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Novel weak acid cation-exchange column

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ABSTRACT

A cation-exchange column with carboxylate cation-exchange sites was developed. Compared with conventional surface-sulfonated or latex agglomerated resins, this weak acid cation exchanger has a high selectivity for hydronium ions. Mono- and divalent cations such as alkali and alkaline earth metals can therefore be determined simultaneously in less than 10 min using a weakly acidic eluent under isocratic conditions. Because the ethylvinylbenzene–divinylbenzene substrate is highly cross-linked, the new separator is solvent compatible, thus allowing the use of organic solvents to alter the selectivity of the separation and to remove organic contaminants from the column. The separation characteristics of this column are presented and various applications are discussed.

INTRODUCTION

Since the introduction of ion chromatography in 1975 [1], there have been numerous publications on chromatographic methods suitable for alkali and alkaline earth metals in which conductimetric detection is applied to the column effluent [2–6]. At first, the large differences in ion-exchange selectivities of alkali *versus* alkaline earth metals necessitated sequential determinations of the two cation classes using surface-sulfonated polystyrene–divinylbenzene resins. While monovalent cations such as alkali metals, ammonium and small aliphatic amines are easily eluted with dilute mineral acids [7], the separation of alkaline earth metals required the use of divalent eluent ions such as *m*-phenylenediamine or ethylenediamine [5]. However, the aim of the inorganic analytical chemist has always been the simultaneous determination of alkali metal, alkaline earth metal and ammonium cations, and various column materials and eluents have been tested for this purpose. Kolla *et al.* [8] were the first to report on an isocratic elution of both cation classes within a reasonable time period using a silica-based weak cation exchanger coated with poly(butadiene–maleic acid) as the stationary phase and mildly acidic complexing agents as the eluent. Thus, cation-exchange and chelating processes take place, the latter being strongly dependent on sample pH. Although the eluent composition occasionally has to be adjusted when using columns from different production batches to compensate for the variations in the coating process, the concept of using a stationary phase with a carboxylate functionality results in an analysis time of *ca.* 20 min for the above-mentioned mono- and divalent cations.

As an alternative concept, a column-switching technique was proposed based on two latex agglomerated strong acid cation exchangers of different dimensions and capacities and switching them to change the flow direction during the elution for the simultaneous determination of alkali and alkaline earth metals [9]. Although the resulting resolution between the monovalent cations was sufficient, the major drawback of this technique was the poor effi-

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ciency for divalent cations. This limitation was overcome with the introduction of a more efficient strong acid latex agglomerated cation-exchange column, IonPac CS10 [10]. In contrast to a conventional latex agglomerated cation exchanger of the IonPac CS3 type, an ethylvinylbenzene–divinylbenzene copolymer was used as the substrate material to ensure solvent compatibility. Thus, it is possible either to alter the selectivity of the separation by adding organic solvents to the eluent or to remove organic contaminants by rinsing the packing material with acetonitrile or methanol. Also, two different monomers have been used to polymerize the latex material, one of which is not readily sulfonated, thus producing a lower charge density ion-exchange material. This, in turn, is important for the ion-exchange process of divalent metal separation. Owing to this lower charge density, the interaction of the divalent cations with the stationary phase is significantly reduced. With a mixture of hydrochloric acid and 2,3-diaminopropionic acid as the eluent, sodium, ammonium, potassium, magnesium and calcium are eluted within 15 min. As shown in the chromatogram in Fig. 1, all ions are separated to the baseline. On the other hand, the tremendous resolution between calcium and magnesium is unnecessary for routine water analysis. Nevertheless, this column concept is well understood, and a good column-to-column reproducibility is obtained [11].

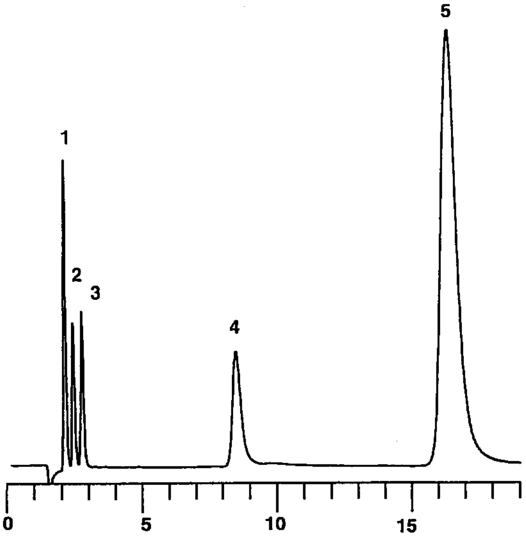

Fig. 1. Simultaneous separation of alkali and alkaline earth metals on IonPac CS10. Eluent, 0.04 mol/l hydrochloric acid + 0.004 mol/l, 2,3-diaminopropionic acid; flow-rate, 1 ml/min; detection, suppressed conductivity; injection volume, 25 μl; solute concentrations, (1) 1 ppm sodium, (2) 0.5 ppm ammonium, (3) 1 ppm potassium, (4) 1 ppm magnesium and (5) 10 ppm calcium.

The major effort during the past 2 years was to combine the benefits of both column concepts, *i.e.*, to develop a polymeric solvent-compatible stationary phase with a carboxylate functionality. The work presented in this paper focuses on the chromatographic properties and the applicability of such a packing material. In order to study this new separation material, chromatographic parameters such as eluent composition, eluent concentration and flow-rate were varied.

EXPERIMENTAL

Apparatus

All experiments were carried out with a DX-300 ion chromatographic system (Dionex, Sunnyvale, CA, USA) consisting of a quaternary gradient pump, a chromatographic module and a conductivity detector. Eluents were degassed by purging them with helium using the eluent degas module. Separations were performed on an IonPac CS12 cation exchanger. A guard column (IonPac CG12) was used at all times. Conductivity detection was carried out in the recycle mode using a cation self-regenerating suppressor (CSRS-1). A chromatographic data system (Al-450; Dionex) was used for instrument control and for data collection and processing.

Reagents

Ultrapure water (18 MΩ cm resistivity at 25°C), used for the preparation of the eluents, was obtained from a water purification system (SERAL, Ransbach-Baumbach, Germany). Methanesulfonic acid (Ventron Alfa Products, Karlsruhe, Germany) was of analytical-reagent grade. Tetrabutylammonium hydroxide (1.5 mol/l in water) was purchased from Riedel-de Haën (Seelze, Germany) and acetonitrile (Chrom AR grade) from Promochem (Wesel, Germany).

Dilute working standards solutions of all the cations under investigation were prepared daily from 1000 ppm stock standard solutions. All standard solutions were stored in polyethylene containers.

RESULTS AND DISCUSSION

The new cation exchanger is commercially available under the trade name IonPac CS12. Its structural and physical properties are summarized in Table I.

In order to overcome the stability problem of polymer-coated silica phases, we used a highly cross-linked, macroporous ethylvinylbenzene–divinylbenzene polymer with a bead diameter of 8 μm, a pore size of 6 nm and a specific surface area of 300 m^2/g as substrate material. In a second step, this substrate material was grafted with another polymer, containing carboxylate groups, resulting in a relatively high ion-exchange capacity of 2.8 mequiv. per column. In contrast to conventional latex agglomerated strong acid cation exchangers such as IonPac CS10, very simple eluents such as hydrochloric acid or methanesulfonic acid can be used to elute mono- and divalent cations rapidly and efficiently under isocratic conditions. As can be seen from Fig. 2, sodium, ammonium, potassium, magnesium and calcium are separated to the baseline in less than 10 min.

TABLE I

STRUCTURAL AND PHYSICAL PROPERTIES OF THE IONPAC CS12 SEPARATOR

Parameter	Valve
Column dimensions	(A) 250 mm × 4 mm I.D. (B) 250 mm × 2 mm I.D.
Substrate	Ethylvinylbenzene cross-linked with 55% divinylbenzene
Bead diameter	8 μm
Pore size	6 nm
Surface area	300 m^2/g
Ion-exchange group	Carboxylic acid ($pK_a < 3$)
Capacity	(A) 2.8 mequiv. per column (B) 0.7 mequiv. per column
Mobile phase compatibility	Acidic eluents; compatible with HPLC solvents. Alcohols should be avoided

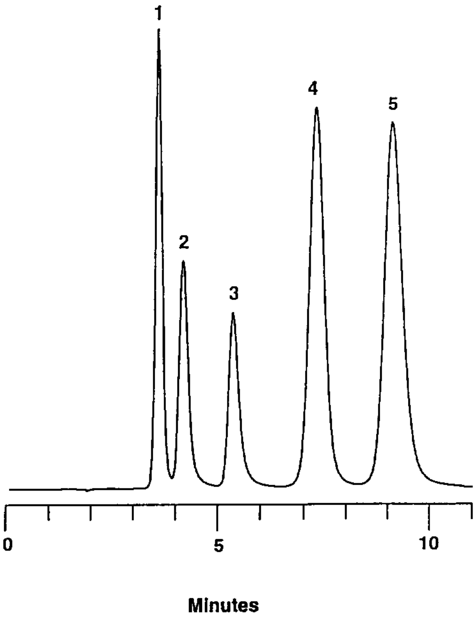

Fig. 2. Simultaneous separation of alkali and alkaline earth metals on IonPac CS12. Eluent, 0.02 mol/l methanesulfonic acid; flow-rate; 1 ml/min; detection, suppressed conductivity; injection volume, 25 μl; solute concentrations, 5 ppm (1) sodium, (2) ammonium, (3) potassium and (4) magnesium and (5) 10 ppm calcium.

Experiments were carried out to investigate the maximum sodium-to-ammonium ratio that still allows a separation of these two ions on the IonPac CS12. Under isocratic conditions, using an eluent concentration of 0.01 mol/l methanesulfonic acid (MSA) and a flow-rate of 2 ml/min, it is possible to analyze samples containing a 250–500-fold excess of sodium in comparison with ammonium (Fig. 3). As can be seen from Fig. 3, even samples with a sodium-to-ammonium ratio of 1000:1 can be analyzed for ammonium. However, the resolution between sodium and ammonium is less than 1.3 at this concentration ratio, and quantification is therefore only possible using the corrected peak height for ammonium. To improve the resolution between sodium and ammonium, a step gradient can be used, as shown in Fig. 4. Starting the analysis with an MSA concentration of 0.004 mol/l and switching it to 0.016 mol/l after 5.1 min, a baseline-resolved separation between sodium and ammonium, even with a 1000-fold excess of sodium, can be obtained. The total analysis time including the re-equilibration step is less than 20 min, thus this technique is suitable for routine water analysis.

A major problem with weak acid cation exchangers is that the dissociation of the carboxylate

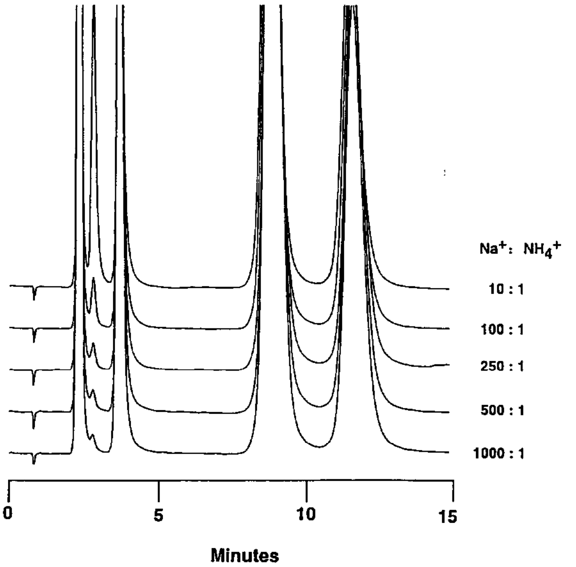

Fig. 3. Separation of sodium and ammonium at different concentration ratios using IonPac CS12. Eluent, 0.01 mol/l methanesulfonic acid; flow-rate, 2 ml/min; detection, suppressed conductivity; injection volume, 25 μl; solute concentrations, 20 ppm sodium, potassium, magnesium and calcium.

functional groups is strongly affected by the sample pH. Polymer-coated silica phases, for instance, such as that according to Kolla *et al.* [8], require an adjustment of the sample pH with either nitric acid or sodium hydroxide. This is time consuming and prone to interferences as the chemicals could contain other cationic impurities. Therefore, experiments with IonPac CS12 were carried out to investigate the influence of the sample pH on the separation of cations. As shown in Table I, the pK_a value of the carboxylate functionality that was chosen for this material is less than 3. This was done to allow the analysis of strongly acidic samples in much the same way as it was possible with sulfonated strong acid cation-exchange columns. A representative chromatogram of an acid soil digest is shown in Fig. 5. The sample was diluted 20-fold, having a final pH of about 2 after dilution. Methanesulfonic acid (0.02 mol/l) at a flow-rate of 1 ml/min was used as the eluent. Suppressed conductivity detection was carried out utilizing the CSRS-1 in the auto-suppression mode [12]. As can be seen from Fig. 5, the baseline performance is not affected by the acid sample matrix and the peak shapes for the divalent metal ions are absolutely symmetrical.

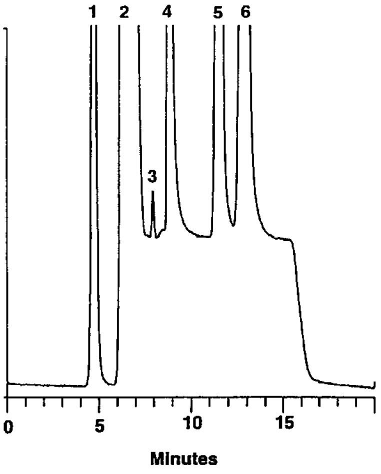

Fig. 4. Determination of ammonium in presence of large amounts of sodium. Separator, IonPac CS12; eluent, 0.004 mol/l methanesulfonic acid with step change at 5.1 min to 0.016 mol/l; flow-rate, 2 ml/min; detection, suppressed conductivity; injection volume, 25 μl; solute concentrations, (1) 0.5 ppm lithium, (2) 52 ppm sodium, (3) 0.05 ppm ammonium, (4) 5 ppm potassium, (5) 2.5 ppm magnesium and (6) 5 ppm calcium.

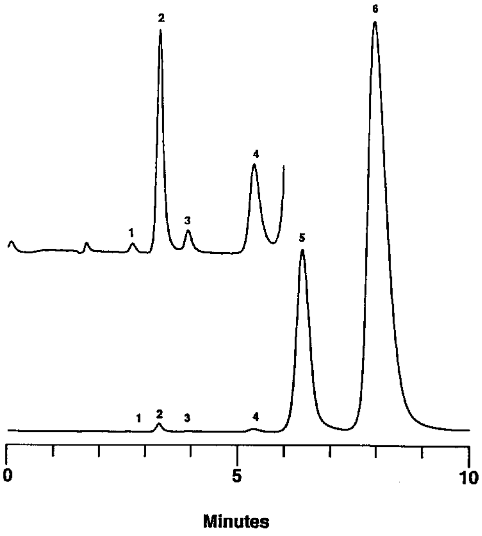

Fig. 5. Determination of inorganic cations in an acid soil digest. Separator, IonPac CS12; eluent, 0.02 mol/l methanesulfonic acid; flow-rate, 1 ml/min; detection, suppressed conductivity; injection volume, 10 μl; sample, acid soil digest (diluted 20-fold) with (1) 0.01 ppm lithium, (2) 1 ppm sodium, (3) 0.1 ppm ammonium (4) 0.9 ppm potassium, (5) 25 ppm magnesium and (6) 130 ppm calcium.

In many European countries, including Germany, there is an increasing demand for the ability to determine simultaneously alkali and alkaline earth metals, including barium, in a variety of water samples. Whereas the required detection limit for barium is in the low mg/l range, the concentrations of the other metal cations are usually several orders of magnitude higher. As is commonly known, barium, the least stable of the alkaline earth elements, is strongly retained on conventional cation-exchange resins, resulting in significant peak broadening which, in turn, leads to a lower sensitivity in comparison with the earlier eluting alkaline earth metals. However, using IonPac CS12 with 0.02 mol/l MSA at a flow-rate of 1 ml/min under isocratic conditions, barium elutes after 13 min (Fig. 6). With suppressed conductivity detection and a larger injection loop (100 μl), barium can be detected down to 0.1 mg/l. Other alkali and alkaline earth metals in higher concentrations do not interfere. Another approach to lowering the detection limit for barium is to use a step gradient starting with an MSA concentration of 0.016 mol/l until calcium is eluted, and than switching to 0.04 mol/l MSA to elute barium. With this procedure, a sharper peak for barium is obtained, resulting in a lower detection limit.

A high sensitivity for barium can also be obtained by applying gradient elution. As shown in Fig. 7, elution of all the alkali and alkaline earth metal cations of interest and ammonium is completed in about 10 min by increasing the MSA concentration in the mobile phase from 0.004 to 0.04 mol/l during the run. Similar gradients have already been tried with conventional strong acid cation exchangers such as IonPac CS10 [13]. The major problem with this method is the magnesium and calcium impurities in the eluent used. These ions are concentrated on the column while equilibrating it with the weak eluent. When starting the gradient, they are eluted at their expected retention times. With a cation trap column between the pump and the injection valve, this problem could be partly solved. When running linear gradients on an IonPac CS12 column with methanesulfonic acid, a cation trap column is no longer necessary.

IonPac CS12 can also be used in combination with non-suppressed conductivity detection. In this mode, the eluent used (0.0025 mol/l HNO_3 + 100

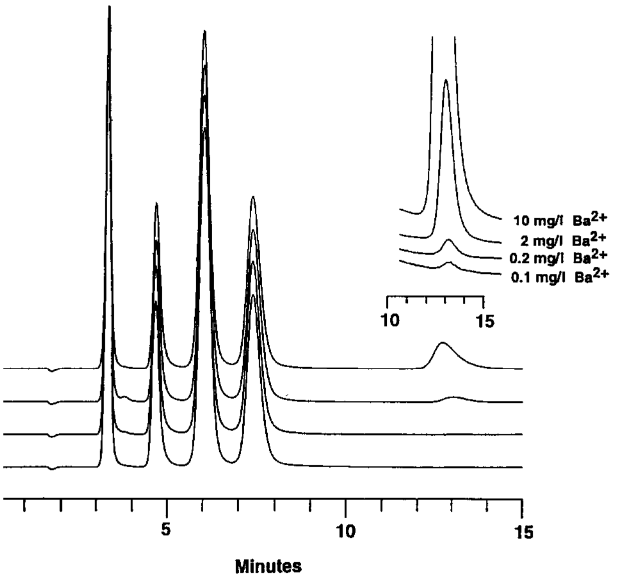

Fig. 6. Determination of barium on IonPac CS12. Chromatographic conditions as in Fig. 5 except injection volume, 100 μl; solute concentrations, 20 ppm sodium, potassium, magnesium and calcium.

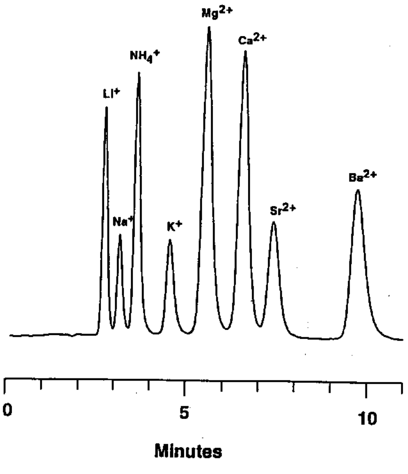

Fig. 7. Gradient elution of alkali and alkaline earth metals on IonPac CS12. Eluent, methanesulfonic acid; gradient, 0.004 mol/l isocratic for 1 min then linear to 0.04 mol/l in 10 min; flow-rate, 1 ml/min; detection, suppressed conductivity; injection volume, 25 μl; solute concentrations, 2.5 ppm lithium and sodium, 5 ppm ammonium and potassium, 10 ppm calcium and strontium and 25 ppm barium.

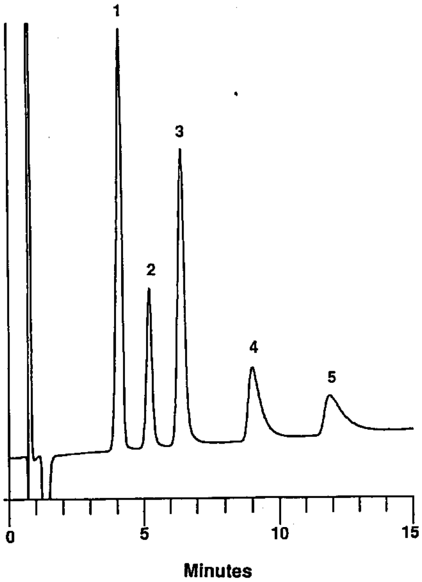

Fig. 8. Separation of alkali metal ions on IonPac CS12. Eluent, 0.0025 mol/l nitric acid; flow-rate, 2 ml/min; detection, non-suppressed conductivity; injection volume, 25 μl; solute concentrations, (1) 5 ppm lithium, (2) 5 ppm sodium, (3) 10 ppm ammonium, (4) 10 ppm potassium and (5) 20 ppm rubidium.

ml/l acetonitrile) exhibits a high background conductivity so that the metal cations are detected as negative signals. In Fig. 8, a typical chromatogram for the separation of alkali metals is shown. Whereas lithium, sodium, ammonium and potassium are eluted within 10 min, divalent cations such as alkaline earth metals cannot be eluted with a dilute mineral acid because the column capacity is too high. As is typical for non-suppressed conductivity work, the temperatures of the eluent, the column and the detector cell have to be closely controlled.

As mentioned above, the support material of IonPac CS12 is a highly cross-linked ethylvinylbenzene–divinylbenzene copolymer ensuring solvent compatibility. Whereas organic solvents as eluent modifiers can alter the selectivity of the stationary phase for organic cations such as organic amines [11,14,15], the retention behavior of inorganic cations is not significantly influenced, especially when using strong acid cation exchangers such as IonPac CS10. On the other hand, for a weak acid cation exchanger such as IonPac CS12, one should expect an influence of aprotic solvents (*e.g.*, acetonitrile) on retention, because aprotic solvents diminish the

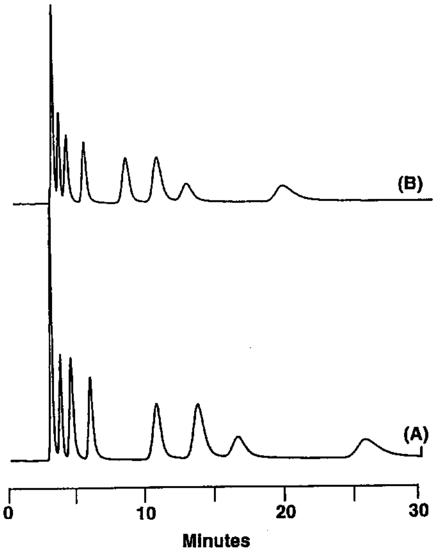

Fig. 9. Effect of acetonitrile on the retention of alkali and alkaline earth metals on IonPac CS12. Eluent, (A) 0.018 mol/l methanesulfonic acid and (B) 0.018 mol/l methanesulfonic acid–acetonitrile (95:5, v/v), flow-rate, 1 ml/min; detection, suppressed conductivity; injection volume, 25 μl; solute concentrations, 20 ppm lithium, sodium, ammonium, potassium, magnesium, calcium, strontium and barium.

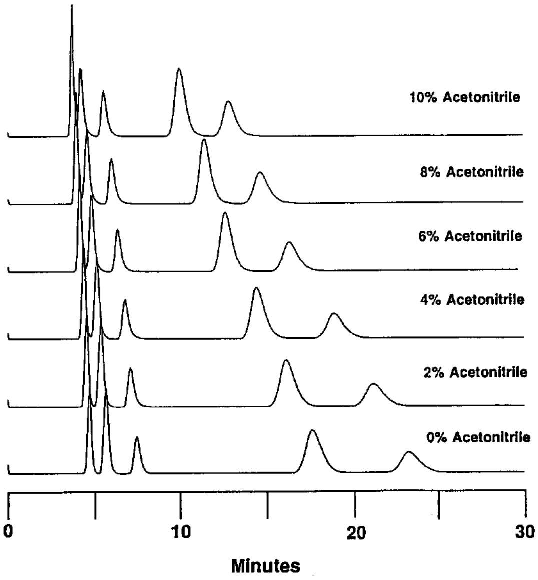

Fig. 10. Effect of acetonitrile on the retention of alkali and alkaline earth metals on IonPac CS12. Eluent, 0.01 mol/l methanesulfonic acid–acetonitrile; flow-rate, 1 ml/min; detection, suppressed conductivity; injection volume, 25 μl; solute concentrations, 10 ppm sodium, ammonium, potassium, magnesium and calcium.

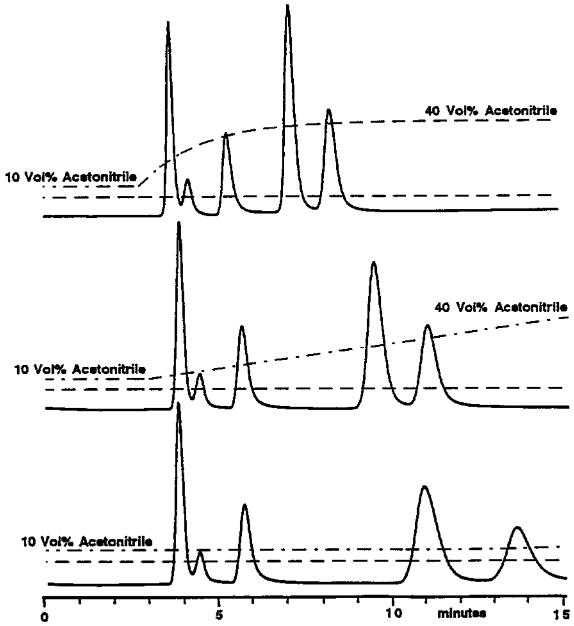

Fig. 11. Effect of different acetonitrile gradients on the resolution of alkali and alkaline earth metals on IonPac CS12. Eluent, 0.01 mol/l methanesulfonic acid–acetonitrile; flow-rate, 1 ml/min; detection, suppressed conductivity; injection volume and solute concentrations as in Fig. 10.

dissociation of the carboxylate ion-exchange groups, thus reducing the effective capacity of the resin. To confirm this assumption, a set of experiments were carried out keeping the MSA concentration in the mobile phase constant 0.01 mol/l and increasing the acetonitrile content in steps of 2% (v/v). As can be seen in Fig. 9, the retention times, especially for the divalent cations, decrease with increasing content of acetonitrile in the mobile phase. Acetonitrile seems to reduce the dissociation of the carboxylate functionality, resulting in a lower effective capacity of the resin. This means that if an organic solvent is added to the mobile phase, the concentration of the acid eluent has to be decreased to obtain the same separation as without organic solvents in the mobile phase. Fig. 10 shows the resulting chromatograms of isocratic alkali and alkaline earth metal separations with different acetonitrile contents in the mobile phase. From Fig. 10, it can be concluded that adding 10% acetonitrile to the eluent reduces the retention times of magnesium and calcium by 45%. In this case, the MSA concentration should be half the starting concentration in order to maintain a constant retention time. As shown in Fig. 11, acetonitrile gradients of different shapes (linear, convex, concave) have also been investigated. The results of these experiments suggest the use of acetonitrile gradients to generate separations for sodium, ammonium, potassium, magnesium, and calcium that look similar to isocratic separations. This application can be used to analyze samples containing large amounts of organic contaminants, because the column is continuously cleaned with acetonitrile during the ongoing separation of the inorganic compounds.

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