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Separation of cations using methacrylate-based low-capacity cation exchangers

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ABSTRACT

The possibility of using macroporous methacrylate-based low-capacity ion exchangers in the separation of cations of alkali, alkaline earth, transition and heavy metals was tested. The separation conditions were optimized with respect to the composition of the eluent (content of ethylenediamine, tartaric acid, organic solvent and pH). The retentions of cations on methacrylate ion exchangers were compared with those on derivatives of styrene–divinylbenzene and silica gel. The detection limits obtained using the usual apparatus and method were $2.5 \cdot 10^{-8}$ g.

INTRODUCTION

The determination of cations is not the most significant field of application of ion chromatography (IC), but it has received considerable attention recently. Benson[1] filled short columns with cross-linked polystyrene selectively sulphonated to a low exchange capacity (on the usual ion exchangers the ions are retained too strongly) and separated cations of alkali metals. These cations were separated on a methacrylate cation exchanger also without suppressed conductivity detection[2]. The ammonium cation, which has properties differing from those of alkali metals, can be separated by using eluents with an admixture of organic solvents[3]. The possibility of using organic solvents appears to be a special feature of the discussed columns compared with the Dionex type.

More than one solution has been proposed for the separation of alkaline earth and transition metals. In addition to the classical separation with a strongly acidic cation exchanger[4], complex-forming sorbents or eluents are also employed in the process. A sorbent containing phosphonic groups[5] or an anion exchanger converted into the EDTA form[6] can also be used. In these instances the concentration of exchange groups of the ion exchanger can be higher[3] (up to 0.4 mmol/g).

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A different approach leading to a more universal method utilizes a complex-forming eluent. The complex-forming agents improve the selectivity of separation and the shape of the peaks[7]. Also, for the separation of transition and heavy metals complex-forming eluents such as ethylenediamine[8,9], tartaric acid[8], citric acid[10], oxalid acid[10] or lactic acid[11,12] are recommended. The sensitivity is reported to be as high as 0.1 ppb if peak detection by the suppressed conductivity detection technique is used[13].

In addition to conductivity detection, in particular for transsition metals, other methods are also applied, *e.g*, UV detection after reaction with 4-(2-pyridylazo)-resorcinol (PAR)[14].

This study is concerned with the chromatographic properties of macroporous methacrylate copolymers possessing sulphopropyl groups for the separation of alkaline earth and transition metals.

EXPERIMENTAL

Materials

The sorbent for ion chromatography was prepared by a consecutive chemical transformation of the copolymer (glycidylmethacrylate–ethylenedimethacrylate) (40 wt.-% of the cross-linking agent) obtained by radical suspension copolymerization[15]. Glycidyl groups of the copolymer, particle size 17–25 μm, were hydrolysed and subsequently modified by reaction with propane sultone[2,16]. The properties of the sorbents used are summarized in Table I.

Chromatography

Chromatographic measurements were carried out using a Cvet 306 liquid chromatograph (Khimavtomatika, Moscow, U.S.S.R.) with conductivity (alkali metals) and UV (transition and heavy metals) detection; a solution of the post-column reagent (0.001% PAR + 0.5% ammonia, pH 12.5) was added to the eluate by means of an extra pump. If not stated otherwise, a mixture of ethylenediamine and tartaric acid with the pH adjusted by the addition of 0.1 mol/l of acid or base was used as the eluent. The standard mixture contained $5 \cdot 10^{-4}$ mol/l of cations.

TABLE I

PROPERTIES OF MACROPOROUS METHACRYLATE LOW-CAPACITY IONEXCHANGERS

Exchanger	*Agent/sorbent ratio*	*Conversion (mol.-%)*	*Particle size (μm)*	*Content of groups (mmol/g)*	
				Elemental analysis	*Chromatography*
A	0.31	17.6	19–25	0.42	0.1
B	0.083	71.5	17–20	0.13	0.02
C	0.36	53.2	19–25	0.11	0.02

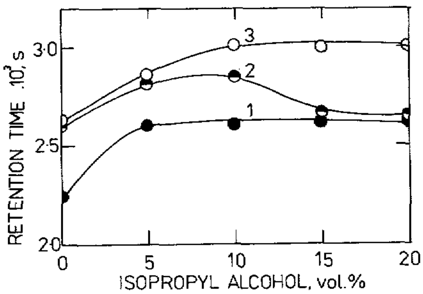
RESULTS

In previous studies[2,3], we demonstrated some possible separations of alkali metals ions and of the ammonium cation on macroporous methacrylate copolymers containing sulphopropyl groups, and the effects of acetone, ethanol and methanol in the eluent. It has been found that methanol can be replaced with isopropanol, which influences the retention of ammonium in a manner different to that of sodium or potassium (Fig. 1). The optimum concentration of isopropanol is 10 vol.-% in 2 mmol/l nitric acid when mixtures of monovalent cations are to be separated within 15 min.

Our methacrylate cation exchanger also makes possible the separation of alkaline earth metals and of transition and heavy metals (Fig. 2). For this purpose, it was necessary to optimize the composition of ethylenediamine and tartaric acid mixtures. The optimization consisted of experimental evaluations of the effects of the ethylenediamine and acetone concentrations in the eluent. The effect of eluent pH was also studied.

At an ethylenediamine concentration below 1 mmol/l the retention times are disproportionately long (Table II); the duration of analysis at a concentration of 2 mmol/l ethylenediamine in the eluate seems to be acceptable. The elution time also increases with increasing pH (Table III), pH 4 being the optimum value.

Similarly to alkali metals, with transition metals an increase in the concentration of the organic solvent (acetone) also increases the retention time; 20 vol.-% of acetone makes the retention time twice as long compared with the use of a reference eluent without the organic solvent. Such long retention times are not advantageous from the practical point of view.



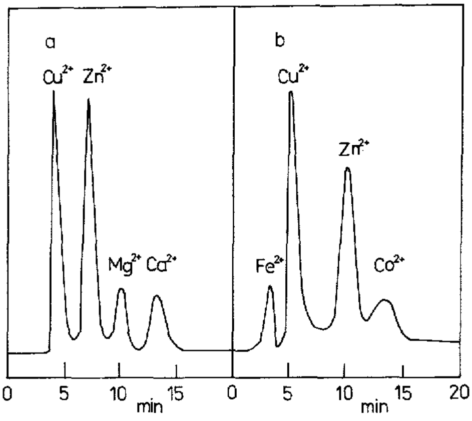


Fig. 1. Dependence of the retention of cations on sample C (0.11 mmol sulpho groups/g) on the content of isopropyl alcohol in 1 mmol/l HNO_3. Conditions: Column, 10 × 0.4 cm I.D.; eluent flow-rate, 1 ml/min. 1 = Na^+; 2 = NH_4^+; 3 = K^+.

Fig. 2. (a) Chromatogram of the separation of alkaline earth and transition metal cations. Conditions: column, 10 × 0.6 cm I.D.; methacrylate cation exchanger (0.11 mmol sulpho groups/g); eluent, 2 mmol/l tartaric acid–2 mmol/g ethylenediamine (pH 4); flow-rate, 1.5 ml/min. (b) Chromatogram of the separation of heavy metal and transition metal cations. Conditions as in (a) except methacrylate cation exchanger (0.42 mmol sulpho groups/g).

TABLE II

EFFECT OF THE ETHYLENEDIAMINE CONCENTRATION ON THE RETENTION TIMES (s) OF TRANSITION METALS

Conditions: Column, 20 × 0.6 cm I.D.; sorbent B (Table I); eluent, 2 mmol/l tartaric acid (pH 4); flow-rate, 2 ml/min.

Cation	*Ethylenediamine concentration (mmol/l)*		
	2	*1*	*0.5*
Cu	310	332	1200
Zn	492	655	1860
Co	587	862	2160

Table IV compares the retention values of alkaline earth metals and transition metals on five cation exchangers for ion chromatography, prepared on the basis of silica gel, styrene–divinylbenzene and glycidylmethacrylate copolymer with different contents of sulphonic groups. The methacrylate copolymers give longer retention times than the ion exchangers based on silica gel and styrene–divinylbenzene copolymer, but they can reliably separate all the cations studies, in particular Mg^{2+} and Ca^{2+}. The time needed for separation varies between 12 and 16 min. The longer retention time can be explained by additional interactions between the cation and further polar groups of the sorbent, *e.g.*, hydroxyl groups. The retention time of cations on methacrylate ion exchangers is proportional to the acidic group content, as follows from Tables I and IV. The efficiency of methacrylate columns, shown as the number of theoretical plates in Table V, is lower than that of the columns in Table IV because of the larger particle size of methacrylate sorbents.

The detection limits (three times the noise) vary between 10^{-4} and 10^{-5} mol/l for concentrations between 10^{-6} and $0.25 \cdot 10^{-7}$ g for the amounts injected. The best and poorest detection limits are observed for Zn^{2+} ($1.5 \cdot 10^{-6}$ mol/l) and Fe^{3+} (10^{-4} mol/l), respectively.

TABLE III

EFFECT OF pH OF THE ELUENT ON THE SEPARATION OF TRANSITION METAL AND ALKALINE EARTH METAL CATIONS

Conditions: Column, 20 × 0.6 cm I.D.; sorbent A (Table I); eluent, 2 mmol/l tartaric acid–2 mmol/l ethylenediamine; flow-rate, 1.5 ml/min.

Cation	*Retention time (s)*		
	pH 4.0	*pH 4.6*	*pH 5.3*
Cu	247	270	255
Zn	420	480	405
Ni	465	495	465
Co	510	600	525
Mg	525	660	645
Ca	705	870	840

TABLE IV

RETENTION TIMES (s) OF TRANSITION METALS ON DIFFERENT SORBENTS

Conditions: Column, 10 × 0.6 cm I.D.; eluent 2 mmol/l tartaric acid–2 mmol/l ethylenediamine (pH 4); flow-rate, 1.5 ml/min.

Cation	*Silica gel*		*Methacrylates*[b]		*Styrene–divinylbenzene IREA*[a]
	Diasorb	*INEOC*[a]	*A*	*B*	
Cu	255	225	225	240	90
Zn	540	225	405	510	142.5
Mg	735	300	570	735	165
Ca	885	300	735	1050	225

[a] Made in U.S.S.R.

[b] See Table I.

TABLE V

SELECTIVITY AND EFFICIENCY OF METHACRYLATE COLUMNS

Conditions[a]	*Cation*	t_R,s	k'[b]	α[c]	R_s[d]	N[e]	
						per column	*per m*
I	Fe	255	4.67			94.4	944
	Cu	300	5.67	1.21	1.45	177	1777
	Zn	480	9.67	1.71	1.67	181	1815
	Co	630	13.00	1.34	1.08	348	3484
	Mn	780	16.33	1.26	1.08	536	5363
II	Cu	255	4.67			94	944
	Zn	465	9.33	2.00	1.88	440	2402
	Mg	630	13.00	1.39	1.37	441	4410
	Ca	840	17.67	1.36	1.40	348	3480

[a] Conditions I: column, 10 × 0.6 cm I.D.; sorbent A (Table I), particle size 19–25 μm; eluent, 2 mmol/l tartaric acid–2 mmol/l ethylenediamine (pH 4); flow-rate, 1.5 ml/min; t_0 = 45 s. Conditions II: column, eluent, flow-rate and t_0 as for I; sorbent C (Table I), particle size 19–25 μm.

[b] Capacity factor $k' = (t_R - t_0)/t_0$.

[c] Selectivity $\alpha = k'_2/k'_1$.

[d] Resolution $R_s = 2(t_{R2} - t_{R1})/(\Delta t_{R2} + \Delta t_{R1})$.

[e] Theoretical plates $N = 16\,(t_R/\Delta t)^2$.

DISCUSSION

Bivalent alkaline earth metal cations and bivalent or trivalent transition and heavy metals are bound by the ion exchanger much more strongly than cations of alkali metals. Their elution from the column requires mineral acids at high concentrations. In practice, two types of eluent components are used in the chromatographic analysis of cations: first diacidic ammonium compounds such as ethylenediamine or phenylenediamine and second di- and tribasic carboxylic acids, such as oxalic, tartaric, lactic and hydroxylactic acid. The di- and tribasic acids form complex compounds with the metals.

The in exchange equation with ethylenediamine as the eluent has the form

$$2\ M^{z+}R_z + z\ E^{2+} \rightleftharpoons z\ E^{2+}R_2 + 2\ M^{z+} \tag{1}$$

where E^{2+} is ethylenediamine, M^{z+} is the metal cation, z is the charge of the metal cation and R is the number of exchange groups of the ion exchanger with the respect to the cation.

The selectivity coefficient is given by[17]

$$K_m^E = \frac{[E^{2+}R_2]^z\ [M^{z+}]^2}{[E^{2+}]^z\ [M^{z+}R_z]^2} \tag{2}$$

At a low metal content in the sample, a condition which is usually met in chromatographic analysis, $[c/2] = [E^{2+}R_2]$ (where c is group content in the ion exchanger) and the capacity of the ion exchanger is then given by $K = [M^{z+}R_z]/[M^{z+}]$. Hence,for the selectivity coefficient we obtain

$$K_m^E = [c/2]^2/[E^{2+}][K] \tag{3}$$

By substituting the retention time of the cation being eluted, $t_R = K\ t_{R_0}$, we obtain

$$K_m^E = \frac{[c/2]^z\ t_{R_0}^2}{[E^{2+}]^z\ t_R} \tag{4}$$

After rearrangement,

$$\log t_R = (z/2) \log (c/2) + \log t_{R_0} - z \log [E^{2+}] - (1/2) \log K_m^E \tag{5}$$

For a cation charge $z = 2$, we have

$$\log t_R = A - \log [E^{2+}] \tag{6}$$

The agreement between the theoretical value ($z = 1$) of the slopes and the experimental values given in Table II suggests an ionic mechanism for separations of cobalt, zinc and copper.

The mechanism of interactions of hydroxy acids with metals is determined by their ability to form complexes of neutral or anionic character. This type of interaction decreases the effective charge of the metal cation and hence also its retention time.

The term $[M^{z+}]$ in eqn. 2 can be replaced with $[M']\alpha_M$, where $[M']$ is the total concentration of both[18] the free and bound metal complex in solution and α_M is that part of metal in solution which is present in the form of free cations. The equation for $\log t_R$ then becomes

$$\log t_R = (z/2) \log \alpha_M + (z/2) \log (c/2) + \log t_{R_0} - (z/2) \log [E^{2+}] - \\ - (1/2) \log K_M^E \tag{7}$$

where α_M is given by the concentration of the complex-forming agent and by the stability constant of the corresponding complex.

Addition of the complex-forming agent to the eluent not only reduces the retention time but also increases the selectivity of separation. For closely eluting metals bearing a charge of the same magnitude (Cu^{2+}, Zn^{2+}, Pb^{2+}, Ni^{2+}, Co^{2+}), the distribution coefficient without the use of complexing acids (D_B = constand/[A], where [A] is concentration of ions of the eluent) differs only slightly. In such a case the separation is given by the ratio of the distribution coefficients of the two metals, D_B/D_C, and does not depend on the eluent concentration.

If complexation becomes part of the separation mechanism, it is possible to observe larger variations in retention behaviour. These variations are mainly caused by the large differences in the values of the equilibrium constants for complex formation. The separations including complex formation can be described by

$$\frac{D_{MB}}{D_{MC}} = \frac{D_B}{D_C} \cdot \frac{K_{compl.B}}{K_{compl.C}} \tag{8}$$

where K_{compl} is the constant of complex formation. At $D_B/D_C \approx 1$, $D_{MB}/D_{MC} \neq 1$.

Experimentally, it was found that the separation depends on the pH of eluent (Table III). In a more acidic medium the retention times are longer and the separation becomes poorer. Clearly, with increasing pH the complex-forming ability of hydroxy acids increases, which in the sense mentioned above leads to shorter retention times and to better separations.

The complex formation may be described by the equation

$$M^{z+} + F'^{u-} \rightleftharpoons MF'^{z-u} \tag{9}$$

where z and u are the charges of the metal cation M and hydroxy acid F′, respectively, [F] is the total concentration of hydroxy acid in all forms in which metal is not bound.

The effective constant of complex formation is given by

$$K_{MF}^{eff} = \frac{[MF]}{[M]\,[F']} = \frac{K_{MF}}{\alpha_H^F} \tag{10}$$

where K_{MF} is the constant of complex formation.

K_{MF} is independent of pH, being a constant of the reaction

$$M^{z+} + F^{s-} \rightleftharpoons MF^{z-s} \tag{11}$$

Here, [F] is the total concentration and α_H^F is the distribution coeffient of hydroxy acid which occurs in variously protonated forms:

$$\alpha_H^F = 1 + [H]\,K_{HF} + [H^2]\,K_{HF}\,K_{H^2F} + \dots \tag{12}$$

The logarithms of the constants K_{HF} and $K_{\mathrm{H^2F}}$ are identical with the pK values of the corresponding acids (pK_1^{F} = log K_{HF}; pK_2^{F} = log $K_{\mathrm{H^2F}}$):

$$\log K_{\mathrm{MF}}^{\mathrm{eff}} = \log K_{\mathrm{MF}} - \log \alpha_{\mathrm{H}}^{\mathrm{F}} \tag{13}$$

With increasing pH, the effective constant of complex formation, $K_{\mathrm{M}}^{\mathrm{eff}}$, approaches K_{MF}, *i.e.*, the stability of the complex increases. These conclusions are of general validity for both cations and anions[19,20].

The results show that cation exchangers based on methacrylate macroporous resins can be applied for separations of complicated mixtures of alkaline earth cations and transition metals.

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