ISSN 0027-1314, Moscow University Chemistry Bulletin, 2007, Vol. 62, No. 5, pp. 290–294. © Allerton Press, Inc., 2007.
Original Russian Text © T.N. Kas'yanova, A.D. Smolenkov, A.V. Pirogov, O.A. Shpigun, 2007, published in Vestnik Moskovskogo Universiteta. Khimiya, 2007, No. 5, pp. 352–356.

Mobile Phases for the Determination of Polarizable Anions on Polystyrene/Divinylbenzene Anion-Exchange Resins

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Received April 24, 2007

Abstract—Anion-exchange resins have been prepared by chloromethylating 50%-crosslinked styrene-divinylbenzene copolymers (PS/DVB) followed by amination with trimethylamine. In addition to ion exchange, interactions with the anion-exchange matrix considerably contribute to the retention of polarizable anions on these sorbents. Additives in the eluent that can suppress adsorption sites of the stationary phase can decrease this effect. p-Hydroxybenzonitrile (0.15 mmol/L) in the eluent increases the NO_3^- peak efficiency from 820 to 5100 theoretical plates per meter.

DOI: 10.3103/S0027131407050161

Ion chromatography is an advanced and highly efficient method for the determination of ionic substances in environmental objects, medicines, and foodstuffs. The search for ways to improve the efficiency and speed of analysis is a focus of chromatography research.

Styrene-divinylbenzene copolymers (PS/DVB) are the most abundant anion-exchange matrices for ion chromatography; copolymers with high degrees of crosslinking (20% and higher) have been used, because they have high mechanical stability [1]. With the use of PS/DVB ion-exchange resins, however, anion retention can be due not only to ion-exchange and but also to non-ion-exchange interactions. Adsorption interactions are as a rule observed for all polarizable inorganic or organic ions that have low hydration energy, low hydrophobicity, and strong π–π interactions with the aromatic matrix of the ion-exchange resin. In some cases, the adsorption properties of the sorbent fully control even separation of simple inorganic anions, such as nitrate and bromide ions [2], which was noted in [3–6]. The enthalpy of sorption $\Delta H_{m \to s}$ for the nitrate and bromide ion was –8.1 and –8.6 kJ/(mol K), respectively; the index $m \longrightarrow s$ denotes mass transfer from the mobile to stationary phase. For fluoride, chloride, phosphate, and sulfate ions, this parameter is either low or zero [2].

Non-ion-exchange interactions generate nonlinear ion-exchange isotherms, a narrow range of linear signal versus concentration dependence, and diffuse peaks. Therefore, minimization of this type of interaction improves chromatographic characteristics and is an important problem for an analyst.

This work was intended to choose mobile phases for the quantitative determination of polarizable anions on PS/DVB anion-exchange resins and to study the effect of additives suppressing adsorption interactions on ion-chromatographic separation.

EXPERIMENTAL

Instruments and Reagents

Experiments were carried out on a Staier chromatograph (Akvilon, Russia) equipped with a conductometric detector. Steel separation columns 4 × 50 mm in size filled by the suspension method under 250 bar were used. A column 4.6 × 150 mm packed with Dowex 50WX8 200–400 mesh cation-exchange resin in the H^+ form (Supelco) was used to suppress the background signal. The ejected sample volume was 50 or 100 μL.

In the synthesis, the following equipment was used: thermostat (Memmert), vacuum pump (Laboport), ultrasonic bath (Sapfir), and mechanical stirrer (Eurostar).

The matrix used to synthesize anion-exchange resins was ST/DVB with 50% crosslinking, grain size 3.3 ± 0.2 μm, surface area 200 m^2/g, total pore volume 0.64 cm^3/g, and average pore diameter 6 nm (prepared in the Chromatography Laboratory, Chemistry Department, Moscow State University) [7].

The following reagents were used to modify the matrix: 40% aqueous formaldehyde (Laverna), thionyl chloride (Merck), chlorosulfonic acid (Aldrich), glacial acetic acid (reagent grade, Reakhim), acetonitrile (high purity grade for liquid chromatography, IREA 2000), hydrochloric acid (Khimmed), sodium hydroxide (reagent grade, Khimmed), and ethanol (analytical grade, Labtekh). The amination was performed with 40% solution of trimethylamine, N,N-diethylethanola-

Table 1. Functional groups and capacities of anion-exchange resins synthesized

Sorbent	Aminating agent	Amine volume, mL	Capacity, mmol/g
TMA	Trimethylamine	15	0.080
DEEA	*N*,*N*-diethylethanolamine	15	0.013
UDMH	*N*,*N*-dimethylhydrazine	10	0.055

mine (99.5%+, Aldrich), or N,N-dimethylhydrazine (Merck).

Analyte solutions and mobile phases were prepared from the following reagents: benzoic acid (99.0%+), sodium hydroxide (98.0%+), perchloric acid (Fluka), sodium carbonate, sodium hydrocarbonate, potassium sulfate, potassium nitrate, lithium chloride (analytical grade), potassium fluoride (reagent grade), and sodium dihydrogen phosphate (analytical grade) purchased from Khimmed or Labtekh.

Stock salt solutions with concentrations of 10 mmol/L were prepared from accurately weighed samples. Working solutions with lower concentrations were prepared by diluting the stock solutions. Eluents were prepared from 200 mM solutions of sodium carbonate, sodium hydrocarbonate, and sodium hydroxide, 5 mM benzoic acid, and 100 mM perchloric acid. Distilled water was used to prepare all solutions.

Anion-exchange resins were synthesized as described in [3]. The volume of the aminating agent added and the chromatographic capacities of the sorbents are listed in Table 1.

RESULTS AND DISCUSSION

Elution with carbonate buffer solution. A two-column version of ion chromatography with a carbonate buffer solution as the eluent was chosen to study the behavior of anions on the test sorbents. However, anomalous nitrate retention is observed for this mobile phase, which is standard for ion chromatography; the relevant peak is very diffuse, making quantitative determination virtually impossible. Figure 1 displays chromatograms for inorganic anions on some anion-exchange resins synthesized.

Elution with sodium hydroxide mixed with perchloric acid. A mixed eluent consisting of perchloric acid, sodium hydroxide, and sodium carbonate was proposed for use with high-capacity anion-exchange resins [8]. The efficiency of perchlorate for these purposes is due to the high affinity of this anion to quaternary ammonium functionalities. If perchlorate anions are added to the mobile phase, stronger sorption interactions with the aromatic stem of the anion-exchange resin are observed for the perchlorate anion than for the nitrate ion. This competing reaction makes it possible to considerably decrease the π–π interactions of the NO_3^- ion with the benzene rings of PS/DVB. Figure 2 exhibits chromatograms for five inorganic anions on the TMA anion-exchange resin with perchloric acid added to the eluent. The use of the 0.1 mM $HClO_4$ + 10 mM NaOH mobile phase provides for the best anion separation; the elution sequence becomes ordinary for ion chromatography. A weakness of addition of pechlorate to an eluent is the high background electrical conductivity of perchloric acid. However, the detection limits we determined (Table 2) signify the possibility of sensitive determination of anions in the concentration ranges characteristic of their determination in natural water analysis.

Elution with benzoic acid. Polarizable anions can interact with the matrix of the ion-exchange resin, generating π–π complexes. This type of complexes can be formed by aromatic compounds. Therefore, the use of aromatic compounds can decrease non-ion-exchange interactions between polarizable anions and the sorbent matrix. This decrease is due to stronger π–π interactions between the π-electron system of PS/DVB and the benzene rings of a component of the mobile phase. Benzoic acid and its derivatives are the most abundant eluents of this type. Figure 3 displays the chromatograms of singly charged inorganic anions in the one-

Table 2. Parameters of the chromatographic determination of inorganic anions on the TMA anion-exchange resin with perchlorate ions added to the eluent (for the conditions, see Fig. 2)

Parameter	F^-	Cl^-	NO_2^-	Br^-	NO_3^-	SO_4^{2-}	PO_4^{3-}
t', min	1.17	3.25	5.19	10.00	12.52	22.22	58.57
k'	0.33	0.91	1.43	2.76	3.52	6.24	16.45
α_{Cl^-}	0.36	1	1.60	3.08	3.85	6.84	18.02
N, TP/m	6600	5700	5000	7300	5700	7900	5200
c_{min}, μg/L	0.2	0.2	0.7	1.3	1.3	1.4	4.9

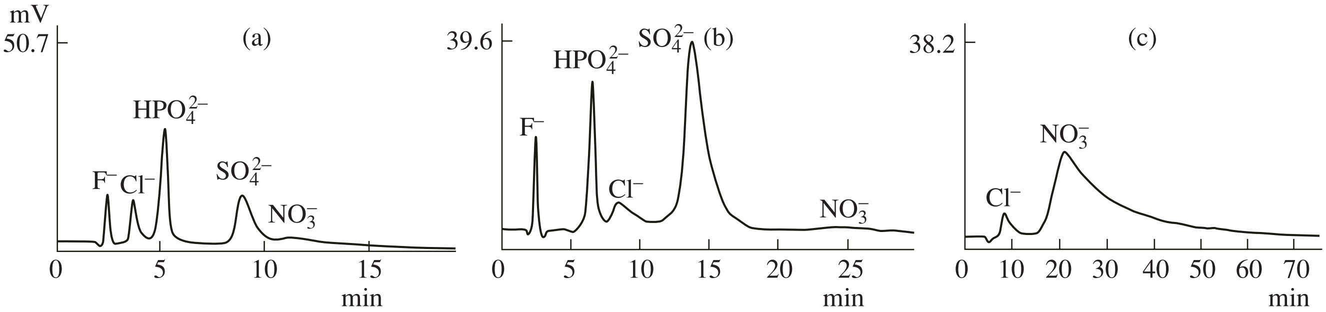

Fig. 1. Separation of inorganic anions with a 1.8 mM Na_2CO_3 + 1.7 mM $NaHCO_3$ eluent: (a) UDMH anion-exchange resin (mobile-phase flow rate, 1.0 mL/min; nitrate ion concentration in the sample, 25 mg/L), (b) TMA anion-exchange resin (mobile-phase flow rate, 1.1 mL/min; nitrate ion concentration in the sample, 25 mg/L), and TMA anion-exchange resin (mobile-phase flow rate, 1.0 mL/min; nitrate ion concentration in the sample, 620 mg/L).

column ion chromatography version, with benzoic acid as an eluent, on an anion-exchange resin bearing N,N-diethylethanolamine functionalities. A system peak is observed in this chromatogram, which increases the analysis time. Table 3 lists some chromatographic parameters.

According to [2], elution with benzoic acid, as a rule, provides for a higher sensitivity than sodium or potassium benzoate; however, the detection limits of ions in one-column ion chromatography are usually higher than in the two-column version. Therefore, in most cases, the two-column version is preferred.

Carbonate eluent with *p*-hydroxybenzonitrile. It is known that *p*-hydroxybenzonitrile in two-column ion chromatography is the best to suppress the surface adsorption sites of the stationary phase. On the one hand, this compound has a benzene ring in its structure; on the other hand, it has a far weaker effect on the background conductivity of the eluent than the perchlorate ion. While the concentration of *p*-hydroxybenzonitrile added ranges from 0.02 to 0.4 mmol/L, the determination sensitivity does not change; the baseline noise remains unchanged: *p*-hydroxybenzonitrile is a weaker acid ($pK_\alpha = 8.0$) than carbonic acid, which forms after suppression. Therefore, the determination occurs on the carbonic acid background, and *p*-hydroxybenzonitrile does not contribute to the baseline noise.

The amount of *p*-hydroxybenzonitrile that should be added to the eluent in order for adsorption sites to be suppressed completely was determined experimentally. Figure 4 shows that *p*-hydroxybenzonitrile added to the eluent decreases the retention times of anions until a certain concentration is reached; when the *p*-hydroxybenzonitrile concentration exceeds 1×10^{-4} mol/L, all accessible adsorption sites are likely suppressed, and anion retention is no longer affected by the additive concentration. As a result, sorption interactions between nitrate ions and the aromatic stem of the ion-exchange resin are no longer observed, which makes it possible to improve the efficiency of sorbents for this anion. This type of effect was demonstrated for the UDMH sorbent. With the carbonate eluent, the efficiency of the anion-exchange resin for NO_3^- ions is 820 theoretical plates per meter; when *p*-hydroxybenzonitrile is added to the eluent, the efficiency increases sixfold (Table 4). A similar situation is observed for

Table 3. Parameters of the chromatographic determination of inorganic anions on the DEEA anion-exchange resin with benzoic acid as the eluent (for the conditions, see Fig. 3)

Parameter	F^-	$H_2PO_4^-$	Cl^-	NO_2^-	Br^-	NO_3^-
t', min	6.34	7.37	11.09	13.80	20.46	28.39
k'	10.23	11.89	17.89	22.26	33.00	45.79
α_{Cl^-}	0.57	0.66	1	1.24	1.84	2.56
N, TP/m	7000	5000	7000	27000	15600	12700
c_{min}, μg/L	3.4	32.6	13.3	14.8	24.7	33.0

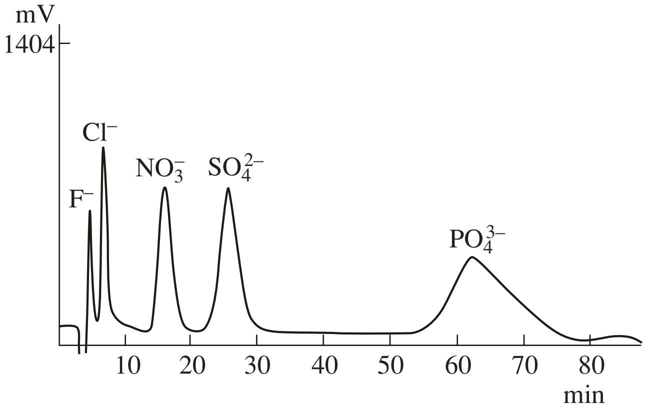

Fig. 2. Chromatograms of inorganic anions on the TMA anion-exchange resin. Chromatographic parameters: eluent, 0.1 mM $HClO_4$ + 10 mM NaOH; mobile-phase flow rate, 0.5 mL/min. The model mixture (mg/L): F^- (2.5), Cl^- (5), NO_3^- (25), SO_4^{2-} (25), and PO_4^{3-} (50).

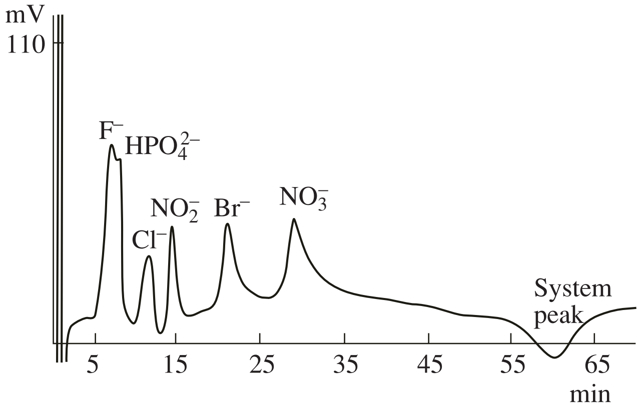

Fig. 3. Chromatograms of inorganic anions on the DEEA anion-exchange resin. Chromatographic parameters: eluent, 1 mM benzoic acid (pH 3.74); mobile-phase flow rate, 1.0 mL/min; conductometric detection. The model mixture (mg/L): F^- (1.9), Cl^- (3.5), NO_2^- (9.2), NO_3^- (12.4), Br^- (16.0), and $H_2PO_4^-$ (38.8).

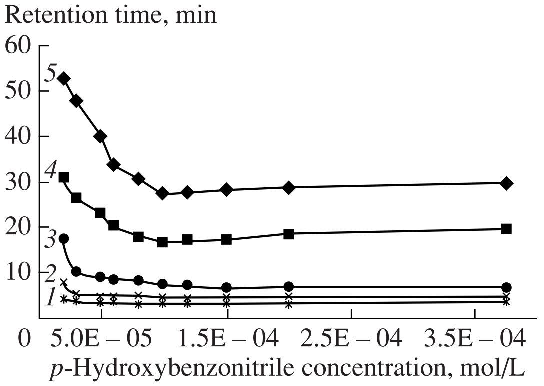

Fig. 4. Anion-retention time vs. *p*-hydroxybenzonitrile concentration in the eluent for (**1**) fluoride, (**2**) chloride, (**3**) nitrate, (**4**) phosphate, and (**5**) sulfate ions.

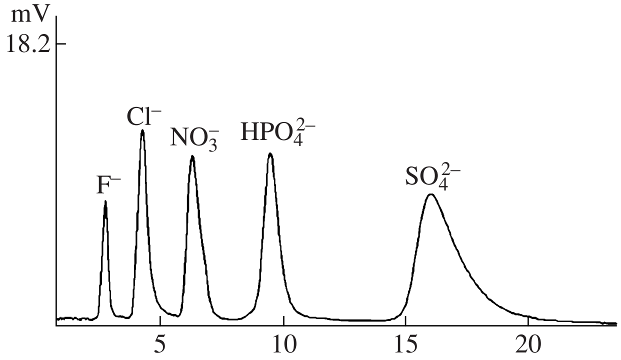

Fig. 5. Chromatograms of inorganic anions on the UDMH anion-exchange resin. Chromatographic parameters: eluent, 0.5 mM Na_2CO_3 + 0.15 mM *p*-hydroxybenzonitrile; mobile-phase flow rate, 1.2 mL/min. The model mixture (mg/L): F^- (1.9), Cl^- (3.5), NO_3^- (15.0), SO_4^{2-} (38.4), and HPO_4^{2-} (38.4).

bromide ions. Figure 5 displays the chromatograms of inorganic anions with *p*-hydroxybenzonitrile added to the eluent.

To summarize, we used chloromethylation followed by amination with trimethylamine, *N*,*N*-diethylethanolamine, or *N*,*N*-dimethylhydrazine to prepare heavily crosslinked PS/DVB sorbents for ion chromatography. Elution with carbonate-buffered solution does not make it possible to determine polarizable ions. We propose to add *p*-hydroxybenzonitrile to eluents for the determination of this type of anion on the PS/DVB matrix in two-column ion chromatography: in this case, the suppresser influences the background electrical conductivity more weakly than perchlorate ions and lower detection limits are achieved than in the one-column version.

Table 4. Parameters of the chromatographic determination of inorganic anions on the UDMH anion-exchange resin with *p*-hydroxybenzonitrile added to the eluent (for the conditions, see Fig. 5)

Parameter	F^-	Cl^-	NO_3^-	HPO_4^{2-}	SO_4^{2-}
t', min	0.19	1.07	3.96	8.01	15.50
k'	0.10	0.57	2.10	4.24	8.20
α_{Cl^-}	0.18	1	3.70	7.49	14.49
N, TP/m	10800	8900	5100	19400	7400

REFERENCES

1. Huck, C.W. and Bonn, G.K., *Chem. Eng. Technol.*, 2005, vol. 28, p. 1457.
2. Weiss, J., *Ion Chromatography*, Weinheim, New York, Basel, Cambridge, Tokyo, 1995, p. 27.
3. Bogolitsyna, A.K., Pirogov, A.V., and Shpigun, O.A., *Izv. Vyssh. Uchebn. Zaved. Sev.-Kavk. Reg., Estestv. Nauki, Prilozhenie*, 2006, no. 8, p. 28.
4. Bogolitsyna, A.K., Pirogov, A.V., Shpigun, O.A., and Bukhberger, V., *Sorbtsionnye i Khromatograficheskie Protsessy (Sorption and Chromatographic Processes)*, 2006, vol. 206, p. 827.
5. Biesaga, M., Schmidt, N., and Seubert, A., *J. Chromatogr., A*, 2004, vol. 1026, p. 195.
6. Schmidt, N., Biesaga, M., and Seubert, A., *Microchem. Acta*, 2004, vol. 146, p. 119.
7. Bogolitsyna, A.K., Pirogov, A.V., and Shpigun, O.A., *Vestn. Mosk. Univ., Ser. 2: Khim.*, 2006, vol. 47, p. 339.
8. Nowak, M. and Seubert, A., *J. Chromatogr., A*, 1999, vol. 855, p. 91.