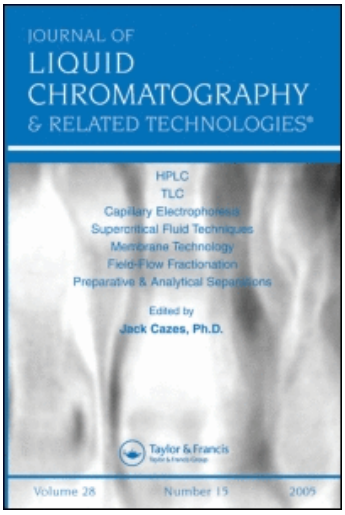

Journal of Liquid Chromatography & Related Technologies
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597273

Separation and Determination of Chosen λ⁵-Silanates by an Isotachophoresis Technique

Mariusz Kluska[a]; Krzysztof Pypowski[a]; Ireneusz Chrząścik[a]; Tatiana Koval[b]; Nikolai Erchak[a]
[a] Institute of Chemistry, University of Podlasie, Siedlce, Poland [b] Brest State University, Brest, Belarus

To cite this Article Kluska, Mariusz , Pypowski, Krzysztof , Chrząścik, Ireneusz , Koval, Tatiana and Erchak, Nikolai(2009) 'Separation and Determination of Chosen λ⁵-Silanates by an Isotachophoresis Technique', Journal of Liquid Chromatography & Related Technologies, 32: 6, 896 — 907
To link to this Article: DOI: 10.1080/10826070902768187
URL: http://dx.doi.org/10.1080/10826070902768187

Journal of Liquid Chromatography & Related Technologies®, 32: 896–907, 2009

ISSN: 1082-6076 print/1520-572X online
DOI: 10.1080/10826070902768187

Separation and Determination of Chosen λ^5-Silanates by an Isotachophoresis Technique

Mariusz Kluska,[1] Krzysztof Pypowski,[1] Ireneusz Chrząścik,[1] Tatiana Koval,[2] and Nikolai Erchak[1]

[1]Institute of Chemistry, University of Podlasie, Siedlce, Poland
[2]Brest State University, Brest, Belarus

Abstract: This work is a continuation of an investigation concerning separation and determination of a mixture of newly obtained pentacoordinated silanates: 1-(N-perhydro-azepiniomethyl)[spirobi(1-sila-2,5-dioxacyclopentane-3-on)]ate, 1-(N-perhydroazepinio-methyl)[spirobi(1-sila-2,5-dioxa-4-methylcyclopentane-3-on)]ate, 1-(N-perhydro-azepinio-methyl)[spirobi(1-sila-2,5-dioxa-4,4-dimethylcyclopentane-3-on)]ate. Because of low mobility of analyzed ions elaboration of a new termination electrolyte was necessary. As a main component of this electrolyte, a newly synthesized compound – 4,4′-bis{1-(N-perhydro-azepiniomethyl)[spirobi(1-sila-2,5-dioxacyclopentane-3-on)]ate} was used. Separation of the analyzed mixture can be carried out in a time under 12 minutes.

Keywords: Hypercoordinated silicon compounds, Isotachophoresis, Separation

INTRODUCTION

Aminomethyltrialkoxysilanes are starting materials in the reaction of the preparation of hypercoordinated ES-silanates. ES-silanates belong to compounds biologically active and related to natural compounds. At present, wide ranging investigations concerning the biological activity of this group of compounds is being conducted.[1–4]

Correspondence: Mariusz Kluska, Institute of Chemistry, University of Podlasie, 54 3-Maja St., 08-110 Siedlce, Poland. E-mail: kluskam@ap.siedlce.pl

Recently, silicon organic compounds played the key role in bioregulation of plant organisms.[5,6] The highest growth stimulating biological activity shows silatrane.[6] However, they possess some disadvantages, e.g., low solubility in water, high hydrolytic instability. As chloroderivatives they can be sources of potential toxic products of their degradation in an environment.

Experimental confirmation of the possibilities of electrostatic stabilization of ES-silanates opens a way to numerous, earlier not known classes of chemical compounds. New compounds are starting materials to new substances, systems, materials, and new solutions. They create expectations for new specific biological activity and consistently, then possibilities of new treatment methods of resistant or even incurably diseases.[7]

Chiral hypercoordinated silicon compounds are engaged in transferring of chirality's from silicon atom to carbon atom[8] and can serve as model compounds for processes of biological silicon transport.[9]

Data from the literature show that hypercoordinated silicon organic complexes can be formed in biologically associated fluids.[10] An existence of a transitional silicon organic complex, generated during a vital cycle, was also reported. A controversial suggestion concerning the important role of hypercoordinated silicon organic compounds in assimilation and transport of silicon through biological systems was also confirmed. The existence of these complexes can explain other questions of biogeochemistry of silicon, e.g., a problem of stability of silica dissolved in concentrated biological fluids, biofractionation of silicon isotopes, and fractionation of germanium from silicon. Silicon organic compounds, which contain pentacoordinated silicon, can effectively increase silicon solubility, transport this element through an organism, and accumulate it in suitable places.[10]

The aim of this work was to elaborate the optimum conditions of separation and determination of three newly obtained pentacoordinated silanates: 1-(N-perhydroazepinio-methyl)[spirobi(1-sila-2,5-dioxacyclopentane-3-on)]ate, 1-(N-perhydroazepiniomethyl)-[spirobi(1-sila-2,5-dioxa-4-methylcyclopentane-3-on)]ate, 1-(N-perhydroazepiniomethyl)-[spirobi(1-sila-2,5-dioxa-4,4-dimethylcyclopentane-3-on)]ate by the capillary isotachophoresis technique. However, in order to do this, it was necessary to apply adequate terminating electrolytes with mobility lower than the mobility of analyzed ions. Therefore, a new pentacoordinated compound: 4,4′-bis{1-(N-perhydroazepiniomethyl)[spirobi(1-sila-2,5-dioxacyclopentane-3-on)]ate} was used.

EXPERIMENTAL

Instrumentation

Analyses were carried out by means of a capillary electrophoresis analysator EA 202 M produced by Villa Labeco s.r.o. in Spisska Nova

Ves (Slovakia) equipped with an injection block with a container for terminating electrolytes, preseparation column (capillary diameter 0.8 mm, length 90 mm), bifurcation block with an electrode block of the preseparational column, analytic column (capillary diameter 0.3 mm, length 160 mm), an electrode block of the analytic column, UV detector, two conductometric detectors with a measurement range between 30 kΩ and 20 MΩ, and steering unit – personal computer PC containing converter AD/DA. After drawing of the standard curves for individual compounds, optimization of the conditions of the isotachophoretic separation of the mixture was carried out.

Spectroscopic Conditions

The ^{1}H, ^{13}C spectra were performed on a Varian Mercury 400 (Varian, Inc., Palo Alto, USA) spectrometer (400 MHz) at 25°C using deuterated methyl sulfoxide as solvent and TMS as internal standard. IR spectra were obtained on a Magna-IR 760, Nicolet (KBr), (Thermo Fisher Scientific, Waltham, GB). The infrared spectra of ES-silanates have been examined in the region 3500–450 cm^{-1} to assign the characteristic group frequencies in the compounds synthesized. The electronic absorption spectra in the visible range were obtained on a Beckman DU68 (Beckman Coulter, Inc., Fullerton, USA) spectrophotometer using 1 mL quartz cells at room temperature. The UV/Vis spectra were recorded digitally (0.5 nm step) over the range 400–900 nm. The samples concentration was 4×10^{-3} mole $\times L^{-1}$ in CH_2Cl_2.

Spectroscopic Data

1-(N-Perhydroazepiniomethyl)[spirobi(1-sila-2,5-dioxacyclopentane-3-on)] ate: ^{1}H NMR (DMSO), δ (ppm): 1.5–1.8 (4H; CCH_2C), 1.6–1.9 (4H; CCH_2C), 2.59 (2H; $SiCH_2$), 3.03–3.18 (4H; NCH_2Si), 3.96 (4H; CH_2COO), 8.06 (1H; NH). ^{13}C NMR (DMSO), δ (ppm): 23.55, 25.41, 25.43, 49.05, 62.73, 173.82.

UV/Vis (CH_2Cl_2): λ_{max} (lg ε) = 303 (2.48), 325 (2.51). IR (KBr) ν_{max}: 3431, 3118, 2939, 2862, 1726, 1472, 1460, 1240, 1100, 579, 533, 489, 457 cm^{-1}.

1-(N-Perhydroazepiniomethyl)[spirobi(1-sila-2,5-dioxa-4-methylcyclopentane-3-on)]ate: ^{1}H NMR (DMSO), δ (ppm): 1.21 (6H; CH_3, $J = 6.73$ Hz), 1.45–1.69 (4H; CCH_2C), 1.71–1.84 (4H; CCH_2C), 2.38 (2H; NCH_2Si), 3.00–3.22 (4H; NCH_2), 4.10 (2H; CCHO, $J = 6.73$ Hz), 8.02 (1H; NH). ^{13}C NMR (DMSO), δ (ppm): 20.36, 23.45, 25.43, 49.72, 65.73, 68.69, 176.29.

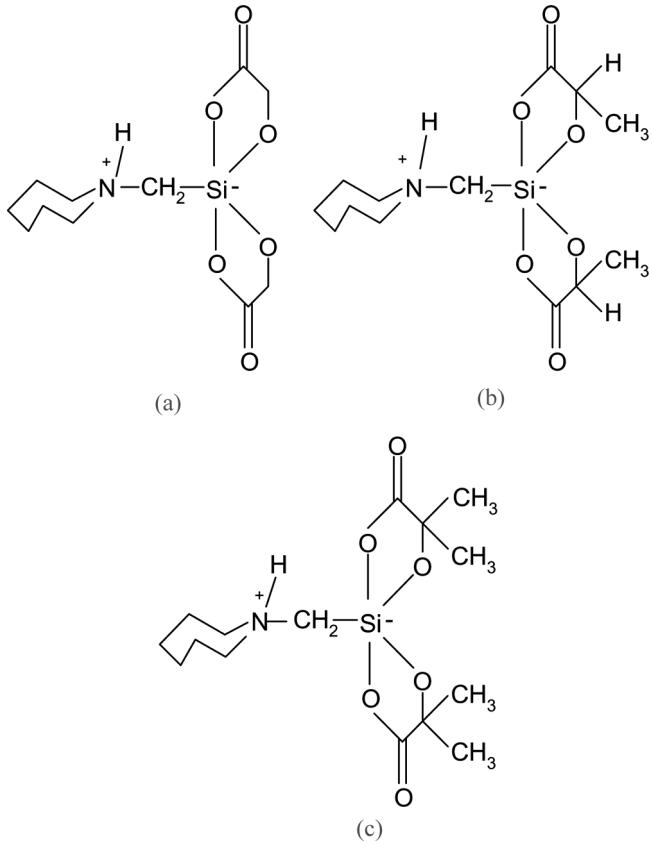

Figure 1. Structures of analyzed compounds (a) 1-(N-perhydroazepiniomethyl) [spirobi(1-sila-2,5-dioxacyclopentane-3-on)]ate (**ES-1**), (b) 1-(N-perhydroazepiniomethyl)[spirobi(1-sila-2,5-dioxa-4-methylcyclopentane-3-on)]ate (**ES-2**), (c) 1-(N-perhydroazepiniomethyl)[spirobi(1-sila-2,5-dioxa-4,4-dimethylcyclopentane-3-on)] ate (**ES-3**).

UV/Vis (CH_2Cl_2): λ_{max} (lg ε) = 283 (2.45). IR (KBr) ν_{max}: 3432, 3163, 2976, 2933, 2862, 1723, 1443, 1369, 1316, 1240, 1062, 550, 453 cm^{-1}.

1-(N-Perhydroazepiniomethyl)[spirobi(1-sila-2,5-dioxa-4,4-dimethyl-cyclo-pentane-3-on)]ate: ^1H NMR (DMSO), δ (ppm): 1.28 (12H; CCH_3), 1.53–1.63 (4H; CCH_2C), 1.68–1.81 (4H; CCH_2C), 2.4 (2H; NCH_2Si), 2.89–3.26 (4H; NCH_2), 8.13 (1H, NH). ^{13}C NMR (DMSO), δ (ppm): 20.30, 23.59, 25.60, 49.23, 64.33, 68.74, 175.59.

UV/Vis (CH_2Cl_2): λ_{max} (lg ε) = 283 (2.45), 325 (2.51), 450 (2.65), 459 (2.66). IR (KBr) ν_{max}: 3430, 2980, 2938, 1728, 1463, 1392, 1343, 1240, 1100, 538, 481 cm^{-1}.

4,4′-bis{1-(N-Perhydroazepiniomethyl)[spirobi(1-sila-2,5-dioxacyclopentane-3-on)]ate}: ^{1}H NMR (DMSO), δ (ppm): 1.48–1.59 (8H, CCH_2C), 1.72–1.89 (8H, CCH_2C), 2.1–2.2 (4H, NCH_2Si), 2.98–3.24 (8H, NCH_2), 4.23 (4H, CCHO), 7.85 (2H, NH), ^{13}C NMR (DMSO), δ (ppm): 25.43, 25.52, 29.59, 49.99, 58.57, 74.99, 173.

UV/Vis (CH_2Cl_2): λ_{max} (lg ε) = 283 (2.45), 302 (2.48), 325 (2.51). IR (KBr) ν_{max}: 3300–3500, 2935, 2862, 1708, 1716, 1473, 1240, 1092, 534, 510, 447 cm^{-1}.

Materials

The ES-silanate compounds were prepared by the method described in the literature.[1–4] As a material of investigation, the following compounds were synthesized in Department of Organic and Applied Chemistry of University of Podlasie (Figure 1), i.e., 1-(N-perhydroazepiniomethyl)[spirobi(1-sila-2,5-dioxacyclopentane-3-on)]ate, 1-(N-perhydroazepiniomethyl)[spirobi(1-sila-2,5-dioxa-4-methylcyclopentane-3-on)]ate and 1-(N-perhydroazepinio-methyl)[spirobi(1-sila-2,5-dioxa-4,4-dimethylcyclopentane-3-on)]ate (Figure 2). In the process of optimization, the following extra pure reagents were applied: deionized water (Merck), muriatic acid (POCh Gliwice), acetic acid (POCh Gliwice), acetate of sodium (POCh Gliwice), terminating electrolyte containing aqueous solution of 4,4′-bis{1-(N-perhydroazepiniomethyl)[spirobi(1-sila-2,5-dioxacyclo-pentane-3-on)]ate}.

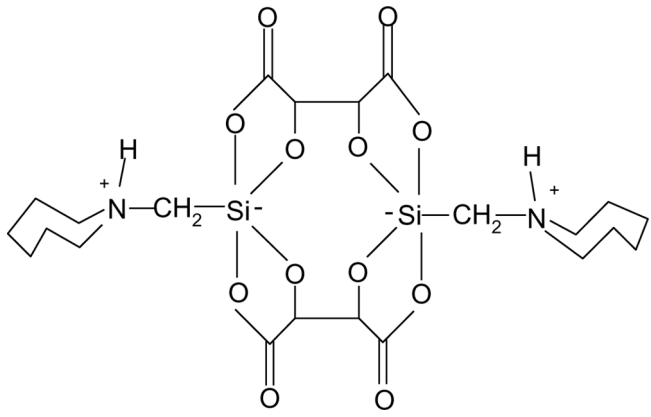

Figure 2. Structure of a compound used in terminating electrolyte 4,4′-bis{1-(N-perhydroazepinio-methyl)[spirobi(1-sila-2,5-dioxacyclopentane-3-on)]ate} (**ES-4**).

Preparation of Samples

In order to prepare the standard solutions (**ES-1** and **ES-3**), adequate amounts of these compounds were weighed to obtain concentrations 1.0×10^{-3} mole $\times$ L^{-1}, 5.0×10^{-4} mole $\times$ L^{-1}, and 7.5×10^{-4} mole $\times$ L^{-1}. 1. The weighed portions were dissolved in deionized water and subjected to analysis. The terminating electrolytes contained an aqueous solution of 4,4′-bis{1-(N-perhydroazepiniomethyl)[spirobi(1-sila-2,5-dioxacyclopentane-3-on)]ate} (Figure 3). Leading electrolytes (Ld-1) and (Ld-2) for an analytic column, exhibiting pH = 3.54, were prepared from equal volumes of the following solutions: HCl solution (2×10^{-3} mole $\times$ L^{-1}), CH_3COONa solution (1.5×10^{-3} mole $\times$ L^{-1}), CH_3COOH solution (1.5×10^{-3} mole $\times$ L^{-1}). Terminating electrolytes (Tm) contained aqueous solution of 4,4′-bis{1-(N-perhydroazepiniomethyl)[spirobi(1-sila-2,5-dioxacyclopentane-3-on)]ate} (10^{-3} mole $\times$ L^{-1}).

RESULTS AND DISCUSSION

The aim of the investigation was to separate and determine the analyzed compounds in the shortest time. Results obtained by the capillary isotachophoresis with conductometric detection are presented in Tables 1–6,

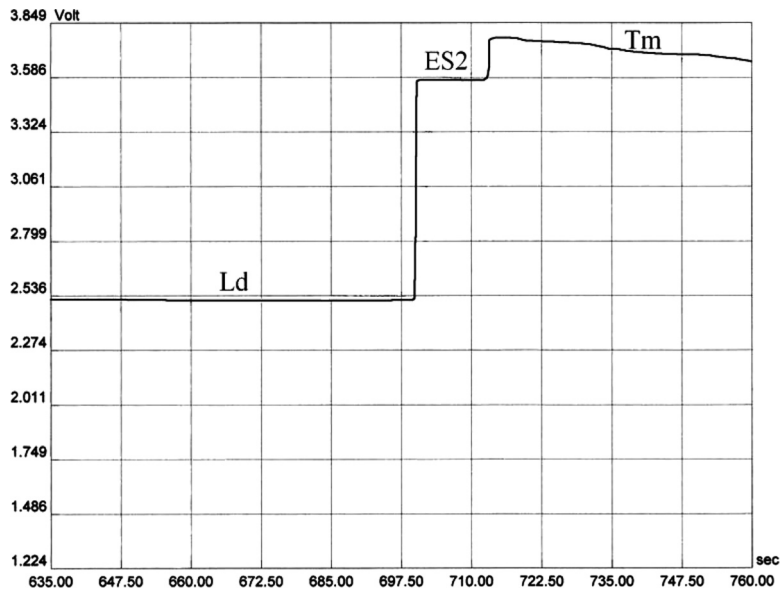

Figure 3. Isotachophoregram of **ES-2**.

Table 1. Composition of electrolytes during optimization of isotachophoretic process for analyzed compounds

Cations					
Ld–1		Ld–2		Tm	
Component	Concentration (mole · L^{-1})	Component	Concentration (mole · L^{-1})	Component	Concentration (mole · L^{-1})
HCl	$8 \cdot 10^{-3}$	HCl	$2 \cdot 10^{-3}$	**ES-4**	$1 \cdot 10^{-3}$
CH_3COONa	$3 \cdot 10^{-3}$	CH_3COONa	$2 \cdot 10^{-3}$		
CH_3COOH	$3 \cdot 10^{-3}$	CH_3COOH	$3 \cdot 10^{-3}$		
PH	3.8	pH	3.54		

optimal conditions of separation and determination on isotachophoregrams (Figures 3–4). Analyses were carried out in aqueous solutions: acidic, neutral, and basic. During an isotachophoretic analysis, only ions with the same sign (cations or anions) were determined. The separation was carried out due to differences in the electrophoretic mobility of the analyzed ions. In Table 1, compositions of leading (Ld-1 and Ld-2) and terminating I electrolytes used in the separation of analyzed compounds are presented. These compositions enable the determination of individual silanates, as well as their mixture in acidic medium.

In the literature, the terminating electrolytes used for analyses of inorganic cations and anions are characterized by higher mobility than the ions investigated in this paper. Therefore, by the process of trial and error and by addition of the standard, a new terminating electrolyte was elaborated and used. It is essential for isotachophoretic separation to possess, in leading electrolytes, ions with mobility higher and in terminating electrolytes, ions with lower mobility than ions in the sample. Double salt: 4,4′-bis{1-(N-perhydroazepiniomethyl)[spirobi(1-sila-2,5-dioxacyclopentane-3-on)]ate} showed to be an excellent terminating electrolyte with suitable mobility.

Table 2. Common parameters of optimal **ES-1**, **ES-2** and **ES-3** separation and determination by isotachophoresis method

Parameters of the method	
UV filter [nm]	200
High Voltage Limit [V]	12000
Sample rate [smp/s]	50
Polarity	+cations

Table 3. Optimum conditions of **ES-1** determination on the preseparation column

Considered parameters				
Stage	Time (s)	Intensity (μA)	Comp (10 mV)	Conductometric detector
1	300	100	0	–
2	120	200	50	–
3	180	200	0	X

Separation and determination of chosen compounds was carried out by the use of capillary isotachophoresis. Optimal conditions for separation and determination of chosen compounds have been elaborated. Quantitative analysis was based on a comparison of the zone height on the isotachophoregram of a sample with the zone height on the isotachophoregram obtained for standard solution.

Analyzed compounds and their mixtures were subjected to various tests in order to maximum separation, to obtain a number of zones containing one kind of ion. Limits of zones are sharp when all zones are characterized by different effective ion mobility. It is also connected with the decrease of conductivity of a zone, i.e., increase of resistance and with changes of ion concentration in this zone.

Analyzed compounds caused many difficulties during isotachophoretic determination, because of small differences of mobility. Until now, attempts to analyze these compounds have been not reported in the literature.

During optimization of the determination, various conditions of this method were tested: time of the analysis, current intensity, level of high voltage limitation, and different columns.

Attempts of optimization of the separation and determination of chosen ES – silanates were carried out by changes of voltage from

Table 4. Optimum conditions of the method of **ES-2** determination on the preseparation column

Considered parameters				
Stage	Time (s)	Intensity (μA)	Comp (10 mV)	Conductometric detector
1	500	100	0	–
2	160	200	50	–
3	100	200	0	X

Table 5. Optimum conditions of **ES-3** determination on the preseparation column

Considered parameters				
Stage	Time (s)	Intensity (μA)	Comp (10 mV)	Conductometric detector
1	150	100	0	–
2	160	200	50	–
3	100	200	0	X

10000 V to 15000 V. Experiments carried out under 10000 V failed. The best results of separation were obtained when high voltage was limited to 12000 V (42, Figures 3–4).

The speed of ions in an electric field depends on the current intensity of the field. Therefore, in various steps of the method, this parameter was changed.

The next stages of the optimization were separations and determinations in different values of pH of solutions of analyzed samples: acidic (pH = 4), neutral (pH = 7), and basic (pH = 10, anions). The best results were obtained in acidic medium. With the increase of pH, differences of the effective mobilities of ions in the analyzed mixture decreased. Therefore, satisfactory results were achieved neither in neutral nor in basic medium.

Analyses of acidic (pH = 4) solutions allowed for complete separation of **ES-1**, **ES-2** and **ES-3** as components of mixtures and for analyses of individual compounds. Optimization of individual component separation on a preseparation column was carried out also. Standard curves were obtained in the same conditions.

Table 6. Optimum conditions of isotachophoretic separation of a mixture of **ES-1**, **ES-2** and **ES-3**

Considered parameters				
Stage	Time (s)	Intensity (μA)	Comp (10 mV)	Conductometric detector
1	490	60	0	–
2	160	130	50	–
3	110	200	0	X
4	510	50	50	–
5	90	50	0	X

Table 7. Characteristic of used analytical method

Parameter	Unit	For examined ion
Precision[1]	%	2.5–3.3
Recovery[2]	%	91.5±6
Linearity[3]	$mg \cdot L^{-1}$	1–30
Limit of identification[4]	$mg \cdot L^{-1}$	1

[1]n = 7, the samples were analyzed twice.
[2]the sample was enriched with 1.5 mL of a solution containing $1\,mg \cdot mL^{-1}$ of examined ion, n = 7.
[3]correlation coefficient above 0.98.
[4]calculated from the limit of identification and coefficients of the calibration curve.

Consideration of the obtained isotachophoregram (Figure 4) and conditions of the method (Table 6) showed that the shortest time of analysis was for compound **ES-3**, longer for **ES-2** and **ES-1**. Good separation for a mixture of both ES-silanates was achieved in a time under 12 min (Figure 4).

The structures of analytes after analysis were examined again. They answered the initial structures of analyzed relationships.

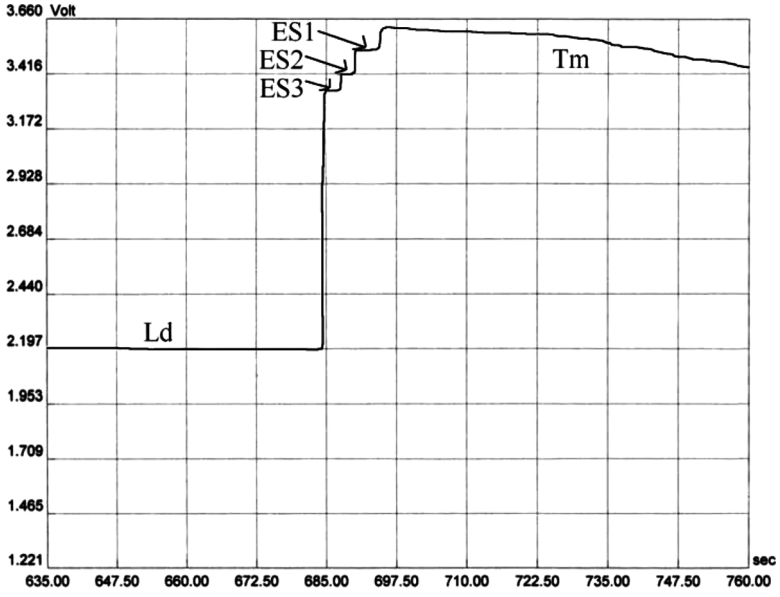

Figure 4. Isotachophoregram of the mixture of **ES-1**, **ES-2** and **ES-3**.

Differences in the speed of charged particles mainly depend on their magnitude, charge, and molecular mass. It allows separation of systems with various magnitude and structure of molecules.

The high efficiency of separation, in comparison with other electrophoretic methods and the short time of analysis, allows capillary isotachophoresis to compete, not only with HPLC, but also with other analytical techniques. However, this method is still in the stage of investigation, as well as the theoretical basis for practical applications.

Isotachophoresis allows determination of chosen ES-silanates in an aqueous solution. The main attribute of this method is simultaneous determination of all macro- and microelements in a short time (up to 25 min), compared with classical chromatographic methods. Preparation of samples is simple (only dissolution in water), the method is cheap, and is suitable for routine analyses. It can be considered as a "green chemistry" technique, because toxic solvents or reagents are not used.

Precision and accuracy of results obtained by the capillary isotachophoresis method is better than these obtained by classical methods.[11] Characteristics of the used analytical method was introduced in Table 7.

CONCLUSIONS

A method of separation of a mixture consisting of three ES-silanates has been elaborated. It takes less than 12 min. A new terminating electrolyte has been worked out. Analyzed compounds, due to numerous difficulties in electrophoretic determinations, and mobilities of their ions, only slightly differ from each other. A new, elaborated method of separation and determination opens wide possibilities of investigation of biological activity of these kinds of substances.

ACKNOWLEDGMENT

We would like to thank Mrs. Joanna Nasiłowska for help during the performing of some analyses.

REFERENCES

1. Erchak, N.P.; Lukevics, E.J.; Matorykina, V.F.; Kemme, A.A.; Blejdelis, J.J. 1-Morpholiniomethyl-1,1'-spirobi(1-sila-2,5-dioxacyclopentanone-3)ate and Method of Its Preparation. **1983**, SU 1059872.

2. Erchak, N.P.; Ancens, G.A.; Kemme, A.A.; Blejdelis, J.J.; Liepinsh, E.E.; Lukevics, E.J. A Method of Preparing Aminiomethylsirobi-(1-sila-2,5-dioxacyclopentanone-3)ates, **1985**, SU 1182788.
3. Erchak, N.P.; Kemme, A.A.; Blejdelis, J.J.; Ancens, G.A. A Method of Preparing N,N-Dimethylaminiomethylsirobi(1-sila-2,5-dioxacyclopentanone-3)ate Crystalloglycolate. **1986**, SU 1274271.
4. Erchak, N.P.; Lukevics, E.J. A Method of Preparing Morpholiniomethylsirobi(1-sila-2,5-dioxacyclopentanone-3)ate. **1987**, SU 1439991.
5. Voronkov, M.G.; Zelchan, G.; Lukevics, E. *Silicon and Life, 2nd* Revised Edition; Zinatne: Riga, 1978; 588 p. (in Russian).
6. Lukevics, E.; Ignatovich, L. Biological Activity of Organosilicon Compounds. in *Metallotherapeutic Drugs and Metal-Based Diagnostic Agents: The Use of Metals in Medicine*; Gielen, M., Tiekink, E.T., Eds.; John Wiley & Sons: 2005, 83–107.
7. Erchak, N. *Electrostatically Stabilized Silanates*, XIth International Symposium of Organosilicon Chemistry, University Montpellier II, France, 1996.
8. Corriu, R.; Jutzi, P., Eds.; *Tailor-made Silicon-Oxygen Compounds: From Molecules to Materials*; Vieweg: Braunschweig: Wiesbaden, 1996; 332.
9. Rogers, J.R.; Bennett, P.C. Mineral stimulation of subsurface microorganisms: release of limiting nutrients from silicates. Chem. Geol. **2004**, *203*, 91–108.
10. Kubicki, J.D.; Heaney, P.J. Molecular orbital modeling of aqueous organosilicon complexes: implications for silica biomineralization. Geochim. Cosmochim. A **2003**, *67*, 4113–4121.
11. Onuska, F.I.; Kaniansky, D.; Onuska, K.D.; Lee, M.L. Isotachophoresis: Trials, tribulations, and trends in trace analysis of organic and inorganic pollutants. J. Microcolumn Sep. **1998**, *10* (7), 567–579.

Received August 17, 2008
Accepted October 27, 2008
Manuscript 6387