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Modified silica as a stationary phase for ion chromatography

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Abstract

The possibility of the rapid preparation of agglomerated anion exchangers was demonstrated on a reversed-phase silica support with the polymeric agents poly(*N*-ethyl-4-vinylpyridinium bromide), poly(dimethyldiallylammonium chloride), poly(hexamethyleneguanidinium hydrochloride) and 2,5-ionene as modifiers. A 90-min sorbent preparation and column packing allowed an efficiency of more than 10000 theoretical plates per metre to be obtained for 10- μ m spherical beads. The polymeric agents showed different selectivity, stability and capacity for the resulting anion exchangers (owing to changes in the structure and the density of functional groups in the polymer chain). The sorbents were used for the simultaneous determination of weakly and strongly retained anions and some heavy metals with EDTA solutions as eluent.

1. Introduction

Many packing materials are available for the separation of anions by ion chromatography (IC) and polymer-based and silica-based sorbents are very common [1]. Silica-based sorbents have the advantage of high mechanical strength and performance. However, eluents of high pH will damage the columns. Vydac IC 302 is one example of a surface-bonded silica packing [2].

Polymer-based materials are more popular for the suppressed ion chromatography of anions as they are stable in alkaline media. Surface-agglomerated resins were prepared by Small et al. [3] in which fine particles of anion-exchange latex are attracted to the superficial sulfonated beads of polymers.

A simple way to prepare anion exchangers for

IC is to coat commercially available reversed-phase material with quaternary ammonium salts [4,5]. Coated anion-exchange resins with various capacities have been produced by static and dynamic procedures.

The aim of this study was the production of new sorbents with different selectivities and to study the factors that influence selectivity. An attempt was made to prepare sorbents for anion IC using the interaction of polymeric anion exchangers with dynamically coated reversed-phase silica.

2. Experimental

A SIC-800 ion chromatograph (Biotronik, Maintal, Germany) with UV and conductivity detectors and a Shimadzu CR-3A integrator was

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used. The separation column used was made of stainless steel (100 × 3 mm I.D.).

The eluents were prepared by dissolving analytical-reagent grade potassium hydrogenphthalate or EDTA (or their mixtures) in deionized water and adjusting the pH value with potassium hydroxide. Stock standard solutions of inorganic anions and heavy metals were prepared from the salts and diluted to the desired concentrations. On-column and precolumn (with potassium hydrogenphthalate as eluent) formation of the metal–EDTA complexes was used.

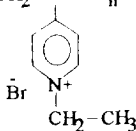
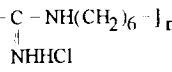
For sorbent preparation, the required amount of 10- μ m spherical Silasorb C₈ (Lachema, Brno, Czech Republic) was shaken with an excess of dodecylbenzenesulfonic acid (DBSA) solution (Johnson Matthey, Karlsruhe, Germany). Polymer solution (from the High-Molecular-Mass Compounds Division of Lomonosov Moscow State University) in deionized water was added

to modified Silasorb C₈ immediately after centrifugation and removal of excess DBSA. The columns were filled using common packing procedures and washed with the eluent for 60 min. The polymer structures are summarized in Table 1.

3. Results and discussion

Dynamically coated cation-exchangers with a low capacity (0.1–0.2 mmol/g) were obtained in the first stage of modification with DBSA. The final capacity of anion exchangers (Table 1) depends on the functional group density of the polymer chain. Thus, PEVP produced a higher capacity than Ionene, because PEVP has one quaternary ammonium group per two atoms in the chain and Ionene has two groups per nine atoms.

Table 1
Polymer structures and capacities of agglomerated anion exchangers

Polymer	Structure	Capacity (mmol/g)
Poly(N-ethyl-4-vinyl Pyridinium bromide) (PEVP)	$\left[-\text{CH}_2-\text{CH}- \right]_n$ 	0.032
Poly(dimethyldiallyl ammonium chloride) (PDMDA)	$\left[\begin{array}{c} \text{CH}-\text{CH}-\text{CH}_2 \\ \quad \\ \text{H}_2\text{C} \quad \text{CH}_2 \\ \diagdown \quad / \\ \text{N}^+ \\ / \quad \backslash \\ \text{CH}_3 \quad \text{CH}_3 \end{array} \right]_n \text{Cl}^-$	0.031
Poly(hexamethylene guanidinium hydrochloride)(PHMG)	$\left[-\text{NH}-\text{C}-\text{NH}(\text{CH}_2)_6- \right]_n$ 	0.012
2,5-Ionene (Ionene)	$\left[-\text{N}^+(\text{CH}_3)_2-(\text{CH}_2)_2-\text{N}^+(\text{CH}_3)_2-(\text{CH}_2)_5- \right]_n \text{Cl}^-$	0.010

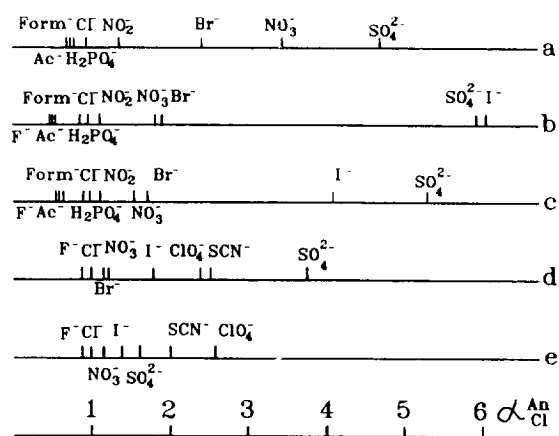


Fig. 1. Scales of selectivity for Silasorb C_8 (a) coated with CTMA and agglomerated with (b) PEVP, (c) PDMDAA, (d) PHMG, and (e) Ionene to some anions. α_{Cl}^{An} = Selectivity factor. Eluent, 1.0 mmol/l potassium hydrogenphthalate (pH 6.0).

The selectivities of the different exchangers were investigated using 1 mmol/l potassium hydrogenphthalate (pH 6.0), as the eluent. The retention times of several anions and the selectivity scales are shown in Table 1 and Fig. 1, respectively. The polymer-coated stationary phases are compared with Silasorb C_8 that was dynamically coated with cetyltrimethylammonium bromide (Silasorb C_8 -CTMA), which is

commonly used for coating reversed-phase silica in IC. The anion retentions decreased with decreasing column capacity, as shown by comparing Tables 1 and Table 2. The behaviour of anions, with the exception of SCN^- and ClO_4^- , does not depend on the type of polymer. It is interesting that an increase in the distance between the silica surface and the exchange layer leads to a decrease in the affinity to the N-containing anions (compare Fig. 1a and c). A linear relationship between $\log k'$ and $\log C_{e1}$ was observed for all packing materials and anions.

The simultaneous determination of strongly and weakly retained anions could be performed using Silasorb C_8 -PHMG and Silasorb C_8 -Ionene (Figs. 2 and 3). Strongly retained anions were not eluted from Silasorb C_8 -PEVP with 1 mmol/l potassium hydrogenphthalate (pH 6.0) as eluent. However, it was demonstrated that the concentration and pH of the mobile phase affected the separation of complex mixtures (Fig. 4).

The possibility of a decrease in capacity for this system should be taken into account. This decrease may be caused by two effects. The first is the desorption of DBSA. Thus, attempts to obtain reproducible results using Silasorb C_2 support were unsuccessful. A tenfold decrease in capacity was observed after 100 ml of the eluent

Table 2
Retention times of some anions on the agglomerated anion exchangers

Anion	Retention time (min)				
	Silasorb C_8 -CTMA	Silasorb C_8 -PEVP	Silasorb C_8 -PDMDAA	Silasorb C_8 -PHMG	Silasorb C_8 -Ionene ^a
F^-	–	0.81	0.93	0.59	0.78
Acetate	1.00	0.83	0.94	–	0.77
Formate	1.05	0.98	1.09	–	0.79
$H_2PO_4^-$	1.17	1.59	1.67	–	0.82
Cl	1.44	1.78	1.77	0.71	0.84
NO_2^-	2.20	2.05	1.84	–	0.86
NO_3^-	4.90	3.37	2.60	0.91	0.90
Br	3.60	3.49	3.01	0.81	0.92
I	–	10.97	7.50	1.25	1.18
SO_4^{2-}	7.05	10.87	9.60	2.65	1.34
SCN	>30	>30	>30	1.85	1.69
ClO_4^-	>30	>30	>30	1.75	2.18

Conditions: column, 100 × 3 mm I.D.; eluent, 1 mmol/l potassium hydrogenphthalate (pH 6.0); flow-rate, 1.5 ml/min; indirect UV detection ($\lambda = 260$ nm).

^aFlow-rate 1.0 ml/min.

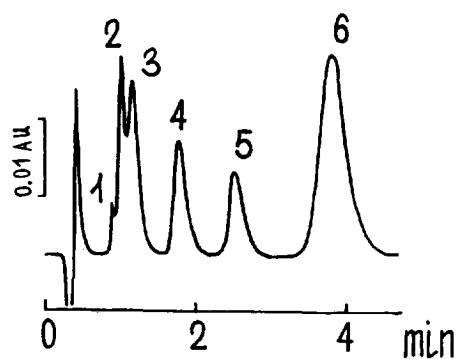


Fig. 2. Rapid separation of strongly and weakly retained anions. Column, Silasorb C_8 -PHMG; eluent, 1 mmol/l potassium hydrogenphthalate (pH 6.0); flow-rate, 1.0 ml/min; indirect UV detection ($\lambda = 260$ nm). Peaks: 1 = F^- ; 2 = Cl^- ; 3 = Br^- ; 4 = I^- ; 5 = ClO_4^- ; 6 = SO_4^{2-} .

(pH 4) had passed through the Silasorb C_2 -PEVP column. The second effect is the weak electrostatic attraction of the PHMG chain to the sulfonated surface, which led to a twofold decrease in the capacity of Silasorb C_8 matrix after 4 l of the eluent had passed through the column.

The highest stability was obtained for the Silasorb C_8 -PEVP system; the retention times and column efficiencies were constant during 2 months of continuous work. An efficiency of more than 10000 theoretical plates per metre was

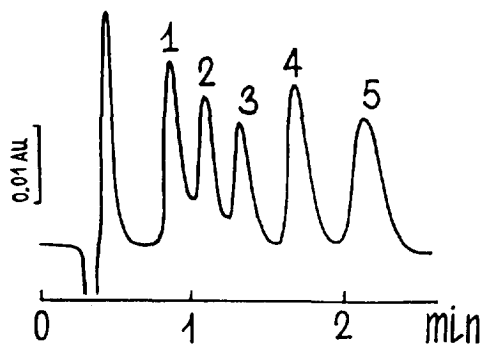


Fig. 3. Rapid separation of strongly and weakly retained anions. Column, Silasorb C_8 -Ionene; eluent, 1 mmol/l potassium hydrogenphthalate (pH 6.0); flow-rate, 1.0 ml/min; indirect UV detection ($\lambda = 260$ nm). Peaks: 1 = Cl^- ; 2 = I^- ; 3 = SO_4^{2-} ; 4 = SCN^- ; 5 = ClO_4^- .

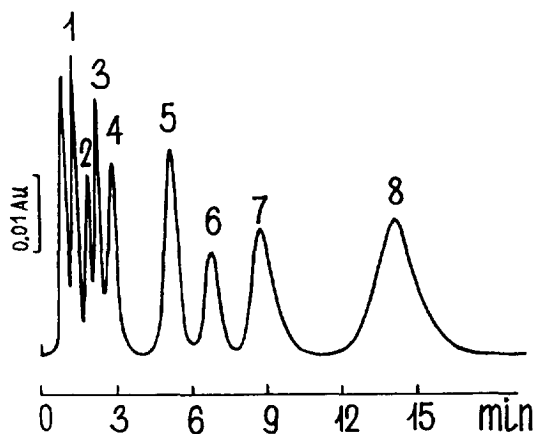


Fig. 4. Chromatographic separation of some anions. Column, Silasorb C_8 -Ionene; eluent, 2.6 mmol/l potassium hydrogenphthalate (pH 7.0); flow-rate, 1.3 ml/min; indirect UV detection ($\lambda = 260$ nm). Peaks: 1 = IO_3^- ; 2 = Cl^- ; 3 = $H_2PO_4^-$; 4 = NO_3^- ; 5 = SO_4^{2-} ; 6 = I^- ; 7 = SCN^- ; 8 = ClO_4^- .

observed for all the packing materials, with the exception of systems showing a large decrease in capacity (Silasorb C_2 -PEVP and Silasorb C_8 -PHMG).

Because of the good stability of the Silasorb C_8 -PEVP column, it was used for the simultaneous determination of inorganic anions and heavy metals. First, retention times of the anions and metal-EDTA complexes were obtained with potassium hydrogenphthalate-EDTA (pH 7) eluent (Fig. 5). Various detection parameters for UV detection ($\lambda = 210$ – 260 nm) or conductivity detection were used for peak identification. Indirect UV ($\lambda = 260$ nm) and direct UV ($\lambda = 210$ nm) or conductivity detection was used for the eluents with predominant potassium phthalate and EDTA, respectively. Thus, the addition of triply charged EDTA to the phthalate eluent led to a decrease in the retention for all of the analytes. The selectivity did not change for the equally charged anions. However, the retention of I^- and SCN^- increased with an EDTA-only eluent, which indicates that the phthalate anions are characterized by strong hydrophobic interactions with the sorbent. Figs. 6 and 7 illustrate the ability of the Silasorb C_8 -PEVP packing for the simultaneous determination of anions and heavy

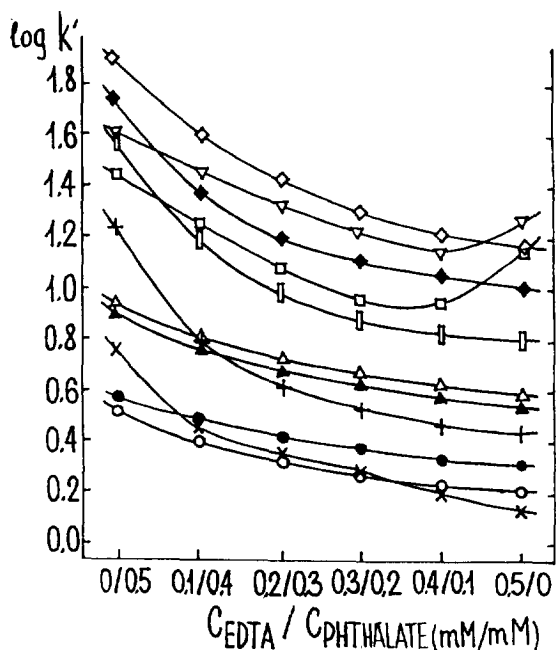


Fig. 5. Influence of the ratio of EDTA to potassium hydrogenphthalate concentration in the eluent (pH 7.0). Column, Silasorb C_8 -PEVP; UV and conductivity detection. \circ = Cl^- ; \bullet = NO_2^- ; \times = $H_2PO_4^-$; \triangle = Br^- ; \blacktriangle = NO_3^- ; $+$ = $Pb(II)$, $Mn(II)$; $=$ SO_4^{2-} , $Co(II)$, $Cd(II)$, $Zn(II)$; \blacklozenge = $Ni(II)$; \diamond = $Cu(II)$; \square = I^- ; ∇ = SCN^- .

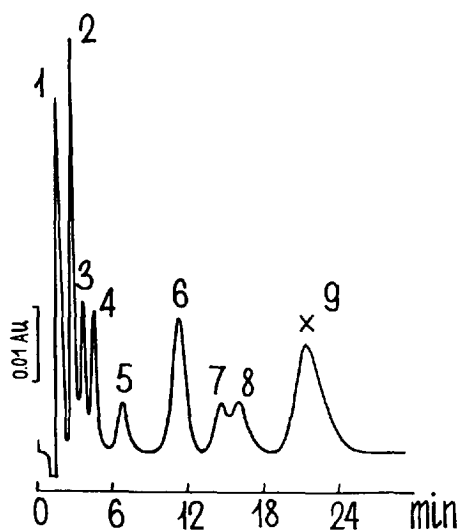


Fig. 6. Simultaneous IC of some anions and metal-EDTA complexes. Column, Silasorb C_8 -PEVP; eluent, 1.5 mmol/l potassium hydrogenphthalate (pH 6.9); flow-rate, 1.0 ml/min, indirect UV detection ($\lambda = 260$ nm). Peaks: 1 = acetate; 2 = Cl^- ; 3 = $H_2PO_4^-$; 4 = Br^- ; 5 = $Mn(II)$; 6 = SO_4^{2-} ; 7 = SCN^- ; 8 = $Ni(II)$; 9 = $Cu(II)$; \times = reversed negative signal.

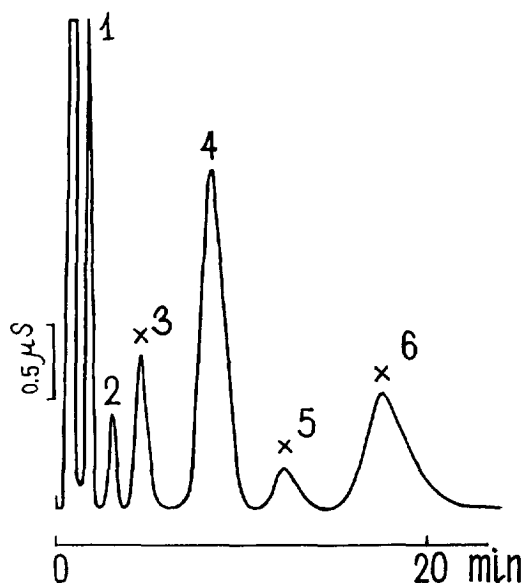


Fig. 7. Simultaneous IC of some anions and metal-EDTA complexes with EDTA as eluent. Column, Silasorb C_8 -PEVP; eluent, 0.2 mmol/l EDTA (pH 7.0); flow-rate, 0.75 ml/min; conductivity detection. Peaks: 1 = Cl^- ; 2 = NO_3^- ; 3 = $Mn(II)$; 4 = SO_4^{2-} ; 5 = $Ni(II)$; 6 = $Cu(II)$; \times = reversed negative signal.

metals. Fig. 5 also shows that the separation of $Pb(II)$ and $Mn(II)$ or SO_4^{2-} , $Co(II)$, $Cd(II)$ and $Zn(II)$ could not be achieved by changing the concentration of the eluent components in the range shown in Fig. 5. Moreover, it is possible to alter the selectivity of this sorbent for non-resolvable analytes, e.g., by simultaneously varying the pH and the eluent concentration of potassium hydrogenphthalate and EDTA (Fig. 8). Under these conditions the peaks of SO_4^{2-} , $Co(II)$, $Cd(II)$, and $Zn(II)$ are successfully resolved. Unfortunately, a complicated composition of the eluent leads to the formation of a system peak and changes in the direction of some peaks.

Acknowledgement

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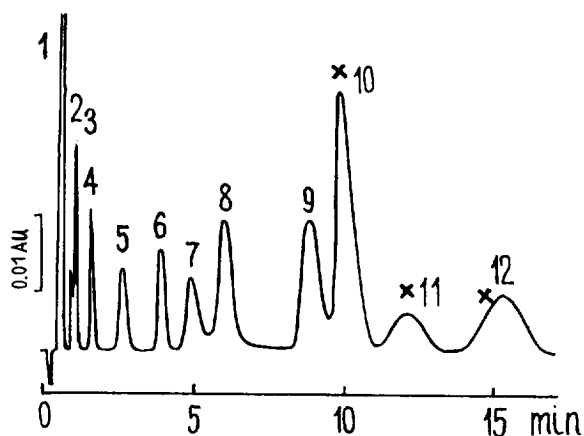


Fig. 8. Simultaneous IC of some anions and metal-EDTA complexes with potassium hydrogen phthalate-EDTA mixture as eluent. Column. Silasorb C_{18} -PEVP; eluent: 1.0 mmol/l potassium hydrogenphthalate-0.5 mmol/l EDTA (pH 6.0); flow-rate. 1.0 ml/min; indirect UV detection ($\lambda = 260$ nm). Peaks: 1 = acetate; 2 = Cl⁻; 3 = NO₂⁻; 4 = NO₃⁻; 5 = Mn(II); 6 = SO₄²⁻; 7 = Zn(II); 8 = Co(II); 9 = Cd(II); 10 = system peak; 11 = Ni(II); 12 = Cu(II); × = reversed negative signal.

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