phase interaction with the substrate. Temperature aids in the resolution of peaks number 2 and 3, 2-aminopyridine and 4-picoline, and reduces the total run time. Efficiency is also improved, especially for
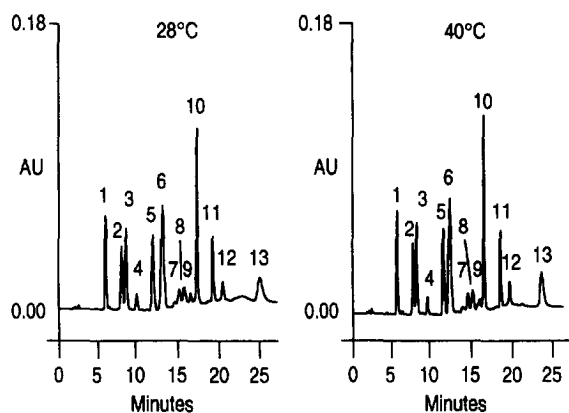
Fig. 15. Gradient elution of anilines on the CS12A. Eluent: 20 mM sulfuric acid–5% acetonitrile to 20 mM sulfuric acid–25% acetonitrile in 10 min, to 20 mM sulfuric acid–60% acetonitrile in 17 min. Detection: UV, 210 nm. Peaks: 1=aniline; 2=N-methylaniline; 3=3-toluidine; 4=N,N'-dimethylaniline; 5=N,N'-diethylaniline; 6=4,4'-methylenedianiline; 7, 8, 9=unknown; 10=4-nitroaniline; 11=2-nitroaniline; 12=N-methyl-N-nitrosoaniline; 13=2,6-dichloro-4-nitroaniline.
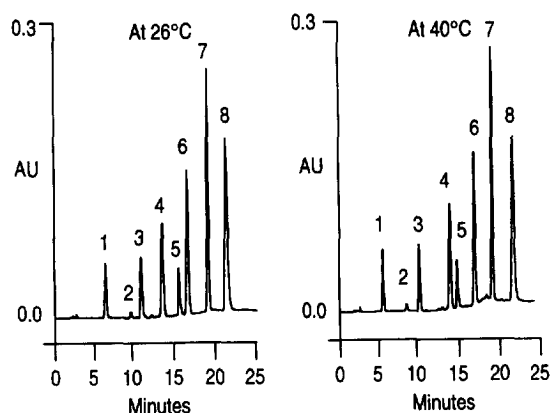

Fig. 17. Gradient elution of benzylamines and amides on the CS12A. Eluent: 5 mM sulfuric acid–5% acetonitrile to 5 mM sulfuric acid–25% acetonitrile in 10 min, to 5 mM sulfuric acid–60% acetonitrile in 17 min. Detection: UV, 210 nm. Peaks: 1=4-hydroxybenzamide; 2, 3=unknown; 4=benzamine; 5=benzamide; 6=N,N'-dimethylbenzylamine; 7=dibenzylamine; 8=tribenzylamine.

2-(2-aminoethyl)pyridine, when the temperature was raised to 60°C.

Fig. 17 shows the separation of benzylamines and amides on the CS12A using an acetonitrile gradient with a constant amount of sulfuric acid. Detection was by UV at 210 nm. Peak number 5, benzamide, moves closer to benzamine (peak number 4) and
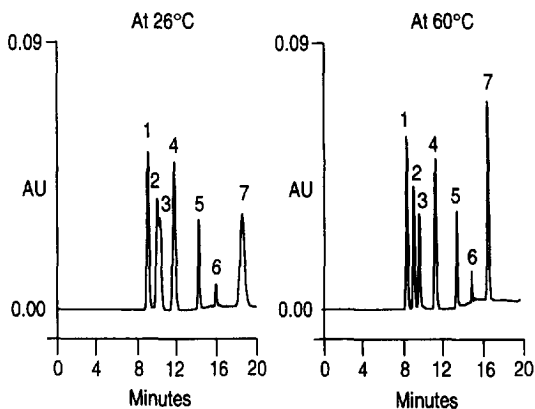

Fig. 16. Gradient elution of pyridines on the CS12A. Eluent: 5 mM sulfuric acid–10% acetonitrile to 9 mM sulfuric acid–25% acetonitrile in 10 min, to 20 mM sulfuric acid–50% acetonitrile in 13 min. Detection: UV, 254 nm. Peaks: 1=pyridine; 2=2-aminopyridine; 3=4-picoline; 4=2-dimethylaminopyridine; 5=2,2'-bipyridine; 6=4-benzylpyridine; 7=2-(2-aminoethyl)pyridine.

away from dimethylbenzylamine (peak number 6) when the temperature is raised to 40°C. In this case, the optimum column temperature would depend on the different concentration ratios of peaks number 4, 5 and 6.

3.9. Separation of arenes and substituted benzenes

The analytes shown in Fig. 18 are either neutral or acidic in nature. Under the acidic eluent conditions (pH 1.7), all except for phenylphosphoric acid (which is negatively charged) are neutral, and retention and separation of these are taking place by reversed-phase adsorption in the macroporous polymeric substrate of the CS12A column. The eluent consists of a constant amount of sulfuric acid and a gradient of acetonitrile. Detection was by UV at 210 nm. Peak efficiencies especially improve for the later eluting peaks when the temperature is raised to 40°C.

4. Conclusions

The starting goal for the development of this column, that is, the separation of manganese and the common six inorganic cations (lithium, sodium, ammonium, potassium, magnesium and calcium)
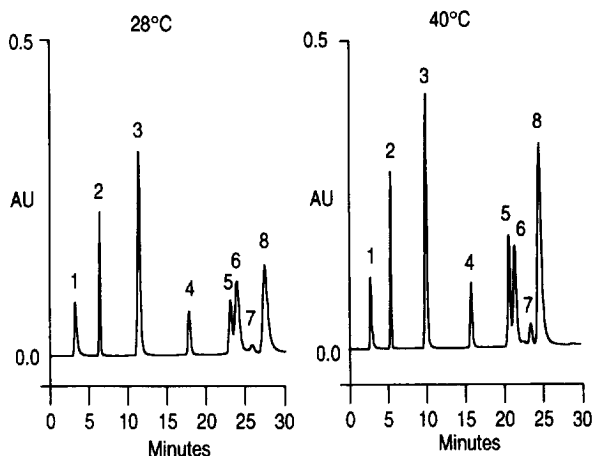
Fig. 18. Gradient elution of arenes and substituted benzenes on the CS12A. Eluent: 10 mM sulfuric acid–30% acetonitrile to 10 mM sulfuric acid–90% acetonitrile in 30 min. Detection: UV, 210 nm. Peaks: 1=phenylphosphoric acid; 2=phenol; 3=2,2'-biphenol; 4=benzene; 5=styrene; 6=benzophenone; 7=cumene; 8=naphthalene.

using a simple acid eluent system was achieved by using a combination of a carboxylic acid monomer and a phosphonic acid monomer.

The CS12A column provides higher overall peak efficiencies and improved peak symmetries for both inorganic cations and amines, than the previous polymeric carboxylate columns, the CS12 and the CS14, due to the way the resin is grafted and the type of monomers used. Furthermore, using the column under elevated temperature conditions improves peak shapes and efficiencies for most inorganic and organic analytes, and this effect is more pronounced in this column than the other two. Temperature has the added potential benefit of aiding separations that are difficult, both through an increase in peak efficiency as well as changes in analyte selectivity. With the help of temperature, it is possible to analyze for the common six inorganic cations in less than 5 min. In many cases, the use of solvent in the eluent can be avoided by increasing the column temperature, thus reducing operating cost.

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