

## Ion-exchange properties of glutamic acid-bonded silica

A.I. Elefterov\*, M.G. Kolpachnikova, P.N. Nesterenko, O.A. Shpigun

*Analytical Chemistry Division, Lomonosov Moscow State University, Lenin Hills GSP-3, Moscow 119899, Russia*

Received 11 October 1996; revised 6 January 1997; accepted 7 January 1997

---

### Abstract

The chromatographic behaviour of alkali, alkaline earth and some transition metals on the glutamic acid-bonded silica stationary phase was investigated using dilute solutions of perchloric acid as eluent. The effect of different classes of organic modifiers as well as the influence of temperature on the retention of cations were studied. Sorption heats for cations under different conditions were calculated. These investigations allowed the chromatographic separation conditions, under which either complex forming or ion-exchange mechanisms prevail, to be determined.

*Keywords:* Mobile phase composition; Temperature effects; Organic modifiers; Stationary phases, LC; Metal cations

---

### 1. Introduction

The synthesis of new selective ion exchangers is one of the topical problems in ion chromatography. Sorbents with attached carboxylic groups provide wider possibilities in varying selectivity of separation of metal cations on changing mobile phase pH in comparison with traditional sulfonic cation exchangers [1,2]. Moreover, besides ion exchange these sorbents allow formation of complexes of metal ions and their functional groups, which have different stability. This can also affect the selectivity of such sorbents.

Recently, sorbents with attached amino acid groups were studied intensively [3–8]. The existence of an amino group in attached molecules in the  $\alpha$ -position relative to the carboxylic group results in an increase of the dissociation constant of the latter. This allows using these sorbents in a wider pH range

– up to 2–3 – contrary to conventional carboxylic cation exchangers with the working pH range not lower than 4.

Preliminary investigations showed interesting ion-exchanging properties of the silica-based sorbents with attached groups of aminodicarboxylic acids. In our opinion, these can be used for separation of metal ions [3,4,9]. In this paper, we studied the cation-exchange properties of a sorbent with attached glutamic acid groups. Glutamic acid is able to form relatively stable complexes with metal cations. Thus, one could expect that ion exchange and chelation would play comparable roles in retaining metal cations, and selecting appropriate conditions would provide a predominant effect of one of these.

The aim of this paper was to investigate the general regularity of retention of metal cations on the amino acid-bonded silica sorbents (by the example of bonded glutamic acid groups) on varying the composition of mobile phase (pH, ionic strength, the concentration of organic solvent) and the temperature of chromatographic column.

---

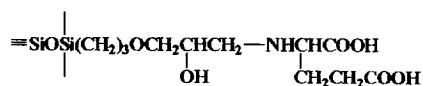
\*Corresponding author.

## 2. Experimental

### 2.1. Chromatographic system

The chromatographic system consisted of a Milton Roy A 802 (USA) high-pressure pump, a Rheodyne 7125 (USA) injector with a 50- $\mu$ l loop, a stainless-steel column (100 $\times$ 4.6 mm), a thermostat, a LKB Conductolyser 5300B (Sweden) conductometric detector, a Beckman 114M (Sweden) high-pressure pump for post-column reagent, a Valko chamber for mixing the eluate and the reagent (USA), a Linear MicroUVis 20 (USA) spectrophotometric detector, and a Spectra-Physics DP-700 (USA) integrator.

Silica gel Silasorb 300 (Lachema, Brno, Czechoslovakia) with 5- $\mu$ m particle size and 300 m<sup>2</sup> g<sup>-1</sup> specific surface area was used as a matrix for preparing the sorbent. The sorbent was prepared by attaching glutamic acid groups to glycidoxypopyl silica [10]. The chromatographic column was packed with glutamic acid-bonded silica by suspension method. The structure of the ion-exchange site is shown below:



### 2.2. Reagents

All the reagents used were analytical grade or purer. The solutions were prepared using doubly distilled water. Solutions of perchloric acid were used as the eluents. The following organic modifiers were used throughout: acetonitrile and methanol (both HPLC grade) from Merck (Darmstadt, Germany) and high-purity grade isopropanol from Reakhim (Moscow, Russia).

A solution of PAR–Zn–EDTA served as a post-column reagent for photometric detection of metal cations at a high ionic strength of eluents. The solution was prepared from PAR [monosodium salt of 4-(2-pyridylazo)resorcinol] from Reanal (Budapest, Hungary) and Zn–EDTA (tetrahydrate of disodium salt of zinc ethylenediaminetetraacetate, C<sub>10</sub>H<sub>12</sub>N<sub>2</sub>Na<sub>2</sub>O<sub>8</sub>Zn·4H<sub>2</sub>O) research grade, from Merck.

### 2.3. Potentiometric titration

A weighed portion of the sorbent (0.1–0.3 g) or the corresponding amount of a solution of glutamic acid was placed into a titration flask with a solution of sodium perchlorate (0.5 mol l<sup>-1</sup>) and was titrated with a solution of 0.01 mol l<sup>-1</sup> sodium hydroxide and 0.5 mol l<sup>-1</sup> of sodium perchlorate with stirring. The process of equilibrium attaining was monitored using the signal from a pH meter on a self-recorder.

## 3. Results and discussion

### 3.1. Ion-exchange properties of the sorbent

Glutamic acid is an ampholyte and can exist as a cation or as an anion depending on pH (pK<sub>1</sub>=2.39, pK<sub>2</sub>=4.21, pK<sub>3</sub>=9.54 [11]). Thus, a sorbent based on glutamic acid can serve as either a cation exchanger or an anion exchanger. Attaching glutamic acid groups to the sorbent surface affects their acid–base properties. First, the primary amine becomes the secondary one and acidity of the carboxylic group increases. Second, the secondary amino groups interact with the remaining silanol groups of the sorbent, which somewhat decreases their basicity. Moreover, this leads to a dependence of acid–base properties on the concentration of the groups on the sorbent surface [5,9].

Cation- and anion-exchange properties of the sorbent were found by studying pH dependencies of the retention of organic ions (aromatic amines, acid and ampholyte) – aniline, trimethylphenylammonium, benzoic and *p*-aminobenzoic acids – using a solution of citric acid as an eluent [9].

Increasing the pH of the eluent from 2.9 to 7.0 leads to an increase of the charge of the functional groups due to their dissociation. Moreover, an increase in pH of the eluent increases the eluting ability of citric acid. Both these factors result in a decrease in retention times of benzoic and *p*-aminobenzoic acids. In the case of trimethylphenylammonium, an increase in pH results in a drastic increase in retention. The curve of pH dependence of retention times of aniline (Fig. 1) shows a maximum at pH 4.8–5.0, the existence of the maximum is connected with a competition of two processes:

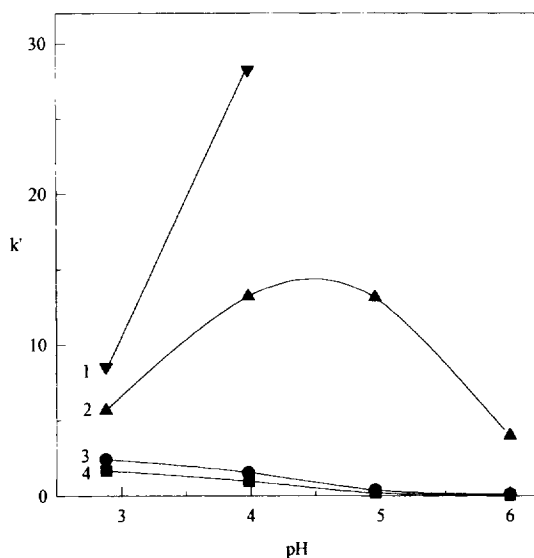


Fig. 1. Effect of eluent pH on capacity factor of some ionogenic organic compounds. Eluent:  $5 \cdot 10^{-3} \text{ mol l}^{-1}$  citric acid. 1: Tri-methylphenylammonium; 2: aniline; 3: benzoic acid; 4: *p*-amino-benzoic acid.

dissociation of the carboxylic groups of the sorbent, which results in an increase of retention times, and deprotonation of the amino group of aniline, which decreases the retention. Thus, it is clear that the cation-exchange properties of the sorbent prevail over the anion-exchanging properties.

### 3.2. Capacity characteristics of the sorbent

Exchange capacity is one of the most important characteristics of the sorbents for ion chromatography. Thus, we determined static and dynamic capacity of the sorbent in question for copper(II) and the capacity from the data of potentiometric titration.

Potentiometric titration of the sorbent with sodium hydroxide was performed under high ionic strength to eliminate the effect of electrostatic repulsion of the titrant ions and negatively charged carboxyl groups of the sorbent, which makes the titration difficult. From the titration curve it was found that the dissociation constant of  $\gamma$ -carboxylic group is  $pK_a = 4.13$ . This value is lower than the value for free glutamic acid under the same conditions,  $pK_a = 3.72$  (for ionic strength close to zero  $pK_a = 4.21$  [11]). This can be accounted for the formation of hydrogen

bonds of the amino groups with silanol groups of silica, which results in a decrease in the basicity of the nitrogen atoms and, thus, in a decrease in the dissociation constants of the carboxylic groups. The sorbent capacity from the data of potentiometric titration was  $55 \mu\text{mol g}^{-1}$ .

In this case, the static exchange capacity of the sorbent for copper(II) is a function of pH, because the degree of dissociation of the bonded groups on the surface increases with an increase in pH. Starting with pH 4, the exchange capacity is nearly constant and equal to  $38 \mu\text{mol g}^{-1}$ .

The dynamic exchange capacity was determined by eluting copper from the chromatographic column after its complete saturation. The dynamic capacity was  $71.7 \mu\text{mol g}^{-1}$ . This value is larger than the static capacity nearly by a factor of two. This can be accounted for by the formation of complexes with a metal–ligand ratio of 2:1 owing to a large excess of copper over the functional groups of the sorbent in comparison with the determination of static exchange capacity.

### 3.3. Dependencies of retention of metal cations on the composition of mobile phase

In a wide pH range the cation-exchange properties of the studied sorbent prevail over the anion-exchange properties and metal ions can form complexes with bonded groups of glutamic acid. Therefore, we studied the retention of cations of alkali, alkaline-earth and several transition metals.

The most frequently used eluents for separation of cations of alkali and alkaline-earth metals are dilute solutions of mineral acids because protons have a high eluting ability. We selected perchloric acid as an eluent because it allows the most sensitive indirect conductometric detection owing to the lowest mobility of its anion, which decreases the background signal and the limits of detection.

The dependencies of the capacity factors of the cations on the concentration of perchloric acid in the eluent in bilogarithmic coordinates are nearly linear (Fig. 2). This is evidence of the predominant ion-exchange character of retention. However, the slopes differ significantly from the theoretical: 1.5 for alkali and 2.1–2.5 for alkaline-earth and transition metals (theoretical values are 1 and 2, respectively). This

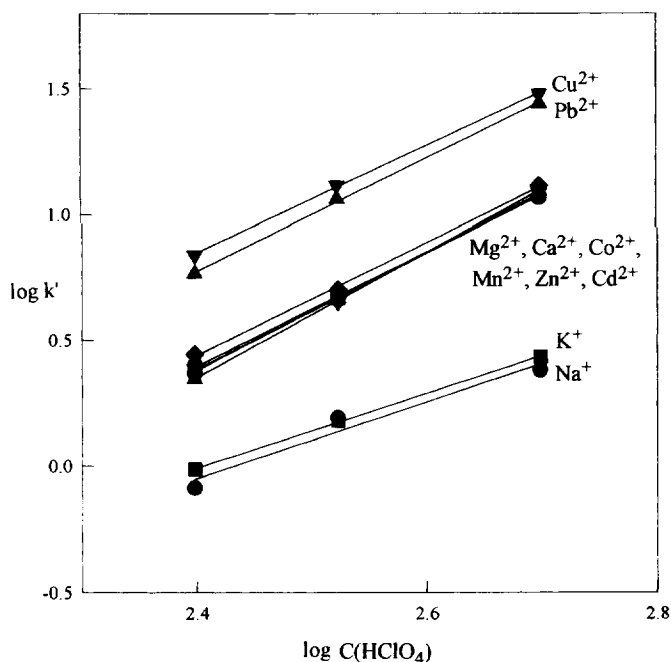


Fig. 2. Dependence of capacity factors for cations on the concentration of perchloric acid in the eluent.

can be accounted for by a change in ionic state of the ion-exchange centre on an increase of pH of the eluent. Moreover, doubly charged cations can also form complexes with glutamic acid groups on the surface of the sorbent. This should also result in an increase in retention, and this process also becomes more pronounced with an increase in pH of the eluent.

Thus, using solutions of perchloric acid as an eluent makes it possible to divide the studied cations into three groups: (i) alkali metals, (ii) alkaline-earth and most transition metals and (iii) lead and copper. The strongest retention of copper among the doubly charged cations can be accounted for its strong affinity to the nitrogen of the amino acid groups (Table 1). In the case of lead, it forms relatively stable mixed-ligand hydroxo complexes ( $\log K [\text{Pb}(\text{OH})\text{Glu}+\text{H}]=8.25$ , where Glu is glutamic acid [11]). In our opinion, no selectivity in separation of

alkaline-earth and several transition metals is accounted for mutual influence of ion exchange and weak chelation of the cations with bonded amino acid groups on the surface of sorbent.

Frequently, eluents in ion chromatography contain organic modifiers (acetonitrile, alcohols, etc.). Their presence in the eluent may change the selectivity of separation, increase the speed of analysis or enhance the shape of chromatographic peaks. Organic modifiers can interact both with test ions, e.g. by replacing part of the water molecules in the solvate shell of an ion or forming complexes, and with functional groups of a sorbent revealing their donor–acceptor properties.

We studied the influence of the solvents most frequently used in liquid chromatography (acetonitrile, methanol and isopropanol) on the cation retention. Adding any of the solvents resulted in a decrease in retention times (Fig. 3). This effect is

Table 1  
Stability constants of complexes of metals with glutamic acid ( $\log K_1$ ) [11]

$\text{Sr}^{2+}$	$\text{Ca}^{2+}$	$\text{Mg}^{2+}$	$\text{Cd}^{2+}$	$\text{Mn}^{2+}$	$\text{Co}^{2+}$	$\text{Zn}^{2+}$	$\text{Pb}^{2+}$	$\text{Cu}^{2+}$
1.37	1.43	1.9	3.9	4.09	4.56	5.34	5.57	8.20

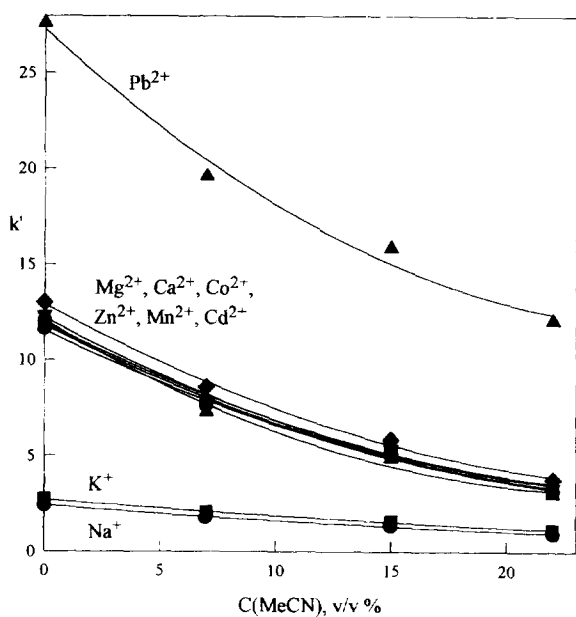


Fig. 3. Dependence of retention of cations ( $k'$ ) on the concentration of acetonitrile in the eluent. Eluent:  $2 \cdot 10^{-3} \text{ mol l}^{-1}$  perchloric acid with acetonitrile.

due to the lower polarity of organic solvents compared to water (Table 2). Therefore, adding them to the eluent decreases permittivity of the solution and weakens electrostatic interactions between the sorbed cations and the carboxylic groups of the sorbent. It also decreases the degree of dissociation of the groups. One could therefore expect that adding equal amounts of organic solvents would cause a lowering of retention times, which would increase as the polarity of the solvent decreases, in the order water > acetonitrile > methanol > isopropanol. However, the experimental data obtained show that the order for the organic modifiers is reversed (Table 3).

Besides polarity, the retention is also affected by the protophylic and protogenic properties of the solvents. These properties can be characterised using solvatochromic parameters of acidity and basicity of the solvents proposed for solvent classifying by Snyder (Table 2) [12]. It is known that attached glutamic acid at the pH of the eluent used (from 2.5 to 3) exists as a zwitterion, and water serves as an acceptor in the reaction of the amino group deprotonation —the carboxylic group protonation:



It is clear that a stronger carboxylic group would be the functional group with stronger cation-exchange properties. Where the eluent contains an organic modifier, which is a stronger proton acceptor (Table 2), the equilibrium is shifted to the right: to the protonated  $\alpha$ -carboxylic group and, therefore, to the sorbent with lower capacity. In addition, the carboxylic group with a protonated amino group in  $\alpha$ -position will be protonated last owing to a strong negative inductive effect. It also shifts the equilib-

Table 2  
Classification of solvents according to Snyder [12]

Solvent	$P'$	$x_c$	$x_d$	$x_n$
Water	10.2	0.37	0.37	0.25
Acetonitrile	5.8	0.31	0.27	0.42
Methanol	5.1	0.48	0.22	0.31
Isopropanol	3.9	0.55	0.19	0.27

$P'$  = polarity,  $x_c$  = proton acceptor parameter,  $x_d$  = proton donor parameter,  $x_n$  = dipolar interaction parameter.

Table 3  
Retention of cations ( $\log k'$ ) for various organic modifiers in the eluent

Organic solvent	$\text{Na}^+$	$\text{K}^+$	$\text{Mg}^{2+}$	$\text{Ca}^{2+}$	$\text{Cd}^{2+}$	$\text{Co}^{2+}$	$\text{Mn}^{2+}$
None	0.50	0.56	1.04	1.06	1.10	1.06	1.04
Acetonitrile	0.21	0.28	0.79	0.82	0.87	0.82	0.81
Methanol	0.23	0.29	0.81	0.85	0.90	0.85	0.84
Isopropanol	0.24	0.40	0.82	0.91	0.90	0.84	0.84

Eluent:  $2 \cdot 10^{-3} \text{ mol l}^{-1}$  solution of perchloric acid with organic modifier, 10 % (v/v); 33°C.

rium to the right in case of a solvent with stronger proton acceptor properties (Table 2). Both these phenomena result in shorter retention times in the case of acetonitrile compared to methanol or isopropanol (Table 3). It should be noted that adding organic modifiers to the eluent does not change the selectivity of separation.

To investigate chelating properties of the sorbents, it is necessary to suppress ion exchange in one way or another. It is known that using eluents with more than  $0.1 \text{ mol l}^{-1}$  of a strong electrolyte allows almost complete suppression of ion exchange in a chromatographic system [13]. In our case, we added sodium perchlorate (from  $0.05$  to  $0.2 \text{ mol l}^{-1}$ ) to the mobile phase.

On increasing pH, we observed a growth of retention of the cations and an increase in selectivity of separation (Fig. 4), and the elution order as a whole corresponds to the stability constants of the metal complexes with glutamic acid (Table 1). This is evidence of the increasing contribution of chelation to the cation retention owing to an increase in the degree of dissociation of the functional groups bonded to the surface and an increase in conditional stability constants of the complexes. An abnormally high retention of cadmium seems to be connected with formation of mixed-ligand hydroxo complexes analogous to the case of lead [11]. At pH higher than

4.5–5, no further increase in retention times is observed due to complete dissociation of glutamic acid residues on the surface of silica.

### 3.4. Influence of temperature on the retention of metal cations

Changing temperature is used in liquid chromatography less frequently than varying the composition of the mobile phase. However, increasing the temperature of a chromatographic column sometimes enhances the selectivity of retention and increases the efficiency. Moreover, a study of temperature dependencies of retention times allows a more profound investigation of the mechanism of the separation process owing to a simple dependence that connects the capacity factors  $k'$ , sorption enthalpy  $\Delta H^\circ$  and temperature:

$$\ln k' = -(\Delta H^\circ/RT) + \text{constant}$$

In the case of a solution of perchloric acid as an eluent, an increase of the column temperature results in a decrease in the retention times of the cations on the silica with attached glutamic acid groups (Fig. 5). The dependencies of logarithms of capacity

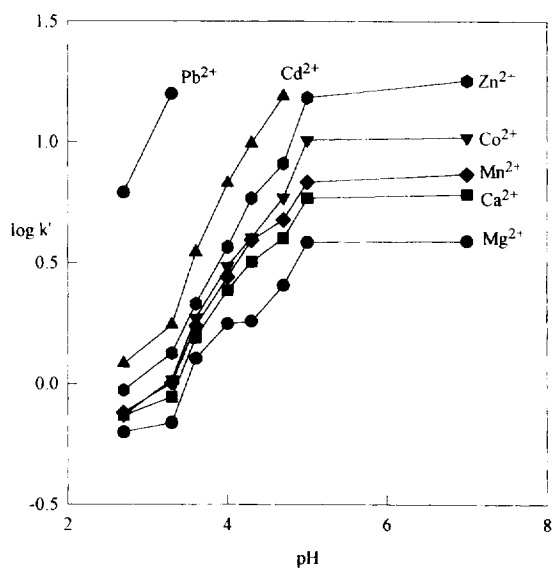


Fig. 4. pH dependence of retention of metal cations. Eluent:  $0.2 \text{ mol l}^{-1}$  solution of sodium perchlorate.

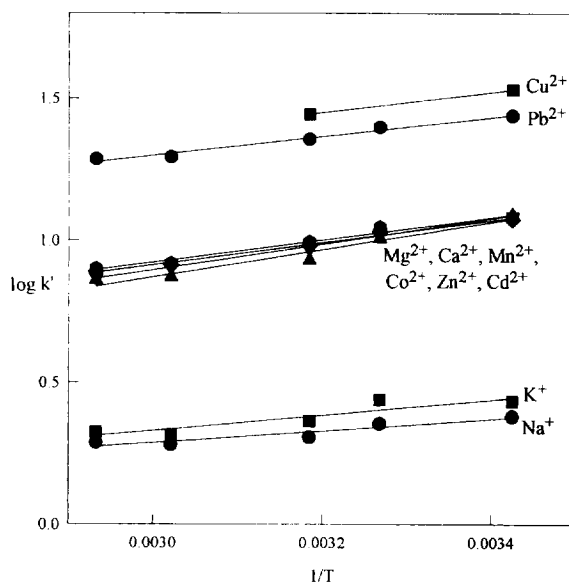


Fig. 5. Temperature dependencies of capacity factors. Eluent:  $2 \cdot 10^{-3} \text{ mol l}^{-1}$  solution of perchloric acid.

Table 4  
Sorption heats ( $-\Delta H^\circ$ , kJ mol $^{-1}$ ) of metal cations

Eluent	Na $^+$	K $^+$	Mg $^{2+}$	Ca $^{2+}$	Mn $^{2+}$	Co $^{2+}$	Zn $^{2+}$	Cd $^{2+}$	Pb $^{2+}$	Cu $^{2+}$
2·10 $^{-3}$ mol l $^{-1}$ HClO $_4$	3.97	5.19	9.29	8.67	8.08	7.51	7.52	6.96	6.45	6.99
2·10 $^{-3}$ mol l $^{-1}$ HClO $_4$ with 10% (v/v) CH $_3$ CN	6.07	4.30	8.63	9.06	8.58	7.50	8.00	6.62	5.59	-1.61
2·10 $^{-3}$ mol l $^{-1}$ HClO $_4$ with 10% (v/v) iso-PrOH	4.62	3.06	9.32	10.1	8.21	6.85	7.73	6.00	7.59	7.22
0.2 mol l $^{-1}$ NaClO $_4$ (pH 4.0)	-	-	-2.08	-2.81	-3.01	-3.95	-5.96	-11.3	-	-
0.2 mol l $^{-1}$ NaClO $_4$ (pH 4.7)	-	-	-10.1	-9.17	-13.1	-18.8	-30.6	-	-	-

factors on reciprocal temperature for the system in question are virtually linear in the studied temperature range for all the studied cations; the sorption process is exothermic (Table 4). This agrees with the existing data on determining the sorption heats of cations using solutions of mineral acids as eluents [14,15].

We also investigated temperature dependencies of retention times of the cations in the presence of organic modifiers – acetonitrile or isopropanol – in the eluent. In all cases, we observed a regular decrease in the retention times with increasing temperature of the system (Fig. 6). The slopes for most cations and, therefore, their sorption heats,

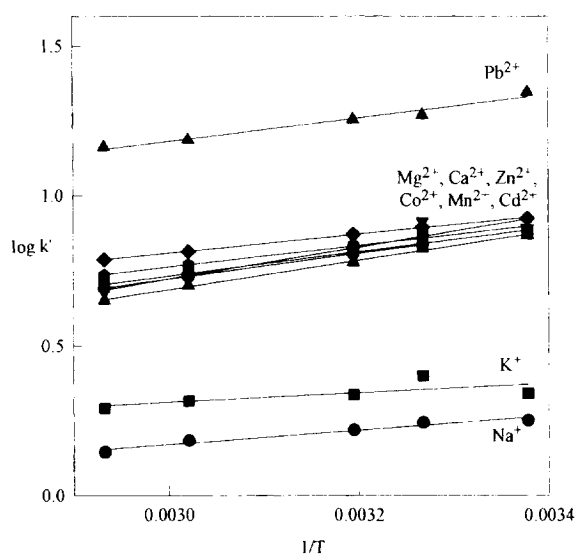


Fig. 6. Temperature dependencies of capacity factors for the cations. Eluent: 2·10 $^{-3}$  mol l $^{-1}$  solution of perchloric acid with 10% (v/v) isopropanol.

changed insignificantly compared to the aqueous mobile phase (Table 3). In the case of the eluent containing acetonitrile, copper was an exception: its retention time increased with an increase in temperature. This is possibly connected with a complete or partial change in the retention mechanism (increased contribution of chelation), for copper forms the most stable complexes with glutamic acid (Table 1). Thus, adding small amounts of organic modifiers (up to 10–20, v/v) to the eluent does not lead to a significant change in the retention mechanism for the most cations in question.

As noted above, high ionic strength of the eluent should suppress ion exchange and chelation should become the predominant mechanism of retention. At high pH values of the eluent, we observed an increase in retention times of the cations on increasing the temperature (Fig. 7a,b), i.e. under these conditions the sorption is endothermic. The heats of sorption calculated from these dependencies (Table 4) and the elution order of the cations are in good correlation with the stability constants of the complexes with glutamic acid (Table 1). This allows us to conclude that under these conditions the effect of chelation on retention prevails over ion exchange.

When pH of the eluent is about 3, i.e. in the pH range that corresponds to millimolar solutions of perchloric acid, the behaviour of temperature dependencies of the retention times (Fig. 7c) is similar to the dependencies for the eluents with low ionic strength (Fig. 5) with exothermic Joule effect. In our opinion, the major contribution to the retention is accounted for by residual ion exchange, and chelation virtually does not affect the retention due to a low degree of dissociation of glutamic acid attached to the sorbent surface.

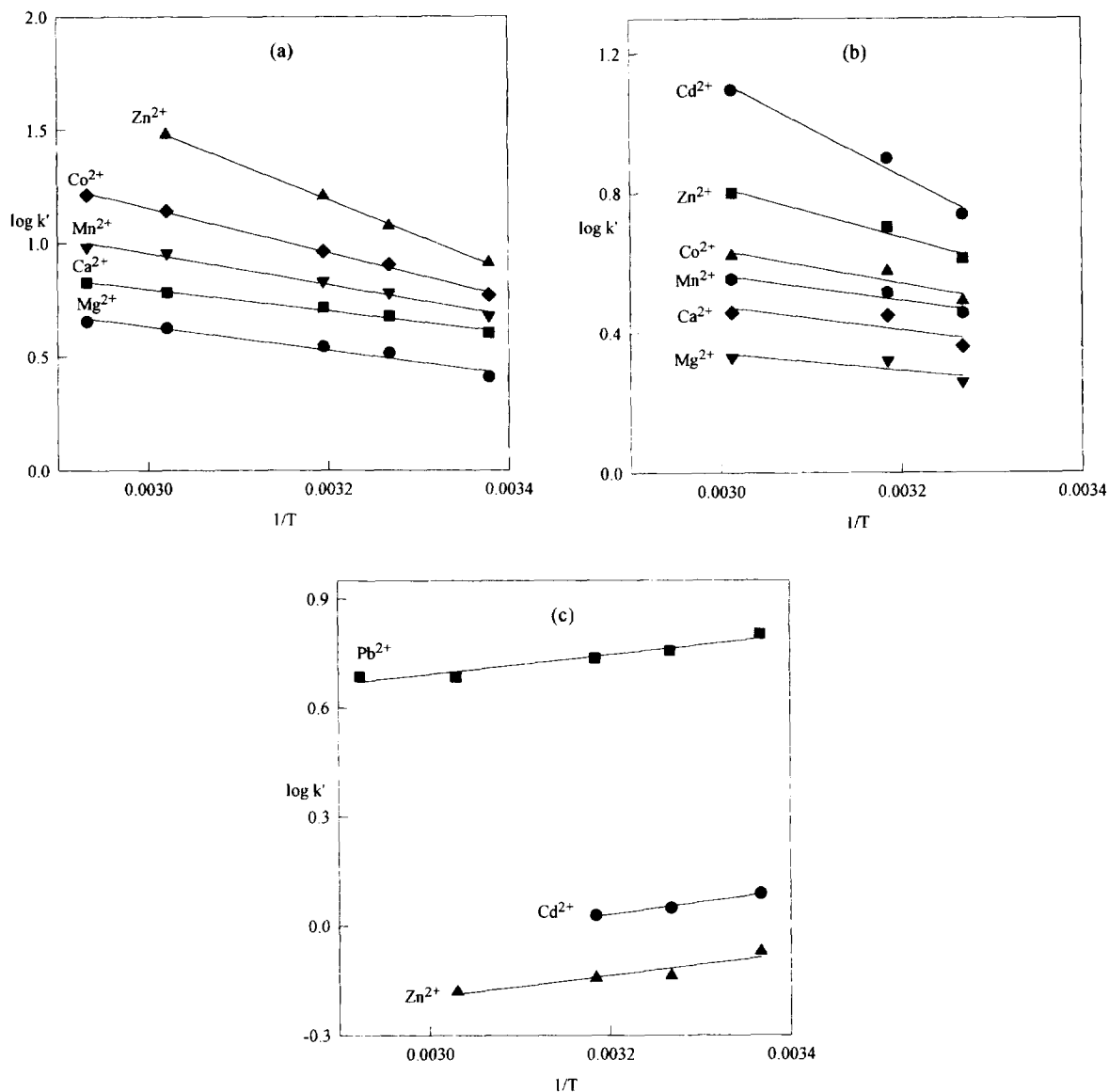


Fig. 7. Temperature dependencies of capacity factors for the cations. Eluent: 0.2 mol l<sup>-1</sup> solution of sodium perchlorate, pH (a) 4.7, (b) 4.0 and (c) 3.0.

### 3.5. Determination of lead

As was mentioned previously, lead can be determined with high selectivity using solutions of perchloric acid as eluents. The selectivity is high enough for all the investigated concentrations of the acid in the eluent. Thus, to increase speed, the

analytical characteristics of the system in question were determined for the concentration of perchloric acid of  $4 \cdot 10^{-3}$  mol l<sup>-1</sup>. The chromatogram of a model mixture is shown in Fig. 8.

The upper limit of linear range of the calibration graph for indirect conductometric detection is  $4 \cdot 10^{-3}$  mol l<sup>-1</sup> of lead for peak heights and  $7 \cdot 10^{-3}$



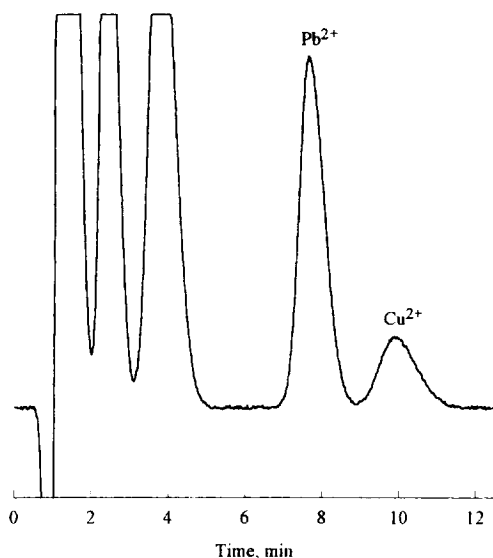


Fig. 8. Chromatogram of a model mixture of metal cations. Eluent:  $4 \cdot 10^{-3}$  mol l<sup>-1</sup> solution of perchloric acid, 1 ml min<sup>-1</sup>; conductometric detection.

mol l<sup>-1</sup> for peak areas (the volume of injected sample is 50  $\mu$ l). The limit of detection calculated by  $3\sigma$  criterion is 0.05  $\mu$ g. The determination is characterised with high precision: the values of R.S.D. are 0.4% for retention times, 1% for peak heights and 3% for peak areas ( $n=3$ ,  $P=0.95$ ). More than 30-fold amounts of alkali and 10-fold amounts of alkaline-earth or transition metals do not interfere with the determination of lead in the mixtures.

The results of the determination of lead in a certified reference sample and in samples of waste and swamp water (with preconcentration on a Diasorb-IDA concentrating cartridge) are in good

Table 5  
Results of determination of lead ( $n=3$ ,  $P=0.95$ )

Sample	Found ( $\mu$ g ml <sup>-1</sup> ) <sup>a</sup>	Pb <sup>2+</sup>
	IC	AAS
Certified reference sample	4.99 $\pm$ 0.07	5.01
Waste water (after preconcentration)	0.33 $\pm$ 0.01	0.31
Swamp water (after microwave digestion and preconcentration)	0.023 $\pm$ 0.002	0.020

<sup>a</sup> IC = developed ion chromatographic procedure for determination of lead; AAS = atomic absorption spectrometry.

agreement with the results of atomic absorption determination (Table 5).

#### 4. Conclusion

The influence of composition of mobile phase (pH, ionic strength and the concentration of organic modifiers in the eluent) on the retention of inorganic cations on silica with bonded groups of glutamic acid was studied.

The effect of temperature on retention for various conditions of separation was investigated. It was shown that an increase in temperature leads to a decrease in the retention times for the ion-exchange mechanism of retention and to an increase of the retention times for the chelation mechanism of retention.

The heats of sorption of the cations were calculated. We found that in the case of the chelation mechanism of retention, they correlate with the stability constants of the complexes. The dependence of heat of sorption on pH of the solution was studied.

#### Acknowledgments

This work is supported by the Russian Foundation for Fundamental Research (projects No. 95-03-09571a and No. 96-03-42597z).

#### References

- [1] D. Jensen, J. Weiss, M.A. Rey and C.A. Pohl, *J. Chromatogr.*, 640 (1993) 65.
- [2] L.M. Nair, R. Saari-Nordhaus and J.M. Anderson, Jr., *J. Chromatogr. A*, 671 (1994) 43.
- [3] L.W. Yu, T.R. Floyd and R.A. Hartwick, *J. Chromatogr. Sci.*, 24 (1986) 177.
- [4] L.W. Yu and R.A. Hartwick, *J. Chromatogr. Sci.*, 27 (1989) 176.
- [5] P. Nesterenko, *J. Chromatogr.*, 605 (1992) 199.
- [6] P.N. Nesterenko, O.A. Shpigun and Yu.A. Zolotov, *Dokl. Akad. Nauk*, 324 (1992) 107.
- [7] P.N. Nesterenko, R.V. Kopylov, D.A. Tarasenko, O.A. Shpigun and Yu.A. Zolotov, *Dokl. Akad. Nauk*, 326 (1992) 838.
- [8] P.N. Nesterenko, *J. High Resolut. Chromatogr.*, 14 (1991) 767.

- [9] P.N. Nesterenko, A.I. Elefterov, D.A. Tarasenko and O.A. Shpigun, *J. Chromatogr. A*, 706 (1995) 59.
- [10] V.A. Malinovskiy, S.M. Staroverov and G.V. Lisichkin, *Vestnik. Mosk. Un-ta., Ser.2, Khim.*, 25 (1984) 80.
- [11] IUPAC — Stability Constants Database. Version 2.62. Academic Software Royal Society of Chemistry IUPAC, 1994.
- [12] L.R. Snyder, *J. Chromatogr. Sci.*, 16 (1978) 223.
- [13] O.J. Chalenger, S.J. Hill and P. Jones, *J. Chromatogr.*, 639 (1993) 197.
- [14] N.E. Fotier and J.S. Fritz, *Talanta*, 34 (1978) 415.
- [15] S. Cerjan-Stefanovic and M. Kastelan-Macan, *Fresenius' Z. Anal. Chem.*, 332 (1988) 817.