Separation of calcium and magnesium ions by ion chromatography with a HEMA–EDMA column

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Abstract. Properties of HEMA–EDMA weak cation exchange sorbent for ion chromatography are discussed. The column prepared was used for experiments with calcium and magnesium ions in single column ion chromatography. The ion chromatographic method was used for measuring the stability constants of complexes of Ca and Mg cations with the binary mixture of tartaric and pyridine-2,6-dicarboxylic acids. A retention model for binary mixtures is proposed to choose and predict the retention times for Ca and Mg ions in single ion chromatography. The stability constants calculated were tabulated for Ca and Mg complexes.

Key words: ion chromatography, HEMA–EDMA column, calcium ions, magnesium ions.

INTRODUCTION

Different types of poly(styrene–*c*o-divinylbenzene) and methacrylate sorbents were used to prepare strong or weak ion exchange resins [1–4]. Recently a poly-vinyl alcohol packing material (5-μm YS-506D) containing carboxyl ion exchange groups was developed for cation analysis [5]. This column (dimensions 150 mm × 6.0 mm) provides a good separation for the ammonium and sodium ions and ensures a good peak shape for the doubly charged calcium and magnesium ions. A 2-hydroxyethyl methacrylate/ethylene dimethacrylate (HEMA–EDMA) type of macroporous material (Separon HEMA), supplied by TESSEK Ltd., was used by various surface modification reactions using the 2-hydroxyethyl moieties on the HEMA particle surfaces as the reactive groups yielding strong anion or cation exchange resins with a capacity of 0.8–2.0 mmol/g [6].

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Calcium and magnesium cations were separated using different eluents based on mineral or organic acids. Lin & Horvath [7] investigated the divalent metal ion stability constants for tartrate complexes and proposed the use of a mixture of 0.2 mM tartaric acid and 0.2 mM ethylenediamine at pH 4.5. Several suppressed and nonsuppressed ion chromatographic methods in which hydrochloric acid and diaminopropionic acid, 18 mM sulphuric acid, and hydrochloric acid and ethylenediamine mixtures are used are recommended by Dionex Corporation (USA). Kolla et al. [8] proposed a polymer coated silica carboxylic cationite compatible with hydrochloric, oxalic, tartaric, and phtalic acid eluents. 2,6-Pyridinedicarboxylic acid can be used as an eluent for UV and conductivity detection of inorganic anions, magnesium, and calcium in natural water [9].

The heavy metals are accumulated in the column when eluents based on mineral acids are used. Special ion-exchange sample treatment is therefore required and a regeneration procedure with complexing eluents can restore the column performance. Eluents based on oxalic acid give a good sensitivity, but are limited in the linear dynamic range because of limited solubility of calcium oxalate.

EXPERIMENTAL

Reagents and procedures

The underivatized HEMA 1000 10 μm was purchased from TESSEK Ltd. Calcium nitrate tetrahydrate, magnesium nitrate hexahydrate, sulphuric acid, oxalic acid, sodium hydrogen carbonate, and potassium permanganate were of analytical grade from Reakhim, Russia. Tartaric acid, 2,6-pyridinedicarboxylic acid (PDCA) from Aldrich and deionized water (Purite HP) were used to prepare the eluent and Ca and Mg salts solutions. The eluent pH was adjusted to 2.5.

Instrumentation

The ultrasonic bath used was from Decon Laboratories Ltd. (UK). The block heater for sorbent synthesis was from Wealtec Corporation (USA). IC experimental work was done with an ion chromatograph equipped with IJD-1 conductivity detector, pump, and column thermostat with manual injector 50 μL (Inkrom, Estonia) and Kromex32 (Akrom-EX Inc., Estonia) data acquisition software. Samples were injected onto a 150×3 mm i.d. column packed with prepared sorbent based on a weak cation exchanger.

RESULTS AND DISCUSSION

Preparation of the ion exchange column

The reaction mixture was prepared from 0.01 M acidic potassium permanganate solution and preweighed (2–3 g) Separon HEMA 1000 sorbent. The mixture was

placed in an ultraconic bath and sonicated for 5 min to obtain a homogenic degassed solution. The resultant slurry was then heated up to 70 °C for 4 h in a block heater with regulated temperature and timer control. Then the sorbent was washed with 100 mL deionized water and with 100 mL 0.1 M solution of oxalic acid followed by 100 mL deionized water to remove the reaction products. The slurry packed column ion exchange capacity was measured converting the column to the sodium form using 0.01 M sodium hydrogen carbonate. The 0.01 M tartrate eluent was used for displacing sodium ions and the sodium amount found in the effluent was used to calculate the column ion exchange capacity. The average measured ion exchange capacity was 0.08 mM/g.

Measurement and calculation of the PDCA stability constants of calcium and magnesium ions

The calculation of the metal complex stability constant is based on the following equation:

$$\frac{1}{k'} = \frac{1}{\Phi D} + \left(\frac{1}{\Phi D}\sum_{i=0}^{n}(\beta_i f_{Li})\right)C_{Li},\qquad(1)$$

where k' is the capacity factor, $\Phi = V_{r}/V_{s}$ is the phase ratio of resin and mobile phase volumes in the column, $D = [M_{r}]/[M_{s}]$ is the equilibrium constant, β_i is the stability constant of the metal complex, f_{Li} is fraction of ionized eluent weak acid (ligand I), C_{Li} is the total concentration of weak acid in the eluent.

If the eluent contains several ligands the additive model can be used. Thus some of the stability constants must be known to calculate the unknown stability constants. It was also assumed that the eluting cation concentration should be kept the same, adjusting the eluent pH and concentration.

If 1–4 mM PDCA and 6 mM tartaric acid eluent are used (Fig. 1), the following relationship must be considered:

$$\frac{1}{k'} = \frac{\{1 + (\beta_{MHDP}^{HDP}[DPA]f_{HDP}) + (\beta_{MHT}^{HT}[T]f_{HT}) + (\beta_{MT}^{T}[T]f_{T})\}}{\Phi D},\qquad(2)$$

where β_{MHDP}^{HDP}, β_{MHT}^{HT}, and β_{MT}^{T} are the stability constants of PDCA and tartaric acid; f_{HDP}, f_{HT}, and f_{T} are the fractions of the respective weak acid ligand, which at constant pH value can be calculated using the PDCA (pK$_1$ = 2.16; pK$_2$ = 4.76) and tartaric acid ionization constants [10–11].

The average ionic strength in the chromatographic experiments was 10 mM. The stability constants of Ca and Mg tartaric acids ($\log\beta_{MgT}^{T} = 1.91$; $\log\beta_{CaT}^{T} = 2.17$; $\log\beta_{MgHT}^{HT} = 0.92$; $\log\beta_{CaHT}^{HT} = 1.11$) measured at $I = 0.09$ M and $I = 0.2$ M, respectively, were corrected by the Debye–Hückel equation [12].

The experimental and thermodynamic stability constants calculated are listed in Table 1.
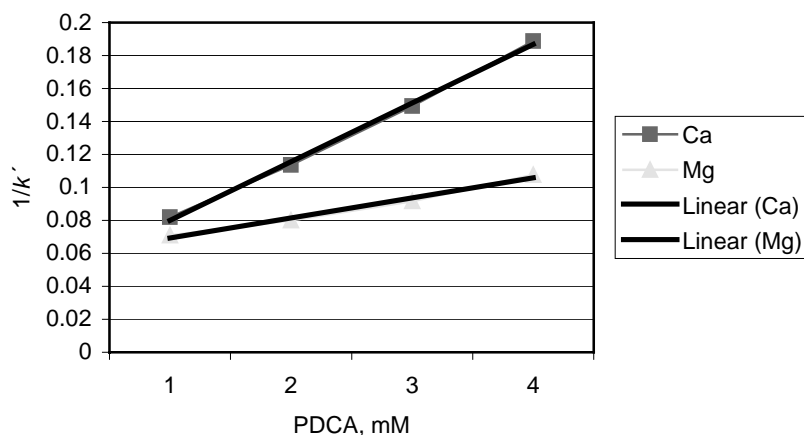
Fig. 1. Reciprocal value of k' versus PDCA concentration in the mobile phase. Eluent 6 mM tartaric acid + PDCA, flow rate 1 mL/min, pH 2.5, $t = 37\,°C$.

Table 1. Stability constants of alkali metal PDCA complexes, $t = 37\,°C$

Metal ion	$\log \beta_{MHDP}^{0.01}$	$\log \beta_{MHDP}^{T}$
Ca	1.67 ± 0.12	1.86 ± 0.12
Mg	2.35 ± 0.30	2.54 ± 0.30

CONCLUSIONS

A HEMA–EDMA sorbent for ion chromatography was prepared and used to evaluate the complexation constants of alkali metal ions (Ca, Mg) measuring the retention factors for binary PDCA and tartrate eluent mixtures. The method enables to predict the retention times of ions. The stability constants are tabulated at different ionic strengths.

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REFERENCES

1. Small, H., Stevens, T. S. & Bauman, W. C. Novel ion exchange chromatographic method using conductimetric detection. *Anal. Chem.*, 1975, **47**, 1801–1809.
2. Gjerde, D. T. & Fritz, J. S. *Ion Chromatography*, 3rd ed. Wiley-VCH, Weinheim, 2000.
3. Haddad, P. R. Ion chromatography retrospective. *Anal. Chem.*, 2001, **73**, 266a–273a.
4. Sarzanini, C. Recent developments in ion chromatography. *J. Chromatogr. A*, 2002, **956**, 3–13.

5. Majors, R. E. New chromatography columns and accessories at the 2005 Pittcon Conference, Part I. *Mar 1*, 2005. LCGC North America.

6. *TESSEK Product Catalog*. TESSEK Ltd., Prague (http://www.tessek.com/cat4.htm).

7. Hung-Jye Lin, F. & Horvath, C. Measurement of stability constants for complexes of divalent cations with tartaric acid by ion chromatography. *J. Chromatogr.*, 1992, **589**, 185–195.

8. Kolla, P., Köhler, J. & Schomburg, G. Polymer-coated cation-exchange stationary phases on the basis of silica. *Chromatographia*, 1987, **23**(7), 465–472.

9. Chen, Z. L. & Adams, M. A. 2,6-Pyridinecarboxylic acid as an eluent for UV and conductivity detection of inorganic anions, magnesium and calcium in water by ion chromatography. *Chromatographia*, 1999, **49**, 496–502.

10. *Handbook of Chemistry and Physics*, 75th ed., 1913/1995, p. 851.

11. Martell, A. & Smith, R. M. *Critical Stability Constants*, Vol. 6. Plenum Press, 1989.

12. Alumaa, P. & Pentchuk, J. Ionic strength dependence of heavy metal tartrate complex stabilities. *Chromatographia*, 1998, **47**, 77–80.

Kaltsiumi ja magneesiumi ioonide ioonkromatograafiline lahutamine, kasutades HEMA-EDMA kolonni

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On sünteesitud ja uuritud HEMA-EDMA nõrga kationiidi ioonkromatograafilisi omadusi. Saadud kolonni on kasutatud kaltsiumi ja magneesiumi ioonide stabiilsuskonstantide mõõtmiseks binaarsetes viinhappe- ja püridiin-2,6-dikarboksüülhappesegudes. Saadud retentsioonimudelit on võimalik kasutada kaltsiumi ja magneesiumi retentsiooni leidmiseks ioonkromatograafias. Leitud termodünaamiliste stabiilsuskonstantide väärtused on ära toodud.