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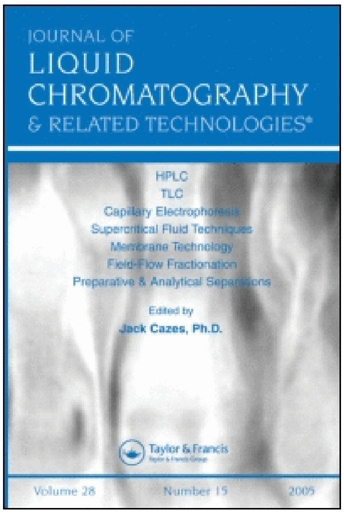

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Separation of Selected Heptacoordinated Derivatives of Goshchava-Silanates for HPLC

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Abstract: Optimum conditions of separation and determination was studied of two newly synthesized heptacoordinated benzyl derivatives from the group of Goshchava-silanates: 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 the carried out investigation, we considered three stationary phases (octadecyl, octyl, phenylbutyl) and two mobile phases (acetonitrile and dichloromethane) in various intensities of flow. The best selectivity and the highest separation factor ($\alpha = 9.08$) was obtained using the mobile phase acetonitrile (100%) and the phenylbutyl column. To reliably optimize the process of separation and determination of the compounds on the phenylbutyl column, the validation of prepared methodology was done.

Keywords: Determination, Heptacoordinated organosilicon derivatives, HPLC, Separation

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INTRODUCTION

In the seventies of the last century, a new scientific trend was created – bioorganosilicon chemistry. Its future prospects were determined. Some were singled out for maximum utilization of the most modern analytical methods, definition of structures, identification of silicon compounds in living organisms, analysis of transport, accumulation of silicon compounds in nature, definition of mechanisms of silicon compounds' participation in physiological processes of living organisms, synthesis of new medicinal preparations, biostimulators, and pesticides on the base of organosilicon compounds.[1]

One of the main problems in the bioorganosilicon chemistry is formation of organomineral complexes of soil and soil solutions (sources of nourishment for flora and fauna), formation of humus, etc. It was confirmed that destruction of silicon minerals in the environment can be an effect of widening of silicon atom coordination.[2] Therefore, many silicon compounds were prepared in order to look for biological activity.[3,4] Hypercoordinated model compounds (penta-, hexa- and heptacoordinated) with bonds silicon-oxygen-carbon in molecules were synthesized. A new group of compounds – ES-silanates (electrostatic stabilized silanates) was produced.[5–8] Heptacoordinated organosilicon derivatives synthesized in Department of Environment Chemistry of University of Podlasie belong to dozens of, untill now, obtained compounds of this class.[9–11]

ES-silanates are biologically active. For this reason, they are more and more frequently subjected to various tests. Electrostatically stabilized silanates are neutral and easily soluble in water. Therefore, microfloras of soil can utilize these compounds for assimilation and transport of silicons.[12–14]

ES-silanates show similar properties as natural systems; they are neither toxic nor mutagenic (except silatranes). Chiral hypercoordinated silicon compounds can serve as model compounds for investigation of biological transport of silicons.[15]

Organosilicon compounds are widely applied in medicine. Numerous anticancer drugs were based on silicon compounds. Multidirectional methods of synthesis based on organosilicon reagents enabled improving the technology of production of antibiotics, which possessed extraordinary activity against gram-positive and gram-negative bacteria.[16]

Heptacoordinated organosilicon derivatives belong to a group (Hoszczawa–) Goshchava-silanates. These polymeric compounds of λ^7 – type, contain heptacoordinated silicon atoms.[17,18] During the synthesis process of this type of compounds, as donors of electrons, serve oxygen atoms of carbonyl groups and hydroxyl groups of oxalic acid. Looking for high resistant materials led to intensification of interest concerning silicone based polymers and products. Aminomethyltrialkoxysilanes as polyfunctional organosilicon monomers proved to be useful in the preparation of cross linked plastics.[19] Amino derivatives of trialkoxysilanes are applied in glass fiber production and as hardeners instead of epoxide resin.

Aminomethyltrialkoxysilanes are important starting materials in reactions of synthesis of ES-silanates and Goshchava-silanates. These compounds are biologically active and their structure is similar to natural systems.[20] Because of the wide possibilities of application, their determination seems to be advisable. Therefore, elaboration of optimum conditions of chromatographic separation and determination of two synthesized heptacoordinated derivatives belonging to the group of Goshchava-silanates, i.e., 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 this work.

EXPERIMENTAL

HPLC Analysis of Hyper Coordinated Compounds

Samples of Homo{O,O′,O″,O‴-oxalic acid's Si-[N-benzylaminiomethyl]-Si,Si-dihydroxysilanate} (ES.1) and Homo{O,O′,O″,O‴-oxalic acid's Si-[N-benzylaminiomethyl]-Si,Si-diethoxysilanate} (ES.2) (Figure 1)[17] were dissolved in DMSO (HPLC purity, Fluka AG, Buchs, Switzerland); to obtain a concentration at about 20 $\mu g \cdot mL^{-1}$. Analyses were performed at 326 nm and at temperature of 20°C. Three stationary phases

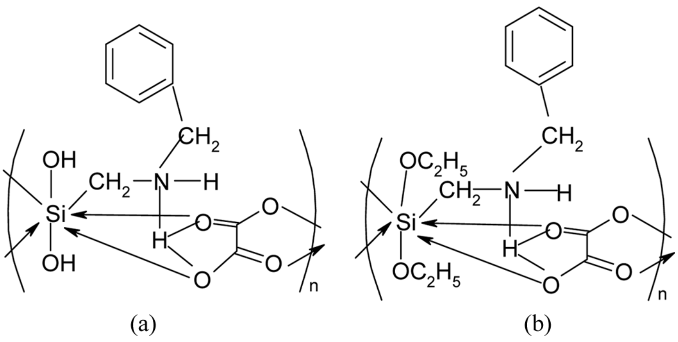

Figure 1. Structures of: (a) Homo{O,O′,O″,O‴-oxalic acid's Si-[N-benzylaminiomethyl]-Si,Si-dihydroxysilanate}, and (b) Homo{O,O′,O″,O‴-oxalic acid's Si-[N-benzylaminiomethyl]-Si,Si-diethoxysilanate}.

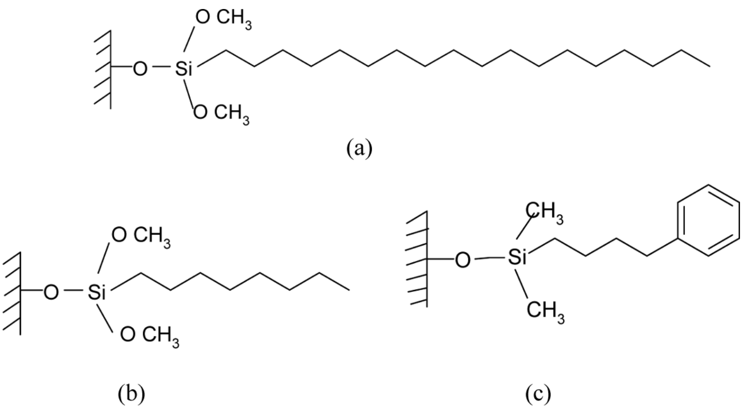

Figure 2. Scheme of chemically bonded stationary phases: (a) octadecyl, (b) octyl, and (c) phenylbutyl.

were examined: octadecyl (S. Witko – J.T. Baker, Łódź, Poland), octyl (S. Witko – J.T. Baker, Łódź, Poland), and phenylbutyl (Si–PB, Figures 2, and 3).[21] Dimensions of the steel columns were: for Si–C_{18} – 250 × 4.6 mm, for Si–C_8 and Si–PB – 125 × 4.6 mm (Table 1). Two anhydrous systems of mobile phase were applied: acetonitrile and dichloromethane.

The hypercoordinated compounds were prepared by the method described in the literature.[17]

Homo{O,O′,O″,O‴-oxalic acid's Si-[N-benzylaminiomethyl]dihydroxy-silanate: ^{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]-diethoxy-silanate: ^{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.

Table 1. Characteristics of bonded phase

Stationary phases	Manufacturer of column	Carbon content vol. (%)	Length of column (mm)
Octadecyl	S. Witko–J.T. Baker	18.09	250 × 4.6
Octyl	Home made	13.49	125 × 4.6
Phenylbutyl	Home made	14.90	125 × 4.6

After optimizing the analytical conditions, the ES.1 and ES.2 detection method was validated in terms of linearity, limit of determination LOD, limit of quantification LOQ, recovery, and correlation coefficient. Eight solutions were prepared: $2.5\,\mu g \cdot mL^{-1}$, $5.0\,\mu g \cdot mL^{-1}$, $10.0\,\mu g \cdot mL^{-1}$, $50.0\,\mu g \cdot mL^{-1}$, $80.0\,\mu g \cdot mL^{-1}$, $100.0\,\mu g \cdot mL^{-1}$, $130.0\,\mu g \cdot mL^{-1}$, $150.0\,\mu g \cdot mL^{-1}$. The validation process was done according to procedure used in literature.[22,23]

Apparatus

^{1}H, ^{13}C, ^{29}Si NMR spectra were recorded on a Varian Mercury 400 MHz in DMSO-d_6, with TMS as internal standard. The UV/Vis spectra were recorded on a spectrophotometer DU-68 (Beckman, USA).

Chromatographic measurements were performed on a liquid chromatograph SPD-6A (Shimadzu, Kyoto, Japan) equipped with a gradient pump LC-6A, UV detector, a sampling valve Rheodyne (Berkeley, CA, USA), model 7125, with a 20 μL sample loop, and a Shimadzu C-R6 A data recorder. The obtained chromatogram was placed in the paper by the use of OriginPro 7.5 program (OriginLab Corporation, Northampton, USA).

RESULTS AND DISCUSSION

In the paper are reported optimum data of chromatographic separation and determination of two heptacoordinated derivatives from the group of Goshchava-silanates: 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}. Obtained results are collected in Table 2.

During optimization of conditions of chromatographic separation and determination, two mobile phases (acetonitrile and dichloromethane) in various intensities of flow and three stationary phases (octadecyl, octyl, and phenylbutyl) were tested. Octadecyl phase is, in HPLC, commonly used and considered as the reference phase. But its application to separation in some groups of compounds does not yield satisfactory effects. Therefore, during elaboration of optimum conditions of separation and determination of newly synthesized compounds, in order to obtain the best results, it is necessary to take into an account special packings of columns.

In this paper, separation has been obtained by means of octadecyl, as well as an octyl column. For the octadecyl (reference) column, the highest value of separation factor (1.18) was obtained at flow $0.5\ mL \cdot min^{-1}$, for

Table 2. Chosen dependence k′ for ES.1 and ES.2 from on type of stationary and mobile phase. Chromatographic conditions: flow – 1.0, 0.5 mL · min^{-1}, wavelength – 326 nm, temperature – 20°C

Type of stationary phase	[a]Mobile phase/flow rate (mL · min^{-1})	k'_1	k'_2	$\alpha = k'_2/k'_1$
Si–C_{18}	Acetonitrile/1.0	2.74	2.87	1.05
	Acetonitrile/0.5	6.29	7.45	1.18
	Dichlomethane/1.0	2.77	2.93	1.06
	Dichlomethane/0.5	6.36	7.51	1.18
Si–C_8	Acetonitrile/1.0	2.71	2.90	1.07
	Acetonitrile/0.5	5.03	5.88	1.17
	Dichlomethane/1.0	2.74	2.95	1.08
	Dichlomethane/0.5	5.11	5.94	1.16
Si–PB	Acetonitrile/1.0	0.37	3.36	9.08
	Acetonitrile/0.5	2.11	8.14	3.86
	Dichlomethane/1.0	0.47	3.47	7.38
	Dichlomethane/0.5	2.18	8.34	3.83

[a]In the table are presented only optimum data of separation of the analyzed derivatives.

both mobile phases. The retention time of the second derivative (ES.2) in the case of acetonitrile was 6.83 min. On the other hand, an application of an octyl column yielded maximum value of separation factor (1.17) using acetonitrile and the same flow. The retention time of the second

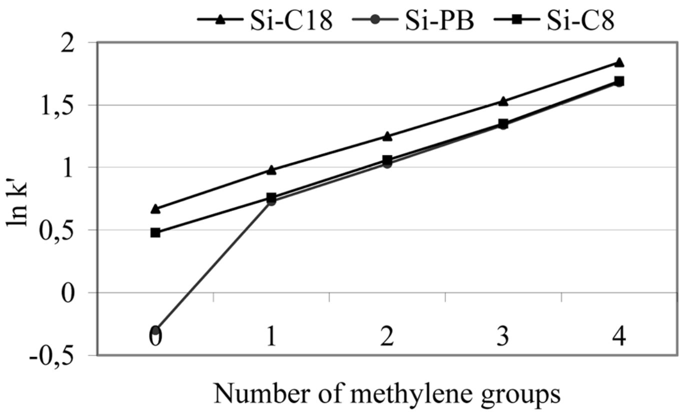

Figure 3. Dependence ln k′ on the number of carbon atoms in alkyl chain of alkyl-benzenes for octyl, octadecyl and phenylbutyl packing. Chromatographic conditions: mobile phase 65/35 vol.% acetonitryle/water, flow – 1 mL · min^{-1}, wavelength – 254 nm, temperature – 20°C.

derivative was 6.61. The selectivity obtained by means of both of these columns was not high and separation factor did not exceed a value of 1.2. A phenylbutyl column was needed for the separation of these compounds. Essential for properties of this column is the content of the phenyl group. Its presence changes a character of interactions between analyzed compounds and column packing. The dominating influence of interactions of the $\pi - \pi$ type can be easily observed on the basis of obtained data (Figures 3–5, Table 2). The phenylbutyl column yielded the highest selectivity and separation factor 9.08. The time of retention of the first derivative was 1.58 min, of the second 4.93 min.

Different compositions of water containing solvent mixtures caused only an elongation of retention times, not improving the selectivity of the separation. Therefore, in Table 2 these results are not reported.

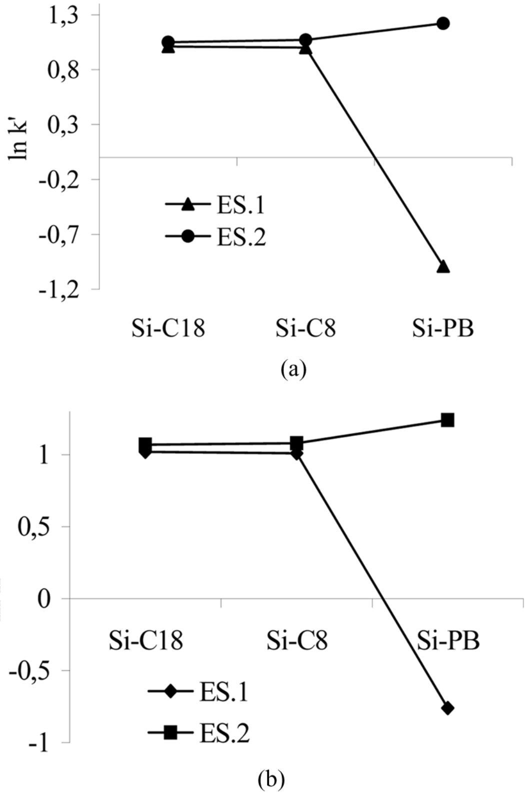

Figure 4. Effect of the separation of ES.1 and ES.2 with the use of stationary phases Si–C_{18}, Si–C_8 and Si–PB. Mobile phase: (a) acetonitrile (vol. 100%), flow rate: 1.0 $mL \cdot min^{-1}$, (b) dichloromethane (vol. 100%), flow rate: 1.0 $mL \cdot min^{-1}$, detection – 326 nm (see Table 2).

Table 2 contains only optimum data obtained in the process of chromatographic separation and determination.

As always, it is desirable to obtain the best results in the shortest time as is possible, the use of the phenylbutyl column showed to be highly indicated. Phenylbutyl phases (Figure 2c) are classified as aryl phases. Usually aryl phases are designed for determination of π electron containing compounds.[24–28] If the chromatographic process involves only a limited group of compounds containing aromatic rings, then, the dominating interactions in the chromatographic process are interactions of $\pi - \pi$ type. Owing to increased selectivity in numerous determinations, as well as in this work, better separation of analyzed hypercoordinated derivatives was achieved.

To recapitulate, the use of the aryl phase significantly improved selectivity of separation of analyzed derivatives: 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 a very short time, under 5 min. Effects of separation on three used stationary phases are shown in Figures 4–6. Optimum conditions of separation and determination of above mentioned derivatives are reported in Table 2. It was shown that the phenylbutyl chemically bonded stationary phase is characterized by the highest selectivity and separation factor (9.08). The best results in utilizing this phase were obtained using acetonitrile (100%) as the mobile phase; however, the use of dichloromethane also achieved good results. The structures of analytes

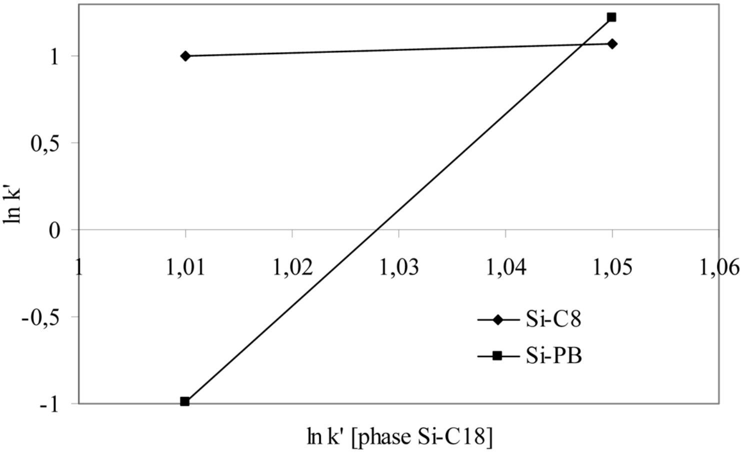

Figure 5. Dependence of ln k′ of the Si–C_8 and Si–PB phases on ln k′ obtained for the octadecyl phase for ES.1 and ES.2. Mobile phase: acetonitrile (100 vol. %), flow – 1 mL · min^{-1}, wavelength – 326 nm, temperature – 20°C.

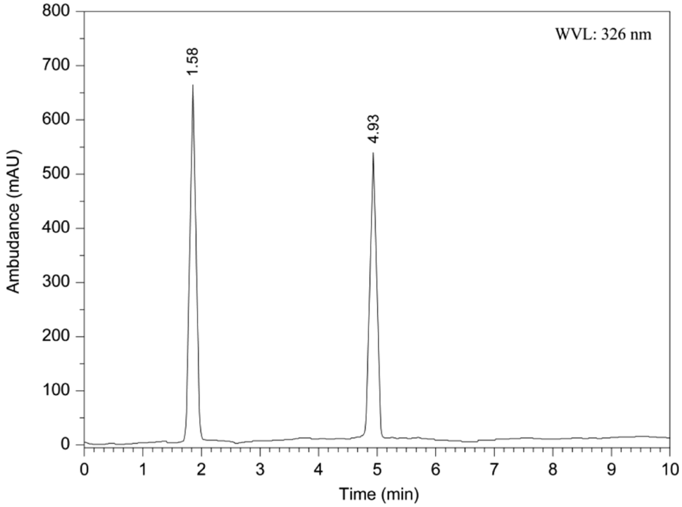

Figure 6. A chromatogram of separation of the Homo{O,O′,O″,O‴-oxalic acid's Si-[N-benzylaminiomethyl]-Si,Si-dihydroxysilanate} (1.58 min) and Homo-{O,O′,O″,O‴-oxalic acid's Si-[N-benzylaminiomethyl]-Si,Si-diethoxysilanate} (4.93 min) on the stationary Si–PB phase. Mobile phase: acetonitrile (100 vol. %), flow – 1 mL · min^{-1}, wavelength – 326 nm, temperature – 20°C.

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

For the reliable optimization process of separation and determination of the ES.1 and ES.2 derivatives mixture on the phenylbutyl column, the validation of the prepared methodology was done (Table 3). Limit of determination LOD was calculated on the basis of results for 8 independently prepared samples, in which the level of analyte concentration was close to the expected LOD. The average value and standard deviation were calculated. Limit of quantification LOQ was calculated as signal to noise ratio (S/N = 3). The method has an LOQ for ES.1 and ES.2 of 5 μg · mL^{-1}.

Table 3. Validation parameters of determination of the ES.1 and ES.2

Compound	Recovery (%)	Limit of quantification LOQ (μg · mL^{-1})	Limit of determination LOD (μg · mL^{-1})	Limit of linearity (μg · mL^{-1})	Correlation coefficient
ES.1	86.2 ± 2.7	5,0	2.5	5–150	0.9871
ES.2	86.9 ± 3.1	5,0	2.5	5–150	0.9882

To resume, the phenylbutyl column, mobile phase – acetonitrile (100%), flow rate 0.5 mL·min^{-1} 326 nm, should be applied to separate the mixture of ES – silanate, using the HPLC technique in the shortest time.

CONCLUSIONS

The best selectivity of separation of two analyzed heptacoordinated benzyl derivatives: 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 obtained using the phenylbutyl column. The highest separation factor ($\alpha = 9.08$) was obtained using acetonitrile (flow 1 mL·min^{-1}) as the mobile phase.

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