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Synthesis and ion-exchange properties of silica chemically modified with aminophosphonic acid

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Abstract

The synthesis of a cation exchanger by conversion of 3-aminopropyl moieties covalently attached to a silica surface to propylaminomethylphosphonic by reaction with sodium hypophosphite and formaldehyde is described. The ion-exchange properties of the prepared sorbent in the pH range from 2.5 to 7.0 were evaluated by investigation of the retention of different ionogenic organic molecules. The ion-exchange selectivity toward alkali and alkaline-earth and transition metals ions was estimated. The effects of concentration of the nitric or perchloric acid, ionic strength and column temperature on the retention of cations were studied. The possibility of ion-chromatographic separation of a standard mixture of seven alkaline-earth and transition metal ions on a short (50×4.6 mm) column packed with 10 μm aminophosphonic-bonded silica using mineral acid solutions as eluents was demonstrated. © 1998 Elsevier Science B.V. All rights reserved.

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1. Introduction

Polymer resins or silica-based phosphorus-containing cation exchangers are widely used for the preconcentration of transition metals, lanthanides, uranium and thorium [1–6]. There are three different types of cation exchangers having phosphorus-containing functional groups: phosphate –OPO(OH)₂, phosphonic –PO(OH)₂ and phosphinic –PO(OH)H. Of these, only cation exchangers with phosphonic acid functional groups can be successfully used in ion chromatography because of poor hydrolytic or oxidative stability of phosphate and phosphinic functionalised substrates. One interesting property of the phosphonic acid cation exchangers relates to the

possibility of changing selectivity with increase of pH because of the presence of two ionizable OH groups in one ion-exchange site. The same is responsible for the complexation ability of phosphonic acid containing ion-exchangers and has been studied by others in detail [5,6]. The abovementioned properties of phosphonic cation-exchange groups produces a selectivity different from that observed for common carboxylic and sulphonic acid cation exchangers. Usually the phosphonate-type of ion exchanger has an increased affinity for trivalent cations, divalent heavy metals like lead, cadmium and copper, and to manganese and calcium. However, no data exists on the application of cation exchangers containing only phosphonic acid functional groups in ion chromatography. There are only two newly developed chromatographic columns [7,8] that contain phosphonic

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functional groups attached to the surface of polystyrene matrix (Dionex CS 12A and Dionex CS 15). It should be noted that both of these cation exchangers have a mixed-mode type functionality and have additionally either carboxylic or carboxylic and crown ether functional groups at the surface, respectively. For both of them the introduction of phosphonic groups seems specifically for the modification of their ion-exchange selectivity to increase the affinity for manganese(II) and calcium(II).

Thus, phosphonic acid-bearing ion exchangers have not yet been studied in ion chromatography except for a recent paper [8], therefore, the main idea of this investigation was to define the ion-exchange selectivity of such a type of substrate, namely, aminophosphonic acid bound to silica. The possibility of its application for the separation of metal ions was additionally considered.

2. Experimental

2.1. Preparation of silica-bound aminophosphonic acid (APAS)

The silica-based ion exchanger containing aminophosphonic functionality was obtained by a Mannich-type reaction of commercially available aminopropylsilica with hypophosphorous acid and formaldehyde using the following scheme:

The process was performed under mild conditions in accordance with modified methods [9,10]. For this purpose, 5 g of Silasorb Amine (Lachema, Brno, Czech Republic), 5 μm , was mixed with 40 ml of propyleneglycol in a 250-ml flask equipped with stirrer and thermometer and was heated up to 60°C under stirring. A mixture of 4.77 g sodium hypophosphite, 3.95 ml of 37% aqueous solution of formaldehyde and 1.52 ml concentrated HCl dissolved in 10 ml of propyleneglycol was added to the obtained suspension of aminopropylsilica. The amino groups of the sorbent were converted to aminophosphonic acid under stirring for 3 h at 60–80°C. The sorbent was collected by filtration, after cooling, and washed with water, then with acetone, and air dried.

2.2. Potentiometric titration

The capacity for hydrogen ions was determined by acid–base potentiometric titration of 1 g of ion-exchangers with 0.1 M nitric acid in the presence of 1 M potassium nitrate. The pH of solutions was monitored by a pH meter equipped with a glass electrode.

2.3. Apparatus

The isocratic ion chromatographic system consisted of a DX-500 HPLC pump (Dionex, Sunnyvale, CA, USA), a Rheodyne 7010 polyether ether ketone (PEEK) liquid six-port injection valve (Rheodyne, Cotati, CA, USA) fitted with a 100- μl sample loop and a post-column detection system. The latter included a Constametric III HPLC pump (LDC, Riviera Beach, FL, USA) used for delivery of PAR–ZnEDTA post-column reagent, a zero dead volume poly(tetrafluoroethylene) (PTFE) tee followed by a 1.4 m \times 0.3 mm I.D. PTFE reaction coil and Dionex spectral array detector (Dionex) set at 495 nm. The post-column reagent was a mixture of $1.2 \cdot 10^{-4}$ M 4-(2-pyridylazo)resorcinol (PAR), $2 \cdot 10^{-4}$ M ZnEDTA in 2 M NH_4OH in water. The flow-rate of the post-column reagent was 1.0 ml/min unless otherwise stated. Two PEEK columns were slurry packed with APAS and Silasorb Amine from an ethanol–water (50:50) mixture. A water bath was used for thermostating the PEEK chromatographic column (50 \times 4.6 mm) packed with 5 μm particle size silica bonded with aminophosphonic acid.

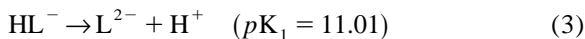
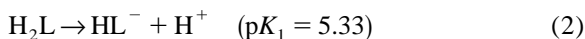
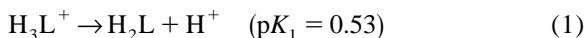
2.4. Reagents

All reagents were of analytical grade unless otherwise stated. Common reagents were supplied by BDH (Poole, UK) except PAR and Zn–EDTA which were obtained from Fluka (Glossop, UK). Metal stock solutions were Spectrosol standard solutions obtained from BDH. All solutions were prepared using deionised water from Milli-Q system) and stored in poly(propylene) bottles (Millipore, Bedford, MA, USA).

3. Results and discussion

3.1. Ion-exchange properties of APAS

The pK values of the dissociation constants known for ethylaminophosphonic acid for the consecutive reactions



are known [11]. The related pK values for amino-phosphonic groups attached to silica are not published elsewhere and may have different values from that known for the homogeneous analog. Only, pK_2 values for N-cyanoethylaminoethylphosphonic acid [12] and pK_1 values for aminodiphosphonic acid [13] attached to the silica surface were found equal to 5.4 and 2.0–2.5, correspondingly. The pK_2 value of the conditional dissociation constant of APAS evaluated from the data of potentiometric titration is equal to 5.6 which is close to the value of 5.4 obtained for the N-cyanoethyl derivative of aminophosphonic acid attached to the silica [12]. So, one can expect ampholyte properties for aminophosphonic acid bound silica in acid solution up to pH 3 and cation-exchange properties in weak acid or neutral solutions.

The previously described approach [14,15] involving the investigation of retention of different ionogenic organic compounds in 5 mM citric acid in the pH range 3 to 7 was used for evaluation of ion-exchange properties. The original aminopropyl silica used for the synthesis contained 0.45 mmol/g of bonded amino groups and demonstrated only weak anion-exchange properties (Fig. 1B) that corresponded to a stronger retention of benzenesulfonic and benzoic acids. In accordance with the results of the potentiometric titration the cation-exchange capacity of the synthesized aminophosphonic silica was equal to 0.1 mmol/g. Thus, the degree of conversion of amino groups into aminophosphonic is about 25%, so the resulting ion exchanger could have both anion- and cation-ex-

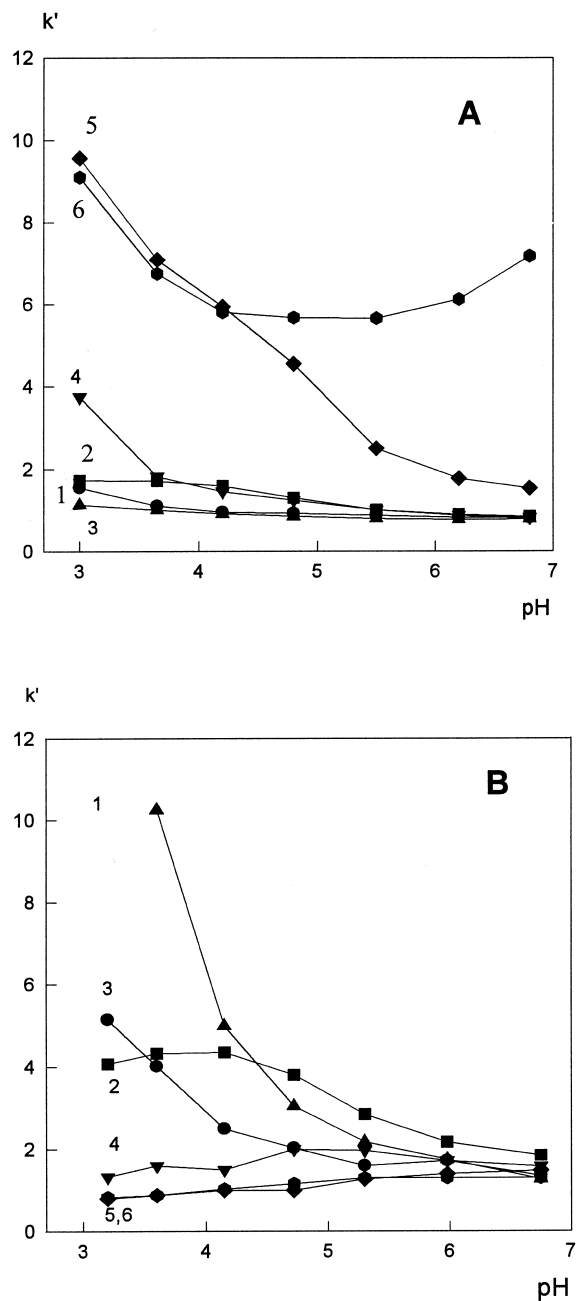
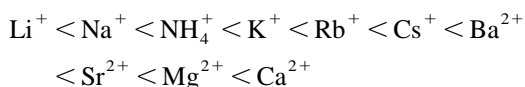


Fig. 1. Effect of eluent pH on capacity factor ($\log k'$) of some ionogenic organic compounds for (A) aminophosphonic acid and (B) aminopropylsilica bound silica. Eluent: 5 mM citric acid. Solutes: 1=benzenesulfonic acid, 2=benzoic acid, 3=aminosulphonic acid, 4=aminobenzoic acid, 5=aniline, 6=trimethylphenyl ammonium bromide.

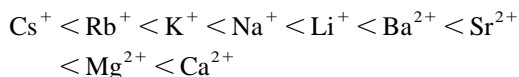
change properties. The aminophosphonic ion exchanger has the properties of a cation exchanger as expressed by the increased retention times of positively charged solutes such as trimethylphenyl ammonium and anilinium ion (Fig. 1A). It should be noted the significant retention of ampholyte solutes such as *p*-aminobenzoic and sulfanilic acids that clearly demonstrates the presence of zwitterionic properties of aminophosphonic acid functionalised silica at pH 3.

3.2. Influence of concentration of nitric acid on the retention of cations

As explained earlier, the ion exchangers containing phosphonic or aminophosphonic acid as ion-exchange functionality have the property to vary the effective charge of the phosphonic group with growth of pH of the eluent. It is a rather well established fact [5] that the ion-exchange selectivity of monodissociated and bidissociated forms of phosphonic acid functional groups is different. So in weak acid solution where only one OH group is dissociated the following selectivity law was observed [8]:



There is a very different selectivity in neutral and alkaline eluents where two groups are dissociated:

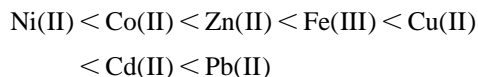


Another factor that should influence the ion-exchange selectivity is the possibility of bidissociated phosphonic acid functional groups forming relatively stable complexes with alkaline-earth and transition metal ions. Little is known about the ion-exchange selectivity of aminophosphonic acid functionalised silica based substrates. There is some data on the sorption of transition and lanthanide ions, uranium and thorium [16–18] and frontal chromatography of copper(II) [13].

It should be noted that no data has been published on the affinity of silica modified with any aminophosphonic functional groups towards alkali cations.

The studied aminophosphonic acid cation exchanger demonstrated low affinity and selectivity to alkali metal ions and significant retention of monovalent cations was obtained only with diluted $5 \cdot 10^{-4}$ M perchloric acid (see Fig. 2). No reasonable selectivity was achieved with either perchloric, acetic, citric or glycolic acid-based eluents. However, the elution order was different from the common one usually observed for sulpho- and carboxylic cation exchangers – $\text{Cs}^+ > \text{Rb}^+ > \text{K}^+ > \text{Na}^+ > \text{Li}^+$. Because of the poor ion-exchange selectivity of amino-phosphonic functional groups only a partial separation of rubidium and lithium can be achieved with diluted perchloric acid. The character of dependence (Fig. 2) is connected with a change in degree of dissociation of the aminophosphonic functional groups with pH.

The alkaline-earth (Fig. 3A) and transition metal ions on an APAS-packed column are retained in a stronger eluent such as $1.0\text{--}3.0 \cdot 10^{-2}$ M nitric or perchloric acid. The elution order of alkaline-earth cations is in accordance with literature data for phosphonic cation exchangers. The retention order of transition metal ions



is better correlated with stability constants of their complexes with chloromethylphosphonic acid than with those for aminophosphonic ligands (Table 1),

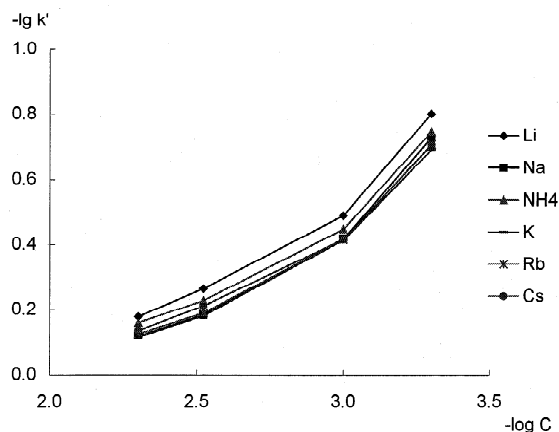


Fig. 2. The dependence of retention ($\log k'$) of alkali metal ions as a function of logarithm of concentration of perchloric acid. $T=20^\circ\text{C}$.

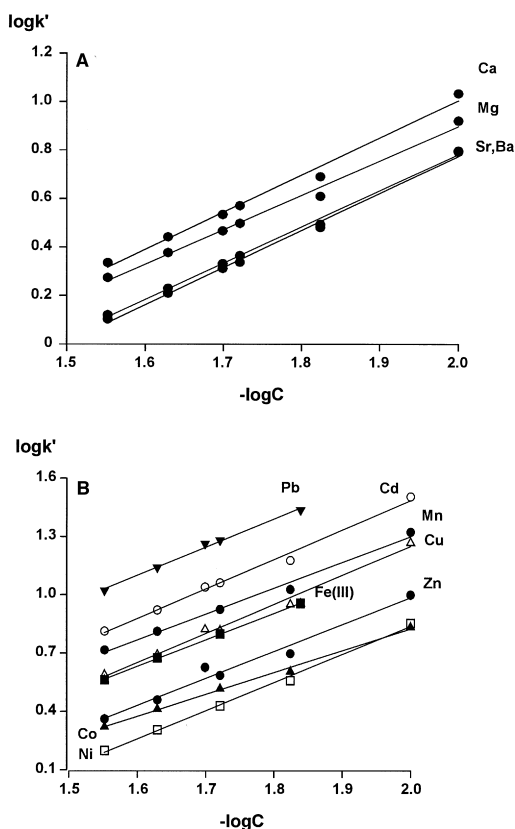


Fig. 3. The dependence of retention ($\log k'$) of (A) alkaline-earth and (B) transition metal ions as a function of logarithm of concentration of nitric acid. $T=20^\circ\text{C}$.

so one can conclude that the nitrogen in the amino-phosphonic group of APA-SiO₂ is not too available for complexation with metal ions, probably due to possible interaction of protonated amino group with

Table 1

Log β_1 values for complexes of metal ions with alkylphosphonic and aminomethylphosphonic ligands [11]

Metal ion	ClCH ₂ PO(OH) ₂	NH ₂ CH ₂ PO(OH) ₂
Mg ²⁺	1.59	2.03
Ca ²⁺	1.46	1.71
Sr ²⁺	1.18	
Ba ²⁺		
Co ²⁺	1.89	4.45
Ni ²⁺	1.81	5.29
Zn ²⁺	2.11	5.0
Mn ²⁺	2.19	
Cd ²⁺	2.43	
Cu ²⁺	2.88	8.12

residual silanols at the surface. A similar effect was obtained earlier for amino acid-bonded silica [14,15]. It should be noted that iron(III) was eluted between copper(II) and zinc(II) which contradicts the literature data published for the phosphonic acid cation exchangers.

3.3. Influence of ionic strength

The role of complexation in retention of cations can be revealed by a change of ionic strength of the eluent. In our previous investigation we demonstrated [19–21] that an increase of ionic strength produced by addition of common electrolytes like sodium perchlorate or potassium nitrate in the eluent can suppress or “swamp” electrostatic interactions between cations and the cation exchanger bearing iminodiacetic functional groups, but has little effect on their chelation ability. Such action led to change in elution order due to change of separation mechanism especially for alkaline-earth metal cations. So one can expect that in the case of other chelating cation exchangers such as APA-SiO₂ a similar effect should be achieved. Fig. 4 shows the effect of ionic strength on the retention of calcium and some transition metal ions on a column packed with APAS. As it was expected, the retention of all cations decreased drastically with increase of ionic

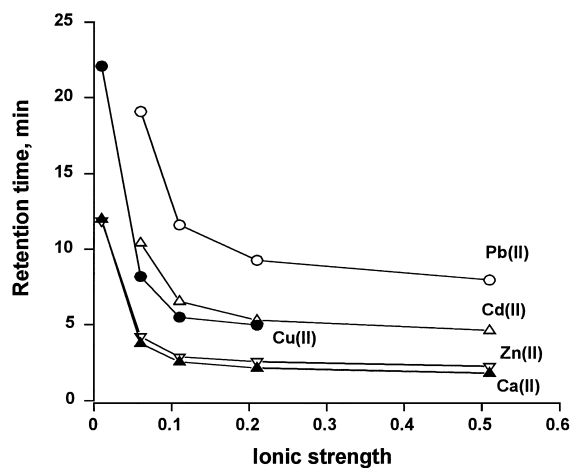


Fig. 4. The effect of ionic strength on the retention of alkaline-earth and transition metal ions. Column: 50×4.6 mm; eluent: 1.0·10⁻² M HClO₄ containing a varied concentration of NaClO₄; flow-rate: 1.0 ml/min.

strength of the eluent that corresponded to the presence of electrostatic interaction in this chromatographic system. However, the selectivity of separation was not changed at all except for the reversal in elution order for the pair $\text{Ca}^{2+}/\text{Zn}^{2+}$. Thus, even in the absence of significant ionic strength the role of chelation in retention of alkaline-earth and transition metal cations on the aminophosphonic phase is still the more dominant.

3.4. Influence of column temperature

Another suitable tool for changing the selectivity of separation is column temperature [19,20,22]. An increase of column temperature can also promote the complexation between separated cations of transition metal ions and chelating functional groups of the cation exchanger. Fig. 5 demonstrates the dependence of retention of metal ions ($\log k'$) as a function of inverse temperature. In the case of APA-SiO₂, the increase of column temperature has a little effect on the retention of most of investigated metal ions except of copper(II) and magnesium(II). In the case of copper(II), the retention increases with a growth of temperature and for magnesium and lead(II) (Table 2) cations the retention decreases. Thus, a separation performed at a column temperature around 50°C corresponds to optimal selectivity, allowing a reasonable separation of a standard

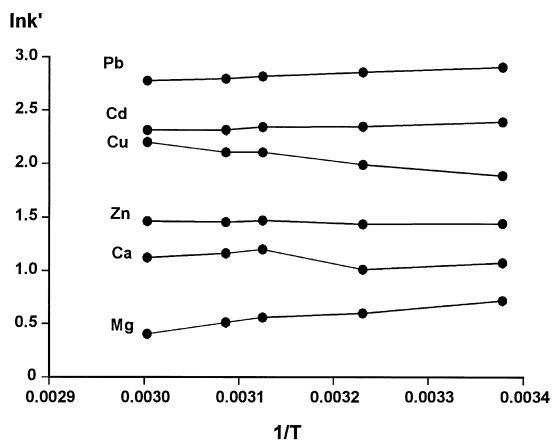


Fig. 5. The dependence of retention of metal ions ($\log k'$) as a function of inversed temperature ($1000/T$). Eluent: $1.6 \cdot 10^{-2} M \text{HNO}_3$ – $0.7 M \text{KNO}_3$.

Table 2

The effect of column temperature on the retention (t_R , min) of alkaline-earth and transition metal ions on APA-SiO₂ column (50×4.6 mm; eluent: $2 \cdot 10^{-2} M$; flow-rate: 1.0 ml/min)

Metal ion	Column temperature (°C)				
	23	36.5	47	51	60
Mg(II)	3.93	3.75	4.32	4.20	4.07
Ca(II)	4.42	4.13	4.07		3.92
Sr(II)	3.15	2.90	2.82		2.67
Ba(II)	3.05	2.82	2.75	2.67	2.50
Fe(III)		6.63	6.72	6.47	6.45
Cu(II)	7.63	8.33	9.22	9.23	10.03
Cd(II)	11.97	11.48	11.42	11.13	11.10
Pb(II)	19.35	18.48	17.78	17.40	17.07
Zn(II)	5.23	5.20	5.35	5.28	5.32

mixture of seven alkaline-earth and transition metal cations on a column of 5 cm length (Fig. 6). The column efficiency calculated for the peak of copper was 500 theoretical plates which gives about 10 000 plates/m. This compares favourably with typical efficiency of ion chromatography separations of metal ions on modern Dionex columns such as IonPak CS 10, which gives about 10 000 to 12 000 plates/m.

However, the asymmetry of some chromatographic peaks is worse on aminophosphonate columns. An unsatisfactory peak shape was observed under all experimental conditions only for manganese(II) (Fig. 7), which can be explained because of its slow kinetics of complexation with the aminophosphonic

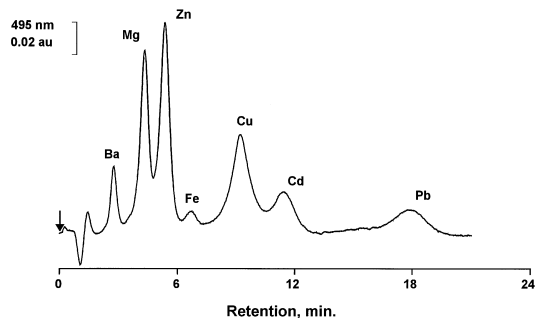


Fig. 6. Chromatogram of standard mixture of metal ions. Column: 50×4.6 mm; eluent: $2.0 \cdot 10^{-2} M \text{HNO}_3$; flow-rate: 1.0 ml/min; 47°C; sample volume: 100 μl . Peaks: 1.89 ppm Ba^{2+} (1), 1.13 ppm Mg^{2+} (2), 1.89 ppm Zn^{2+} (3), 3.37 ppm each of Fe^{3+} (4), Cu^{2+} (5), Cd^{2+} (6) and 7.75 ppm Pb^{2+} (7). Detection: PCR with PAR-ZnEDTA, 495 nm.

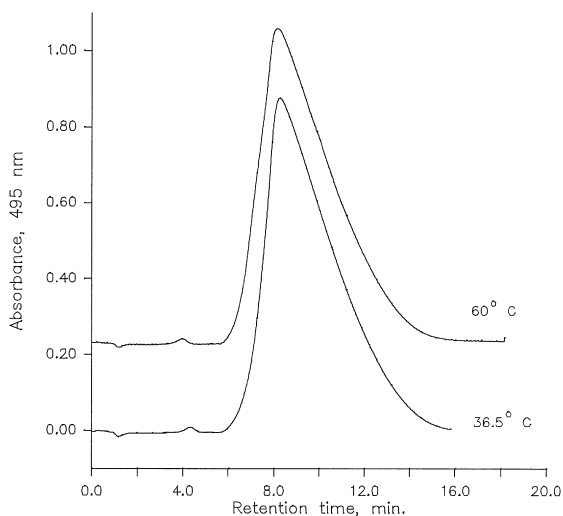


Fig. 7. The peak shape of manganese(II) under different column temperatures (a) 36.5°C and (b) 60°C. Column: 50×4.6 mm; eluent: $2.0 \cdot 10^{-2}$ M HNO_3 ; flow-rate: 1.0 ml/min; sample: 100 μl of 10 ppm standard solution of Mn(II).

ligand. It should be noted that an increase of column temperature does not significantly improve the peak shapes for cations under study.

4. Conclusions

Aminophosphonic acid bonded to silica shows a useful selectivity and kinetics of ion-exchange is quite good and is comparable with the commonly used small particles sulphonated resins. It could be applied to on-column preconcentration followed by ion chromatographic separation, allowing the determination of heavy metal ions such as lead(II), copper(II), cadmium(II) and zinc(II) strongly retained on a chromatographic column. The affinity of aminophosphonic functional groups towards alkali metal ions is low and a reversed elution order as compared with traditional sulpho and carboxylic cation exchangers was observed. This should make possible the determination of alkaline-earth metal ions in the presence of increased concentrations of alkali metal cations in samples.

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