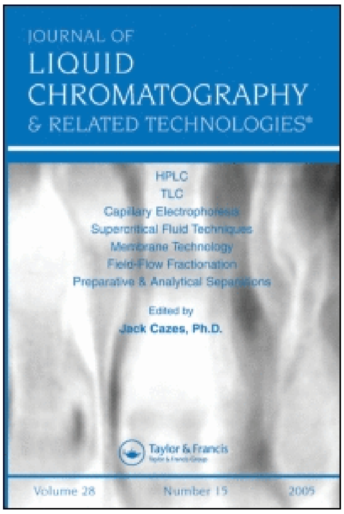
This article was downloaded by:
On: *23 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Liquid Chromatography & Related Technologies

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597273

Separation of Azepinio-Methyl Derivatives of ES-Silanates by the Use of Aryl Stationary Phases in HPLC

Mariusz Kluska[a]; Edvards Liepinsh[b]; Krzysztof Pypowski[a]; Nikolai Erchak[a]
[a] Department of Environmental Chemistry, Institute of Chemistry, University of Podlasie, Siedlce, Poland [b] Department of Physical-Organic Chemistry, Latvian Institute of Organic Synthesis, Latvia

To cite this Article Kluska, Mariusz , Liepinsh, Edvards , Pypowski, Krzysztof and Erchak, Nikolai(2008) 'Separation of Azepinio-Methyl Derivatives of ES-Silanates by the Use of Aryl Stationary Phases in HPLC', Journal of Liquid Chromatography & Related Technologies, 31: 5, 675 — 682

To link to this Article: DOI: 10.1080/10826070701853826

URL: http://dx.doi.org/10.1080/10826070701853826

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Journal of Liquid Chromatography & Related Technologies®, 31: 675–682, 2008

ISSN 1082-6076 print/1520-572X online
DOI: 10.1080/10826070701853826

Separation of Azepinio-Methyl Derivatives of ES-Silanates by the Use of Aryl Stationary Phases in HPLC

Mariusz Kluska,[1] Edvards Liepinsh,[2] Krzysztof Pypowski,[1] and Nikolai Erchak[1]

[1]Department of Environmental Chemistry, Institute of Chemistry,
University of Podlasie, Siedlce, Poland
[2]Department of Physical-Organic Chemistry, Latvian Institute of Organic
Synthesis, Latvia

Abstract: Optimal conditions of chromatographic separation and determination of chosen higher coordinated compounds belonging to a group of ES-silanates have been elaborated. In the analysis were considered: $^5\lambda$-Si-[(azepinio)methyl]bis[2-methyllactic(2 −)-0^1, 0^2]silicate and $^5\lambda$-Si-[(azepinio)methyl]bis[2-methylglycolic(2-)-0^1, 0^2]silicate. Investigations were carried out applying three stationary phases (phenylbutyl, naphthylpropyl, and hypercarb), two mobile phases (acetonitrile, dichloromethane) and various flows. The shortest retention times were observed when a hypercarb column containing graphitized coal was used. However, the highest separation factor ($\alpha = 3.05$) was obtained using the naphthylpropyl column and the mobile phase consisting of pure acetonitrile (flow 1 mL · min^{-1}).

Keywords: Aryl stationary phases, HPLC, $^5\lambda$-Si-[(azepinio)methyl]bis[2-methyllactic(2-)-0^1, 0^2]silicate, $^5\lambda$-Si-[(azepinio)methyl]bis[2-methylglycolic(2-)-0^1, 0^2]silicate

INTRODUCTION

Silicon organic derivatives with higher than 4 coordination numbers belong to a group of higher coordinate compounds. Synthesis of compounds of this type is based on an ability of silicon to coordinate ligands with easily accessible

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

electron pairs. In the formation of ES-silanates oxygen atoms of carboxyl and hydroxyl groups of the carboxyl acids are taking part, e.g., 2-methylglycolic, 2,2-dimethylglycolic, tartaric or mandelic acid.[1,2]

One of the substrates to ES-silanates is an aminomethyl derivative of trialkoxysilane. An analysis of published data showed that aminomethyltrialkoxysilanes were used as inhibitors of corrosion. If we take into account that attacks of the pollution environment on steelworks, bridges, etc., are stronger and stronger, searching for good agents to resist this harmful process is reasonable; on the other hand, the results that have been hitherto obtained, seems hopeful.[3,4]

ES-silanates can serve as examples of higher coordinate organic silicon compounds. They are electrostatically stabilized and belong to pentacoordinate compounds of the λ^5 type. They contain Si-C-N and Si-O-C bonds in their molecules.[5−8]

Penta- and hepta-coordinated silicon compounds are widely known. In the case of the preparation of heptacoordinated compounds, so called Hoszczawa-silanates, as donors of electrons, serve as oxygen atoms of the carbonyl group and hydroxyl group of the oxalic acid.[2]

An analysis of the chemical literature concerning properties of ES-silanates lead to the conclusion that they show biological activity.[9] Especially, interesting, these properties exhibit silsesquioxanes (belonging to ES-silanates). These compounds can be used as membrane materials for the production of optical fibers. However, after adequate modification, silsesquioxanes can also possess properties of liquid crystals.[10] Investigations reported in this paper and concerning $^5\lambda$-Si-[(azepinio)methyl]bis[2-methyllactic(2-)-0^1, 0^2]silicate (**ES-1**) and $^5\lambda$-Si-[(azepinio)methyl]bis[2-methylglycolic(2-)-0^1, 0^2]silicate (**ES-2**) are a continuation of previous work, which referred to optimization of the process of their chromatographic separation and determination.[11] This chromatographic investigation is, in our opinion, reasonable, because they show important properties and their structures approximate natural systems.

EXPERIMENTAL

HPLC Analysis of ES-Silanates

Samples of $^5\lambda$-Si-[(azepinio)methyl]bis[2-methyllactic(2-)-0^1, 0^2]silicate and $^5\lambda$-Si-[(azepinio)methyl]bis[2-methylglycolic(2-)-0^1, 0^2]silicate (Figure 1) were dissolved in dichloromethane (HPLC purity, Fluka AG, Buchs, Switzerland), in order to obtain a concentration at about 21 $\mu g \cdot mL^{-1}$. The samples were subjected to analysis performed by the use of HPLC at 325 nm and at temperature of 20°C. Three stationary phases (commercial hypercarb column, packed by porous graphitized coal (RP Si—PGC, Figure 2a,

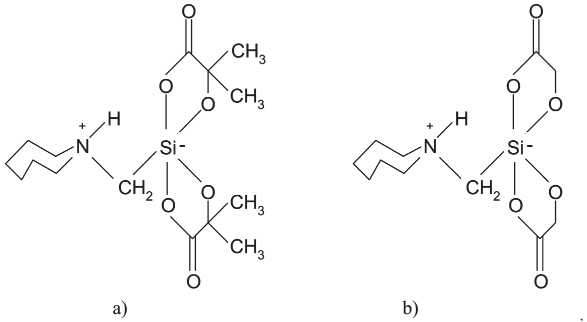


Figure 1. Structures of: a) $^5\lambda$-Si-[(azepinio)methyl]bis[2-methyllactic(2-)-0^1, 0^2]silicate, b) $^5\lambda$-Si-[(azepinio)methyl]bis[2-methylglycolic(2-)-0^1, 0^2]silicate.

Thermo Electron Corporation, UK), phenylbutyl phase (RP Si—PB, Figure 2b,[12–15] and naphthylpropyl (RP Si—NAF, Figure 2c,[12–15] were used. Dimensions of the columns were: for RP Si—PGC – 100 × 4.6 mm, for RP Si—PB – 125 × 4.6 mm, for RP Si—NAF – 125 × 4.6 mm, respectively (Table 1). Two mobile phases (acetonitrile and dichloromethane) and different flow intensities (1.0, 0.5, 0.3 mL · min^{-1}) were tested during the research. The ES-silanate compounds were prepared by the method described in the literature.[2]

$^5\lambda$-Si-[(azepinio)methyl]bis[2-methyllactic(2-)-0^1, 0^2]silicate: ^{1}H NMR (DMSO), δ (ppm): 1.27 (s; 12H; CCH_3), 1.53–1.64 (m; 4H; CCH_2C),

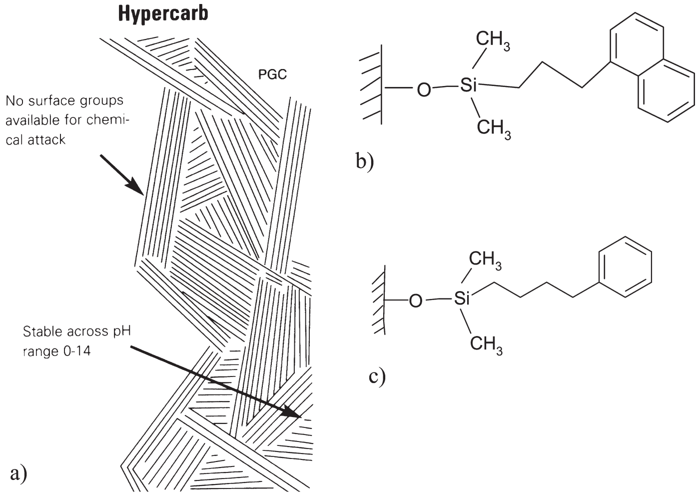


Figure 2. Scheme of chemically bonded stationary phases: a) hypercarb (RP Si—PGC) b) naphthylpropyl (RP Si—NAF), and c) phenylbutyl (RP Si—PB).

Table 1. Characteristics of aryl bonded phase

Column name	Reversed phase code	Carbon (%)	Column dimensions (mm)	Manufacturer of column
Hypercarb	Si—PGC	100	100 × 4.6	Thermo Electron Corporation
Naphthylpropyl	Si—NAF	16.1	125 × 4.6	Home made
Phenylbutyl	Si—PB	14.9	125 × 4.6	Home made

1.68–1.82 (m; 4H; CCH_2C), 2.5 (s; 2H; NCH_2Si), 2.88–3.26 (m; 4H; NCH_2), 8.12 (bs; 1H, NH).

^{13}C NMR (DMSO), δ (ppm): 20.29 (s), 23.58 (s), 25.61 (s), 49.23 (s), 64.32 (s), 68.73 (s), 175.59 (s).

UV/Vis (CH_2Cl_2): λ_{max} ($\lg\varepsilon$) = 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}.

$^5\lambda$-Si-[(azepinio)methyl]bis[2-methylglycolic(2-)-0^1, 0^2]silicate: ^1H NMR (DMSO), δ (ppm): 1.5–1.7 (m; 4H; CCH_2C), 1.7–1.9 (m; 4H; CCH_2C), 2.58 (s; 2H; $SiCH_2$), 3.02–3.18 (m; 4H; NCH_2Si), 3.95 (s; 4H; CH_2COO), 8.05 (bs; 1H; NH).

^{13}C NMR (DMSO), δ (ppm): 23.54 (s), 25.40 (s), 25.43 (s), 49.04 (s), 62.72 (s), 173.81 (s).

UV/Vis (CH_2Cl_2): λ_{max} ($\lg\varepsilon$) = 303 (2.51), 325 (2.51).

IR (KBr) ν_{max}: 3431, 3118, 2939, 2862, 1726, 1472, 1460, 1240, 1100, 579, 533, 489, 457 cm^{-1}.

The infrared spectra of ES-silanates have been examined in the region of 3500–450 cm^{-1} to assign the characteristic group frequencies in the compounds synthesized.

Apparatus

Chromatographic measurements were performed on a liquid chromatograph (model SPD-6A, Shimadzu, Kyoto, Japan), equipped with a gradient pump (Shimadzu, model LC-6A, Kyoto, Japan), UV/Vis detector, a sampling valve (Rheodyne, model 7125; Berkeley, CA, USA), with a 20 μL sample loop, and a Shimadzu model C-R6A data recorder.

The ES silanates compounds were prepared by the method described in the literature,[2] ^1H NMR spectra were recorded on a Bruker-200 in $CDCl_3$, with HMDS as internal standard. The infrared (IR) spectra were recorded on a Nicolet Magna-IR 760 in potassium bromide.

RESULTS AND DISCUSSION

The obtained data of the chromatographic separation of chosen 1-[silanyl)-methyl]azepane are presented in Table 2. Investigated derivatives of ES-silanates (Figure 2) are members of a very important group of biologically active compounds.[9,10] Their valuable properties and structures, which are similar to the structures of natural compounds, are of increasingly wider interest; therefore, they are the reason for the chromatographic research being undertaken.

In looking for optimal process conditions, two mobile phases (acetonitrile and dichloromethane) with different flow intensities (1.0, 0.5, 0.3 mL · min^{-1}) were considered. During the investigation three stationary phases were used: phenylbutyl (RP Si – PB), naphthylpropyl (RP Si—NAF), and hypercarb (RP Si—PGC). The best separation was obtained by the use of pure acetonitrile as the mobile phase (Table 2, Figures 3–5). Because this paper is a continuation of an earlier work, which referred to the optimization of the process of chromatographic separation and determination of chosen ES-silanates, data concerning octadecyl columns (as reference phase and already published),

Table 2. Chosen dependence ln k′ for **ES-1** and **ES-2** from on type of stationary and mobile phase. Chromatographic conditions: flow–1.0, 0.5 or 0.3 mL · min^{-1}, wavelength–325 nm, temperature–20°C

Type of stationary phase	Mobile phase	Flow rate (mL · min^{-1})	k'_1	k'_2	$\alpha = k'_2/k'_1$
RP Si—PGC	Dichloromethane	1.0	0.17	0.18	1.06
		0.5	0.52	0.55	1.06
		0.3	3.38	3.73	1.10
	Acetonitrile	1.0	0.29	0.30	1.03
		0.5	0.41	0.41	1.00
		0.3	3.12	3.78	1.21
RP Si—NAF	Dichloromethane	1.0	0.49	0.78	1.59
		0.5	4.14	5.18	1.25
		0.3	14.28	19.27	1.35
	Acetonitrile	1.0	0.41	1.25	3.05
		0.5	3.46	7.54	2.18
		0.3	12.56	24.96	1.99
RP Si—PB	Dichloromethane	1.0	1.17	1.32	1.13
		0.5	5.24	6.13	1.17
		0.3	17.21	23.96	1.39
	Acetonitrile	1.0	0.94	1.25	1.33
		0.5	5.01	7.13	1.42
		0.3	16.13	21.28	1.32

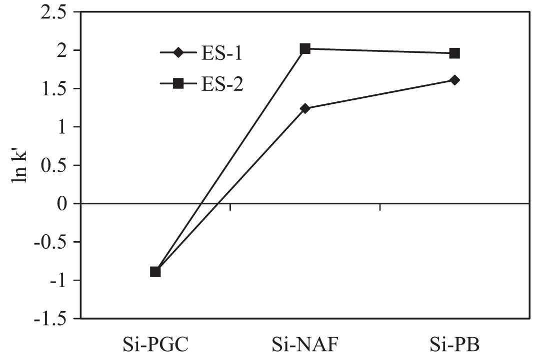


Figure 3. Effect of the separation of $^5\lambda$-Si-[(azepinio)methyl]bis[2-methyllactic(2-)-0^1, 0^2]silicate (**ES-1**), $^5\lambda$-Si-[(azepinio)methyl]bis[2-methylglycolic(2-)-0^1, 0^2]silicate (**ES-2**) with the use of aryl stationary phases: RP Si—PGC, RP Si—NAF, and RP Si—PB. Mobile phase: acetonitrile (100 vol. %), flow–0.5 mL · min^{-1}, detection–325 nm (see Table 2).

are here omitted. The best selectivity of determined compounds has been obtained using an RP Si—NAF column and acetonitrile (flow 1.0 mL · min^{-1}). In this case, retention time of **ES-1** was 1.68 min and retention time of **ES-2**–2.70 min. On the other hand, an RP Si—PGC column and the same solvent system yielded a slightly shorter retention time, but the separation was unsatisfactory. The RP Si—PB column was characterized by better selectivity; however retention times were a little longer (Figures 3 and 4). A commercial hypercarb column is characterized by a different surface structure than the two remaining stationary phases (Figure 2). This difference causes shortening of retention times and decreasing of selectivity. The effect achieved with the help of the RP Si—NAF column was the best from among five tested columns (hypercarb, naphthylpropyl,

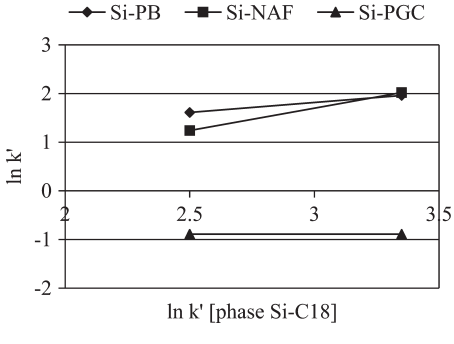


Figure 4. Dependence of ln k′ of the RP Si—PB and RP Si—NAF and RP Si-PGC phases on ln k′ obtained for the octadecyl phase for **ES-1** and **ES-2**.

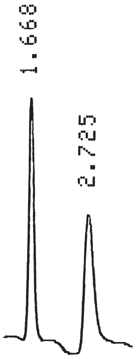


Figure 5. A chromatogram of separation of the $^5\lambda$-Si-[(azepinio)methyl]bis[2-methyllactic(2-)-0^1, 0^2]silicate (time 1.668 min), and $^5\lambda$-Si-[(azepinio)methyl]bis[2-methylglycolic(2-)-0^1, 0^2]silicate (time 2.725 min) on the stationary RP Si—NAF phase. Mobile phase: acetonitrile (100 vol.%); flow–1 mL · min^{-1}, wavelength –325 nm, temperature –21°C.

phenylbutyl columns (aryl columns) and two columns recommended as standard, i.e., octyl and octadecyl).[11] Good results of optimization of the chosen ES silanates confirm the reasonableness of our investigation (Figure 5).

Decreasing of the flow to 0.5 mL · min^{-1} caused slight elongation of retention time of ES-silanates (to at about 14 min for aryl columns), whereas for earlier tested alkyl columns,[11] retention time for **ES-2** was 20.27 min in the case of RP Si-C_{18} column and 36.01—in the case of RP Si-C_8. Retention time of **ES-2**, when flow of acetonitrile was 0.3 mL · min^{-1}, came up to 109 min for octadecyl column,[11] while naphthylpropyl columns in the same conditions yielded retention time of 31 min. Proportional results were obtained using anhydrous dichloromethane as a mobile phase. In recapitulation, data presented in Table 2 show, that independently of the composition of a mobile phase, RP Si-NAF phase is characterized by the highest selectivity. However, the hypercarb phase is characterized by the shortest retention times. This phase differs from the former mainly in the surface structure. Slightly lower separation factors (α) and longer retention times of the analyzed ES-silanates show the phenylbutyl phase. Retention times obtained by means of these three aryl phases are considerably shorter in comparison with results obtained using an octadecyl (standard) phase.

CONCLUSIONS

The course of the optimization of the separation and determination of chosen ES-silanates by HPLC as examples: $^5\lambda$-Si-[(azepinio)methyl]bis[2-methyllactic(2-)-0^1, 0^2]silicate and $^5\lambda$-Si-[(azepinio)methyl]bis[2-methylglycolic(2-)-

0^1, 0^2]silicate, showed that these compounds can be determined by means of phases considered as standard (octadecyl) as well as by means of hypercarb, naphthylpropyl, phenylbutyl columns (aryl columns). Application of these phases considerably reduced retention times of analyzed compounds. Naphthylpropyl stationary phase was characterized by the highest selectivity (separation factor $\alpha = 3.05$) from among the tested phases.

REFERENCES

1. Lukevics, E.; Dremowa, V.P.; Simchenko, L.I.; Voronkov, M.G. Khim-Farm. Zh. **1974**, *8* (10), 29.
2. Szymanik, A. Master's thesis, University of Podlasie, Poland, 2005, p. 83.
3. Klyuchnikov, N.G.; Karabadzhk, F.I.; Losev, V.B. Zh. Prikl. Khim. **1970**, *43* (12), 2763.
4. Shreiber, G.K.; Saakiyan, L.S.; Losev, V.B.; Al'khamedan, K.; Skripchenko, V.I. Zh. Prikl. Khim. **1970**, *43* (1), 200.
5. Tace, R.; Becht, J.; Dannappel, O.; Ahlrichs, R.; Schneider, U.; Sheldrick, W.S.; Hahn, J.; Kiesgen, F. Organomet. **1996**, *15* (8), 2060.
6. Bertermann, R.; Biller, A.; Krupp, M.; Penka, M.; Seiler, O.; Tace, R. Organomet. **2003**, *22* (20), 4104.
7. Erchak, N.; Liepinsh, E.**1991**, SU N. 1710561 (USSR).
8. Erchak, N.; Liepinsh, E.**1991**, SU N. 1685954 (USSR).
9. Lukevics, E.; Lapsina, A.F.; Zelcans, G.; Dauvarte, A.; Zidermane, A. Latv. PSR Zinat. Akad. Vestis, Kim. Ser. **1978**, *3*, 338.
10. Guliński, J. Chemia w szkole **2003**, *1*, 4.
11. Kluska, M.; Liepinsh, E.; Pypowski, K.; Erchak, N. Anal. & Bioanal. Chem. **2007** (in press).
12. Gadzała-Kopciuch, R.M.; Kluska, M.; Wełniak, M.; Buszewski, B. Mat. Chem. & Phys. **2005**, *89*, 228.
13. Kluska, M.; Pypowski, K.J. Liq. Chromatogr. & Rel. Technol. **2007**, *30*, 2059.
14. Kluska, M.; Pypowski, K.; Erchak, N.J. Liq. Chromatogr. & Rel. Technol. **2007**, *30*, 2385.
15. Kluska, M.; Pypowski, K.; Erchak, N.J. Liq. Chromatogr. & Rel. Technol. **2007**, *30*, 1777.

Received June 28, 2007
Accepted September 10, 2007
Manuscript 6200