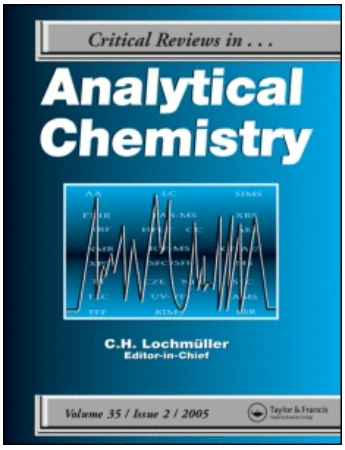

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Analytics of Biologically Active Heptacoordinated Goshchava-Silanates

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The present work attempts at a synthesis of information on a so far little known group of heptacoordinated compounds—Goshchava-Silanates. There are only a dozen or so known silicon derivative compounds of this type. These compounds show biological activity and thereby are very important for the entirety of the ecosystem, although they have not been thoroughly studied. Some of the derivatives of this compound class can easily hydrolyze which creates additional difficulties in their isolation from various matrices and chromatographic assay and separation. The present work examines two techniques of assay and separation of derivatives from the Goshchava-Silanates group: high performance liquid chromatography and isotachophoresis. Five stationary phases have been considered. The aforementioned techniques have been successfully applied in the analysis of this group of compounds.

Keywords Goshchava-Silanates, biological activity, organosilicon compounds, capillary electrophoresis, HPLC

INTRODUCTION

The chemistry of organosilicon compounds began over 150 years ago. The first organosilicon compound, tetraethoxysilane, was synthesized by Ebelman in 1845. And in 1863, Ch. Friedel and J. M. Crafts, who were working in Germany at the time, obtained the first compound with a silicon-carbon bond (tetraethylosilane) as a result of the reaction of diethyl zinc with silicon tetrachloride (1–7). Their work was continued by Ladenburg, who introduced alkyl compounds of sodium and mercury as reagents to the synthesis of organosilicon compounds. It was in the year 1900 that F. S. Kipping, for the first time, applied Grignard's method to obtain organosilicon compounds. In his experiments he obtained diphenylsilicone, from which the name "silicones" was derived. Kipping is recognized to be the father of organosilicon chemistry due to his enormous contribution to the development of this filed. The proof of his contribution to the development of organosilicon chemistry is the Kipping medal, awarded every 2 years by the American Chemical Society to the most distinguished researchers in this field of chemistry (5–8).

In the years preceding the Second World War, the number of publications concerning organosilicon compounds had decreased considerably (1). In 1935, Sztetter patented a new method of organosilicon compounds synthesis, and the industrial production of ethyl silicate was commenced—the first organosilicon compound ever produced on a larger scale. Two years later, K. A. Andrianov published a method of obtaining organosilicon synthetic resins by the hydrolysis of alkyl- or aryl- derivatives of orthosilicic acid. In the year 1939, Andrianov published, almost simultaneously with Koton, a method for obtaining polymers by hydrolysis and condensation of alkyl- or aryl-orthosilicic acid esters. Both scientists pointed out to the possibility of the utilization of these polymers as insulation materials with good dielectric properties and high heat resistance (1, 2).

In the year 1941, E.G. Rochov announced new ways of obtaining chloromethylsilanes and methylpolysiloxanes. A year later R. Miiller (who already in 1934 had discovered the catalytic action of copper in the process of silicochloroform synthesis from silicon and hydrogen chloride) patented the application of this reaction for obtaining chloromethylsilanes. Since that time Miiller has been acknowledged to be the discoverer of silicone monomer synthesis from silicon and organic halogen derivative (1).

Production of organosilicon compounds containing a silicon-carbon bond increased significantly only towards the end of the Second World War. In the year 1947, the total production of silicones amounted to approximately 40 tons a year; in 1955, 10,000 tons a year; in 1960, 20,000 tons a year; and in 1965, 50,000 tons a year. At present, the global production of silicones reaches 500–700 thousand tons a year, 45% of which is the production of silicone rubber (9, 10).

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As many as 14,000 organosilicon compounds had been known by the year 1956, and the interest in them was continually growing due to the broad spectrum of possible uses (1,4).

BIOLOGICAL ACTIVITY OF ORGANOSILICATES

The first reports on the biological activity of silicon-carbon bonds date back to the year 1960 (11–16). During the last 50 years there has been a significant development of organosilicon compounds [silatranes with the formula of R-Si(OCH2CH2)3N]. A particular interest has been attracted by l-(chloromethyl)silatrane (CMS). The stimulation of the connective tissue development by silatranes (by 1-ethoxysilatrane in particular) was noticed for the first time in 1971.

Later research of over 20 compounds of this group, with various substituents attached to the silicon atom, revealed their action stimulating the connective tissue multiplication which was demonstrated in accelerated healing of wounds, ulcers, and burns. The CMS mentioned above also exhibits anti-inflammatory action and stimulates the hair growth process (hair follicles appear in the application site). CMS significantly accelerates the recovery of the eye cornea damaged by burns caused by alkalis and acids, with no development of scars or stitches on wounds. This compound prevents the loss of calcium in bones and, thus, strengthens them. Furthermore, it promotes the healing of open fractures through the stimulation of the bone tissue remodeling process. CMS has an antineoplastic effect (13,14).

Most biologically active molecules contain functional groups (OH, NH) in which the hydrogen atom can be replaced with an organosilicon substituent [e.g., $Si(CH_3)_3$]. The so-obtained compounds often exhibit more affinity to fats than their carbon analogs. The silicon-nitrogen or silicon-oxygen bonds found in such molecules break easily and recreate the initial system; therefore, the silicon derivatives can be used as prod rugs. Such compounds penetrate through cell membranes more efficiently thanks to their physicochemical properties, and their hydrolysis, occurring inside cells, leads to the creation of an active form of the molecule (17,18).

Some organosilicon compounds have an effect on the central nervous system; for example, organosilicon barbiturates, amides, carbamates, 2-imidazolylsilanes, 1-alkyl- and alkenylsilatranes, dialkilo[2-(alkoxycarbonyl)alkoxo]silanes, and propargyloxysilanes have a sedating effect. The soporific effect is exhibited by triethylsilanol and N-trimethylsilylpyrrolidine. Moreover, other compounds, e.g., 1-methyl- and 1-vinylsilatranes as well as organosilicon derivatives of urea, have an analgesic effect (19–23).

On the other hand, organosilicon amines, spirobarbiturates, 2-aminoalkoxysilylamines, and silatranes can trigger disturbances of motor coordination. Administration of 5–10 mg/kg of (3-aminopropyl)silane to white mice and rats reduced their motor activity, but only after the administration of 10–20 mg/kg dose some animals showed disturbances of motor coordination. As soon as within 5–10 minutes of administration of 30–50 mg/kg of (3-aminopropyl)silane there appeared symptoms of muscle relaxation which lasted for 1 hour. On the other hand, after administration of methylbis(2-furyl)(3-aminopropyl)silane, the muscle relaxation and loss of coordination occurred only after 45–60 minutes and with a higher dose (13).

Analysis of the biological activity dependence on the structure shows that the toxicity of 3-aminopropylsilanes increases with the increase in the number of phenyl groups attached to the silicon atom. In the case of dimethyl(2-furyl)- and dimethyl(2-theino)(3-aminopropyl)silane, an additional anticonvulsant effect was observed. Also numerous N-heterocyclic compounds containing silicon exhibit biological activity (12).

The existence of a wide range of effective drugs administered in anti-tumor therapies does not reduce the intensity of the search for new, less toxic substances. Swift development of bioheteroorganic chemistry has made it possible to develop new drugs based on organosilicon compounds. Research of many years has showed that introduction of the silicon atom into a drug molecule reduces its toxicity, not modifying the essential function of the drug (13).

Toxicity (LDso) of most organosilicon compounds demonstrating an anti-tumor effect is in the 800–1200 mg/kg range. These compounds do not have any direct effect on the cancer cells, but rather work through the immune system, stimulating some defense reactions, and through hormones (13, 15).

The stereochemistry of the compounds is very important, e.g., *2,6-cis*-diphenylhexamethylcyclotetrasilane is very frequently used in the treatment of prostate cancer (as it is 100 times more active than the isomer *trans).* It turns out that their effect on dopamine levels in the brain is comparable (15).

Anti-tumor activity is also shown by silsesquioxanes based on silanes with substituents, e.g., phenyl ones. Antineoplastic activity is also found in organosilicon oximes, polysilanols, tetrasiloxanes containing fluoroalkyl substituents, organosilicon carboxylic acids and their salts, carbofunctional silatranes, silanes, and silatranes containing the quinoline ring (17).

Biological activity of organosilicon compounds is manifested not only in their pharmacological or toxic actions. There is an entire range of combinations characterized by a specific fragrance, e.g., organosilicon perfume. Research is mainly focused on the synthesis of silicon analogs of known odor agents. The replacement of the central carbon atom in a molecule of an odor agent with the silicon atom may result in, inter alia: deeper scent, increased intensity, or altered tone. Silicon derivatives exhibit a characteristic scent, e.g., compounds of the carbinol type—flower scent (18).

Isoxazolines are a separate group of compounds whose pharmacological uses are of the utmost importance. Some silylisoxazolines demonstrate neurotropic activity, whereas others, for example with pyridine substituent, show antithrombotic action (15). On the other hand, derivatives of thiophenol show psychotropic action (5).

Some compounds with isoxazoline rings exhibit the ability to influence the excitatory amino acid receptors, e.g., alpha-amino-3-hydroxy-5-methyl-4-isoxazolepropionic acid. On the

other hand, 3-(4-alkoxyphenyl)isoxazolines show anti-platelet activity in the presence of some glycoprotein receptors. After the introduction of a silyl group into such a molecule, its lipophilicity increases (which means a greater ability to penetrate through the blood-brain barrier). The geometry of the isoxazoline ring also changes in comparison to the carbon analog and the molecule can be modified). Therefore, the synthesis of compounds containing silyl and isoxazoline group is important for both organic and medical chemistry (15).

Biological activity is also exhibited by organic compounds containing silicon-nitrogen bonds with polycyclic structure, e.g., fungicide-containing nitric and additionally fluoroorganic compounds. Some time later organosilicon plant growth stimulators were developed (14, 24, 25).

CHARACTERISTICS OF SELECTED GOSHCHAVA-SILANATES

Organosilicon derivatives of compounds with a coordination number higher than four belong to the group of hypercoordinated compounds. Hypercoordinated organosilicon compounds, due to their specific biological, physicochemical, and structural properties, are in the center of attention of many scholars. Results of research related to this group of compounds have been published in scientific press for many years. Each available publication raises or discovers new, unusual, and fascinating properties or uses of hypercoordinated silanates. At the same time each consecutive publication contributes to better understanding of this group of compounds.

Increasingly fast development of modern organic synthesis utilizing silicon compounds and their derivatives results in obtaining compounds with more and more complicated structure. It frequently happens that the synthesis of a new compound with a natural system as its basis is carried out bearing in mind its biological activity and possible application. Examples of this type of compounds are hypercoordinated silanates (26–31). Synthesis of these compounds is based on the ability of the silicon atom to coordinate ligands with readily accessible electron pairs (28, 31–34).

Hypercoordinated organosilicon compounds are undergoing intensive research due to their interesting structure and synthetic usability. Penta-, hexa-, and heptacoordinate ionic silicon compounds are believed to be intermediate products or transitory structures in the nucleophilic substitution of the hypercoordinated silicon atom (27, 33, 34).

Synthesis of such ionic compounds is a nucleophilic attack of anions (e.g., F^-) on the neutral silicon atom accompanying bidentate ligands, stabilizing the state of the hypercoordination by the effect of the five-membered ring. On the other hand, neutral silicon compounds with a coordination number of five to seven can by synthesized using bi- or tridentate ligands with intramolecular coordination bonds (van Koten type ligands or 8-(dimethylamino)naphthyl ligand) (7, 35–40).

Most of these compounds exhibit coordinating interaction with the central atom to which they are attached. Another type

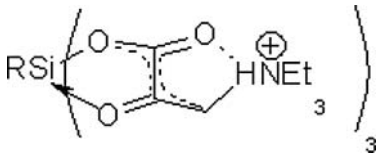

FIG. 1. Structure of heptacoordinated silicon derivative obtained in reaction of silicon tetraacetate with Schiff s bases in benzene.

of interaction is known in which the coordinating interaction is shown by atoms adjacent to ligands attached to the central atom. In the first case the number of ligands required for the synthesis increases with the coordination number of the compound we want to obtain. In the second case, however, only one ligand is required, even for the synthesis of a heptacoordinated compound, enabling the attachment to the central silicon atom of more than two functional groups (7).

Heptacoordinated organosilicon compounds belong to Goshchava-Silanates, i.e., to electrically stabilized silanates. Only a dozen or so heptacoordinated organosilicon compounds are known. In order to obtain them the oxygen atom from the carbonyl group and hydroxyl group of oxalic acid is used as the electron donor (41–47).

Synthesis of hypercoordinated silicon compounds occurs successfully due to the ability of silicon to coordinate with ligands which contain readily accessible electron pairs. Seven-coordinate silanates, whose structure is shown in Fig. 1, are obtained as a result of mutual interaction of silicon tetraacetate with Schiff base in benzene (42, 45).

Various derivatives with a chemical structure similar to the discussed class of compounds are described in detail in literature, e.g., triethylamine derivatives (l-sila-2,5-cyclopentane-3-on-4-ol)ate (Fig. 2) (40–45). Some of the obtained products are hydrolytically unstable and can hydrolyze in humid air, e.g., into trimethylammonium hydrooxalate and derivatives of 4-coordinate silicon (48).

The product obtained according to the diagram in Fig. 3 is characterized by the fact that the silicon atom is bound with carbon and six oxygen atoms. Three out of six silicon-oxygen bonds are of the coordinating type. The changing order of groups

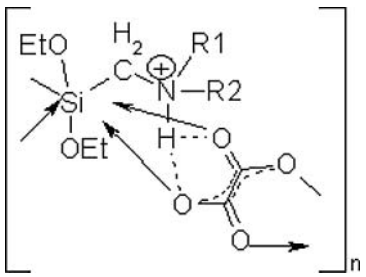

FIG. 2. An example of a structure of heptacoordinated diethoxy silicon derivative.

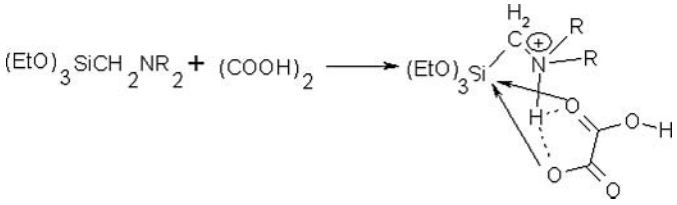

FIG. 3. General reaction schema of Goshchava-Silanates preparation (42).

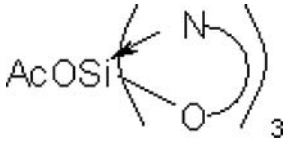

FIG. 5. Structure of heptacoordinated organosilicon derivative containing four oxygen atoms and three nitrogen atoms.

and fragments of oxalic acid (in the name of the compound indicated by "homo") illustrates the polycyclic system of anionic character (42).

Seven-coordinate silanates are polymer compounds in solid form (Fig. 4). The synthesis method of these derivatives consists in mutual interaction of aminomethyltriethoxysilanes with anhydrous oxalic acid in organic solvent (ethanol or tetrahydrofuran) in an atmosphere of argon (40).

The structure of another seven-coordinate silicon compound in which the silicon atom coordinates with four oxygen atoms and three nitrogen atoms is shown in Fig. 5 (42). The silicon-oxygen bond plays a very important role in structures of hypercoordinated silanates. High electronegativity of this bond makes the oxygen atom stabilize the hypercoordinated bonds on the silicon atom (46). X-ray examinations of individual derivatives helped determine the shape and length of bonds in the molecule between atoms (36).

Seven-coordinate silanates dissolve in DMSO, however, they do not dissolve in numerous organic solvents, e.g., acetone, dimethylformamide, or acetonitrile (41–44). Some of them can hydrolyze in aqueous solutions.

Another example of heptacoordinated organosilicon compound is trichlorosilane with tris(2-methoxy-5-t-biphenyl) four donor ligand (Fig. 6) (23). The structure of each aforementioned hypercoordinated silanate has also been confirmed by X-ray analysis.

For example, in the case of the last compound the x-ray analysis revealed an axis of symmetry C_3 running along the Si-C bond. Three methoxyl groups rotate in the same direction and position themselves towards the silicon atom. Each of the three Si-O interatomic distances is shorter that the corresponding sum of van der Waals radii. On the other hand, the Cl-Si-O angles indicate that the coordinating oxygen atoms are located opposite the chlorine atoms. Three free electron pairs derived from the oxygen atoms interact with σ^*_{Si-C} orbitals and this is why the Si-Cl bond lengths are a bit extended in comparison to the sum of relevant covalent bond radii. Bond angles around the silicon atom indicate tetrahedral structure. More specifically, it is a tri-capped tetrahedral structure if we consider the [4 + 3] coordination of the central silicon atom (23).

Preparation of Samples for Analysis

Hypercoordinated organosilicon compounds exhibit biological activity and this is one of the reasons behind so much interest in them. Goshchava-Silanates belong to this group of compounds (Fig. 7). Some of them easily undergo hydrolysis, which causes difficulties during their isolation from various matrices in order for them to undergo chromatographic analysis. In

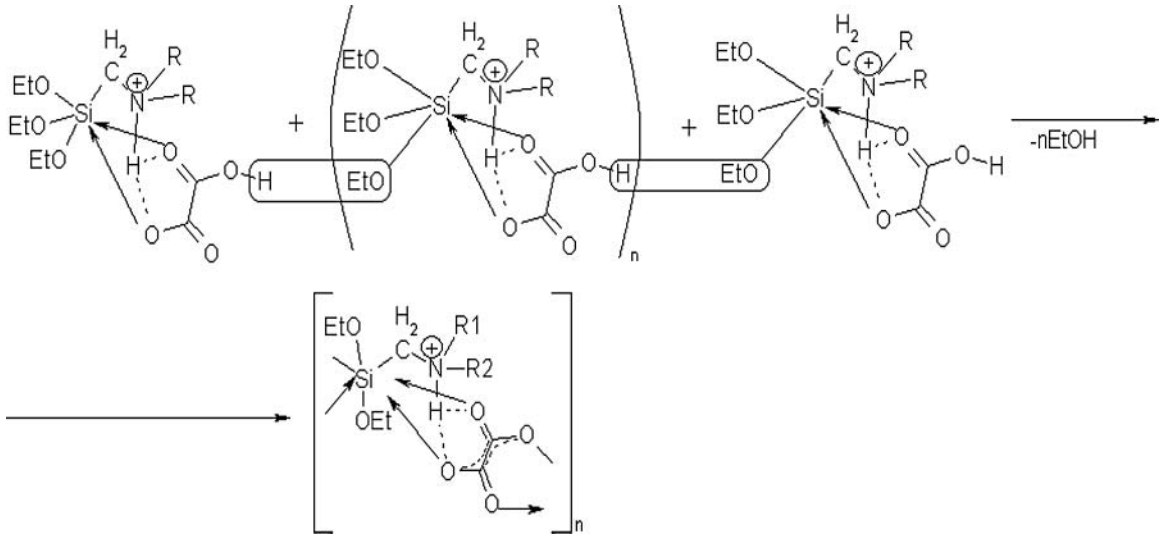

FIG. 4. Scheme of polymerization reaction of silicon ethoxy derivative (40).

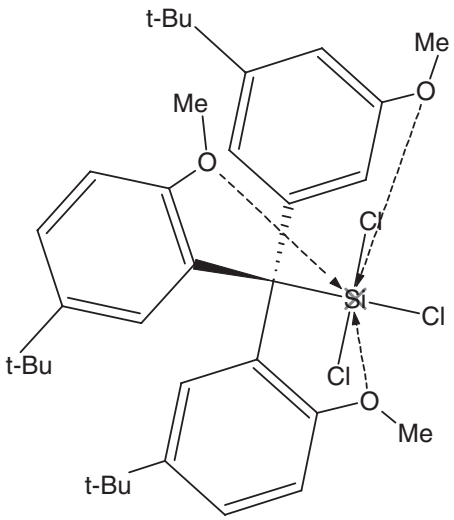

FIG. 6. Structure of trichlorosilane derivatives with tetradonor ligand tris(2-methoxy-5-t-butylphenyl).

such a case, dried and high-grade purity solvents are used most frequently during the entire analysis process.

Some organosilicon derivatives can pose a tremendous problem as, due to slightly different properties, they show the ability to modify the column packing, in both the extraction and chromatographic column. This fact is the source of additional difficulties during isolation, regardless of the applied extraction type or chromatographic column used.

At present, due to the great development of specific packings, the most frequently used isolation method of compounds from various matrices is still the solid state extraction (SPE) and the most popular chromatographic technique is still high performance liquid chromatography (49–56). With a view to developing optimal conditions for the assay and separation of several heptacoordinated silanates using HPLC and capillary electrophoresis techniques (48, 57–59), the present work describes these methods in detail.

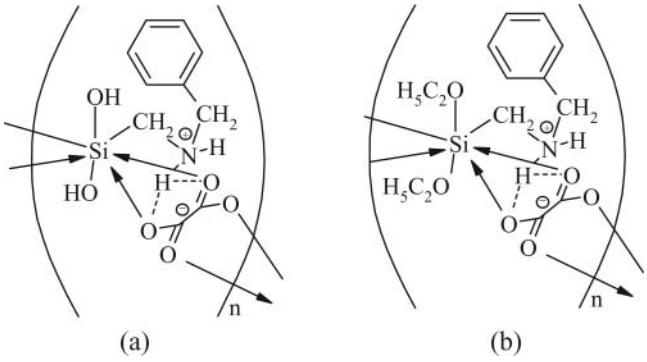

FIG. 7. Structures of: (a) Homo{O,O′,O″,O‴-oxalic acid's Si-[N-benzylaminiomethyl]-Si,Si-dihydroxysilanate} and (b) Homo{O,O′,O″,O‴-oxalic acid's Si-[N-benzylaminiomethyl]-Si,Si-diethoxysilanate}.

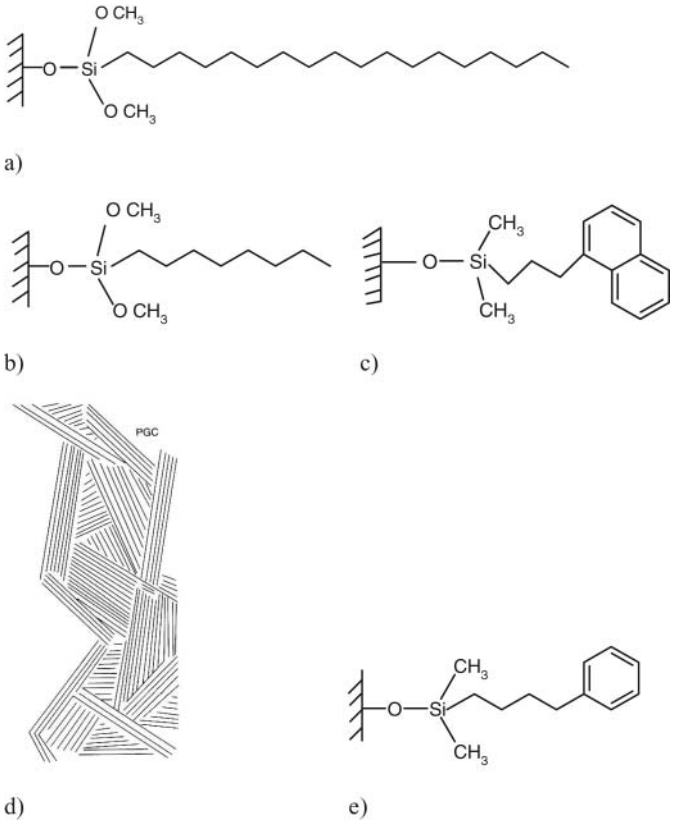

FIG. 8. Scheme of chemically bonded stationary phases: (a) octadecyl, (b) octyl, (c) naphthylpropyl, (d) PGC, (e) phenylbutyl.

A lot of attention is attached to the analysis of biologically active substances, especially in pharmaceutics and medicine. However, in order to perform isolation and proper separation of complex mixtures, in most cases selective packings must be used. Stability and repeatability of both extraction and chromatographic packings are necessary for the analytical procedure to be performed correctly. In chromatography and allied techniques, the most important aspect is the selection of mobile phase, and stationary phase in relation to the analytes being assayed. The heart of the entire chromatographic system is its column, as the most important physicochemical processes take place in it, and the success of the performed analysis depends on these processes.

SPE and HPLC make use of column packings of various polarities. The most common in both extraction and liquid chromatography are stationary phases based on silica. Chemically modified sorbents are the most important in the reversed-phase system (Fig. 8).

The retention process in reversed-phase chromatography is based on specific and non-specific interactions between stationary phase, mobile phase, and separated substance. Optimization of the chromatographic process is achieved through: change of type, composition, and character of the mobile phase or change of type, property, and topography of the stationary phase

(60–62). Whether the particular mobile and stationary phase will cause the mixture to separate depends on the thermodynamic properties of the chromatographic system.

Preparation of a sample for chromatographic analysis usually requires initial separation of the examined substance, usually from a very complicated matrix. This applies in particular to the HPLC technique. Samples analyzed using the electrophoresis technique are an exception. This technique does not require thickening and slight differences in concentrations of analyzed components. Still, the analyzed substances must be hydrolytically stable, at least for the time of the analysis process. Stability of the compounds the discussed in the present 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}] differed. The first was hydrolytically stable, whereas the latter's stability was limited. Ethoxyl derivative, 30 minutes after dissolution in water, underwent visible hydrolysis. However, this property did not cause difficulties in assays performed using isotachophoresis technique, as the optimal analysis period lasted 9 minutes. In the case of longer analyses of the discussed compounds, DMSO should be used, as both compounds dissolve very well in it.

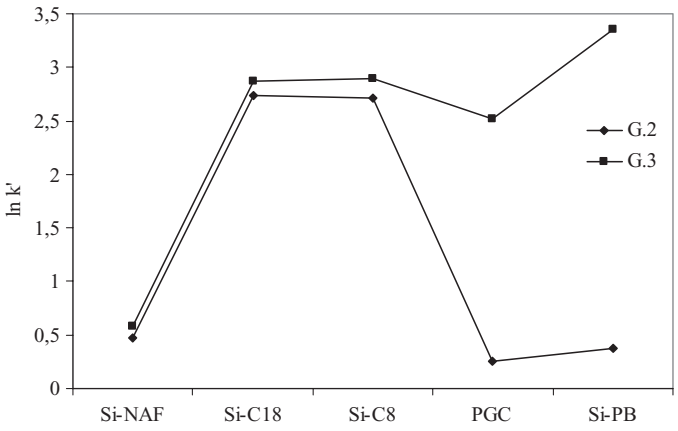

FIG. 9. Results of separation of the (G.2) Homo{O,O′,O″,O‴-oxalic acid's Si-[N-benzylaminiomethyljdihydroxysilanate and (G.3) Homo{O,O′,O″,O‴-oxalic acid's Si-[N-benzylaminiomethyljdiethoxysilanate on the stationary phases: naphthylpropyl, octadecyl, octyl, PGC, and phenylbutyl. Chromatographic conditions: mobile phase—acetonitrile (100%), flow—1.0 mL min^{-1}, wavelength −326 nm, temperature −20°C.

Analytics of Individuals by Chromatography and Isotachophoresis Techniques

One of the techniques employed in assays of Goshchava-Silanates was a high performance liquid chromatography. Analyses were performed at the wave length of 326 nm, using anhydrous mobile phases: acetonitrile and methylene chloride with different flow rates. Due to the limited hydrolytic stability of the ethoxyl derivative, the following types of mixtures of mobile phases were not used: acetonitrile/water, methanol/water, or methylene chloride/water.

In order to develop optimal conditions for the chromatographic assay and separation of analyzed compounds, five different stationary phases were used: octadecyl, octyl, phenylbutyl, naphthylpropyl, and graphitic PGC (Fig. 8) (57–59).

The octadecyl column was used as a reference. The best separation results were obtained using pure acetonitrile as the mobile phase and graphitic (PGC) column. Optimal separation retention time of the Goshchava-Silanates mixture in the HPLC technique did not exceed 5 minutes.

On the other hand, for the same system and phenylbutyl column, the retention time was slightly longer. This column was characterized by good separation of analyzed compounds, too. Slightly smaller selectivity and longer retention times were characteristic of the naphthylpropyl column. At the same time good separation of analyzed compounds was achieved in this column (60). Obtained results indicate a dominant effect of TT-TT interactions between the stationary phase and the analyte.

Comparatively, the weakest interactions were characteristic of octyl and octadecyl phases. Retention time of the assayed Goshchava-Silanates was longer by a few minutes. Poor separation of analytes was also observed in these columns, regardless of the mobile phase used. Reducing the mobile phase flow rate resulted in prolonged retention times of the compounds assayed on alkyl columns. On the other hand, aryl columns showed a significantly smaller extension of retention time than in case of alkyl columns (Fig. 9).

To sum up, the PGC column, compared with the other phases, was characterized by a slightly different surface structure and manner of interactions with analyte (Fig. 10). Graphite can interact as a donor or recipient of a proton. The visible effect of

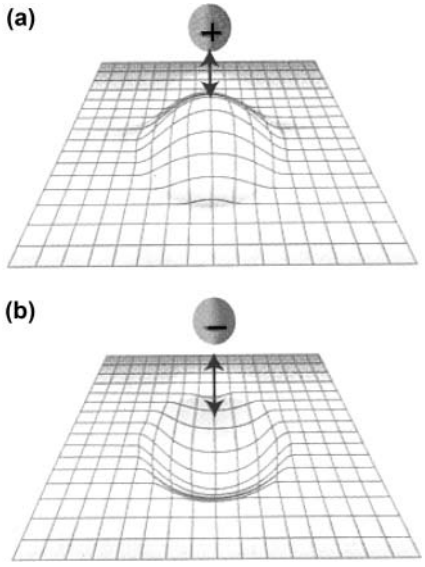

FIG. 10. Scheme of interactions between analyzed compound and graphite surface (PGC column).

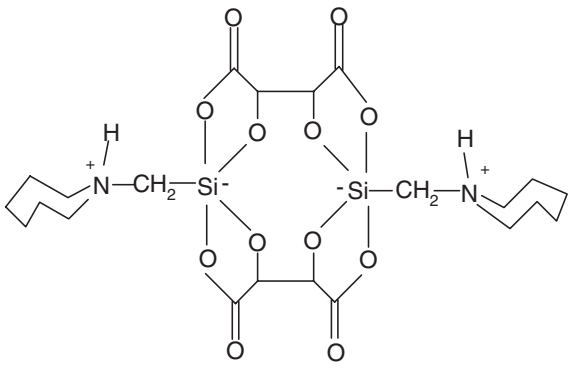

FIG. 11. Schema of structure of the terminating electrolyte constituent used to isotachophoretic determination: 4,4′-bis{l-(perhydroazepiniomethyl)[spirobi(l-sila-2,5-dioksacyklopentan-3-on)]at}.

these differences was the shortest retention time of the assayed compounds and the best selectivity. Obtained results for five columns are shown in Fig. 9.

Another technique employed in assays of Goshchava-Silanates was capillary electrophoresis. Capillary electrophoresis analyzer of EA 202M Villa Labeco (Slovakia) series was used in the analyses.

Separation 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} took place based on the differences in electrophoretic mobility of analyzed ions. The compounds were difficult to analyze due to the negligible mobility and limited hydrolytic stability of the ethoxyl derivative. Another problem was the use of an appropriate terminator for this type of compounds, one which would have the lowest mobility. In the assays of Goshchava-Silanates, an ionic compound was used, being a double salt 4,4″-bisl-[N,N-dimethyl)aminomethyl]spirobi(l-sila-2,5-dioxacyclopentan-3-on)ate (Fig. 11) (63, 64).

Development of optimal conditions for the assay and separation of analyzed compounds is confirmed by the obtained isotachophoregram (Fig. 12, Table 1). Optimal separation time of the analyzed mixture was just under 9 minutes. High efficiency of the separation, comparable to electrophoretic methods, and

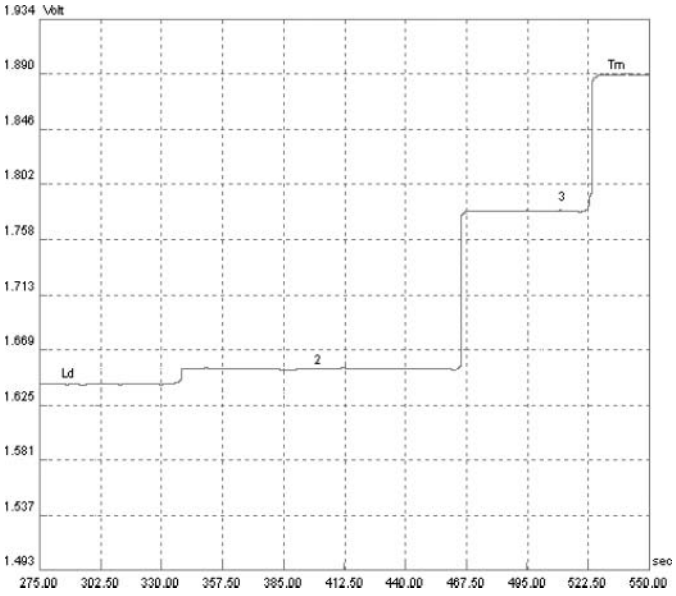

FIG. 12. Isotachophoregram of the mixture (2) of Homo{O,O′,O″,O‴-oxalic acid's Si-[N-benzylaminiomethyl]-Si,Si-dihydroxysilanate} and (3) Homo{O,O′,O″,O‴-oxalic acid's Si-[N-benzylaminiomethyl]-Si, Si-diethoxy silanate}.

short analysis time make capillary isotachophoresis competitive in many aspects not only to HPLC, but also to other analytical techniques.

Isotachophoresis allows one to assay heptacoordinated compounds of the Goshchava-Silanates group. The main advantage of this technique is the fact that it makes it possible to simultaneously assay macro- and micro-components in only several minutes. It does not require complicated preparation of the sample prior to the analysis, and is also perfectly suitable for routine analyses. Isotachophoresis does not require the use of toxic reagents or solvents and therefore can be classified as one of the so-called green chemistry techniques. The applied technique was characterized by high precision and accuracy of results obtained in the analyses (Table 2). The linearity range was 2–31 mg/L, and the detection limit was 1 mg/L. Precision and accuracy of results obtained by the capillary isotachophoresis method is better than that of classical methods.

TABLE 1
Optimum Conditions of Isotachophoretic Separation of a mixture of (*2*) Homo{O,O′,O″,O‴-oxalic acid's Si-[N-benzylaminiomethyl]-Si,Si-dihydroxysilanate} and (*3*) Homo{O,O′,O″,O‴-oxalic acid's Si-[N-benzylaminiomethyl]-Si,Si-diethoxysilanate}.

Considered parameters					
Stage	Time [s]	Intensity [HA]	Composition [10 mV]	Column	Conductometric detector
1	100	150	0	Upper	—
2	210	200	50	Upper	X
3	240	240	0	Lower	X

TABLE 2
Characteristics of Analytical Methods used

Parameter	Unit	For examined ion
Precision[1]	%	2.4–3.3
Recovery[2]	%	91.5±6
Linearity[3]	mg/L	2–31
Limit of Identification[4]	of mg/L	1

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

[2]The sample was enriched with 1 .5 mL of a solution containing 1 mg/mL of examined ion, n = 7.

[3]Correlation coefficient above 0.98.

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

At present, in order to develop optimal conditions for assay and separation of compounds, sometimes chemometrics is used, which is based on computer aided modeling. This method works when dealing with a known group of compounds. However, it is impossible in the case of Goshchava-Silanates.

Another problem is the fact that chemometrics is not a perfect technique, as from the viewpoint of separation selectivity there are no universal packings (in which separation of every group of compounds is possible). Therefore, effective separation of compounds belonging to, for example, the same homologous series is not always feasible. Results obtained in this way can be misleading for the analyst. Computer aided modeling is especially problematic when working on new or barely known compounds. It does not work at all if, during syntheses, poor yield of products is obtained, often in the form of mixtures. In such cases chromatography and allied techniques are irreplaceable.

SUMMARY

To sum up, both high performance liquid chromatography and capillary electrophoresis can be applied to assay heptacoordinated compounds of the Goshchava-Silanates group. A successful separation of a mixture of compounds was performed: 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}. In spite of the fact that the analyzed Goshchava-Silanates differed slightly in electrophoretic mobility, optimal conditions for their assay and separation were developed with the use of isotachophoresis with conductivity detection. For the assays, a new terminating solution was used in the form of an aqueous solution 4,4′-bisl-[N,N-dimethyl)aminomethyl]spirobi(l-sila-2,5-dioxacyclopentan-3-on)ate.

Optimal conditions for the assay and separation of the aforementioned Goshchava-Silanates with the use of HPLC technique were also determined. Regardless of the type and flow rate of the mobile phase, the highest selectivity was characteristic of the commercial PGC stationary phase. Apart from the highest selectivity, this phase was characterized by the shortest retention times of assayed compounds. The main reason for increased selectivity was the occurrence of additional TT electron interactions between the stationary phase and the analyte. The phases used in the analyses differed mainly in the surface structure. The lowest separation factor and the longest retention times of the analyzed Goshchava-Silanates were revealed in alkyl phases. Retention times of analyzed compounds on aryl stationary phases were significantly shorter in comparison to alkyl phases.

Optimization of conditions for the assay and separation of this class of compounds using HPLC and capillary electrophoresis techniques will certainly contribute to the development of chemistry of hypercoordinated compounds. It indicates new possibilities for research of biological activity of this type of combinations. The present work is a synthesis of information on heptacoordinated compounds of the Goshchava-Silanates group and compliments information on hypercoordinated organosilicon compounds.

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