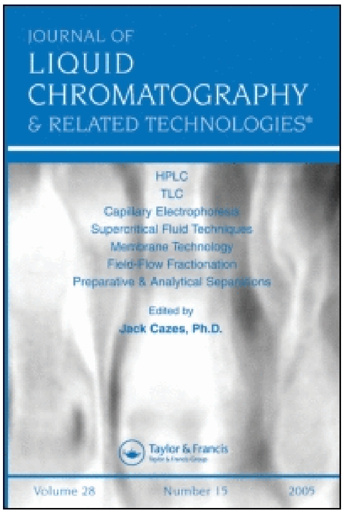

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Isotachophoresis of Chosen Heptacoordinated Goshchava Silanates

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Abstract: In the course of our work we have carried out an optimization of conditions for the separation and determination of selected derivatives belonging to the group of Goshchava-Silanates by a capillary isotachophoresis technique. Analyzed heptacoordinated compounds show biological activity. In the investigations, we considered homo{O,O′,O″,O‴-oxalic acids Si-[N-benzylaminiomethyl]-Si,Si-dihydroxysilanate} and homo{O,O′,O″,O‴-oxalic acids Si-[N-benzylaminiomethyl]-Si, Si-diethoxysilanate}. A new terminating electrolyte was proposed for determination of these compounds in a form of aqueous solution of 4,4′-bis{1-[(N,N-dimethyl) aminiomethyl]spirobi(1-sila-2,5-dioxacyclopentan-3-on)at}. Optimum time of analysis did not exceed 9 minutes. The newly elaborated method allows for wider research of biological activity of the analyzed compounds and increases the possibilities of their applications. Until now, information concerning the use of above mentioned technique for heptacoordinated organosilanates has not been published.

Keywords: Determination, Heptacoordinated organosilicon derivatives, Isotachophoresis, Separation

INTRODUCTION

Organosilicon compounds with coordination number higher than four belong to a group of hypercoordinated compounds. Hypercoordinated

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organosilanates are intensively investigated because of their interesting structures and their exhibited biological activity.[1]

In the beginning of the 1970s a new scientific trend became apparent-biosiliconorganic chemistry. Soon, its main challenges were determined. Among them can be distinguished the determination of structures and identification of hypercoordinated organosilicon compounds in living organisms, analysis of transport and accumulation of silicon in nature, establishment of mechanisms of silicon compounds' participation in physiological processes of living organisms, synthesis of new therapeutic preparations, i.e., biostimulators and pesticides on the base of organosilicon compounds, and maximum use of modern techniques for the analysis of these types of compounds.[2–5]

Biosiliconorganic chemistry presents numerous problems. One of them is formation of organomineral complexes of soil and soil solutions as well as silicon transport in organisms. These problems concern, among others, sources of nutrition of flora and fauna as well as formation of humus. It was confirmed that solution or decomposition of the majority of silicon compounds can be an effect of an increase of silicon atom coordination.[6–8] Therefore, numerous organosilicon compounds were intentionally synthesized for research of their biological activities.[9–12]

At the beginning of the 1990s, some model hypercoordinated, penta-, hexa-, and hepta-coordinated compounds containing silicon-oxygen-carbon bonds in molecules were synthesized.[13–15] Then, a new group of compounds – ES-silanates (electrostatically stabilized) appeared. Compounds which are analyzed in this paper belong to a dozen, until now, synthesized organic derivatives of heptacoordinated silicon.[16]

Heptacoordinated organosilicon derivatives belong to a group of substances known as Goshchava-Silanates. They are polymeric compounds of λ^7 type, where the silicon atom is heptacoordinated.[17,18] In the process of synthesis of this type of compound, oxygen atoms from hydroxy and carbonyl groups of suitable organic acids are the donors of electrons. Ionic penta-, hexa-, and hepta-coordinated silicon compounds are considered to be intermediate or transitory structures in nucleophilic substitution of a hypercoordinated silicon atom. Synthesis of these ionic compounds is based on a nucleophilic attack of anions (e.g., F^-) on a neutral silicon atom, accompanied by two ligands that stabilize hypercoordination by the effect of a pentacyclic ring.

Neutral silicon compounds with coordination number 5–7 can be synthesized also by the use of two- or tridonor ligands containing intermolecular coordination bonds (e.g., ligands of van Koten type or 8-(dimethylamino)naphthyl ligand).[19] The weak intramolecular coordination significantly influences on the reactivity. As precursors of every type of organosilicon compounds mainly chlorosilanes were used. An intermediate form heptacoordinated compound can be formed also in a chemical reaction during a nucleophilic attack on hexacoordinated silicon atom.[20]

Research in area of high performance materials led to increased interest in polymers and materials based on silicon. Organosilicon compounds are widely applied also in medicine. Multiple methods of synthesis using silicon compounds allowed for improvement of technology of antibiotic possessing extraordinary activity against wide spectrum of Gram-positive and Gram-negative bacteria.[21,22]

Taking into consideration biological activity and wide, not completely known possibilities of application of hypercoordinated compounds belonging to Goshchava-Silanate group, continuation of different investigations of compounds of this type, seems justified. Therefore elaboration of optimum conditions for isotachophoretic separation and determination of two synthesized heptacoordinated derivatives belonging to Goshchava-Silanate group: homo{O,O′,O″,O‴-oxalic acid's Si-[N-benzylaminiomethyl]-Si,Si-dihydroxysilanate} and homo{O,O′,O″,O‴-oxalic acid's Si-[N-benzylaminiomethyl]-Si,Si-diethoxysilanate} was the aim of our work.

EXPERIMENTAL

Instrumentation

Analyses were carried out by means of a capillary electrophoresis analyzer 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 electrolyte, a preseparation column (capillary diameter 0.8 mm, length 90 mm), a bifurcation block with an electrode block of the preseparational column, an analytical column (capillary diameter 0.3 mm, length 160 mm), an electrode block of the analytical column, a UV detector, two conductometric detectors with a measurement range between 30 kΩ and 20 MΩ, a steering unit – personal computer PC containing an AD/DA converter. After drawing of standard curves for individual compounds, optimization of conditions of the isotachophoretic separation of the mixture was carried out.

Spectroscopic Conditions

The ^{1}H, ^{13}C, ^{29}Si NMR spectra were performed with a Varian Mercury 400 (Varian, Inc., Palo Alto, USA) spectrometer (400 MHz) at 25°C using deuterated dimethylsulfoxide as solvent and TMS as an internal standard. The UV/Vis spectra were recorded digitally (0.5 nm step) over the range 230–900 nm. The samples' concentration was 3×10^{-3} mole $\times$ L^{-1} in DMSO.

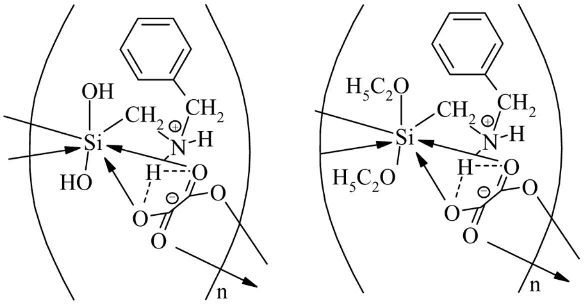
Spectroscopic Data

Homo{O,O′,O″,O‴-oxalic acids Si-[N-benzylaminiomethyl]dihydroxysilanate: ^{13}C NMR (DMSO-d_6) δ (ppm) = 52.5, 63.3, 129.4, 129.8, 130.3, 131.3, 160.0. ^{1}H NMR, (DMSO-d_6).[17] ^{29}Si NMR (DMSO-d_6) δ (ppm) = −174.2. UV (DMSO): λ_{max} = 324.5, 325–327, 340, 358, 373.5 nm.

Homo{O,O′,O″,O‴-oxalic acid's Si-[N-benzylaminiomethyl]diethoxysilanate: ^{13}C NMR (DMSO-d_6) δ (ppm) = 19.1, 52.0, 56.6, 67.6, 129.3, 129.6, 130.3, 132.5, 160.2. ^{1}H NMR, (DMSO-d_6).[17] ^{29}Si NMR (DMSO-d_6) δ (ppm) = −174.0. UV (DMSO): λ_{max} = 325.5, 326, 327, 374, 457.5 nm.

Material

The Goshchava-Silanate compounds were prepared by the method described in the literature.[23] As a material of investigation the compounds synthesized in the Department of Organic and Applied Chemistry of University of Podlasie, i.e., following compounds: Homo{O,O′,O″, O‴-oxalic acid's Si-[N-benzylaminiomethyl]-Si,Si-dihydroxysilanate} (**2**) and Homo{O,O′,O″,O‴-oxalic acid's Si-[N-benzylaminiomethyl]-Si,Si-diethoxysilanate} (**3**) (Fig. 1). In the process of optimization, the following reagents were applied: deionized water from Merck (Darmstadt, Germany), DMSO from Merck (Darmstadt, Germany), prepared from equal volumes of following solutions: HCl, CH_3COONa, CH_3COOH solution from POCH (Gliwice, Poland).



(a) (b)

Figure 1. Structures of: (a) homo{O,O′,O″,O‴-oxalic acid's Si-[N-benzylaminiomethyl]-Si,Si-dihydroxysilanate}, and (b) homo{O,O′,O″,O‴-oxalic acid's Si-[N-benzylaminiomethyl]-Si,Si-diethoxysilanate}.

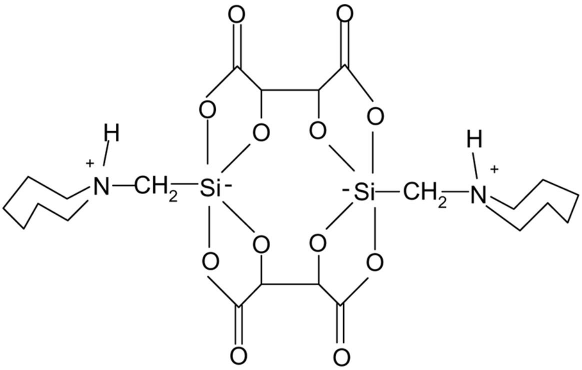


Figure 2. Structure of a compound used in terminating electrolyte 4,4′-bis{1-(N-perhydroazepinio-methyl)[spirobi(1-sila-2,5-dioxacyclopentane-3-on)]ate}.

Preparation of Samples

In order to prepare the standard solutions (**2**) and (**3**), suitable amounts of these compounds were weighed to obtain concentrations of 2.0×10^{-3} mole × L^{-1}, 5.0×10^{-4} mole × L^{-1} and 8.0×10^{-4} mole × L^{-1}. The weighed portions were dissolved in deionized water and subjected to analysis. Leading electrolytes Ld-1 and Ld-2 for an analytical column, pH = 3.4, prepared from equal volumes of the following solutions: HCl solution (2×10^{-3} mole × L^{-1}), CH_3COONa solution (1.5×10^{-3} mole × L^{-1}), and CH_3COOH solution (1.5×10^{-3} mole × L^{-1}). Terminating electrolyte (Fig. 2) contained an aqueous solution of 4,4′-bis{1-(N-perhydroazepiniomethyl) [spirobi(1-sila-2,5-dioxacyclopentane-3-on)]ate} (2×10^{-3} mole × L^{-1}).

RESULTS AND DISCUSSION

The heptacoordinated derivatives belonging to the Goshchava-Silanate group, analyzed in this work, homo{O,O′,O″,O‴-oxalic acid's Si-[N-benzylaminiomethyl]-Si,Si-dihydroxysilanate} and homo{O,O′,O″,O‴-oxalic acid's Si-[N-benzylaminiomethyl]-Si,Si-diethoxysilanate} were subjected to investigations in order to separate and determine them in the shortest time. In the ITP technique, samples containing ions are placed in a system of two electrolytes, between leading electrolyte and terminating electrolyte. An application of an electric field causes ions to migrate toward adequate potential and move in order from the highest velocity to the lowest velocity.

In the work, an optimization of parameters of separation and determination method of derivatives belonging to Goshchava-Silanate has been performed. Obtained results are shown in Tables 1–4. Isotachophoregrams, performed at the optimum conditions, are shown in Figs. 3 and 4.

Table 1. Common parameters of optimal homo{O,O′,O″,O‴-oxalic acid's Si-[N-benzylaminiomethyl]-Si,Si-dihydroxysilanate} and homo{O,O′,O″,O‴-oxalic acid's Si-[N-benzylaminiomethyl]-Si,Si-diethoxysilanate} separation and determination by isotachophoresis method

Parameters of the method	
UV filter [nm]	200
High Voltage Limit [kV]	12
Sample rate [smp/s]	50
Polarity	+cations

During optimization of separation and determination of ES-silanates, various conditions of the method were tested; time of analysis, intensity of the electric current, pH range, and level of limitation of high voltage were changed with the use of preseparational column or system of two columns: preseparational and analytical. Analyses were carried out, changing the voltage from 9 kV to 15 kV. At a voltage lower than 9 kV, separation was not achieved. The best separations were obtained at limitation of the voltage to 12 kV.

Analysis of chosen derivatives belonging to the Goshchava-Silanate group was carried out in acidic solutions. During the analysis, only cations were determined. The separation was performed on the basis of differences of electrophoretic mobility of the analyzed ions. Analyzed compounds showed very similar electrophoretic mobilities. We used a solution of terminating electrolyte characterized by significantly lower mobility than analyzed isomers.

The terminating electrolyte for analysis of the investigated mixture was selected by a process of trial and error. It consists of an aqueous solution of 4,4′-bis{1-[(N,N-dimethyl)aminiomethyl]spirobi(1-sila-2,5-dioxacyclopentan-3-on)at}. This compound belongs to a group of ES-silanates (hypercoordinated organosilicon compounds) and was already used successfully in earlier works.[24,25] Common conditions of analyzed heptacoordinated derivatives are shown in Table 1.

Table 2. Conditions of the method of individual determination of homo {O,O′,O″,O‴-oxalic acid's Si-[N-benzylaminiomethyl]-Si,Si-dihydroxysilanate} (**2**)

Considered parameters				
Stage	Time (s)	Intensity (μA)	Comp (10 mV)	Conductometric detector
1	70	80	0	–
2	50	120	50	–
3	60	50	0	X

Table 3. Optimum conditions of isotachophoretic separation of a mixture of homo{O,O′,O″,O‴-oxalic acid's Si-[N-benzylaminiomethyl]-Si,Si-dihydroxysilanate} (**2**) and homo{O,O′,O″,O‴-oxalic acid's Si-[N-benzylaminiomethyl]-Si,Si-diethoxysilanate} (**3**)

Considered parameters				
Stage	Time (s)	Intensity (μA)	Comp (10 mV)	Conductometric detector
1	100	150	0	–
2	210	200	50	X
3	240	240	0	X

Table 4. Characteristic of used analytical method

Parameter	Unit	For examined ion
Precision[a]	%	2.4 – 3.3
Recovery[b]	%	91.5 ± 6
Linearity[c]	$mg \times L^{-1}$	2 – 31
Limit of identification[d]	$mg \times L^{-1}$	1

[a] n = 7, the samples were analyzed twice.

[b] The sample was enriched with 1.5 mL of a solution containing $1\,mg \times mL^{-1}$ of examined ion, n = 7.

[c] Correlation coefficient above 0.98.

[d] Calculated from the limit of identification and coefficients of the calibration curve.

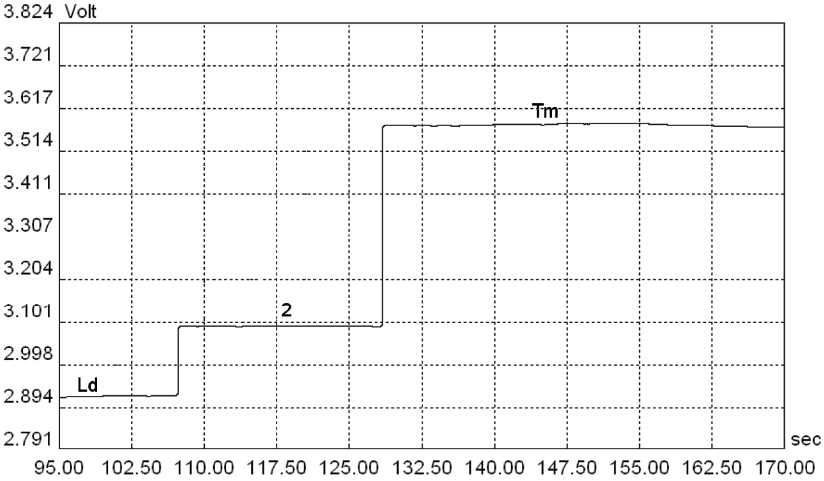


Figure 3. Isotachophoregram of homo{O,O′,O″,O‴-oxalic acid's Si-[N-benzylaminiomethyl]-Si,Si-dihydroxysilanate} (**2**).

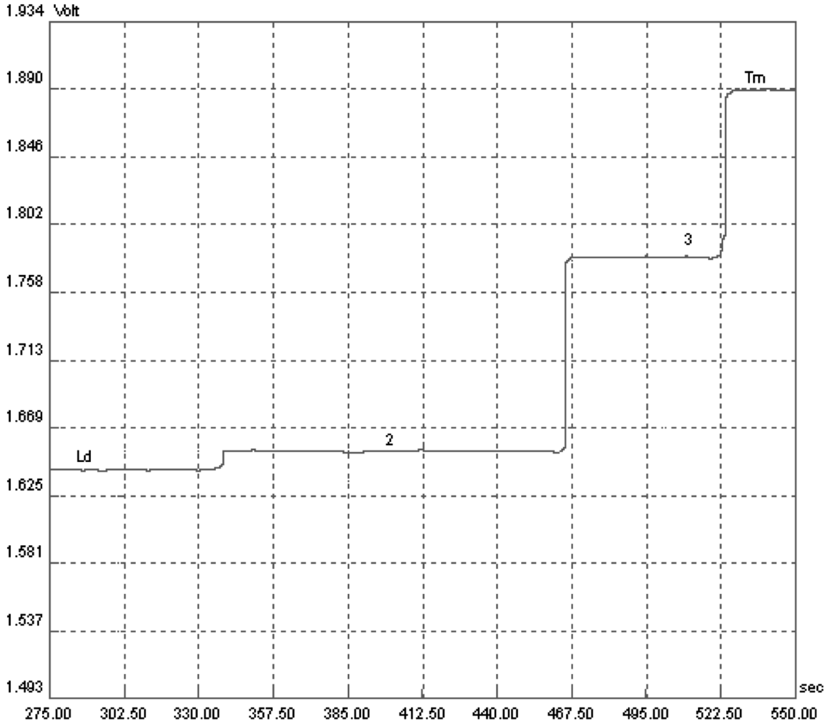


Figure 4. Isotachophoregram of the mixture of homo{O,O′,O″,O‴-oxalic acid's Si-[N-benzylaminiomethyl]-Si,Si-dihydroxysilanate} (**2**) and homo{O,O′,O″,O‴-oxalic acid's Si-[N-benzylaminiomethyl]-Si,Si-diethoxysilanate} (**3**).

Using capillary electrophoresis, proper separation and determination of the components of the analyzed mixture was carried out. The mixture consisted of homo{O,O′,O″,O‴-oxalic acid's Si-[N-benzylaminiomethyl]-Si, Si-dihydroxysilanate} and homo{O,O′,O″,O‴-oxalic acid's Si-[N-benzylaminiomethyl]-Si,Si-diethoxysilanate}. All analyses were performed with the use of two dimensional analysis with column switching. Qualitative analysis was carried out on the basis of height identification of a zone. Obtained heights of zones were compared with isotachophoregrams recorded for standard solutions.

The separation of the mixture was difficult, since the compounds differed only by an ethyl group ($-C_2H_5$) and showed similar mobilities. During the optimization process, time of analysis, intensity of the electric current, pH of solutions of leading electrolytes and samples were changed. By a process of trial and error, we proved that the optimum pH for analyzed isomers was 3.4. At pH close to neutral, the isotachophoregram was characterized by sharp zones for the investigated mixture and diffuse zone for the terminating electrolyte. The time of analysis was changed depending on the number of compounds in the analyzed samples. The shortest optimum time of analysis (at about 130 sec) was obtained for one derivative (Table 2, Fig. 3). On the other hand, optimum time of analysis of was extended four times, to 530 sec (Table 3, Fig. 4). Well matched parameters allowed obtaining optimum separation of analyzed derivatives.

The method applied to separation and determination of homo {O,O′,O″,O‴-oxalic acid's Si-[N-benzylaminiomethyl]-Si,Si-dihydroxysilanate} and homo{O,O′,O″,O‴-oxalic acid's Si-[N-benzylaminiomethyl]-Si,Si-diethoxysilanate} was characterized by high precision and accuracy of obtained results (Table 4). Linearity of the method was between 2 and 31 mg × L^{-1}, detection limit was 1 mg × L^{-1}. Precision and accuracy of results obtained by capillary isotachophoretic method are better than by classical methods.

The compounds described here have different stabilities. The first one (dihydroxy derivative) is hydrolytically stable; on the other hand, the second (diethoxy derivative) has limited stability. In an aqueous solution of diethoxy derivatives, after 30 minutes, significant hydrolysis can be observed. This property did not cause difficulties during determinations because the optimum time of isotachophoretic analysis was shorter than 9 minutes. In the case of longer analyses of these compounds, DMSO should be used as the solvent because both compounds are easily soluble.

To sum up, the aim of our investigation has been fully executed, i.e., optimum conditions of isotachophoretic separation and determination of chosen Goshchava-Silanates. Chromatographic investigation concerning this group of compounds and their derivatives was attended by numerous difficulties, independent of selection of the analytical technique.[26] However, for reasons of biological activities of these compounds, and still not exactly known possibilities of their applications, research in this area seems to be justified.

CONCLUSIONS

Optimum conditions of isotachophoretic separation and determination of two heptacoordinated derivatives belonging to Goshchava-Silanate group: homo{O,O′,O″,O‴-oxalic acid's Si-[N-benzylaminiomethyl]-Si, Si-dihydroxysilanate} and homo{O,O′,O″,O‴-oxalic acid's Si-[N-benzylaminiomethyl]-Si,Si-diethoxysilanate} have been elaborated. For the determination, we used a terminating electrolyte consisting of an aqueous solution of 4,4′-bis{1-[(N,N-dimethyl)aminiomethyl]spirobi (1-sila-2,5-dioxacyclopentan-3-on)at}. Goshchava-Silanates can be successfully analyzed by means of capillary electrophoresis. The elaborated method certainly allows for a wider range of investigation of biological activity of the analyzed derivatives and their applications.

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