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## ION CHROMATOGRAPHY ON METHACRYLATE ION EXCHANGERS

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### SUMMARY

The preparation and properties of ion chromatography sorbents based on glycidyl methacrylate–ethylene dimethacrylate macroporous copolymers are described. Anion exchangers were suitable for the separation of inorganic anions and possessed a high selectivity towards the  $\text{NO}_3^-$  anion. Alkaline metal cations and  $\text{NH}_4^+$  were separated under the conditions of non-suppressed ion chromatography. In general, the addition of organic compounds (methanol, ethanol and acetone) increased the retention of cations in the column.

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### INTRODUCTION

At present, ion chromatography is carried out with modified silica and sorbents based on macroporous styrene–divinylbenzene copolymers<sup>1</sup>. Strongly acidic sulpho groups or strongly basic trimethylammonium groups are used as the exchange groups<sup>2</sup>. These groups are introduced into the polymer by a consecutive chemical transformation<sup>3</sup>, by splitting off or blocking (poisoning) of the excess exchange groups<sup>4</sup> and also of dynamically or statically coated polyelectrolytes present at low concentrations on the polymer matrix<sup>5–7</sup>. Ion exchangers based on methacrylate copolymers were prepared containing sulphonate and trimethylammonium groups and possessing sufficient hydrolytic stability, which can undergo more than 100 exchange cycles without any essential decrease in their exchange capacity<sup>8,9</sup>. A more common strongly basic group bonded to the methacrylate matrix is triethylammonium. The ion exchangers used in ion chromatography have a very low exchange-site concentration<sup>1, 2</sup> 3 orders of magnitude lower than those employed in ion exchange or ion-exchange chromatography. The concentration of ion-exchange groups in most exchangers is 1 mmol/g and higher, which may perhaps be used in suppression columns, but not in ion chromatography.

As far as we know, ion exchangers based on methacrylates have not yet been employed in ion chromatography. We therefore thought it worthwhile to examine the behaviour of modified methacrylate copolymers in ion chromatography.

TABLE I  
 PROPERTIES OF MACROPOROUS METHACRYLATE ION EXCHANGERS FOR ION CHROMATOGRAPHY

Ion exchange <sup>a</sup>	Sample No.	Ratio between agent and sorbent (mmol/g)	Conversion (%)	Solvent	Particle size ( $\mu\text{m}$ )	Exchange-site concentration		Chromatographically
						Elemental analysis	Titrimetrically	
Anion exchangers, P-N(CH <sub>3</sub> ) <sub>3</sub> <sup>+</sup>	1	20.120	—	None	19–25	2.26	1.51	—
	2	1.007	—	Water	19–25	1.33	0.94	—
	3	0.250	—	Diethyl ether	17–20	0.15	Undeterminable	0.02
	4	0.013	—	Diethyl ether	19–35	0.07	Undeterminable	0.007
Cation exchangers, P-SO <sub>3</sub> <sup>-</sup>	5	2.000	5.48	—	19–25	0.75	—	—
	6	0.312	17.6	—	19–25	0.42	—	0.1
	7	0.083	71.5	—	17–20	0.13	—	0.02
	8	0.036	53.2	—	19–35	0.11	—	0.02

<sup>a</sup> P- denotes polymeric matrix.



where  $c_0$  is the exchange-site concentration (mmol/g),  $z_i$  is the ion charge,  $c_1$  is the concentration of the elution agent (mol/l),  $K_i$  is the equilibrium constant of the ion exchange ( $K_{\text{Na-H}} = 1.2$ ,  $K_{\text{Cl-OH}} = 4.32$ ) and the adsorption coefficient  $H_i$  (ml/g) is defined by

$$H_i = \frac{(t - t_0)u}{w_i} \quad (2)$$

where  $t$  is the elution time (min),  $t_0$  is the elution dead time (min),  $u$  is the flow-rate of the eluent (ml/min) and  $w_i$  is the weighed amount of the ion exchanger in the column.

Using the ion exchangers thus prepared, columns 15 cm (or 10 cm) long and with I.D. 3.3 or 6 mm were filled by employing the slurry technique in a stream of distilled water under a pressure of up to 20 MPa. The anion exchangers were converted into the  $\text{OH}^-$  form with 0.5 mol/l potassium hydroxide solution, the cation exchangers were converted into the  $\text{H}^+$  form with 0.1 mol/l nitric acid, and both were washed with distilled water, until the conductivity of the eluate had fallen below 10  $\mu\text{S}$ .

The ion separation was investigated using a system consisting of an HPP 4001 high-pressure pump, a CDLC 1 conductimetric detector and a CI 100 computing integrator (Laboratory Instruments, Prague, Czechoslovakia). The samples were injected by means of an LCI 20 injection head using the stop-flow method, in a volume between 5 and 35  $\mu\text{l}$ . The standard mixture of anions contained 10 mg/l  $\text{F}^-$  and  $\text{Cl}^-$ , 50 mg/l  $\text{PO}_4^{3-}$  and  $\text{SO}_4^{2-}$ , 15 mg/l  $\text{NO}_2^-$  and 25 mg/l  $\text{NO}_3^-$ . A suppressor column containing a strong acid cation exchanger in the  $\text{H}^+$  form was placed behind the separation column.

The standard mixture of cations consisted of 25 mg/l  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$  and  $\text{NH}_4^+$ . The suppressor column was not needed in the separation of cations.

## RESULTS AND DISCUSSION

The anions were separated using macroporous methacrylate copolymers containing various amounts of trimethylammonium groups (Scheme 1) as given in Table I. High-capacity anion exchangers (2.8 and 1.3 mmol/g) can be used as packings of suppressor columns able to reduce the conductivity of the eluent (0.001 mol/l nitric acid) during the separation of cations from 700  $\mu\text{S}$  to less than 20  $\mu\text{S}$ . Anion exchangers with a lower exchange-site concentration (0.15 and 0.07 mmol/g) were suitable for use in the separation of anions ( $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{PO}_4^{3-}$ ,  $\text{NO}_2^-$ ,  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$ ). Fig. 1 shows the dependence of the retention of the particular anions on the concentration of sodium hydrogencarbonate in the eluent, *i.e.*, in a solution of sodium carbonate (2.4 mmol/l). The retentions of all anions decrease with increasing content of sodium hydrogencarbonate. The retention of sulphate varies most. Ions from the anion exchanger containing 0.07 mmol/g of groups are eluted with the solution of sodium hydrogencarbonate alone, although this solution has a lower eluting power than the solution containing sodium carbonate. The dependence of the retention of the individual anions on this anion exchanger is shown in Fig. 2. The largest decrease in retention, depending on the concentration of sodium hydrogencarbonate in the eluent, was observed with  $\text{SO}_4^{2-}$  and  $\text{PO}_4^{3-}$ , in accordance with their higher valency.

Fig. 3 shows chromatograms of the separation of a mixture of anions on anion

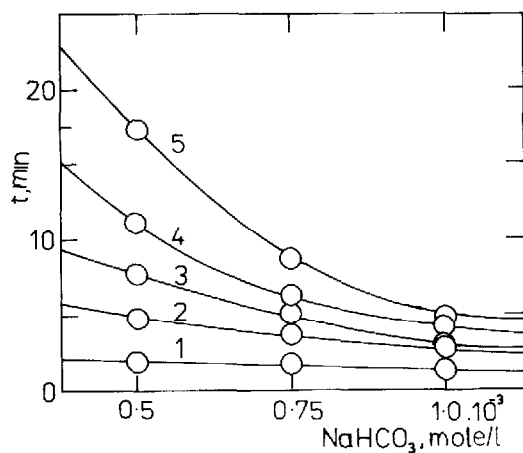


Fig. 1. Dependence of the retention of anions on the concentration of  $\text{NaHCO}_3$ . Column,  $10 \times 0.6$  cm I.D.; flow-rate of eluent, 2 ml/min; sorbent No. 4. 1,  $\text{F}^-$ ; 2,  $\text{Cl}^-$ ; 3,  $\text{PO}_4^{3-}$ ; 4,  $\text{NO}_2^-$ ; 5,  $\text{SO}_4^{2-}$ .

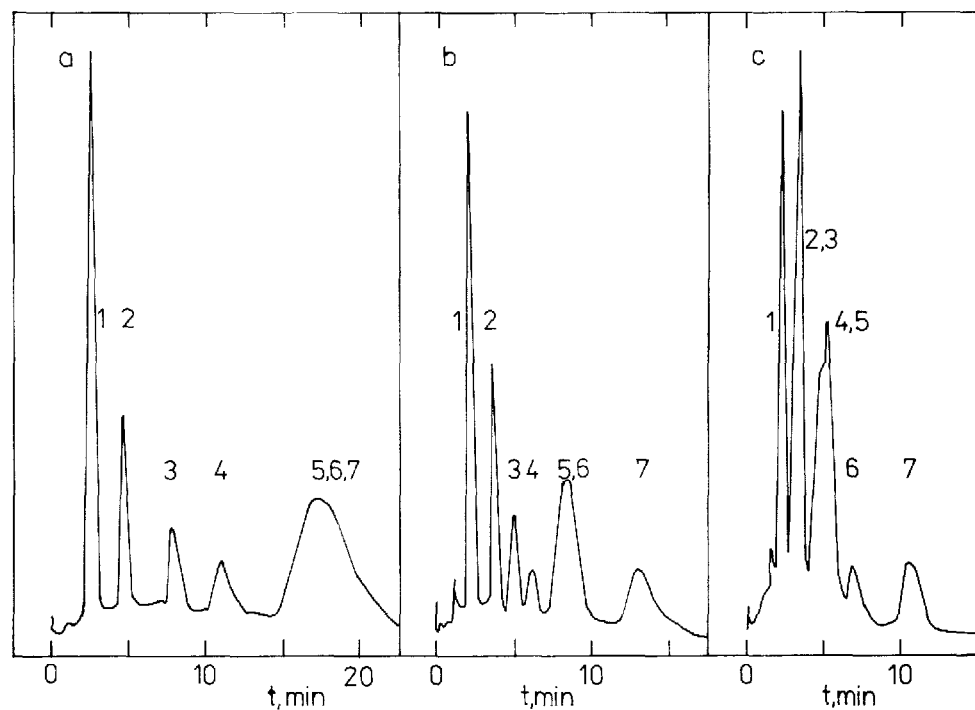


Fig. 2. Chromatogram of the separation of anions at various concentrations of  $\text{NaHCO}_3$  in the eluent. Column,  $10 \times 0.4$  cm I.D.; eluent, 2.4 mmol/l  $\text{Na}_2\text{CO}_3$ ; flow-rate, 2 ml/min; sorbent No. 4. Peaks: 1,  $\text{F}^-$ ; 2,  $\text{Cl}^-$ ; 3,  $\text{PO}_4^{3-}$ ; 4,  $\text{NO}_2^-$ ; 5,  $\text{SO}_4^{2-}$ ; 6,  $\text{Br}^-$ ; 7,  $\text{NO}_3^-$ .

TABLE II

## CHARACTERISTICS OF SEPARATION POWER OF METHACRYLATE ION EXCHANGERS

$n = 5.54 (l/\omega)^2$  plates/m, where  $l$  is the retention time and  $\omega$  is the peak width at half-height; HETP in mm;  $R_s = (t_2 - t_1)/(\omega_1 + \omega_2)$ , given here for adjacent peaks.

Ion	Anion exchanger and eluent <sup>a</sup>											
	No. 4, 0.0005 M NaHCO <sub>3</sub>			No. 4, 0.00075 M NaHCO <sub>3</sub>			No. 4, 0.001 M NaHCO <sub>3</sub>			No. 3, 0.0024 M Na <sub>2</sub> CO <sub>3</sub>		
	<i>n</i>	HETP	<i>R<sub>s</sub></i>	<i>n</i>	HETP	<i>R<sub>s</sub></i>	<i>n</i>	HETP	<i>R<sub>s</sub></i>	<i>n</i>	HETP	<i>R<sub>s</sub></i>
F <sup>-</sup>	1121	0.89	2.00	1385	0.72	1.25	1994	0.50	1.25	2164	0.46	4.08
Cl <sup>-</sup>	4002	0.25	2.33	3116	0.32	1.00	1737	0.57	2.00	4740	0.21	
PO <sub>4</sub> <sup>3-</sup>	3327	0.30	1.44	2463	0.40	1.00	—	—	0.08	—	—	
NO <sub>2</sub> <sup>-</sup>	4290	0.23	1.25	8656	0.11	1.25	556	1.80	0.67	4409	0.23	2.00
SO <sub>4</sub> <sup>2-</sup>	1140	0.88	—	1887	0.53	—	678	1.47	1.67	9245	0.11	1.56
Br <sup>-</sup>	—	—	—	—	—	—	4787	0.22	—	—	—	—
NO <sub>3</sub> <sup>-</sup>	—	—	—	4163	0.24	1.42	2714	0.37	—	—	—	—

Cation exchanger No. 8 and eluent <sup>b</sup>																	
HNO <sub>3</sub> (pH 2.5)						HNO <sub>3</sub> (pH 2.5)-CH <sub>3</sub> OH (2:1)						HNO <sub>3</sub> (pH 2.5)-CH <sub>3</sub> OH (1:1)					
<i>n</i>	HETP	<i>R<sub>s</sub></i>	<i>n</i>	HETP	<i>R<sub>s</sub></i>	<i>n</i>	HETP	<i>R<sub>s</sub></i>	<i>n</i>	HETP	<i>R<sub>s</sub></i>	<i>n</i>	HETP	<i>R<sub>s</sub></i>	<i>n</i>	HETP	<i>R<sub>s</sub></i>
Li <sup>+</sup>	2713	0.37	0.67	3693	0.27	1.74	7706	0.13	1.67	4743	0.21	3693	0.27	2.86	6051	0.16	2.86
Na <sup>+</sup>	2828	0.35	2.86	5771	0.17	2.19	4743	0.21	0.86	3693	0.27	6051	0.16	2.86	—	—	—
NH <sup>+</sup>	3693	0.27	0.69	4469	0.22	—	—	—	—	—	—	—	—	—	—	—	—
K <sup>+</sup>	3246	0.31	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—

<sup>a</sup> Column, 10 × 0.6 cm I.D.; flow-rate of eluent, 2 ml/min.

<sup>b</sup> Column, 15 × 0.4 cm I.D.; flow-rate of eluent, 2 ml/min.

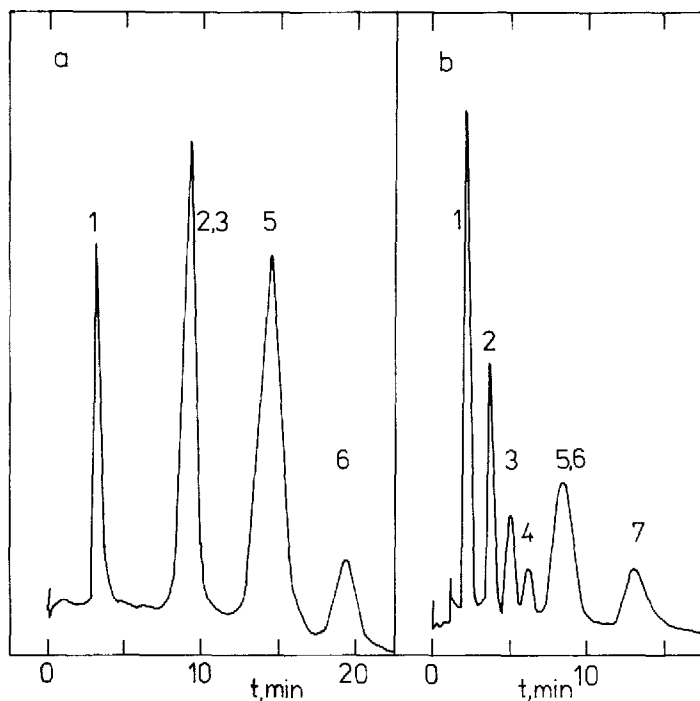


Fig. 3. Chromatogram of the separation of anions. (a) Sample No. 3 (exchange-site concentration 0.15 mmol/g); eluent, 2.4 mmol/l  $\text{Na}_2\text{CO}_3$ . (b) Sample No. 4 (exchange-site concentration 0.07 mmol/l); eluent, 0.75 mmol/l  $\text{NaHCO}_3$ . Other conditions and peaks as in Fig. 2.

exchangers having exchange-site concentrations 0.15 and 0.07 mmol/g. As can be seen (Fig. 3a), on the sorbent with the higher concentration of strongly basic groups the anions are retained longer than on that with the lower concentration. The anion  $\text{F}^-$  is separated better. On the sorbent with the lower exchange-site concentration (Fig. 3b) all anions, with the exception of  $\text{SO}_4^{2-}$  and  $\text{Br}^-$ , are separated within 13 min, with  $\text{NO}_3^-$  having the highest retention.

Table II shows the resolving powers  $R_s$ , defined by

$$R_s = \frac{t_2 - t_1}{\omega_2 + \omega_1} \quad (3)$$

where  $t_2$  and  $t_1$  are the retention times of ions eluted next to each other and  $\omega_1$  and  $\omega_2$  are their respective peak widths at half-height. The resolving power observed on methacrylate anion exchangers was higher than that with styrene-divinylbenzene<sup>1</sup>. Good stability of methacrylate anion exchangers was also confirmed under chromatographic conditions; the resolving power of the column remained virtually the same during 6 months of use.

The separation of cations by ion chromatography was carried out using macroporous methacrylate copolymers with the strongly acid groups (Scheme 2) bound to them. The procedure used in the synthesis allows the groups to be introduced

predominantly on the surface of globulus of the sorbent, thus accelerating the sorption and desorption process. The cation exchanger with the highest content of sulpho groups could be employed in the suppressor column in the separation of anions; the  $20 \times 0.6$  cm I.D. column decreases the conductivity of the eluent containing 2 mmol/l sodium hydrogencarbonate and 4 mmol/l sodium carbonate from 2000 to 35–40  $\mu$ S. The cation exchanger having an exchange-site concentration of 0.42 mmol/g, which cannot be used in the suppressor column, separates the individual cations but the retention values are too high.

In the separation of cations on the cation exchanger having an exchange-site concentration of 0.11 mmol/g (sorbent No.8) using nitric acid as the eluent, the cations were separated within 20 min in the order  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{NH}_4^+$  and  $\text{K}^+$  (Fig. 4).

Fig. 5 shows the effect of the addition of organic solvents (methanol, acetone and ethanol) to the eluent (nitric acid of pH 2.5). The addition of organic compounds generally increase the retention of cations in the column. Methanol at a concentration of 30–50 vol.-% increases the retention of  $\text{K}^+$  considerably, that of  $\text{Li}^+$  and  $\text{Na}^+$  less and that of  $\text{NH}_4^+$  only insignificantly. This can be explained by the lower dissociation of cations of alkali metal ions bound on the ion exchanger compared with the ammonium ion. A complete separation of these four cations was achieved within 20 min in with nitric acid (pH 2.5)–methanol (1:1) (Fig. 5). The separation of  $\text{NH}_4^+$  and  $\text{K}^+$  is characterized by a good resolving power ( $R_s = 2.9$ ). The column efficiency is 9000 theoretical plates per metre, which can be regarded as satisfactory with respect to the particle size used in the experimental arrangement (19–25  $\mu$ m).

The results show that owing to their easy modification with ionogenic groups

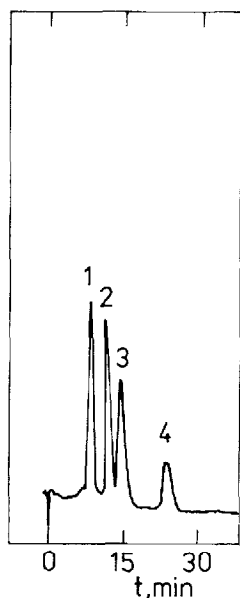


Fig. 4. Chromatograms of the separation of cations of alkali metals on sample No. 8 (exchange-site concentration 0.11 mmol/g). Column,  $15 \times 0.3$  cm I.D.; eluent,  $\text{HNO}_3$  (pH 2.5)–methanol (1:1); flow-rate, 1 ml/min. Peaks: 1,  $\text{Li}^+$ ; 2,  $\text{Na}^+$ ; 3,  $\text{NH}_4^+$ ; 4,  $\text{K}^+$ .



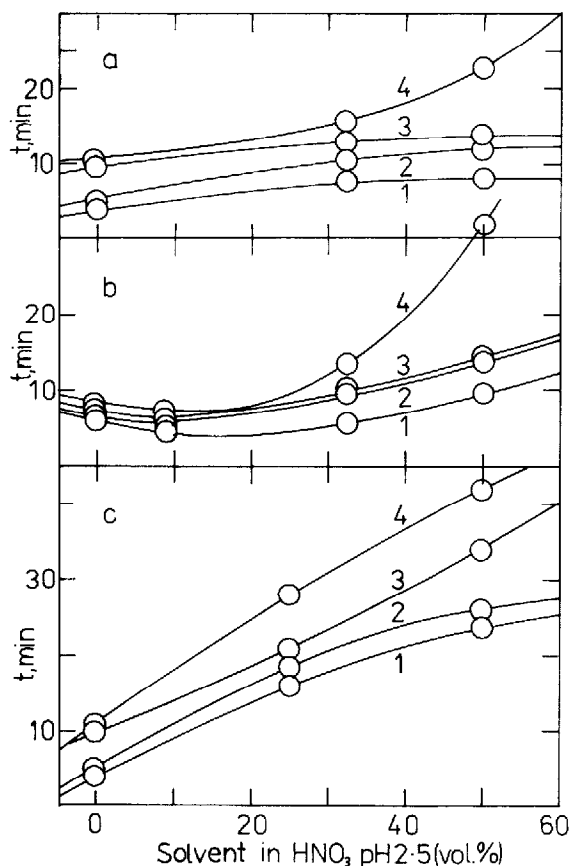


Fig. 5. Dependence of the retention of cations of sample No. 8 (exchange-site concentration 0.11 mmol/g) on the content of solvent in  $\text{HNO}_3$  (pH 2.5). Conditions and cations as in Fig. 4, except eluent: (a)  $\text{HNO}_3$  (pH 2.5)-methanol; (b)  $\text{HNO}_3$  (pH 2.5)-acetone; (c)  $\text{HNO}_3$  (pH 2.5)-ethanol.

and sufficient hydrolytic stability, glycidyl methacrylate matrices can be used as column packings in the ion chromatography of both cations and anions. This new hydrophilic type of matrix allows the selectivity of separation to be altered.

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