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Simultaneous separation of alkali and alkaline-earth cations on polybutadiene–maleic acid-coated stationary phase by mineral acid eluents

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ABSTRACT

The simultaneous separation of alkali and alkaline-earth cations on polybutadiene–maleic acid-coated silica columns can be achieved with mineral acid eluents. Simple ion-exchange retention mechanisms and the high selectivity of eluent hydronium ions towards the carboxylate group are the basis for the separation. Use of mineral acid eluents allows using this column in both single column and suppressor-based IC systems. Both types of ion chromatography systems provide detection limits in the low-ng/ml range with excellent linearity.

INTRODUCTION

Since the introduction of ion chromatography (IC) in 1975, the technique has been widely applied for analyzing various aqueous samples such as waste and drinking water, food and beverages, pharmaceuticals, metal plating solutions, etc. Alkali, alkaline earth, and ammonium cations are often found together in these samples and the demand for determining these species is increasing. Conventional IC methods for the analysis of these cations are time consuming and complicated. Alkali metal ions, ammonium and cations of several monovalent amines are separated by low capacity sulfonic acid cation-exchange columns along with dilute solutions of inorganic acids such as nitric acid or hydrochloric acid [1]. The divalent and trivalent cations, due to their affinity to the resin, will not be eluted with monovalent acid eluents. Divalent cations are separated by divalent cations such as *m*-phenylenediamine or ethylenediamine [1]. An effective, isocratic separation of both monovalent and divalent cations in one run by single column IC was not established until recently [2].

In suppressor-based IC, a gradient separation has been shown to be useful for the simultaneous separation of monovalent and divalent cations [3]. A gradient of 7 to 100% of the 40 m*M* HCl–20 m*M* DAP (2,3-diaminopropionic acid) · HCl eluent and water is able to separate monovalent lithium, sodium, ammonium and potassium, and divalent magnesium, calcium and ethylenediammonium in one run. Even though gradient elution is useful for the initial investigation of unknown samples, it faces disadvantages such as the need for a scavenger column to remove the impurities from the eluent, baseline shift due to changing eluent composition, long retention times and lengthy re-equilibration periods between runs. The overall operational cost is also higher because of the expensive eluents, regenerants and gradient pumps. Stillian *et al.* [4] reported an isocratic separation of mono/divalent cations on a sulfonic acid cation-exchange column using 60 m*M* hydrochloric aicd–6 m*M* DAP eluent by suppressed conductivity. This method simplifies the mono- and divalent cation analysis by suppressor-based IC.

A column switching (dual column) technique was

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also reported for the simultaneous separation of both mono- and divalent cations [3]. Samples are eluted through two separate columns each optimized for the chromatography of one group of cations. The separation is accomplished by switching the eluent flowpaths between the columns. This method has several advantages compared to the gradient technique including: isocratic operation, shorter run times and no re-equilibration period between runs. However this technique requires sophisticated instrumentation and sensitivity for divalent cations is poor.

Other approaches use inorganic eluents followed by indirect UV detection. Small and Miller [5] first developed an IC system consisted of two separate columns with different cation-exchange capacities for the separation of sodium, potassium, magnesium, and calcium using copper sulfate eluent and indirect UV detection. Mayazaki *et al.* [6] reported the separation of alkali earth cations as well as magnesium and calcium on a Zipax cation-exchange column with copper sulfate eluent. However, lithium, barium and strontium are not separated using this method. Sherman and Danielson [7] used a styrene–divinylbenzene (ST-DVB)-based sulfonic acid cation exchanger along with cerium(III) as the eluent. This method is effective for the separation of sodium, potassium, magnesium and calcium. However ammonium and potassium coelute and a system peak due to cerium(III) interferes with the magnesium peak. A combination of benzylamine–citric acid–N-hydroxyethylenediamine-N,N′,N′-triacetic acid (EDTA-OH) and a combination of 1,1′-di-*n*-heptyl-4,5′-bipyridimium (DHBP) ion–citric acid along with indirect UV detection was developed by Sato [8] for the separation of mono/divalent cations. With these eluents no interference was reported, but the sensitivity for divalent cations was poor.

A new cation-exchange stationary phase made of polybutadiene–maleic acid (PBDMA) coated on silica was developed by Schomburg *et al.* [2] for the isocratic and simultaneous separation of monovalent and divalent cations by single column IC (SCIC). The separation was accomplished using different organic acid eluents and indirect electrical conductivity detection. The eluents used for the separation such as citric acid, phthalic acid, tartaric acid, salicylic acid, and pyridine-2,6-dicarboxylic acid, were all capable of complexing divalent cations. The authors report that the separation takes place due to ion-exchange and complex formation mechanisms, both of which reportedly have an important and sometimes opposing effect on the separation of cations. Yan and Schwedt [9] reported the influence of eluents containing organic complexing acids such as 1-hydroxyisobutyric, tartaric, oxalic, pyridine-2,6-dicarboxylic acid and EDTA with this column.

These authors report that the elution of monovalent ions depends on the hydronium concentration in the eluent while the elution of divalent ions is greatly influenced by the type and concentration of organic acid counter ion. The use of an EDTA–nitric acid eluent on the PBDMA-coated silica column is also reported [10]. Monovalent cations are reportedly separated through an ion-exchange mechanism while divalent cations are reportedly separated through the formation of coordination complexes with the eluent and stationary phase.

This paper focuses on the applications of PBDMA-coated silica stationary phase using non-complexing mineral acid eluents, such as hydrochloric acid and nitric acid. Contrary to previous work with this type of column, the separation appears to take place by ion-exchange mechanisms only, with no contribution from complexation mechanisms. The column's compatibility with mineral acid eluents allows it's use on both single-column and suppressor-based IC systems.

EXPERIMENTAL

Instrumentation

SCIC was performed on an Alltech modular ion chromatography system (Alltech, Deerfield, IL, USA) which consists of a Model 325 metal-free pump, Model 320 conductivity detector, Model 330 column heater and Model 9125 Rheodyne injection valve (Rheodyne, Cotati, CA, USA). The temperature of the column heater and the detector cell were maintained at 35°C. For suppressor-based IC, a Dionex BioLC System (Dionex, Sunnyvale, CA, USA) was used. A cation micromembrane suppressor (Model CMMS-11, Dionex) was used to suppress the background conductance of the eluent. All the data were recorded with a Model SP 4400 Chromjet integrator (Spectra Physics, Santa Clara, CA, USA).

Columns

Two types of carboxylic-acid based ion-exchange columns were used in this work. PBDMA coated on silica (Alltech universal cation column, 100 mm × 4.6 mm I.D.) was used to investigate retention mechanisms with a stationary phase capable of forming coordination complexes with divalent cations. A second column packed with a methacrylate-based mono-functional carboxylic acid ion-exchange material (Alltech HEMA CM, 10 μm, 150 mm × 4.6 mm I.D.) was used to investigate the separation of magnesium and calcium on a non-chelating stationary phase. A cation scavenger column (30 mm × 4.6 mm I.D.) (Alltech), packed with a high capacity sulfonic acid cation-exchange material, was connected between the pump and the injector. The scavenger column is needed only when mineral acid eluents are used. Traces of transition metals from the eluent will irreversibly retain on the analytical column causing deactivation of the column. The symptom can be identified as a decrease in retention time as the column exchange sites are tied up by the strongly bound ions. The scavenger column traps the transition metals from entering the analytical column.

Reagents

All eluents were prepared from 99.99% pure chemicals (Aldrich, Milwaukee, WI, USA) and deionized (18 mΩ) water. A Barnstead Nanopure 11 system (Sybron Barnstead, Boston, MA, USA) was used to produce the water used for eluent and sample preparation. A stock solution of 100 m*M* hydrochloric acid was prepared by diluting 99.99% hydrochloric acid in deionized water. This solution was diluted with deionized water to make 5 m*M* hydrochloric acid eluent. The 3 m*M* nitric acid eluent was prepared by diluting 99.99% nitric acid with deionized water. The suppressor regenerant (50 m*M* tetrabutyl ammonium hydroxide [TBAOH]) was prepared by diluting a 55% aqueous solution of TBAOH (Sachem, Austin, TX, USA) with deionized water. The eluents and the regenerant were prepared daily and filtered through a 0.45-μm nylon filter (Alltech).

Sample preparation

All samples except coffee and soil extracts were diluted 10 times with deionized water before injection. The coffee and the soil extracts were filtered through a 0.2-μm Anotop IC syringe filter (Alltech) before injection.

RESULTS AND DISCUSSION

Conventional cation chromatography using sulfonic acid cation-exchange columns requires either two separate conditions or addition of diamino propionic acid to mineral acid eluent for the analysis of mono/divalent cations. A low capacity cation-exchange column along with a dilute acid eluent containing hydrogen (hydronium) ions is used for the separation of monovalent cations and an eluent containing a divalent cation such as ethylenediamine or *m*-phenylenediamine, is used for the separation of divalent cations. An eluent containing hydrochloric acid and diamino propionic acid has been found successful to separate both groups of cations in one run using these columns [4].

The cation-exchange stationary phase, made of PBDMA-coated silica, is capable of achieving the simultaneous, isocratic separation of lithium, sodium, ammonium, potassium, rubidium, magnesium, calcium and barium [2]. The eluents used for the separation are citric acid, tartaric acid, phthalic acid, salicylic acid, 1-hydroxyisobutyric acid, pyridine-2,6-dicarboxylic acid, oxalic acid and ethylene diamine tetraacetic acid, all of which are capable of forming coordination complexes with divalent cations. The monovalent cations are reportedly separated by IC mechanism while the divalent cations are reportedly separated by ion exchange and the formation of coordination complexes with the maleic acid stationary phase and the organic acid eluent.

In this report we will show the separation of mono/divalent cations using mineral acid eluents such as nitric and hydrochloric acid. Because the anionic counter ions of these mineral acids do not form coordination complexes with the divalent cations in this study, we believe the separation is based only on ion-exchange. Complexing eluents are not required. The compatibility of this column with mineral acid eluents opens the possibility of using the column with suppressor-based IC.

Separation by SCIC

Nitric acid eluent. The column performance with

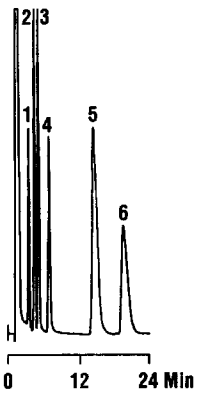

Fig. 1. Simultaneous SCIC separation of mono/divalent cations using 3 m*M* nitric acid. Flow-rate: 1.0 ml/min; column: Alltech universal cation (100 mm × 4.6 mm I.D.); detector: conductivity (negative polarity), 1.0 μS full scale; injection volume: 100 μl. Peak identification: 1 = lithium (0.2 μg/ml), 2 = sodium (1.5 μg/ml), 3 = ammonium (1.5 μg/ml), 4 = potassium (2.5 μg/ml), 5 = magnesium (2 μg/ml), 6 = calcium (2 μg/ml).

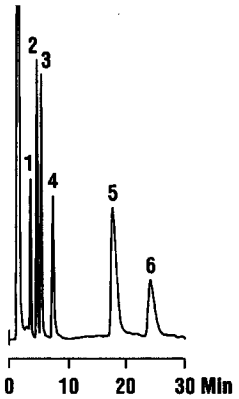

Fig. 2. Simultaneous SCIC separation of mono/divalent cations using 5 m*M* hydrochloric acid. Flow-rate: 1.0 ml/min; column: Alltech universal cation (100 mm × 4.6 mm I.D.); detector: conductivity (negative polarity), 1.0 μS full scale; injection volume: 100 μl. Peak identification: 1 = lithium (0.2 μg/ml), 2 = sodium (1.5 μg/ml), 3 = ammonium (1.5 μg/ml), 4 = potassium (2.5 μg/ml), 5 = magnesium (2 μg/ml), 6 = calcium (2 μg/ml).

nitric acid eluent and SCIC is demonstrated in Fig. 1. Nitric acid is the most common eluent used for the monovalent cation analysis by SCIC when sulfonic acid cation-exchange columns are used. However, the separation of divalent cations on these columns is not possible with this eluent due to the strong affinity of the divalent cations towards the sulfonic acid functional groups. By using a carboxylate-functionalized PBDMA-coated silica column, both groups of cations can be separated isocratically with nitric acid eluents.

Hydrochloric acid eluent. Fig. 2 shows the separation of lithium, sodium, ammonium, potassium, magnesium and calcium on a silica based PBDMA stationary phase using 5 m*M* hydrochloric acid eluent by SCIC. The separation of mono/divalent cations including rubidium and barium are shown in Fig. 3. The sensitivity for monovalent rubidium and divalent barium are quite good. The separation of ethanolamines using PBDMA-coated silica is shown in Fig. 4. Chromatograms of some real world samples are shown in Fig. 5A–C.

In SCIC, indirect conductivity is used for cation analysis. The equivalent conductance of the sample cations are lower than the equivalent conductance of the hydronium ion in the eluent, hence the sample ions are detected as a decrease in conductance. This decrease in conductance is proportional to the concentration of the sample solute cations. The peaks appear positive in the figures by reversing the polarity of the detector.

Separation by suppressor-based IC

Hydrochloric acid is the most common eluent used for monovalent cation analysis by suppressor-

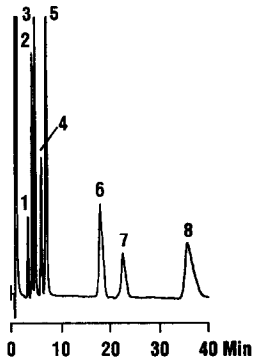

Fig. 3. Simultaneous SCIC separation of mono/divalent cations including rubidium and barium using hydrochloric acid. Chromatographic conditions as in Fig. 2. Peak identification: 1 = lithium (0.2 μg/ml), 2 = sodium (1.5 μg/ml), 3 = ammonium (1.5 μg/ml), 4 = potassium (2.5 μg/ml), 5 = rubidium (2 μg/ml), 6 = magnesium (2 μg/ml), 7 = calcium (2 μg/ml), 8 = barium (5 μg/ml).

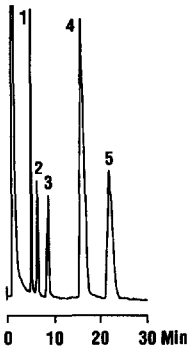

Fig. 4. SCIC separation of ethanolamines using hydrochloric acid. Chromatographic conditions as in Fig. 2. Peak identification: 1 = monoethanolamine, 2 = diethanolamine, 3 = triethanolamine, 4 = magnesium, 5 = calcium.

based IC. However, this eluent is not capable of eluting the divalent cations when conventional sulfonic acid cation-exchange columns are used. With

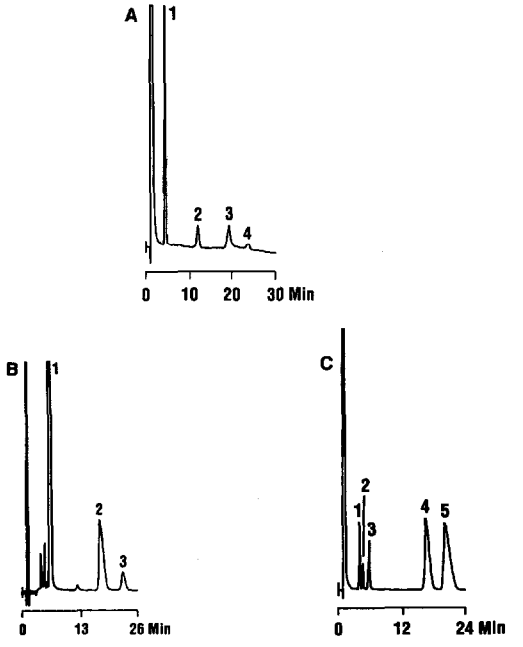

Fig. 5. Cation separations using hydrochloric acid eluent by SCIC. Chromatographic conditions are as in Fig. 2. (A) L-Carnitine and choline in vitamins. Peak identification: 1 = sodium, 2 = L-carnitine, 3 = choline, 4 = calcium. (B) Cations in coffee extract. Peak identification: 1 = potassium, 2 = magnesium, 3 = calcium. (C) Cations in soil extract. Peak identification: 1 = sodium, 2 = ammonium, 3 = potassium, 4 = magnesium, 5 = calcium.

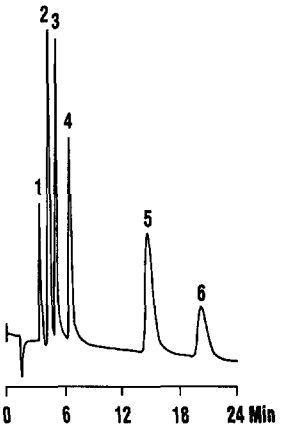

Fig. 6. Simultaneous separation of mono- and divalent cations by suppressor-based IC. Eluent: 5 m*M* hydrochloric acid; flow-rate: 1.0 ml/min; column: Alltech (100 mm × 4.6 mm I.D.); detector: suppressed conductivity, 1.0 μS full scale; injection volume: 100 μl; regenerant: 50 m*M* TBAOH; flow-rate: 7 ml/min. Peak identification: 1 = lithium (0.2 μg/ml), 2 = sodium (1.5 μg/ml), 3 = ammonium (1.5 μg/ml), 4 = potassium (2.5 μg/ml), 5 = magnesium (2 μg/ml), 6 = calcium (2 μg/ml).

the PBDMA-coated silica stationary phase, hydrochloric acid eluent is able to separate both mono- and divalent cations in one isocratic run.

The separation of mono/divalent cations on PBDMA-coated silica column using a suppressor-based IC system is shown in Fig. 6. The suppressor-based cation IC system consists of a suppressible eluent, a column that is capable of separating the cations, a micromembrane suppressor in the hydroxide form and a regenerant solution to regenerate the suppressor. The cation micromembrane suppressor is used to suppress the background conductivity and to enhance the sensitivity of the analytes. 5 m*M* hydrochloric acid is used as the eluent and 50 m*M* TBAOH is used for regenerating the suppressor. When the hydrochloric acid eluent passes through the suppressor, chloride in the eluent is exchanged with hydroxide which reacts with hydronium ions to form water. Conversion of eluent to water reduces background conductivity to near zero. The sample ions are converted to corresponding aqueous hydroxide salt solutions which have much higher conductance than the suppressed eluent; hence they are detected as positive peaks.

Analysis of some real samples such as tap water, well water, lemonade and cola using suppressor-

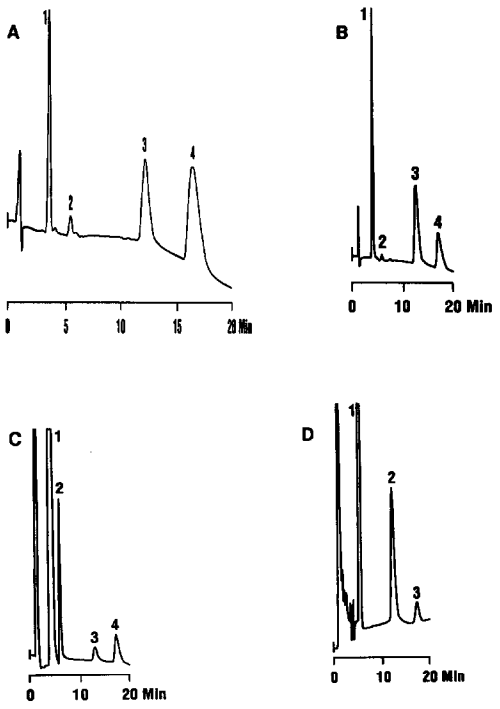

Fig. 7. Cation separations using hydrochloric acid eluent by suppressor-based IC. Chromatographic conditions as in Fig. 6. (A) Cations in tap water. Peak identification: 1 = sodium, 2 = potassium, 3 = magnesium, 4 = calcium. (B) Cations in well water. Peak identification: 1 = sodium, 2 = potassium, 3 = magnesium, 4 = calcium. (C) Cations in lemonade. Peak identification: 1 = sodium, 2 = potassium, 3 = magnesium, 4 = calcium. (D) Cations in cola. Peak identification: 1 = potassium, 2 = magnesium, 3 = calcium.

based IC are shown in Fig. 7A–D respectively. No chromatographic interferences were observed and filtering the samples was not necessary.

The background conductance on the suppressor-based system was not stable from day to day. This problem could be due to the quality of the regenerant and the deionized water used for the eluent preparation. The background conductance of the eluent was greatly influenced by the flow-rate of the regenerant through the micromembrane suppressor and the concentration of the regenerant solution. If the flow-rate and the concentration are too low suppression will not be quantitative and background conductance will increase. However, if the flow-rate or concentration is too high permeation of the regenerant solution through the micromembrane may occur [11]. A concentration of 50 m*M* TBAOH solution, at a flow-rate of 7 ml/min was adequate for the work presented here.

Detection limits and detection linearity of cations by SCIC and suppressor-based IC

The detection limits (calculated as a signal-to-noise ratio of 3) obtained for mono/divalent cations using both types of IC systems (hydrochloric acid eluent) based on a 100-μl injection volume are listed in Table I. SCIC gave slightly better detection limits; however, both types of IC are capable of separating and detecting cations at a very low concentration levels. The higher detection limits for cations for SCIC can be explained by the greater change in conductance for SCIC than for the suppressor-based IC [1]. For example, the equivalent conductance for eluent is $H^+ + Cl^- = 350 + 76 = 426$ and for sample peak is $Li^+ + Cl^- = 39 + 76 = 115$, a net signal of 311. In suppressor-based IC, hydroxide is the counter ion that accompanies the cations. Based on an equivalent concentration, the lithium peak will have an equivalent conductance of 237 ($Li^+ + OH^- = 39 + 198$). A net signal of 237 is observed against water, with equivalent conductance near zero. The higher signal observed in SCIC is partially offset by increased noise associated with high-conductivity of the mineral acid eluent. Close linear dependence between the peak area and the concentration of the ions over a wide range of concentrations are observed for both SCIC and suppressor-based IC.

TABLE I

DETECTION LIMITS (ng/ml) FOR MONO/DIVALENT CATIONS USING SCIC AND SUPPRESSOR-BASED IC

Column: universal cation (100 mm × 4.6 mm I.D.).

Cations	SCIC (HCl eluent)	Suppressor-based IC (HCl eluent)
Lithium	1	3
Sodium	2	3
Ammonium	3	4
Potassium	8	8
Magnesium	4	7
Calcium	3	9

When inorganic acid eluents are used, traces of transition metals from the eluent may irreversibly retain on the analytical column causing column deactivation. The symptom can be identified by a gradual decrease in retention time with each run. In order to protect the colum from deactivation, a cation scavenger column packed with a high capacity sulfonic acid cation-exchange material was connected between the pump and the injector. This column traps traces of transition metals in the eluent before they reach the separator column. Column deactivation due to transition metals in the eluent does not occur when complexing eluents are used. Complexing eluents interact with the metals and elute them from the column. This is one advantage of using complexing eluents for cation analysis on this stationary phase.

Separation mechanisms on PBDMA stationary phase

Earlier studies on PBDMA stationary phases report that the separation of divalent cations on this column using complexing eluents are based on both ion-exchange and complex formation with the stationary phase and eluent anions. Monovalent cations are reportedly separated by ion exchange.

The data presented in this report shows that complexation between the divalent cations and the eluent anion is not necessary to elute divalent cations from the column. The separation of divalent cations using nitric and hydrochloric acid is an example for this. We believe that ion-exchange retention mechanisms coupled with the high selectivity of the hydronium ions towards the carboxylate group provides the significant driving force for the separation [12]. The ion-exchange selectivity for carboxylic acid ion exchangers is significantly different than for sulfonic acid ion exchangers traditionally employed for cation analysis. More specifically, hydronium ions have very high affinity for carboxylic acid ion exchangers, even exceeding the affinity of divalent magnesium and calcium. By contrast, hydronium ions are only weekly attracted to sulfonic acid ion-exchange groups with far less affinity for the support than the divalent cations. The order of selectivity of the analyte cations is identical on both carboxylic and sulfonic acid stationary phases. The high ion-exchange affinity of hydronium ions for the PBDMA stationary phase allows elution of divalent cations from this type of column using dilute acid eluents. Complexation with eluent anions is not necessary. Elution of divalent cations from sulfonic acid ion-exchange columns by dilute acid eluents is not possible due to the low selectivity of hydronium ions with this support.

The successful use of mineral acid eluents demonstrates conclusively that complex formation with eluent anions is not necessary to elute divalent cations from PBDMA stationary phases. However, it does not address the question of whether formation of coordination complexes between divalent cations and the PBDMA stationary phase is necessary for retention of divalent cations on PBDMA columns. Because the maleic acid functional group on the PBDMA polymer can act as both an ion exchanger and a metal chelator, ion exchange and/or chelation may be responsible for retention of those cations capable of forming complexes with maleic acid. Ion exchange alone must be responsible for retention of the alkali metal cations and ammonium because these cations do not form complexes with maleic acid.

A second type of carboxylate-based ion-exchange column (HEMA CM, 150 mm × 4.6 mm I.D.) was used to investigate the importance of chelation as a retention mechanism for divalent cations. The HEMA packing material consists of highly crosslinked hydroxyethylmethacrylate particles functionalized with carboxymethyl (CM) ion-exchange groups. Unlike the maleic acid ion-exchange groups on the PBDMA support, the carboxymethyl ion-exchange groups on the HEMA support will not form stable metal complexes with calcium or magnesium. As demonstrated in Fig. 8, calcium and magnesium are retained and well resolved on the HEMA CM column using dilute hydrochloric acid as the eluent. Consequently, retention of magnesium and calcium on the HEMA CM column must be due to ion exchange alone. While this result does not rule out the possibility that coordination complexes are formed between divalent cations and the PBDMA stationary phase, it does demonstrate that formation of such complexes is not critical to the separation.

We believe the above data strongly suggests that the separation of alkali and alkaline earth cations on PBDMA stationary phases takes place predominantly, if not entirely, by ion-exchange mecha-

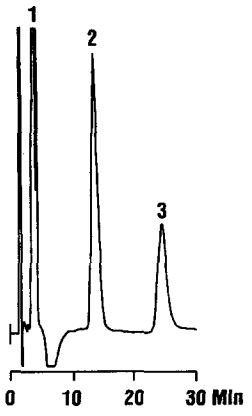

Fig. 8. Analysis of cations on HEMA CM stationary phase. Eluent: 2 m*M* hydrochloric acid; flow-rate: 1 ml/min; column: HEMA CM 10 μm (150 mm × 4.6 mm I.D.); detector: conductivity (negative polarity), 1.0 μS full scale; injection volume: 100 μl. Peak identification: 1 = monovalent cations, 2 = magnesium, 3 = calcium.

nisms, fueled by the high selectivity of hydronium ions for the carboxylic acid functional groups.

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