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# Sulfoacylated polystyrene–divinylbenzene copolymers as resins for cation chromatography

## Influence of capacity on resin selectivity

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### Abstract

To compare the effects of different ion-exchange capacities, a highly crosslinked polystyrene–divinylbenzene resin of 5  $\mu\text{m}$  has been functionalized by sulfoacylation with exchange capacity varying from 0.1 to 0.75 mmol/ml. Theoretically, the separation factor of two cations with the same charge should be independent of the exchange capacity. To study the influence of specific capacity, the retention behavior of a mixture of nine divalent cations (Cu, Pb, Zn, Ni, Co, Cd, Mn, Ca, Mg) has been investigated with tartaric acid–sodium hydroxide as eluent. The logarithm of adjusted retention times was found to be a linear function of the specific capacity. However, the slopes differ significantly from the presumed value of 2 for divalent cations. The observed trend is correlated to the sequence of diameters of the hydrated ions obtained from electrochemical measurements. Considering the deviations from the nominal charge the observed dependencies of separation factors on specific capacity can be explained semiquantitatively. © 1998 Elsevier Science B.V.

**Keywords:** Stationary phases, LC; Polystyrene–divinylbenzene resins; Metal cations

### 1. Introduction

Ion chromatography has become a widely used method for the determination of charged species in complex mixtures [1–3]. In the present sense it comprises a combination of classical ion-exchange methods with modern instrumentation and resins of high performance. One way to optimize ion chromatographic separations is the development of new resins with better properties. Therefore, it is necessary to know how to control selectivity and efficiency. Recently, a powerful new type of sulfoacylated polystyrene–divinylbenzene (PS–DVB) cation-exchangers has been reported [4]. By inserting

a spacer group between the exchange site and the core this new cation exchanger shows an increased chromatographic performance of nearly one order of magnitude. The selectivity of an ion chromatographic resin is influenced by the resin matrix, the type of functional group and, of course, by the ion-exchange capacity. A widely accepted retention model for cation chromatography assumes a linear dependence between the logarithm of the retention factor ( $\log k$ ) and the logarithm of the concentration of the cationic part of the eluent. The slope should be the ratio of the charge of analyte and eluent cation. This dependence has been used for evaluation of the effective charge of cations and anions [2]. The retention model also assumes a linear dependence between  $\log k$  and the logarithm of the volume capacity of the exchanger. For cation exchangers used as chromatography support this dependence has never been

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validated. For this purpose it is necessary to synthesize a number of polymers with identical substrate and with a wide range of capacity. The recently reported functionalization of HPLC-grade PS–DVB polymers using Friedel-Crafts acylation allows the variation of the exchange capacity over a wide range and is therefore ideally suited for the study of the influence of exchange capacity.

## 2. Experimental

### 2.1. Instrumentation

The HPLC system consisted of a HPLC pump (Type 64, Knauer, Berlin, Germany), a pneumatic injection valve (Knauer) fitted with a 20  $\mu$ l sample loop and a variable-wavelength detector (Type 87.00, Knauer). The eluent flow rate was 1 ml/min throughout all experiments. Postcolumn detection of the cations was realized by reaction with 4-(2-pyridylazo)resorcinol (PAR), Zn-EDTA,  $0.25 \times 10^{-4}$  mol/l Zn-EDTA,  $1 \times 10^{-4}$  mol/l PAR, 2 mol/l  $\text{NH}_3$ . The postcolumn reagent was added to the eluate in a postcolumn reactor (3 m  $\times$  0.7 mm I.D.) by a single piston HPLC-pump (LDC Analytical) at a flow rate of 0.3 ml/min and absorption was monitored at 495 nm. All retention factors were calculated using the column dead time. The control of the whole system and the readout of the detector were processed by a computing system.

### 2.2. Columns

All resins were made from a highly crosslinked PS–DVB polymer originally designed for organic phase size-exclusion chromatography. The physical properties of the 5  $\mu$ m diameter BioGel SEC 7 (Bio-Rad Labs., Munich, Germany) were summarized elsewhere [4]. The sulfoacylation was performed as described in Ref. [4] using only  $\omega$ -chloropropionyl chloride as acylation reagent. The exchange capacity varied from 0.1 to 0.75 mmol  $\text{H}^+$  per ml of bed volume. All resins were filled into 100 mm  $\times$  4 mm I.D. stainless steel columns (Vertex, Knauer) in the manner described in Ref. [4].

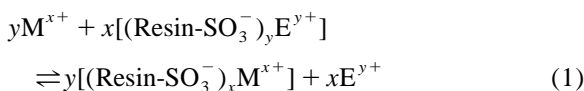
### 2.3. Reagents

All reagents were of analytical or high purity grade. Aliquots of commercially available stock solutions (1000 mg/l) were used to prepare standard mixtures containing the ions to be investigated in a range of 2–60 mg/l. All eluents were prepared with tartaric acid (Fluka, Switzerland, microselect grade) and Millipore water with a minimum resistance of 18 M $\Omega$ . The pH was adjusted with 4 mol/l NaOH solution (from analytical-reagent grade NaOH containing less than 0.0002%  $\text{K}^+$ , Merck, Darmstadt, Germany). The concentration and the pH of the eluents varied from 0.1 to 0.25 mol/l tartaric acid and pH 2.7 to 3.96.

## 3. Results and discussion

### 3.1. Retention model for cation chromatography of multivalent cations

In ion chromatography, separations are based on differences in the relative attraction of sample ions and eluent ions for the oppositely charged functional groups on the stationary phase. The most important properties of an ion-chromatographic resin, i.e. selectivity, retention behavior, chemical and mechanical stability, nonspecific interactions as well as kinetic properties are influenced by the resin matrix, functional group character and ion-exchange capacity [5]. The theoretical basis for this behavior can be shown by studying ion-exchange equilibria, which can be described in terms of equilibria equations [1,6]:



Considering that the amount of metal cations available to exchange is reduced by the addition of complexing agents like tartaric acid to the fractional value  $\alpha_M$  [7]:

$$K_{M,E} = \frac{[\text{M}_R^{x+}][\text{E}_M^{+}]^x}{\alpha_M[\text{M}_M^{x+}][\text{E}_R^{+}]^x} \quad (2)$$

The subscripts R and M denote the resin and the mobile phase,  $x$  represents the charge of the sample

cation eluted by the monovalent sodium-ions in the mobile phase. The technically correct activities are not considered for simplicity [2,8]. The equilibrium equation can be rearranged to predict the chromatographic behavior. The simplified Eq. (3) is showing how the retention factor is dependent from the resin capacity [2]:

$$\log k_M = \log \alpha_M + \log K_{M,E} + (x \log Q) - (x \log [E^+]) + C, \quad (3)$$

$k$  is the retention factor,  $Q$  is the resin capacity and  $[E^+]$  is the eluent concentration. The constant  $C$  includes the ratio of column volume occupied by the stationary and mobile phase [1,5,8,9]. Important conclusions regarding the separation of cations can be drawn from these equations. The separation factor of two ions of the same charge depends only on the selectivity coefficient  $K_{M,E}$ . The separation factor of two ions with different charges depends on the retention factor  $k$ , which can be changed by changing the eluent concentration or the resin capacity. Keeping the eluent composition constant, Eq. (3) can be simplified to:

$$\log k = x \log Q + B \quad (4)$$

### 3.2. Effect of resin capacity

To investigate the influence of resin capacity on

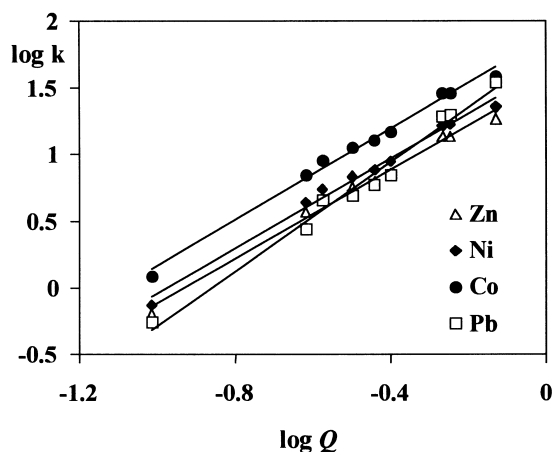


Fig. 1. Plot of  $\log k$  for Zn, Ni, Co and Pb versus  $\log Q$  (specific resin capacity in mmol/ml) for sulfopropionylated resins. Eluent composition was 0.175 mol/l tartaric acid, pH 3.10 with NaOH.

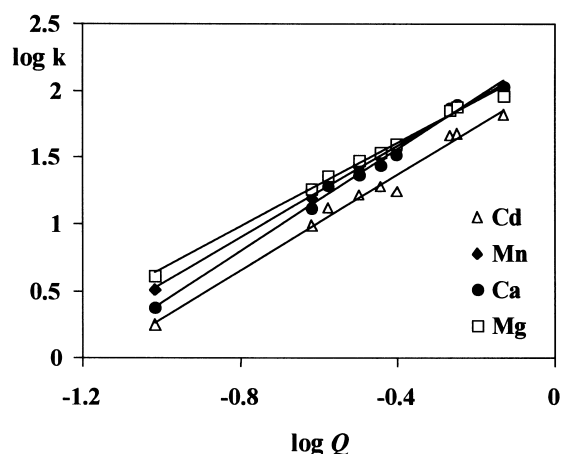


Fig. 2. Plot of  $\log k$  for Cd, Mn, Ca and Mg versus  $\log Q$  (specific resin capacity in mmol/ml) for sulfopropionylated resins. Eluent composition was 0.175 mol/l tartaric acid, pH 3.10 with NaOH.

the separation factor a series of polystyrene–divinylbenzene resins were sulfopropionylated. The retention factors were determined using a tartaric acid based elution system on resins with a specific capacity of 0.1–0.75 mmol/ml. The eluent composition was 0.175 mol/l tartaric acid with pH 3.10 adjusted with NaOH. This moderately strong eluent elutes the most strongly retained cation  $Mg^{2+}$  at  $t_R = 4.0$  min and  $t_R = 79.5$  min for the resin with the lowest and highest capacity, respectively. The results as shown in Figs. 1 and 2 confirm the assumed linear dependence between  $\log k$  and  $\log Q$ .

## 4. Discussion

Assuming the selectivity coefficient to remain constant, the slope of the plot  $\log k$  vs.  $\log Q$  should correspond to the charge of the sample ion relative to the charge of the eluent coion,  $Na^+$  in this work. Indeed, linear plots are obtained with good linear regression coefficients ( $r > 0.99$ ).

However, the slopes of the investigated cations differ significantly from the presumed values (Table 1), which are in good agreement with the values obtained from isoionic displacement studies with sodium nitrate eluents of various concentrations [10]. In these experiments an eluent based on  $NaNO_3$  has been used. By varying the  $Na^+$ -concentration from

Table 1

Effective charge of several divalent ions on a sulfopropionylated PS–DVB cation exchanger using 0.175 mol/l tartaric acid, pH 3.1 adjusted with NaOH, as eluent

Ion	Effective charge by variation of $Q$	Effective charge by variation of $c(\text{Na}^+)$	Ionic radius/ $10^{-8}$ (cm)
Zn <sup>2+</sup>	1.65	1.60	3.49
Ni <sup>2+</sup>	1.69	1.69	3.68
Pb <sup>2+</sup>	2.04	1.97	2.59
Co <sup>2+</sup>	1.71	1.73	3.45
Cd <sup>2+</sup>	1.80	1.87	3.41
Mn <sup>2+</sup>	1.71	1.79	3.44
Ca <sup>2+</sup>	1.89	1.87	3.10
Mg <sup>2+</sup>	1.57	1.78	3.47

The charge is determined by the plot of  $\log k$  versus the exchange capacity. The ionic radii were calculated from limiting conductance data taken from [11].

0.1 to 2 mol/l a plot of  $\log k$  vs.  $\log c(\text{Na}^+)$  should give information about the ratio of the charge of the analyte and the eluent coion [see Eq. (3)].

The best conformity with theory appears to occur with small hydrated ions. The deviations increase in the order Pb, Ca, Cd, Mn, Co, Ni, Zn and Mg. The diameters of the hydrated cations calculated from the conductivity values increase in the same order [11,12]. The electrophoretic mobility of the cations depends on the volume of the hydrated ion and on the total charge. Ca is more mobile than Mg having a larger mass but a lower hydration ability resulting in a higher effective charge [6,13]. This is also evident for Pb, which has a greater mass but a very small hydrate sphere and a high mobility. The Pb ion shows the highest effective charge which is even slightly higher than two, which might be due to nonspecific interaction [14,15].

#### 4.1. Practical consequences

The practical applications of this work are twofold. First, up to now nearly every discussion in literature has concerned either the influence of eluent concentration on the retention factors at a given pH or the influence of the pH whilst maintaining the eluent concentration at a constant value [6,16,17]. An alternative approach is to vary the resin capacity as a powerful parameter to alter the resolution of two cations [13]. Since the chromatographic resolution of two ions is strongly dependent on their differences in

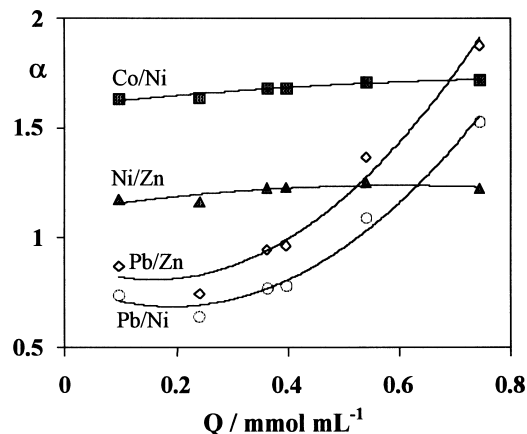


Fig. 3. Plot of the separation factor  $\alpha$  for the peak pairs Co/Ni, Ni/Zn, Pb/Zn and Pb/Ni versus the specific resin capacity  $Q$  for sulfopropionylated resins. Eluent composition was 0.175 mol/l tartaric acid, pH 3.10 with NaOH.

effective charge, it is possible to change relative retention times by changing the degree of resin functionalization.

The second practical application deals with the optimization of specific capacity to produce the desired separation. Figs. 3 and 4 show the plot of the separation factor  $\alpha$  versus the specific resin capacity for a given column. The separation of ions with a comparable effective charge such as Zn, Ni and Co is nearly independent from the specific resin capaci-

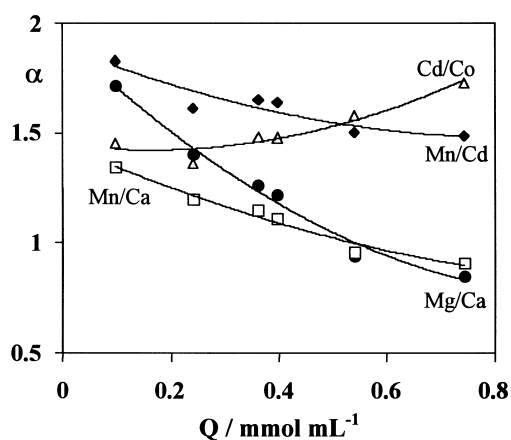


Fig. 4. Plot of the separation factor  $\alpha$  for the peak pairs Cd/Co, Mn/Cd, Mn/Ca and Mg/Ca versus the specific resin capacity  $Q$  for sulfopropionylated resins. Eluent composition was 0.175 mol/l tartaric acid, pH 3.10 with NaOH.

ty. On the other hand, for cations with large differences in effective charge the resolution is strongly dependent on the degree of functionalization. For low capacities, Pb is eluted in front of Zn and Ni (Fig. 5), whereas at high capacities the retention order is reversed (Fig. 6). With a separation factor of higher than 1.5 the ions  $\text{Cd}^{2+}$  and  $\text{Mn}^{2+}$  are always well resolved with a slight decrease in separation factor at higher capacities.

The resolution of the alkaline earth cations Mg and Ca is also strongly dependent on the resin capacity. For low capacities Ca is eluted in front of Mg with a separation factor of 1.7.

The resolution of the two elements decreases rapidly with higher resin capacities (Fig. 2). The electrostatic attraction of the sulfonic acid groups to Ca caused by the higher effective charge is much higher than the attraction of Mg [3]. Mn, Mg and Ca are well separated from each other at low specific capacities. Ca is eluted in front of Mg with a separation factor of 1.4. Mn is eluted long before Mg with a comparable resolution factor.

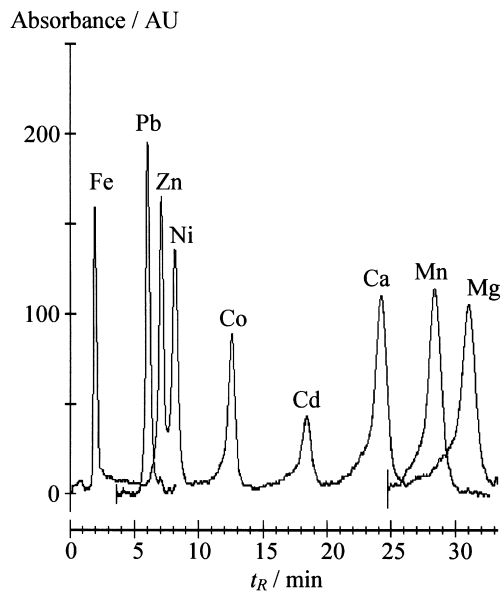


Fig. 5. Separation of di- and trivalent metal cations on a low capacity sulfopropionylated BioGel SEC 7 cation exchanger ( $Q = 0.295$  mmol/ml bed volume). Overlay of several chromatograms. Chromatographic conditions: 0.1 mol/l tartaric acid, pH 3.42 adjusted with NaOH, 1 ml/min flow rate, postcolumn detection with Zn-EDTA-PAR.

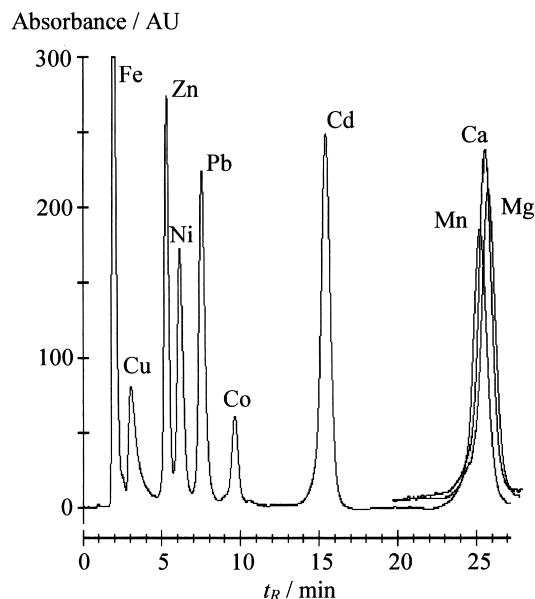


Fig. 6. Separation of di- and trivalent metal cations on a high capacity sulfopropionylated BioGel SEC 7 cation exchanger ( $Q = 0.744$  mmol/ml bed volume). Overlay of several chromatograms. Chromatographic conditions: 0.175 mol/l tartaric acid, pH 3.42 adjusted with NaOH, 1 ml/min flow rate, postcolumn detection with Zn-EDTA-PAR.

## 5. Conclusions

Isocratic single ion chromatography using a sulfopropionylated PS-DVB polymer can be used for the rapid separation of common divalent cations. This study has shown that the linear relationship existing between  $\log k$  and the log of the resin capacity can be used as a basis for the selection of the capacity of the stationary phase. The exchange capacity is a powerful parameter which can be varied in chromatographic separations. The separation factor of cations can be predicted based on the differences in effective charges of the hydrated species. The above relationships provide for systematic selection of resin capacity at fixed eluent composition.

## Acknowledgements

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