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Sulfoacylated poly(styrene–divinylbenzene) copolymers as resins for cation chromatography

Comparison with sulfonated, dynamically coated and silica gel cation exchangers

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Abstract

Most important properties of an ion chromatographic resin are influenced by the resin matrix, the type of functional group and the ion-exchange capacity. Highly crosslinked PS–DVB resins of 5 μm diameter have been functionalized by sulfoacylation, by sulfonation and by dynamic coating over a wide range of exchange capacities. These materials allow a study of the influence of different ion-exchange sites and capacities. The influence of the degree of functionalization on resin performance is completely reverse for sulfoacylated and sulfonated resins. The HETP values for all observed analytes (Cu, Pb, Zn, Ni, Co, Cd, Mn, Ca, Mg) in a tartaric acid elution system decrease for sulfoacylated resins with increasing capacity, for sulfonated resins with decreasing capacity. The performance of sulfoacylated exchangers is better than for dynamically coated ones and far better than for sulfonated resins. The performance of silica gel based cation-exchangers such as BioSil CAT is in most cases better than observed for sulfoacylated resins. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Cation exchangers; Stationary phase, LC; Sulfoacylated poly(styrene–divinylbenzene) copolymers

1. Introduction

Ion chromatography has become a powerful, widely used analytical method enabling simple, selective and fast determination of a variety of inorganic and organic anions and cations [1–4].

In the present sense it comprises a combination of classical ion-exchange techniques with modern instrumentation and high-performing stationary phases.

However, for some sample categories the obtained resolution is not satisfying. Even if the resolution is sufficient, the separation can be optimized in order to shorten the run time. An example is the separation of multivalent metal cations on strong cation-exchangers [1–4]. The well performing silica gel type exchangers are not suitable for acidic or alkaline samples because of either loss of functional groups at low pH or complete dissolution at high pH [1–4]. Those separations are important in the field of ultra trace analysis with sophisticated techniques such as online coupling IC–ICP–(AES, MS) [5].

One possible way to optimize ion chromatographic

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separations such as the type described before is the development of new sorbents with better properties. Recently the characteristics i.e. selectivity, retention behavior, chemical and mechanical stability of a powerful new type of sulfoacylated PS–DVB cation-exchanger has been reported [6,7]. In this paper the influence of sorbent matrix, functional group character and specific capacity on column performance, i.e. HETP values, kinetic properties and non-specific interactions is compared to those of sulfonated and dynamically coated PS–DVB resins and commercially available silica based materials.

1.1. Theoretical considerations

An efficient separation of different ions can be achieved with a column of small height equivalent to a theoretical plate (HETP) values in addition to a large separation factor [8]. For a column packed with porous particles, the general plate height expression was described [9]:

$$H_g = 2\lambda d_p + \frac{2\delta D_m}{u} + \frac{k'}{1+k'} \frac{d_p^2}{D_{\text{eff}}} u + f(\theta, k') \frac{d_p^2}{D_m} u \quad (1)$$

where λ and δ are geometrical factors, D_m and D_{eff} are the diffusion coefficients of the solute in the mobile and the stationary phase respectively, k' is the retention factor, θ is the fraction of the mobile phase inside the pores, $f(\theta, k')$ is a mathematical function, u is the mobile phase linear velocity (cm/s).

In this study, the efficiencies of functionalized PS–DVB-resins were compared by investigating the dependence of the HETP on the functional group

structure and the specific resin capacity. For this purpose, three different types of cation-exchangers were generated from the same basic substrate.

2. Experimental

The properties of the PS–DVB polymer and the sulfoacylated sorbents made of it, as well as the instrumentation and chemicals were described in detail in [6,7] and summarized in Tables 1 and 2.

2.1. Sulfonation procedure

A portion of 20 ml of concentrated sulfuric acid 96% (w/w) and 0.1 g Ag_2SO_4 as the catalyst was placed in a 50-ml single neck flask and thermostated to the desired reaction temperature. After addition of 1 g of the PS–DVB polymer, the suspension turned brown. Coagulation of the polymer was eliminated by rigorous shaking of the flask. Then the reaction proceeded in a thermostated ultrasonic bath to prevent new coagulation. The reaction was stopped by pouring into 200 ml of cold 9 M sulfuric acid. The sulfonated polymer was filtered off and subsequently suspended in 3 M hydrochloric acid and then in ethanol. The final product was yellow–brown depending on reaction temperature and time and was packed into columns as described in [6].

2.2. Dynamic coating procedure

Dynamic coating of the polymer was performed by using the unfunctionalized polymer as reversed-phase packing and using dodecyl sulfate as ion pair reagent in the mobile phase at a concentration of

Table 1
Chromatographic conditions used for comparison of sulfonated, sulfoacylated and dynamically coated PS–DVB resins

Column	Vertex, Knauer, 100×4 mm stainless steel, packed with different sorbents, i.e. Table 2
Eluents	Tartaric acid 0.1–0.25 M, adjusted to pH 2.7–3.96 with NaOH
Flow rate	1 ml/min ⁻¹
Pressure	50–70 MPa/m
Detection	Photometry at 495 nm after post column derivatization with 1×10^{-4} M 4-(2-pyridylazo)-resorcinol (PAR), 0.25×10^{-4} M Zn-EDTA, 2 M NH_3
Injection	20 μl , by six port sampling valve
Sample	Mixture of standard-cations (Zn, Ni, Pb, Co, Cd, Mn, Ca, Mg), 2–60 mg/l

Table 2
Physical properties of the functionalized resins

Physical property	BioGel SEC 7	BioGel SEC 7	BioGel SEC 7	BioSil CAT
Type	PS–DVB	PS–DVB	PS–DVB	Silica
Functionalization	sulfonated	sulfopropionylated	coated with Dodecyl sulfate	silylated
Specific capacity	0.51 mmol/ml	0.54 mmol/ml	0.45 mmol/ml	0.55 mmol/ml
Particle Size	5 μm	5 μm	5 μm	5 μm
Crosslinkage	high	high	high	–
BET-surface	450 m^2/g	450 m^2/g	450 m^2/g	250 m^2/g
Pore volume	1.3 ml/g	1.3 ml/g	1.3 ml/g	0.65 ml/g
Mean pore diameter	7 nm	7 nm	7 nm	9 nm
Maximum pressure	20 MPa	20 MPa	20 MPa	80 MPa

0.002 *M*. In contrast to ion pair chromatography no organic modifier was added. The exchange capacity was measured for H^+ by a static method using the H^+/Na^+ exchange [10].

2.3. Data handling

The whole system control and the read-out of the detector were processed by a computer system. The capacity factors and HETP-values were calculated from the chromatograms using the width at half peak height assuming a Gaussian peak shape.

2.4. Evaluation of column performance

A standard mixture containing 2–60 mg/l each of Fe^{3+} , Cu^{2+} , Pb^{2+} , Zn^{2+} , Ni^{2+} , Co^{2+} , Cd^{2+} , Mn^{2+} , Ca^{2+} and Mg^{2+} in dilute HNO_3 was selected for the evaluation of column performance. With an injection

loop of 20 μl these injection volumes corresponded from 40 to 400 ng of sample and represent a typical working range for photometric detection. The chromatograms obtained with the tartaric acid eluent (0.1–0.25 *M* tartaric acid, pH 2.7–4 adjusted with 4 *M* sodium hydroxide solution) were used to calculate the column efficiency at capacity factors above 11 in order to minimize the influence of the post-column derivatization. The results are given in Table 3

3. Results and discussion

3.1. Influence of functional group structure and type of attachment

Figs. 1–3 show the influence of functional group structure on column performance while using the same basic substrate. Typical plate counts under

Table 3
Performance comparison for the silica based BioSil CAT and the sulfonated, sulfopropionylated and dynamically coated BioGel SEC 7 PS–DVB resins under equal chromatographic conditions (0.175 *M* tartaric acid, pH 3.30 adjusted with NaOH)

	Sulfonated Q: 0.51 mmol/ml Plates/m	Sulfopropionylated Q: 0.54 mmol/ml Plates/m	Coated with dodecyl-sulphate Q: 0.45 mmol/ml Plates/m	BioSil CAT Q: 0.55 mmol/ml Plates/m
Zn	3125	23 800 ^a	7040 ^a	27 000 ^a
Ni	2700	20 400 ^a	6575	25 500 ^a
Co	3350	23 800	7690	37 000
Cd	3350	23 800	7350	38 000
Mn	4200	31 250	9900	52 500
Ca	3700	37 000	6410	55 500
Mg	6250	32 250	7875	55 500
Pb	800	22 700	1980	3300

^a The values are slightly reduced due to the post-column-derivatization.

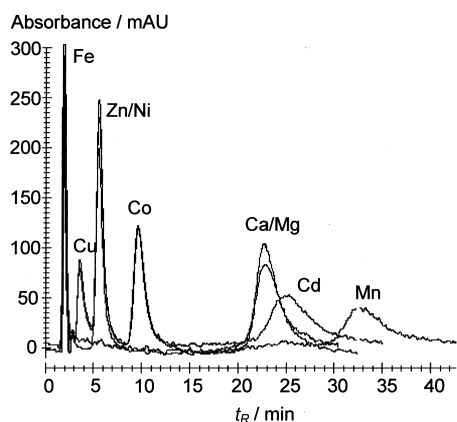


Fig. 1. Separation of di- and trivalent metal cations on a sulfonated BioGel SEC 7 PS-DVB-resin (Specific capacity Q: 0.6 mmol/ml, chromatographic conditions: 0.175 M tartaric acid, pH 3.43 adjusted with NaOH).

identical chromatographic conditions are given in Table 3. All resin used for Figs. 1–3 are based on a highly crosslinked, macroporous PS-DVB core called BioGel SEC 7 (Fig. 4). In Fig. 1 it has been sulfonated to a capacity of 0.51 mmol/ml bed volume. The performance of this column is relatively poor with typically 3000–6000 plates/m. Plate counts for the same but non-functionalized polymer coated with dodecyl sulphate for the generation of a dynamic ion-exchanger (Fig. 2) are within a medium range of 2000–10 000 plates/m. Superior perform-

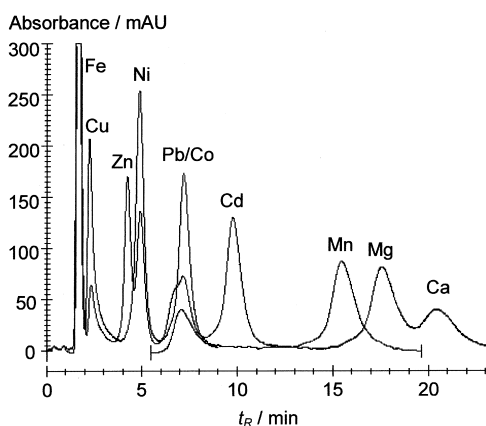


Fig. 2. Separation of di- and trivalent metal cations on a dynamically coated (0.002 M dodecylsulphate) BioGel SEC 7 PS-DVB-resin (Specific capacity Q: 0.45 mmol/ml, chromatographic conditions: 0.175 M tartaric acid, pH 3.30, adjusted with NaOH).

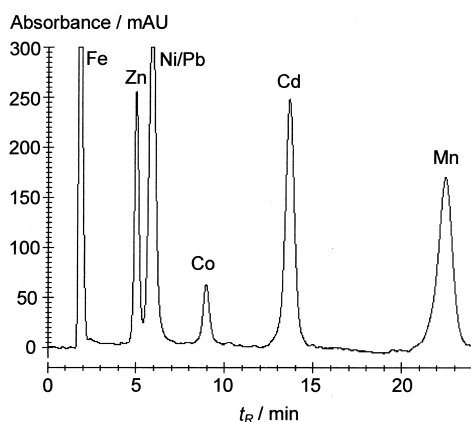


Fig. 3. Separation of di- and trivalent metal cations on a sulfopropionylated BioGel SEC 7 PS-DVB-resin (Specific capacity Q: 0.54 mmol/ml, chromatographic conditions same as for Fig. 2).

ance with 20 000–37 000 plates/m are obtained using sulfopropionylated resins as shown in Fig. 3. On one hand, the plate counts for the less complexed Mg^{2+} -ion differ from 6250 plates/m for the sulfonated resin over 7880 plates/m for the dynamically coated material to 32 250 plates/m for the sulfopropionylated material. On the other hand, the Pb^{2+} -ion shows a huge performance difference for the three different types of functional groups. An explanation may be the high stability constant of the Pb^{2+} tartaric acid complex, which is $K_L = 3890$ [10–12] and therefore one order of magnitude higher than those of Ni^{2+} and other transition metal cations.

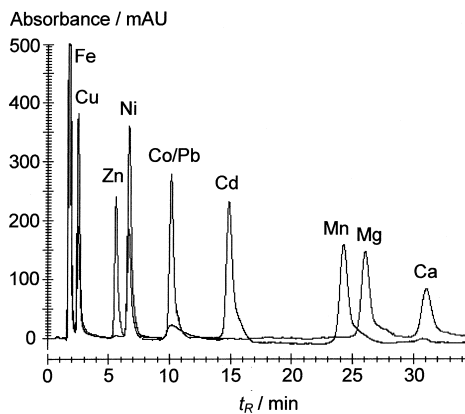
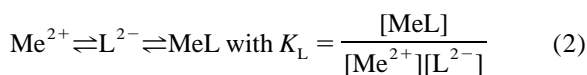


Fig. 4. Separation of di- and trivalent metal cations on a silica based BioSil CAT ion-exchanger (Specific capacity Q: 0.55 mmol/ml, chromatographic conditions same as for Fig. 2).

The observed behavior is likely an example for a well known effect described as reaction-retarded diffusion [13].

3.2. Influence of complexation

Ion exchange is often accompanied by processes other than only ionic mass transfer, which are not considered in the Nernst-Planck equation. While for the dynamically coated and the sulfopropionylated resins, no significant influence of mobile-phase composition on efficiency were found, the sulfonated resins show significant increase of HETP as function of the degree of complexation. When a solute cation Me^{x+} is eluted by a competing cation, E^{y+} and the eluent also contains a complexing reagent capable of reacting with Me^{x+} , the whole retention model has to consider this complex formation process [14]. The fraction of the total concentration of metal ion in the eluent which is present in free form can be expressed as:



$$\alpha_M = \frac{[Me_m^{x+}]}{[Me_m^x] + [MeL^{x-2}] + [MeL_2^{x-4}]} \\ = \frac{[Me_m^{x+}]}{C_M} \quad (3)$$

where C_M is the total concentration of the metal ion in the mobile phase

The effect of complexation on HETP can be seen in Table 4. The peak widths increase for the sulpho-

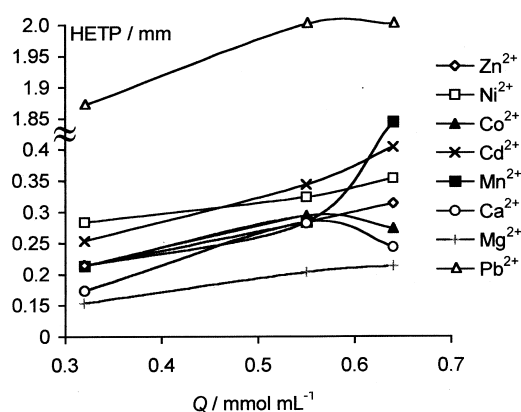


Fig. 5. Comparison of HETP values as function of specific resin capacity for sulfonated BioGel SEC 7 PS-DVB resins for comparable retention factors k' .

nated resins with increased degree of complexation of the cations. The HETP for Zn^{2+} and Ni^{2+} with stability constants of 479, respectively, 398 decrease about 30% by increasing the fraction of non-complexed metal ion from 7.7 to 30%, respectively, 9.1 to 33.7%. The HETP for Mg with a one order of magnitude lower stability constant remains nearly unchanged [15,16].

3.3. Influence of specific capacity

As demonstrated in Fig. 5 the HETP values for the sulfonated resins are increasing with increasing specific capacity. Whereas for the sulfoacylated resins the effect is completely reverse, i.e. the HETP values are decreasing over the investigated range with increasing specific capacity (Fig. 6).

Table 4

HETP values as function of eluent composition for a sulfonated BioGel SEC 7 PS-DVB resin ($Q=0.74$ mmol/ml) and the corresponding degree of complexation

Eluent Metal ion	0.175 M Tartaric acid, pH 3.30, $c(Na^+) 0.17 M$			0.25 M Tartaric acid, pH 2.75, $c(Na^+) 0.12 M$		
	k'	HETP (mm)	$\alpha (Me^{2+})$ (%)	k'	HETP (mm)	$\alpha (Me^{2+})$ (%)
Zn	8.1	0.32	7.7	9.2	0.22	30
Ni	8.6	0.37	9.1	10.6	0.23	33.7
Co	16	0.30	18.6	17.7	0.18	53.8
Cd	51.7	0.30	17.6	35.7	0.25	52.1
Mn	63	0.24	33.8	35.2	0.16	72.3
Ca	47.4	0.29	20.6	38.2	0.19	30.8
Mg	53.6	0.16	38.1	35.6	0.15	47.1
Pb	~50	>1	0.1	~35	>1	0.4

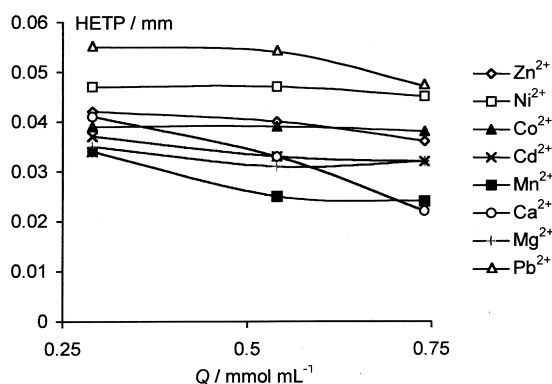


Fig. 6. Comparison of HETP values as function of specific resin capacity for sulfopropionylated BioGel SEC 7 PS–DVB resins for comparable retention factors k' .

The observed phenomena might be explained by refining the Nernst-Planck mass transfer model by referring to a percolation process as described by Broadbent and Hammersley [17]. The functionalized PS–DVB-resins are highly porous materials. More than 98% of the surface area is due to pores and therefore a mainly internal area. When the PS–DVB is reacted with the concentrated sulfuric acid the small SO_3^+ can easily penetrate the pores resulting in deeper functionalization of the core. Using the random walk model and the Einstein equation for molecular diffusion, the cation has to diffuse a longer distance from the bottom of a pore needing more time, resulting in higher peak broadening and higher HETP.

The better HETP values for the sulfoacylated resins are a good indication of possible clogging or filling of smaller pores due to the bonding process of a sterically hindered reagent-catalyst complex resulting in higher diffusion coefficients and obstruction factors in the stationary phase as well as lower fraction of the mobile phase and shorter diffusion distance inside the porous bed, which are in good conformity with the percolation theory [18].

3.4. Comparison of chromatographic performance with commercial silica based ion-exchangers

The theoretical plate counts for the three polymer based cation-exchangers and for the BioSil CAT exchange column (capacity: 0.55 mmol/ml) as an

example for a silica gel based cation-exchanger were shown in Table 3. The data were obtained with an optimized eluent 0.175 M tartaric acid, pH 3.10 (by NaOH). The concentration and pH of the eluent was selected so that the k' -value of each element was comparable on the investigated columns and high enough to minimize the contribution of the post-column derivatization equipment.

BioSil CAT was selected because of the similar exchange capacity. The results for the in different ways modified polymers had been discussed before in Section 3.1 and the sulfopropionylation turned out to be the best choice. It is obvious from Table 3 and from Figs. 3 and 4 that with the exception of Pb^{2+} the HETP values for the BioSil CAT exchanger are slightly lower than the values observed for the sulfopropionylated resin. This effect may be explained by the superior regularity of the particle size distribution of the commercially available material or by the more hydrophilic surface of silica gel.

A surprising result is the high value of 0.3 mm for Pb^{2+} on BioSil CAT, which is close to that of the dynamically coated material. One can only hypothesize that this phenomenon is due to non-specific interaction of the highly complexed Pb^{2+} on the stationary phase, but another commercial silica gel cation-exchanger, the Nucleosil SA material, did not show significant higher HETP values for Pb with similar eluents.

4. Conclusions

It has been shown that column performance for the separation of cations by ion chromatography is controlled by a variety of factors. The main conclusions of this work may be summarized as follows:

(1) This, and our previous three publications [6,7,19], show two selected cases where one or a series of surface reactions can lead to the introduction of permanently bonded sulfonic acid groups onto PS–DVB resins in order to produce strong cation-exchangers which are stable over a wide range of solvent composition and pH. Other modifications, i.e. surface coating, are also possible. Nevertheless, the chromatographic performance of the functionalized materials are dramatically depending on the functional group structure. The plate height obtained

with the sulfopropionylated material is one order of magnitude lower than for the direct sulfonated material.

(2) The work indicates that the primary retention mechanism is ion-exchange, there are certain properties of the bonded phases which are somewhat not covered by the Nernst-Planck approach. Thus, HETP values are depending on the degree of functionalization. The directly sulfonated materials show an increase of HETP as a function of specific capacity, whereas the sulfoacylated resins show significantly lower plate heights with increasing capacity.

(3) While changes in mobile phase composition can be used to affect analyte retention as based on the Nernst Planck equation, the contribution of non-specific interaction can be quite significant under certain circumstances. Thus, the cations show for the directly sulfonated sorbents, a dependance of HETP from the degree of complexation.

(4) The performance of the sulfoacylated resins is comparable to that of commercially available silica based materials. The resins are stable over a pH-range of 0–14, inert against oxidizing reagents such as HNO₃ up to a concentration of 4 M and stable against fluoride and hydrofluoric acid.

(5) The development of new chemically modified sorbents leading to new materials is likely to have a profound effect on optimizing column technology and is therefore highly desirable.

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