Oceanological and Hydrobiological Studies

International Journal of Oceanography and Hydrobiology

Volume 49, No. 3, September 2020
pages (247-254)

ISSN 1730-413X
eISSN 1897-3191

Development of an extraction procedure and analysis of electrostatically stabilized silanates from aqueous solutions

by

Joanna Jabłońska[1], Mariusz Kluska[1,*], Nikolai Erchak[2], Stanisław Popiel[3]

DOI: **10.1515/ohs-2020-0022**
Category: **Original research paper**
Received: **February 21, 2020**
Accepted: **April 9, 2020**

[1]*Siedlce University of Natural Sciences and Humanities, Faculty of Exact and Natural Sciences, ul. 3 Maja 54, 08-110 Siedlce, Poland*

[2]*Latvian Institute of Organic Synthesis, Aizkraukles 21, LV-1006 Riga, Latvia*

[3]*Military University of Technology, ul, gen. Sylwestra Kaliskiego 2, 00-908 Warszawa, Poland*

* Corresponding author: kluskam@uph.edu.pl

Abstract

The analyzed organosilicon derivatives of electrostatically stabilized silanates belong to a group of pentacoordinated compounds. These derivatives are: 1-(N-morpholiniomethyl)spirobi(1-sila-2,5-dioxacyclopentan-3-on)at, 1-(N-morpholiniomethyl)spirobi(1-sila-2,5-dioxa-4-methylcyclopentan-3-on)at, 1-(N-morpholiniomethyl) spirobi(1-sila-2,5-dioxa-4-(i-propyl)cyclopentan-3-on)at.

In the course of the work, the extraction process and optimization of conditions for separation and determination of a mixture of electrostatically stabilized silanates were carried out using capillary isotachophoresis. Proper leading electrolytes were elaborated developed and the terminating electrolyte: 4,4'-bis[(1-morpholiniomethyl)spirobi(1-sila-2,5-dioxacyclopentan-3-on)at] was proposed. The extraction process involved the use of three stationary phases: octadecyl, octyl and phenylpropyl. The highest recovery values, approx. 94%, were obtained on the phenylpropyl column. The optimum time of analysis by the isotachophoretic technique did not exceed 12 min. The developed method of separation and determination of electrostatically stabilized silanates expands the possibility of research on biological activity of this group of compounds in aqueous solutions and surface water vegetation.

Key words: extraction, aqueous solutions, ES-silanates, determination

DE GRUYTER

The *Oceanological and Hydrobiological Studies* is online at www.oandhs.pl

Introduction

In the 1970s, the first methods of synthesis of hypercoordinated compounds containing germanium, silicon, iron, vanadium, and thallium were developed. Many of these elements are the subject of recent research (Lukevics et al. 2007; Kluska & Pypowski 2007; Kluska et al. 2007; Pypowski et al. 2006). Organosilicon derivatives with a coordination number higher than four belong to the group of hypercoordinated compounds. Their preparation is based on the ability of silicon to coordinate ligands containing groups of atoms with easily accessible electron pairs (Kluska 2008a).

Penta- and heptacoordinated silicon compounds are commonly known. When preparing heptacoordinated compounds, oxygen atoms of the carbonyl and hydroxyl groups of oxalic acid serve as donors of electrons (Lukevics et al. 2007). Electrostatically stabilized silanates are biologically active, e.g. 1-(N-morpholiniomethyl)spirobi(1-sila-2,5-dioxacyclopentan-3-on)ate is used as a stimulator of plant growth (Erchak et al. 2005). Electrostatically stabilized silanates are neutral, easily soluble in water and hydrolytically stable (Kluska et al. 2009; Böhme et al. 2006).

ES-silanates show similar properties as natural systems; they are neither mutagenic nor toxic. Chiral hypercoordinated silicon compounds can serve as model compounds in research on biological transport of silicon (Böhme et al. 2006; Oestreich 2006). The information available in the literature indicates that hypercoordinated silicon organic complexes occur in a biologically bound liquid. It is also presumed that there is a transitional organosilicon complex formed during the life cycle of an organism. Hypercoordinated organosilicon compounds play an important role in the assimilation and transport of silica through biological systems (Kenla et al. 2013). Organosilicon compounds containing pentacoordinated silicon are characterized by increased solubility. They can be transported through tissues and accumulated in places selected for their utilization. The presence of hypercoordinated silicon compounds explains the process of biofractionation of Si isotopes and fractionation of Ge with Si (Kubicki & Heaney 2003). In addition, Si improves the water storage within plant tissues and mitigates toxic effects of heavy metal salts in sand (Romero-Aranda et al. 2006; Guo-Chao et al. 2018).

Some organosilicon compounds are applied in the medicine (Durka et al. 2019; Hu et al. 2017; Jabłońska et al. 2018). Numerous anticancer drugs were based on silicon compounds. Multidirectional methods of synthesis based on organosilicon reagents have contributed to the improvement of the technology of production of antibiotics, which are extremely active against gram-positive and gram-negative bacteria (Singh et al. 2017). Numerous organosilicon compounds are effective agents taking part in biocontrol of a plant organism, e.g. morpholine derivatives of electrostatically stabilized silanates.

Nevertheless, among many biologically active organosilicon compounds, some are strongly toxic (usually used against rodents). Silatranes are examples of compounds that are growth stimulators (Lin et al. 2011). However, they belong to chloroorganic compounds, hence the possibility of forming environmentally toxic products (Kluska 2008a).

Given the biological activity and the wide range of uses of this class of compounds, research on this type of substances is very important. Therefore, the main objective of our work was to develop the extraction process and to optimize the conditions for the determination of selected ES-silanates and the separation of constituents of the mixture of these compounds in aqueous solutions. For this purpose, it was necessary to select adequate leading electrolytes and to develop a suitable terminating electrolyte.

Materials and methods

The compounds synthesized at the Institute of Chemistry of the University of Natural Sciences and Humanities in Siedlce served as research material (Erchak et al. 2015), i.e. 1-(N-morpholiniomethyl) spirobi(1-sila-2,5-dioxacyclopentan-3-on) at (**72**), 1-(N-morpholiniomethyl)spirobi(1-sila--2,5-dioxa-4-methylcyclopentan-3-on)at (**73**), 1-(N-morpholiniomethyl)spirobi(1-sila-2,5-dioxa-4-(i-propyl)cyclopentan-3-on)at (**79**) (Fig. 1). The terminating electrolyte contained aqueous solution of 4,4′-bis[1-morfoliniometylo]spirobi(1-sila--2,5-dioxacyclopentan-3-on)at] (Fig. 2).

During the experiment, the concentration of ES-silanate derivatives was 100 μg l^{-1}. The solutions were concentrated by solid phase extraction. The process was carried out in three extraction columns of different chemical structures: octyl (RP Si–C8), octadecyl (RP Si–C18) and phenylpropyl (RP Si–FP, Fig. 3; Gadzała-Kopciuch et al. 2005; Kluska 2008b; Kluska et al. 2019b; Prukała et al. 2008).

The conditioning of each column consisted in rinsing with 4 ml of cyclohexane (Merck, Darmstadt, Germany), 4 ml of methanol (Merck, Darmstadt, Germany) and 4 ml of triple distilled water. The extraction columns were then dried for 15 s under a stream of air. The next step consisted in passing 100 ml of distilled water solution and analyzing derivatives

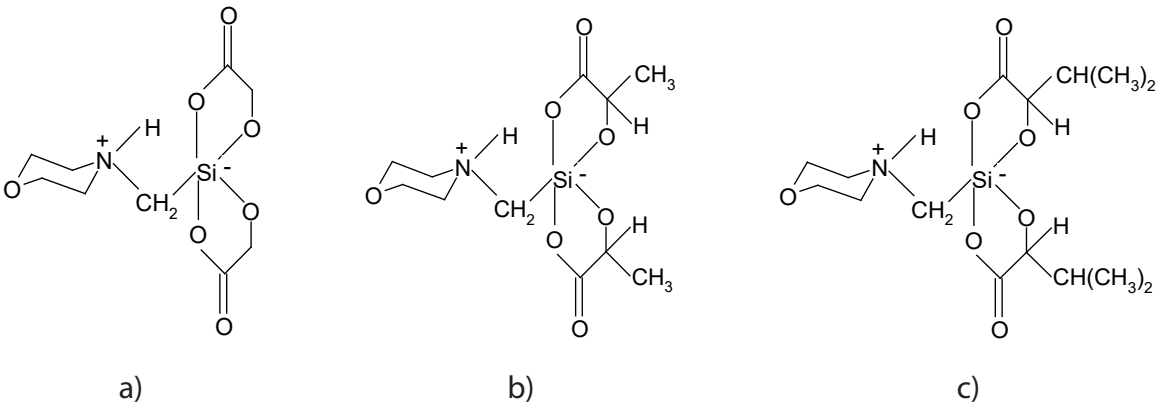

Figure 1

Structures of analyzed compounds: a) 1-(N-morpholiniomethyl)spirobi(1-sila-2,5-dioxacyclopentan-3-on)at (**72**), b) 1-(N-morpholiniomethyl)spirobi(1-sila-2,5-dioxa-4-methylcyclopentan-3-on)at (**73**), c) 1-(N-morpholiniomethyl) spirobi(1-sila-2,5-dioxa-4-(i-propyl)cyclopentan-3-on)at (**79**)

of ES-silanates through the columns in vacuo at a flow rate of 3–4 drops per second. Each column was then dried under a stream of air for 10 min. The adsorbed derivatives of ES-silanates were eluted with 8 ml of methanol and then concentrated under a stream of air to 1 ml. Each sample prepared in this way was then analyzed using the ITP technique.

Optimization of the conditions for the analysis of compounds involved preparation of solutions with specific concentration, creation of standard curves, separation and determination of selected ES-silanates. Electrolytes were prepared: acetic acid (POCh Gliwice), hydrochloric acid (POCh Gliwice), deionized water (Merck) and sodium acetate (POCh Gliwice). Leading electrolytes LE-1 (pH = 3.9) and LE-2 (pH = 4.2) were obtained by mixing adequate volumes of solutions of acetic acid and sodium acetate.

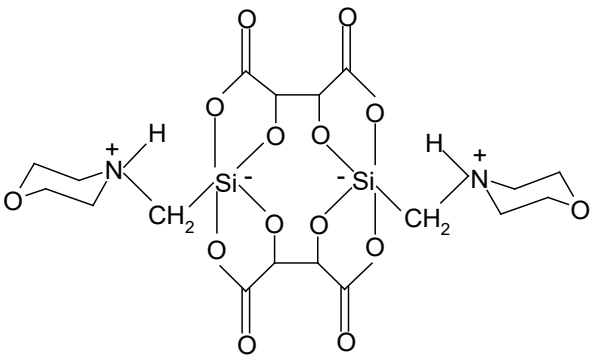

Figure 2

Structure of a compound used in terminating electrolyte 4,4'-bis[(1-morpholiniomethyl)spirobi(1-sila-2,5-dioxacyclopentan-3-on)at]

Solution of 4,4'-bis[(1-morpholiniomethyl)spirobi(1-sila-2,5-dioxacyclopentan-3-on)at] with a concentration of 40 µg l^{-1} was used as a terminating electrolyte (TE).

To determine the validation parameters and to draw calibration curves, standard solutions with concentrations: 0, 2, 5, 10, 20, 50 and 100 µg l^{-1} were prepared.

Different conditions of the method were tested during optimization of ES-silanate analysis. The time of analysis, the level of high voltage limitation, and electric current intensity were changed using preseparation or preseparation and analytical columns.

Apparatus

An octadecyl column from S. Witko, Łódź, Poland was used in the research. The octyl and phenylpropyl columns were developed at the Department of Environmental Chemistry and Bioanalysis of Nicolaus Copernicus University (UMK) in Toruń, Poland.

Optimization of separation and determination of derivatives of ES-silanates was carried out using a capillary electrophoresis analysator EA 202M produced by Villa Labeco s.r.o. in Spisska Nova Ves, equipped with: an injection block with a container for the terminating electrolyte, a preseparation column (capillary diameter 0.8 mm, length 90 mm), a bifurcation block with an electrode block of the preseparation column, an analytical column (capillary diameter 0.3 mm, length 160 mm), and a UV detector, an electrode block of the analytical column, two conductometric detectors with a measurement range between 20 kΩ and 30 MΩ and a steering unit – a personal computer PC containing an AD/DA converter.

Results and discussion

The study included: 1-(N-morpholiniomethyl) spirobi(1-sila-2,5-dioxacyclopentan-3-on)at, 1-(N-morpholiniomethyl)spirobi(1-sila-2,5-dioxa-4-methylcyclopentan-3-on)at, 1-(N-morpholiniomethyl)spirobi(1-sila-2,5-dioxa-4-(i-propyl)cyclopentan-3-on)at. The initial sample preparation procedure should be fast, selective, and environmentally friendly (Buszewski & Szultka 2012; Popiel & Nawała 2013; Popiel et al. 2014; Małkiewicz et al. 2015; Nawała et al. 2016; Wrona et al. 2019). In order to select optimal extraction conditions for ES-silanates, the tests were carried out on three extraction columns differing in the chemical structure of the stationary phase (Fig. 3). Characteristics of the extraction column filling material used in the research indicate that the percentage of carbon and hydrogen and the degree of surface coverage of the extraction phases are at a sufficiently high level (Gadzała-Kopciuch et al. 2005). The octadecyl phase was characterized by the highest surface coverage density (4.68 µmol m^{-2}). Whereas the chemically bonded phenylpropyl phase was characterized by the lowest coverage density (4.21 µmol m^{-2}) and the highest percentage of carbon (12.60%). On the other hand, the octyl phase was characterized by the lowest percentage of carbon (11.04%).

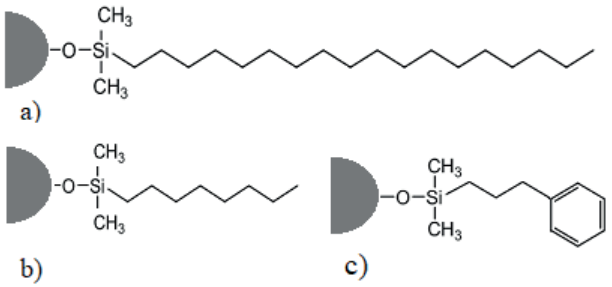

Figure 3

Chemical structures of bonded stationary phases used in the study: a) octadecyl, b) octyl, c) phenylpropyl stationary phases

To select the best conditions for the liquid-solid extraction process, solutions of ES-silanate derivatives in distilled water at 100 µg l^{-1} were prepared. The solutions were mixed and concentrated, and recovery values for three ES-silanate derivatives on three different extraction columns were determined. The obtained results of the research are presented in Table 1. The highest recovery value of 93.9 ± 4.1% was obtained for compound (**79**) on the column packed with phenylpropyl. The lowest recovery value (82.2 ± 4.3%) was determined using the octyl column for derivative (**72**). The highest recovery values were observed for the chemically bonded phenylpropyl phase.

The high recovery values obtained on the phenylpropyl column are probably due to the presence of an aryl group attached to the alkyl chain. It participates in the process of isolating substances from various matrices, using mainly π-π interactions in the terminal part of the attached ligand together with the isolated analyte. Low values of standard deviations and the high recovery values indicate a high rate of reproducibility of the obtained results. In the case of the octadecyl and octyl phases, there are only two types of active centers on the surface of the support, i.e. residual silanols and hydrophobic alkyl chains (Gadzała-Kopciuch et al. 2005).

The qualitative and quantitative analyses of (ES)-silanates were conducted with ITP. The best conditions of separation and determination are shown in Tables 2 and 3 and on the isotachophoregram (Fig. 4). At the beginning, ES-silanates were investigated separately to determine the shortest time of analysis, then on mixed solutions. Isotachophoresis with conductometric detection was used as the method.

Tables 2 and 3 show common parameters of the optimum separation and determination of (**72**), (**73**) and (**79**) by the isotachophoretic technique. The analyses were carried at voltages ranging from 11 kV to 15 kV, wherein at voltage lower than 11 kV no separation was achieved. The best results of separation were obtained at voltage reduced to 12 kV (Fig. 4).

The proposed composition of electrolytes enables the optimum individual determination of these compounds as well as the determination of their mixture in acidic medium. The mobility of ions of an analyzed sample must be lower than that of the terminating electrolyte and higher than the mobility of the leading electrolyte (Mala et al. 2017; Kluska et al. 2019a; Kluska et al. 2020). A new terminating electrolyte was developed and used: 4,4'-bis[(1-morpholiniomethyl)spirobi(1-sila-2,5-dioxacyclopentan-3-on)at] by adding the standard. The terminating electrolyte was selected considering its ion mobility, which is lower than the ion mobility of the analyzed mixture.

The qualitative analysis was based on the identification of zone heights compared to the height of zones obtained on standard isotachophoregrams and based on the comparison of lengths of zones of the analyzed ES-silanates with the standard isotachophoregrams.

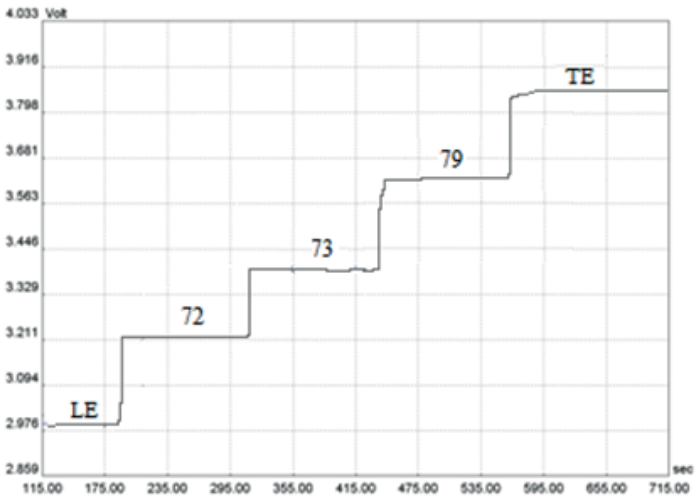

Figure 4

Isotachophoregram of the mixture of 1-(N-morpholiniomethyl)spirobi(1-sila-2,5-dioxacyclopentan-3-on)at **(72)**, 1-(N-morpholiniomethyl)spirobi(1-sila-2,5-dioxa-4-methylcyclopentan-3-on)at **(73)**, 1-(N-morpholiniomethyl) spirobi(1-sila-2,5-dioxa-4-(i-propyl)cyclopentan-3-on)at **(79)**

Table 1

Mean recovery values [1-(N-morpholiniomethyl)spirobi(1-sila-2,5-dioxacyclopentan-3-on)at **(72)**, 1-(N-morpho liniomethyl)spirobi(1-sila-2,5-dioxa-4-methylcyclopentan-3-on)at **(73)**, 1-(N-morpholiniomethyl)spirobi(1-sila-2,5-dioxa-4-(i-propyl)cyclopentan-3-on)at **(79)**] obtained on the columns used in the study (n = 5)

Type of extraction column	Mean recovery values and SD (%)		
	(**72**)	(**73**)	(**79**)
RP Si–C_{18}	85.3 ± 4.2	84.7 ± 3.9	85.1 ± 3.5
RP Si–C_8	82.2 ± 4.3	82.9 ± 4.9	83.7 ± 4.6
RP Si–FP	89.3 ± 3.9	91.3 ± 3.6	93.9 ± 4.1

Table 2

Common parameters of optimal **(72)**, **(73)** and **(79)** separation and determination by the isotachophoresis method

Parameters of the method	
UV filter (nm)	200
High Voltage Limit (kV)	12
Sample rate (smp s^{-1})	50
Polarity	+ cations

Table 3

Optimum conditions for isotachophoretic separation of a mixture 1-(N-morpholiniomethyl)spirobi(1-sila-2,5-dioxacyclopentan-3-on)at **(72)**, 1-(N-morpholiniomethyl)spirobi(1-sila-2,5-dioxa-4-methylcyclopentan-3-on)at **(73)**, 1-(N-morpholiniomethyl)spirobi(1-sila-2,5-dioxa-4-(i-propyl)cyclopentan-3-on)at **(79)**

Considered parameters				
Stage	Time (s)	Intensity (μA)	Comp (10 mV)	Conductometric detector
1	50	80	0	
2	70	120	50	
3	20	90	0	X
4	250	50	50	
5	325	120	0	X

The analyzed mixture was tested to obtain a number of zones containing only one type of ion of the separated mixture. The boundaries of the obtained zones are sharp, because each zone has a different effective ion mobility. This is due to the decreasing conductivity of these zones, which results in an increase of resistance and changes in the ion concentration in the analyzed zone. The increase in pH reduced the differences in the effective mobility of ions in the analyzed mixture. The analysis carried out at pH = 4.2 with the use of acetic buffer allowed the full separation of the constituents of the investigated mixture (**72**), (**73**), and (**79**) (Fig. 4).

The differences between the mobility of ions in the mixture were small and therefore caused problems. So far, attempts to separate and determine analyzed ES-silanates using the ITP or other chromatographic method have not been reported in the chemical literature. Optimization of isotachophoretic separation and determination was changed at individual stages: time of analysis, electric current intensity, the voltage limit level and the use of columns: preseparation and analytical. The optimum separation of the mixture constituents was obtained only on the analytical column within 12 min.

The increasing use of isotachophoresis for the separation and determination of ionic compounds means that ITP can compete with the ion chromatography (Railean-Plugaru et al. 2016; Kosobucki & Buszewski 2010). Capillary isotachophoresis enables the determination of hypercoordinated compounds of ES-silanates in aqueous solution. The main advantage of the ITP method is the possibility of simultaneous analysis of micro and macro amounts of constituents in a short time, while samples are dissolved in water.

After the optimum conditions for the separation and determination of the mixture of ES-silanates were developed, the method was validated (Table 4). It was found that the recovery of ES-silanates ranges from 91 ± 5% to 92 ± 4%; linearity from 2.8–49.6 μg l^{-1} (**73**) and 3.1–50.4 μg l^{-1} (**72**), and the detection limit of the analyzed compounds was 2.1 μg l^{-1} (**73**).

Conclusions

The study presents a new extraction method for three ES-silanates derivatives, namely: 1-(N-morpholiniomethyl)spirobi(1-sila-2,5-dioxacyclopentan-3-on)at, 1-(N-morpholiniomethyl)spirobi(1-sila-2,5-dioxa-4-methylcyclopentan-3-on)at, 1-(N-morpholiniomethyl)spirobi(1-sila-2,5-dioxa-4-(i-propyl)cyclopentan-3-on)at. The highest recovery values of about 94% were obtained in the extraction column with the chemically bonded phenylpropyl stationary phase. The best conditions for the analysis of the mixture of ES-silanates from aqueous solutions were determined, and the optimum time of their analysis did not exceed 12 min. A new terminating electrolyte for the analyzed mixture was proposed: 4,4'-bis[(1-morpholiniomethyl)spirobi(1-sila-2,5-dioxacyclopentane-3-on)at]. The new method of analysis increases the possibilities of research on biological activity of ES-silanates.

Acknowledgements

This work was supported by the Ministry of Science and Higher Education.

Abbreviations

ES-silanates – Electrostatically stabilized silanates
ITP – Isotachophoresis
LE – Leading electrolyte
SPE – Solid phase extraction
TE – Terminating electrolyte

References

Böhme, U., Wiesner, S. & Günther, B. (2006). Easy access to chiral penta-and hexacoordinate silicon compounds. *Inorg. Chem. Comm.* 9(8): 806–809. DOI: 10.1016/j.inoche.2006.05.002.

Buszewski, B. & Szultka, M. (2012). Past, present, and future

Table 4

Characteristic of the applied analytical method

Analyte	Linearity[1] (μg l^{-1})	Coefficient of variation[2] (%)	Limit of detection[3] (LOD) (μg l^{-1})	Limit of quantification[4] (LOQ) (μg l^{-1})	Recovery[5] (%)
(**72**)	3.1–50.4	3.0–4.2	2.2	7.3	91 ± 5
(**73**)	2.8–49.6	3.2–4.5	2.1	6.9	92 ± 3
(**79**)	2.9–51.3	2.8–4.1	2.3	7.6	92 ± 4

[1] – determination coefficient above 0.9987
[2] – n = 6, the samples were analyzed twice
[3]– calculated from the limit of identification and coefficients of the calibration curve
[4]– LOQ = 3.3 x LOD
[5]– the sample was enriched with 4 ml of a solution containing 2 μg · l-1 of the examined ion, n = 6

of solid phase extraction: A review. *Crit. Rev. Anal. Chem.* 42(3): 198–213. DOI: 10.1080/07373937.2011.645413.

Durka, K., Laudy, A.E., Charzewski, Ł., Urban, M., Stępień, K. et al. (2019). Antimicrobial and KPC/AmpC inhibitory activity of functionalized benzoiloxaboroles. *Eur. J. Med. Chem.* 171: 11–24. DOI: 10.1016/j.ejmech.2019.03.028

Erchak, N., Lukjanchik, I.D., Koval, T. & Andrijak, O.O. (2005). Stimulator rosta rostienij, Patent 7079 Republic of Belarus, National Centre of Intellectual Property. *Off. Biull.* 2: 114–118.

Erchak, N., Olszewska, E., Kalvinish, I., Liepinsh, E., Belyakov, S. et al. (2015). Synthesis of pentacoordinated Si-(morpholiniomethyl)silanates. *Chem. Heterocycl. Comp.* 50: 1505–1508. DOI: 10.1007/s10593-014-1617-x.

Gadzała-Kopciuch, R., Kluska, M., Wełniak, M. & Buszewski, B. (2005). Silicon dioxide surfaces with aryl interaction sits for chromatographic applications. *Mater. Chem. Phys.* 89(2–3):228–237. DOI: 10.1016/j.matchemphys.2004.03.022.

Guo-Chao, Y., Nikolic, M., Mu-jun, Y., Zhuo-xi, X. & Yong-Chao, L. (2018). Silicon acquisition and accumulation in plant and its significance for agriculture. *J. Integr. Agr.* 17(10): 2138–2150. DOI: 10.1016/S2095-3119(18)62037-4.

Hu, Y., Wanh, Y., Li, F., Ma, C. & Wang, J. (2017). Design and expeditious synthesis of organosilanes as potent antivirals targeting multidrug-resistant influenza A viruses. *Eur. J. Med. Chem.* 135: 70–76. DOI: 10.1016/j.ejmech.2017.04.038.

Jabłońska, J., Kluska, M. & Erchak, N. (2018). Analytics of biologically active derivatives of electrostatically stabilized by isotachophoresis. *J. Liq. Chromatogr. Rel. Technol.* 41(19–20): 1098–1103. DOI: 10.1080/10826076.2019.1566139.

Kenla, T.J., Tatong, M.D., Talontsi, F.M., Dittrich, B., Frauendorf, H. et al. (2013). Si-enterobactin from the endophytic Streptomyces sp. KT-S1-B5-a potential silicon transporter in nature? *Chem. Commun.* 49: 7641–7643. DOI: 10.1039/C3CC44437F.

Kluska, M. (2008a). Analytical techniques in determination of biologically active organosilicons of the ES-silanate group. *Crit. Rev. Anal. Chem.* 38(4): 216–226. DOI: 10.1080/10408340802341096.

Kluska, M. (2008b). Some aspects of the analysis of biologically active organogermanium substances. *Crit. Rev. Anal. Chem.* 38(2): 84–92. DOI: 10.1080/10408340701804459.

Kluska, M., Jabłońska, J. & Erchak, N. (2019a). Analytics and application of biologically active pentacoordinate electrostatically stabilized silanates. *Crit. Rev. Anal. Chem.* DOI: 10.1080/10408347.2019.1666249.

Kluska, M., Jabłońska, J., Prukała, W. & Kondrzycka-Dąda, A. (2020). Problems related to the isotachophoresis technique employed for separation and determination of alkaloids used in the treatment of malaria. *J. Liq. Chromatogr. Rel. Technol.* 43(1–2): 45–52. DOI: 10.1080/10826076.2019.1666276.

Kluska, M., Krajewska, E., Jabłońska, J. & Prukała, W. (2019b). New applications and analysis of (E)-azastilbenes in environmental samples. *Crit. Rev. Anal. Chem.* 49(5): 395–402. DOI: 10.1080/10408347.2018.1537120.

Kluska, M. & Pypowski, K. (2007). Separation of tribenzylhydrogermanium nitrile derivatives by means of HPLC with participation of π–π interactions. *J. Liq. Chromatogr. Rel. Technol.* 30(14): 2059–2067. DOI: 10.1080/10826070701435061.

Kluska, M., Pypowski, K. & Erchak, N. (2007). Separation of hexabenzyldigermoxane and hexabenzyldigermanium by HPLC. *J. Liq. Chromatogr. Rel. Technol.* 30(12): 1777–1785. DOI: 10.1080/10826070701360418.

Kluska, M., Pypowski, K., Chrząścik, I., Koval, T. & Erchak, N. (2009). Optimization of conditions of isotachophoretic separation and determination of new class of pentacoordinated silanes. *J. Liq. Chromatogr. Rel. Technol.* 32(14): 2001–2012. DOI: 10.1080/10826070903126807.

Kosobucki, P. & Buszewski, B. (2008). Isotachophoretic separation of selected imidazolium ionic liquids. *Talanta* 74(5): 1670–1674. DOI: 10.1016/j.talanta.2007.08.043.

Kubicki, J.D. & Heaney, P.J. (2003). Molecular orbital modeling of aqueous organosilicon complexes: implications for silica biomineralization. *Geochim. Cosmochim. Acta* 67(21): 4113–4121. DOI: 10.1016/S0016-7037(03)00093-0.

Lin, Y., Song, B., Han, A., Hu, S., Ye, F. et al. (2011). Synthesis of γ-arylmethylene-aminopropyl-3,7,10-trimethyl-silatrane derivatives and their activities of regulating plant growth. *Phosphorus Sulfur Silicon Relat. Elem.* 186(2): 298–303. DOI: 10.1080/10426507.2010.496747.

Lukevics, E., Ignatovich, L., Shestakova, I., Romanov, V., Grinberg, S. et al. (2007). A new method for the synthesis of silicon- and germanium- containing 2-acetylfurans and 2-acetylthiophenes. *Chem. Heterocycl. Compd.* 43: 143–150. DOI: 10.1007/s10593-007-0024-y.

Mala, Z., Gebauer, P. & Bocek, P. (2017). Analytical capillary isotachophoresis after 50 years of development: Recent Progress 2014–2016. *Electrophoresis* 38(1): 9–19. DOI: 10.1002/elps.201600289.

Małkiewicz, K., Turło, J., Marciniuk-Kluska, A., Grzech-Leśniak, K., Gąsior, M. et al. (2015). Release of bisphenol A and its derivatives from orthodontic adhesive systems available on the European market as a potential health risk factor. *Ann. Agric. Environ. Med.* 22(1): 172–177. DOI: 10.5604/12321966.1141390.

Nawała, J., Czupryński, K., Popiel, S., Dziedzic, D. & Bełdowski, J. (2016). Development of the HS-SPME-GC-MS/MS method for analysis of chemical warfare agent and their degradation products in environmental samples. *Anal. Chim. Acta* 933: 103–116. DOI: 10.1016/j.aca.2016.05.033.

Oestreich, M. (2006). Chirality transfer from silicon to carbon. Chem. Eur. J. 12(1): 30–37. DOI: 10.1002/chem.200500782.

Popiel, S. & Nawała, J. (2013). Detoxification of sulfur mustard by enzyme-catalyzed oxidation using chloroperoxidase. *Enzyme Microb. Technol.* 53(5): 295–301. DOI: 10.1016/j.enzmictec.2013.06.002.

Popiel, S., Nawała, J. & Czupryński, K. (2014). Preparation and application of sol-gel acrylate and methacrylate solid-phase microextraction fibres for gas chromatographic analysis of organoarsenic compounds. *Anal. Chim. Acta* 837: 52–63. DOI: 10.1016/j.aca.2014.05.039.

Prukała, W., Prukała, D., Pypowski, K., Chrząścik, I. & Kluska, M. (2008). Chromatography of biologically active chlorides of (E)-N-o-(m- or p-)chlorobenzyl-γ-azastilbenols-2′(3′ or 4′). *J. Liq. Chromatogr. Rel. Technol.* 31(17): 2612–2620. DOI: 10.1080/10826070802352850.

Pypowski, K., Uszyńska, I. & Kluska, M. (2006). Chromatographic separation of isomers of tribenzylgermanium nitrile derivatives using chemically bonded aryl stationary phases. *J. Liq. Chromatogr. Rel. Technol.* 29(20): 2989–2996. DOI: 10.1080/10826070600981157.

Railean-Plugaru, V., Pomastowski, P., Rafinska, K., Wypij, M., Kupczyk, W. et al. (2016). Antimicrobial properties of biosynthesized silver nanoparticles studied by flow cytometry and related techniques. *Electrophoresis* 37(5–6): 752–761. DOI: 10.1002/elps.201500507.

Romero-Aranda, M.R., Jurado, O. & Cuartero, J. (2006). Silicon alleviates the deleterious salt effects on tomato plant growth by improving plant water status. *J. Plant Physiol.* 163(8): 847–855. DOI: 10.1016/j.jplph.2005.05.010.

Singh, H.L., Singh, J.B. & Bhanuka, S. (2017). Synthesis and spectral, antibacterial, molecular studies of biologically active organosilicon(IV) complexes. *Arab. J. Basic. Appl. Sci. En.* 23(1): 1–9. DOI: 10.1016/j.jaubas.2016.05.003.

Wrona, O., Rafińska, K., Walczak-Skierska, J., Mozeński, C. & Buszewski, B. (2019). Extraction and determination of polar bioactive compounds from alfalfa (Medicago sativa L.) using supercritical techniques. *Molecules* 24: 4608. DOI: 10.3390/molecules24244608.