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IMPACT OF SOL MIXTURE COMPOSITION ON ORGANOSILICA COATINGS FORMATION ON GLASS SUBSTRATES

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In this study, hybrid organosilica coatings on glass substrates were synthesized using mixtures of the active polymer OH-terminated PDMS and one or more precursors, namely methyltrimethoxysilane bis(3-trimethoxysilylpropyl) amine, phenyltrimethoxysilane, cyanopropyltrimethoxysilane, aminopropyltriethoxysilane in the presence of modifiers (polyethylene glycol, organic solvents) and trifluoroacetic acid catalyst. The aim of this work was to obtain new sorption materials for the extraction of nonpolar and semi-polar analytes, for example, carbonyl compounds in the form of PFBHA derivatives, azo dyes, phthalates, and others, and to purify samples with a complex matrix for further gas chromatographic analysis. The advantages of the obtained sorption coatings are the effective separation of micro quantities of target compounds of nonpolar and semi-polar nature from polar compounds present in aqueous samples in rather high concentrations.

The paper describes the synthesis of organosilica coatings of various compositions, the volume ratio of the active polymer, precursors, deactivating agent, catalyst, and modifiers. The coatings were applied to glass substrates using two methods: spin-coating and dip-coating. Sometimes the application was complicated due to uneven distribution of the sol when the solution mixture was too viscous or required a long drying time. Bis(3-trimethoxysilylpropyl) amine and N-(2-aminoethyl)-3-aminopropyltriethoxysilane proved to be effective crosslinking agents with similar properties of the obtained coatings; the addition of these precursors significantly improved the characteristics of the obtained coatings. It has been shown that mixtures containing OH-terminated PDMS form thick coatings (up to 325 μm) without cracks in the presence of most of the studied precursors, and the addition of titanium isopropoxide improves the thermal stability and leads to the formation of a more uniform coating in the case of substrates of complex shape (stir bars).

The IR spectra of the studied coatings were obtained, most of the spectral bands are typical of the PDMS polymer, and the presence of covalently bound titanium in the coatings is confirmed by a peak at 924 cm^{-1}. All the coatings were hydrophobic, and the contact angles with water were measured, which ranged from 99.7 to 105.6. Thermogravimetric analysis (TG and DTA) was performed to verify the thermal stability of the coatings for further use in solid-phase microextraction with gas chromatography, and it was shown that the coatings could withstand heating up to 350–425 °C.

For sorption in analytical quantitative methods, it is necessary to use coatings that are homogeneous, uniform, durable, less prone to swelling, and reproducible in synthesis and during sorption. The synthesized coatings are effective for further use in chemical analysis to purify samples from interfering components or for preconcentration of analytes. The coatings have sufficient stability to be used in the hybrid methods of analysis.

***Keywords**: sol-gel synthesis, sorption, microextraction, sample preparation, coatings, thin films, polydimethylsiloxane, spectrophotometry*

INTRODUCTION

Thin films and coatings have a wide range of applications, including optics, engineering, surface and material protection, catalysis, and sensors. An interesting area of coating application is solid-phase microextraction and extraction, either to preconcentrate analytes or to clean the sample before chromatographic analysis. The most well-known is solid-phase microextraction on a fiber, in which the coating is deposited on a thin fiber [1–4]. Also stir-bar sorptive extraction (SBSE) is gaining popularity and the cases of thin film SPME are known [1, 5]. Coating based on hydroxyterminated polydimethylsiloxane (OH-terminated PDMS) and phenyltriethoxysilane SBSE was developed for the extraction and preconcentration of benzene, naphthalene, anthracene, and fluorene from aqueous solutions [6]. Tetraethoxysilane-polydimethylsiloxane for use in SBSE of chlorpyrifos and malathion (organophosphorus pesticides) was successfully synthesized using sol–gel technology [7]. Most of investigations were focused on developing stir-bar coatings for liquid desorption rather than thermal desorption [8].

There are works that study transparent titania-polydimethylsiloxane hybrid materials for various optical applications. The results demonstrate that titanium alkoxide was successfully used as a cross-linker. The authors analyzed different molar ratios of titanium isopropoxide to OH-terminated PDMS and found that titania-like nanodomains are formed during the process [9]. However, in the paper authors obtained films through molding and spin coating and were interested in transparent films. The addition of Ti to the PDMS coating structure is also known for SPME materials [4, 10].

PDMS coatings can be synthesized via sol-gel or polymerization reactions. It appears that sol-gel method is one of the most effective methods of coating synthesis because it is simple to perform and allows for variation of the starting precursors and components, partially affecting the polarity of the coating [4, 11]. There are siloxane precursors with different functional groups. However, this also means that the synthesis of the coatings requires careful study and wisely chosen sol components. For example, different titanium alkoxides can be used to implement Ti into the structure, but it was shown that significant differences in the rate of hydrolysis and condensation reactions were observed for different titanium precursors, that resulted in differences in the morphology of TiO_2 films [12].

Some commercial coatings for analytical methods of solid-phase extraction and microextraction are available from Supelco and Gerstel. Despite the wide selection, such materials have drawbacks, such as fragility and high cost, and require proper selection for specific applications.

The purpose of this work is to develop efficient coating for sorption of non-polar and semi-polar compounds using sol-gel technique suitable for analytical application, which can be produced by easy, fast and cheap in-lab synthesis with sufficient characteristics and repeatability. This requires the following steps: searching for the optimal composition of the sol-mix, selecting the best application technology and testing the properties of the resulting coatings.

MATERIALS AND METHODS

Reagents. For this work the following reagents were used: OH-terminated PDMS (750 cSt.), methyltrimethoxysilane (MTMOS), methyltriethoxysilane (MTEOS), tetraethoxysilane (TEOS), bis(3-trimethoxysilylpropyl) amine (BIS), phenyltriethoxysilane (-Ph), cyanopropyl-triethoxysilane (-CN), aminopropyl-triethoxysilane (-NH_2), hexamethyldisilazane (HMDS), titanium isopropoxide (TIP), polyethylenglycol 300 (PEG), 2-[4-(2,4,4-trimethylpentan-2-yl)phenoxy]ethanol (Triton X-100), methanol, isopropanol, ethylacetate, hexane, dichloromethane, trifluoroacetic acid (TFA), hydrochloric acid, sodium hydroxide. Reagents were purchased from Sigma-Aldrich company (ALSI Ltd., Kyiv, Ukraine). N-(2-aminoethyl)-3-aminopropyltriethoxysilane (GENIOSIL® GF 91, Geniosil) from Wacker company was used.

Glass substrate preparation. The microscope slides (Cat. No.7101 and 7105, China) with the original size 25.4×76.2 mm with 1.0–1.2 mm thickness made from clear optical glass were cleaned and cut into squares with the area approximately 100 mm^2, with dimensions 10×10 mm. For the purpose of ATR-FTIR, optical microscopy and thermogravimetry (for the last one the coating material had to be separated from glass) the coating was applied to full uncut slides covering area around 25×50 mm. The squares 10×10 mm were chosen to fit into the lab-made spin-coating setup and to be used prior to the stir bars for sorption. Glass-encapsulated magnetic stir bars were made 10 mm in length and 4 mm in diameter.

Glass substrates (i.e. glass plates and glass-encapsulated magnetic stir bars) were first rinsed with acetonitrile and then with distilled water. They were immersed in an aqueous 1.5 M sodium hydroxide solution for 2 h. Then washed with distilled water until neutral. After that substrates were immersed in an aqueous 0.1 M hydrochloric acid solution for 30 min. After that, they were washed with distilled water until neutral. All substrates were dried and stored in a desiccator. Such preparation procedure with variation in concentration is well-known from the literature [1, 7]. All substrates were weighed to determine the weight of the applied coating.

PDMS-coating preparation. The coating preparation was done by sol gel technique. The sol-gel precursors react with water under the acidic catalyst, then hydrolyses sol-gel precursor forms sol-gel network throughout condensation integrating OH-terminated PDMS [1]. Upon deposition reaction of condensation results in chemical bonding on the glass surface. Deactivation reagents react with the surface OH-groups of coating increasing hydrophobicity. It should be noted that the water required by the reaction was not added directly, and it was present with TFA as 95 % TFA (5 % H_2O) was used. The coatings were prepared using precursors (MTMOS, TIP, BIS, Geniosil, phenyltriethoxysilane, aminopropyltriethoxysilane, cyanopropyltriethoxysilane), solvents (propan-2-ol, dichloromethane), deactivation agent (HMDS), and catalyst (TFA) as described below.

For obtaining 4.5 ml of the mixture to an Eppendorf microtube were added 1000 mg of OH-terminated PDMS, 500–1000 μl of MTMOS (when MTMOS was present), 375–500 μl of TIP (when TIP was present), 250–375 μl of BIS (when BIS was present), 200–375 μl of phenyltriethoxysilane (when -Ph was present), 250 μl of N-(2-aminoethyl)-3-aminopropyl-triethoxysilane (when Geniosil was present), 500 μl of PEG (if PEG was present), 500–2000 μl of aminopropyltriethoxysilane (when -NH_2 was present), 500–2000 μl of cyanopropyltriethoxysilane (when –CN was present), 150 μl of HMDS, 750 μl of propan-2-ol (when TIP was present in the mixture), 750 μl of dichloromethane (when TIP was present in the mixture), 400–500 μl of TFA (always added as last component with proper mixing). After adding each component, the microtube was tightly closed and shaken thoroughly. Then the mixture was exposed to ultrasound for 10 min, shaken, centrifuged for 10 min. The upper phase was separated into clean Eppendorf microtube. Mixtures with general volume less than 1.5 ml was prepared to be used for coating of 10×10 mm glass plates, and at least 4.5 ml of mixtures were prepared for dip-coating of stir bars, with the same proportion between components.

Further in the text the coatings are named by their mixture components, excluding solvents, deactivating agent HMDS and acidic catalyst TFA.

PDMS-MTMOS. This coating was reproduced method proposed by Malik, although it was done with some changes [13]. In our study we used OH-terminated PDMS, MTMOS, HMDS, TFA.

PDMS-MTMOS-BIS coating mixture contained OH-terminated PDMS, MTMOS, BIS, HMDS, TFA.

PDMS-MTMOS-TIP-BIS coating mixture contained OH-terminated PDMS, MTMOS, TIP, BIS, HMDS, propan-2-ol, dichloromethane, TFA.

PDMS-MTMOS-TIP-Ph coating mixture contained OH-terminated PDMS, MTMOS, TIP, phenyltriethoxysilane, HMDS, propan-2-ol, dichloromethane, TFA.

PDMS-MTMOS-TIP-BIS-Ph coating mixture contained OH-terminated PDMS, MTMOS, TIP, BIS, phenyltriethoxysilane, HMDS, propan-2-ol, dichloromethane, TFA.

PDMS-MTMOS-TIP-Geniosil coating mixture contained OH-terminated PDMS, MTMOS, TIP, N-(2-aminoethyl)-3-aminopropyltriethoxysilane, HMDS, propan-2-ol, dichloromethane, TFA.

PDMS-MTMOS-TIP-PEG300 coating mixture contained OH-terminated PDMS, MTMOS, TIP, PEG, HMDS, propan-2-ol, dichloromethane, TFA.

PDMS-MTMOS-TIP-BIS-CN coating mixture contained OH-terminated PDMS, MTMOS, TIP, BIS, cyanopropyltriethoxysilane, HMDS, propan-2-ol, dichloromethane, TFA.

PDMS-MTMOS-TIP-BIS-NH_2 coating mixture contained OH-terminated PDMS, MTMOS, TIP, BIS, aminopropyltriethoxysilane, HMDS, propan-2-ol, dichloromethane, TFA.

PDMS-TIP-BIS-CN coating mixture contained OH-terminated PDMS, TIP, BIS, cyanopropyltriethoxysilane, HMDS, propan-2-ol, dichloromethane, TFA.

PDMS-TIP-BIS-NH_2 coating mixture contained OH-terminated PDMS, TIP, BIS, aminopropyltriethoxysilane, HMDS, propan-2-ol, dichloromethane, TFA.

The application of ultrasound not only affected the reaction speed but also removed the air that might have been trapped due to high viscosity of the mixture. The centrifugation step was originally aimed to separate precipitate if condensation occurs too quickly with big particle formation. However, it turned out that there were no or very small amount of precipitate. But the separation of two phases occurred and it seemed that the upper phase contained OH-terminated PDMS and its reaction products and the bottom phase by the volume and properties contained mostly TFA. We can assume that the separation of two phases was due to the difference in polarity. Reducing amount of TFA was not optimal as it would have resulted in water concentration increase that lead to precipitation and gel-like material formation, making it impossible to obtain coating. Some distribution of components between phases occurred, based on the fact that when the bottom phase (presumably containing mostly TFA) was applied to the glass plates then after drying it gave residuals of very shrunken, cracked film pieces that were not bonded to the glass surface. The upper phase demonstrated the properties of the sol, e.g. scattering of light, and as the condensation reaction between the components continued it was possible to use it for coating as described further.

Coating application onto the substrates. In order to apply a thick layer of coating on glass plates, the measured volume of sol (10–30 μl) was taken with a micropipette and quickly dripped or spread over the surface of the plate. Also the spin-coating technology was used to apply a thin coating on glass plates. Spin-coating depositing was performed on lab-made setup based on magnetic stirrer motor. A glass plate (10×10 mm) was placed on a setup, then the measured volume of sol was taken with a micropipette and applied on top of plate, and the plate was started to rotate for 2 min.

Coatings on the stir bars were deposited by dip-coating. Stir bars were tied with steel wire and immersed in the sol for a certain period of time, keeping them rotating in the sol with a magnetic stirrer. Then the anchors were slowly pulled from the solution and hung by the wire to dry in the desiccator. If necessary, the coating was applied in several layers, by repeating the procedure after drying the previous layer.

After application, all the substrates were placed or hung in such way as to protect the coating from damage and touch. The coatings were dried for 24–72 h in a desiccator, and then dried in the oven. The temperature program started at room temperature and reached 260 °C. In most cases, drying included a 4-hour step at 250 °C.

Coating characterization. Among the methods used are the following: water contact angle measurement, infrared spectroscopy (IR), and coating thickness measurement. The coating thickness was calculated by difference between thickness of plates with and without coating, measured directly using digital micrometer screw gauge (MKC 25, Ukraine, with range 0–25 mm, resolution 0.001 mm). Water contact angle was obtained by sessile drop technique. The ATR-FTIR spectra in the range from 500 to 4000 cm^{-1} were obtained using a Perkin Elmer Spectrum BX FT-IR system with Pike MIRacle Single Reflection ATR. The thermogravimetric analysis was done on a Thermal Analyzer NETZSCH STA 449 F1 Jupiter by heating at 20 °C/min up to 600 °C. Optical microscopy images were done with an optical microscope MICROmed XS-8530 equipped with a camera.

Solutions of Sudan I (industrial azo dye used to color oils, waxes, and polishes, insoluble in water) were used for the preliminary study of the sorption characteristics of obtained coating for Sudan I. a Shimadzu Double Beam UV-2401PC UV-Vis Spectrophotometer was used to measure the absorbance of the Sudan in solutions after the desorption from coatings and the results were calculated as amount of substance using calibration curve obtained from standard solutions of known concentration of Sudan on the same spectrophotometer.

RESULTS AND DISCUSSION

The preliminary research was conducted by obtaining different sol mixtures and their deposition on glass plates in order to find the starting point – the PDMS coating, completely dry and covalently bonded to the surface of plate, was obtained. It was done by the method proposed by Malik research group [13], although with minor modifications due to some missing information and according to available equipment. By performing the literature search and proving them right or wrong by experiment it was found out that MTMOS are more suitable for coatings than TEOS or MTEOS. Coatings containing MTEOS have slower gelation and are drying longer, and TEOS tend to quickly form solid particles. The TIP was used because of the suggested in literature conclusion that higher quality oxide coatings can be obtained from titanium isopropoxide compared to other titanium alkoxides [12]. Among the possible OH-terminated PDMS macromonomers with different viscosities the one of 750 cSt was chosen as to available data of better sorption properties of PDMS materials compared to OH-terminated PDMS of higher and lower viscosity [14].

The coatings are shown in the photo (Fig. 1, Fig. 2). The coating without MTMOS were with obvious defects, meaning there was cracking during the drying. Coatings containing larger amount of BIS (more than 20 %) or with precursors containing -CN or -NH_2 functional groups were colored (varying from slightly yellow to bright orange).

There are many factors that lead to the formation of uneven or damaged coatings, these factors are connected with sol mixture composition and drying process. Upon formation of sol there were two different phases in the mixture. In cases when phases were not separated enough many defects and cracking occurred (the example is in Fig. 2 *d*). Some coatings were completely detached from glass upon drying, other had cracks seen visually. In some cases, cracks were seen only under microscope magnification. The images in Fig. 2 *a–c* show that these coatings do not contain separate particles, for example TiO_2 particles might have been formed, or other defects like cracks.

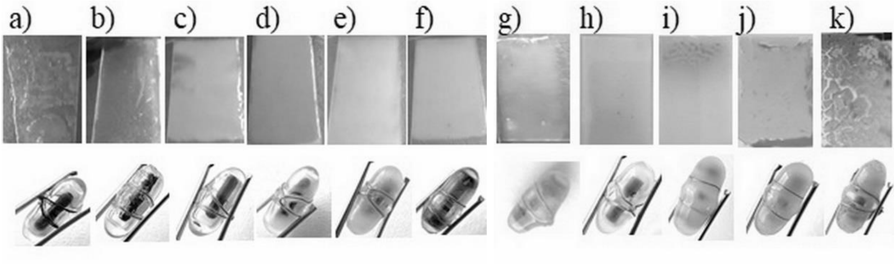
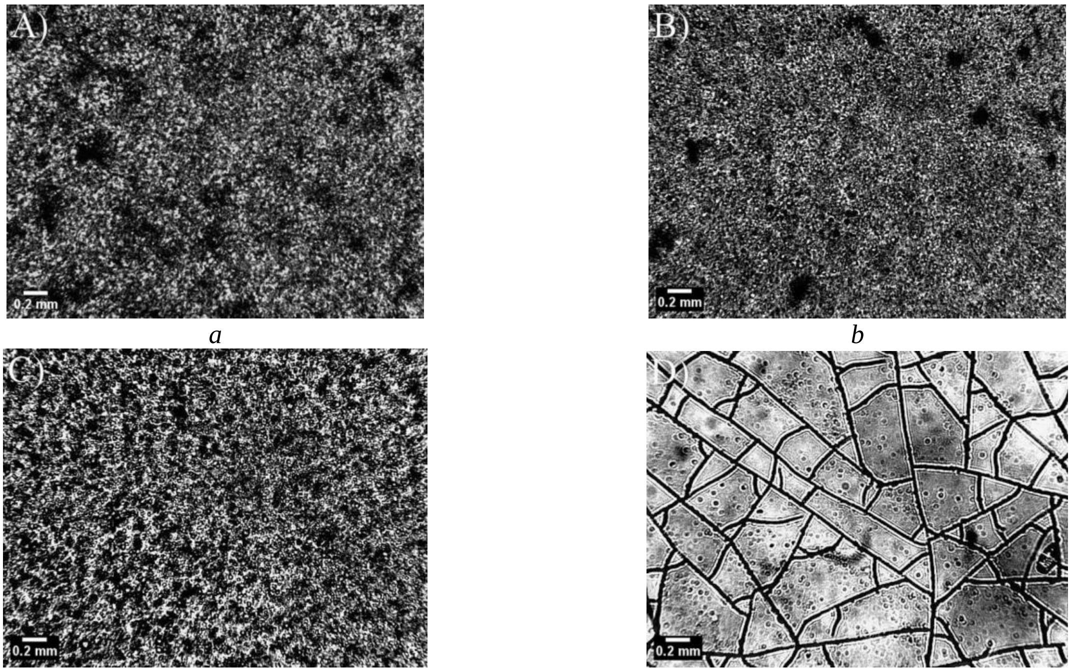


Fig. 1. Photos of coatings deposited on glass plates and on glass stir bars: *a*) PDMS-MTMOS, *b*) PDMS-MTMOS-BIS, *c*) PDMS-MTMOS-TIP-BIS, *d*) PDMS-MTMOS-TIP-Ph, *e*) PDMS-MTMOS-TIP-BIS-Ph, *f*) PDMS-MTMOS-TIP-Geniosil, *g*) PDMS-MTMOS-TIP-PEG300, *h*) PDMS-MTMOS-TIP-BIS-CN, *i*) PDMS-MTMOS-TIP-BIS-NH_2, *j*) PDMS-TIP-BIS-CN, *k*) PDMS-TIP-BIS-NH_2



a *b*

c *d*

Fig. 2. Optical microscopy images of coatings (processed with ImageJ 1 image analysis program): *a*) PDMS-MTMOS-TIP-Ph, *b*) PDMS-MTMOS-TIP-PEG300, *c*) PDMS-MTMOS-TIP-Geniosil, *d*) PDMS-MTMOS (area with cracks)

The coating thickness of the same coating type obtained by different methods was approximately measured by micrometer screw gauge, and it seems that spin-coating results in less than 2 mg of coatings left per glass plate with 5–25 μm thickness films, and mixtures applied directly from micro-pipette (set volume 10–30 μl) resulted in thickness 168–324 μm (Table 1). Thinner coatings that were deposited by spin-coating result in less or no cracking, but small mass of coating means low sorption capacity. The coatings on substrate were designed to be used in analytical chemistry methods for cleaning or separation. Thus, even to be used for small volumes of sample the amount of coating had to be sufficient. Commercial coatings for SPME have thickness up to 100 μm, and commercial stir bars – 500 or 1000 μm as they are used for extraction and preconcentration [1, 15].

Table. 1. Measured coating thickness on 10×10 mm glass plates obtained by different deposition methods

Deposition method	Coating type	Weight, mg	Thickness, μm
Micro-pipette drop	PDMS-MTMOS-TIP	7.8	168
Micro-pipette drop	PDMS-MTMOS-TIP	16.1	283
Micro-pipette drop	PDMS-MTMOS-TIP-PEG	11.9	253
Micro-pipette drop	PDMS-MTMOS	19.8	324
Spin-coating	PDMS-MTMOS	1.4	≤ 7
Spin-coating	PDMS-MTMOS-TIP	1.4	≤ 5

The process applying coating to stir bars showed the need to balance between fast gelation so all the surface of stir bar is coated evenly (that was a problem for the PDMS sol without modifiers and additives) and formation of separate gel clots. Mixtures with TIP and BIS were drying faster, however such sol mixture required solvents (isopropanol and dichloromethane) to ensure that mixture during the reaction and application is as homogeneous as possible.

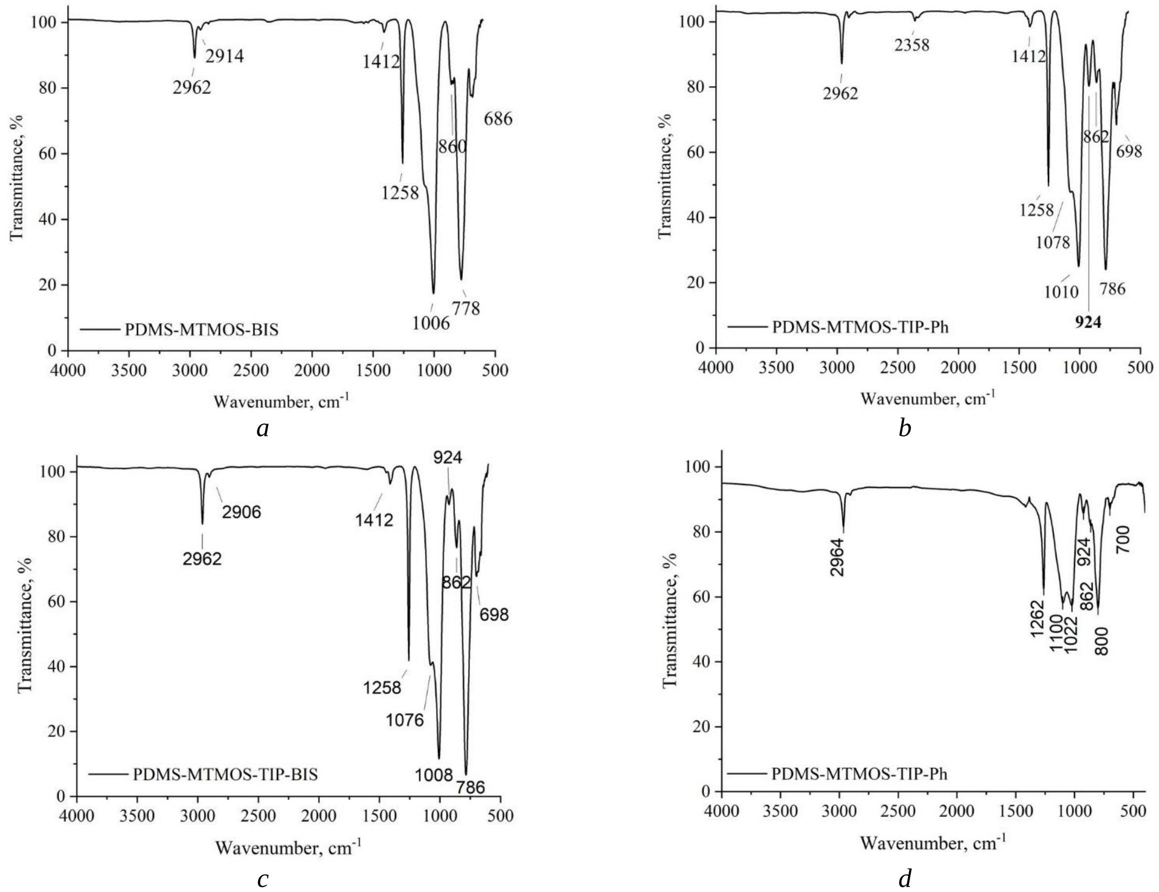
Water contact angle measurement results are shown in Table 2. All the coatings are hydrophobic due to hydrophobicity of the active polymer and are expected to be suitable for sorption of non-polar and semi-polar compounds. Water contact angle might differ depending on the polarity of functional groups on the surface. Also sometimes increase in contact angle indicates more cross-linked dense structure of PDMS [16].

Table. 2. Measured water contact angles of coatings deposited on glass plates

Coating type	Water contact angle
PDMS-MTMOS	99.7
PDMS-MTMOS-TIP-BIS	104.43
PDMS-MTMOS-TIP-Geniosil	105.64
PDMS-MTMOS-TIP-PEG300	103.84
PDMS-MTMOS-BIS	99.28
PDMS-MTMOS-TIP-BIS-Ph	103.31
PDMS-MTMOS-TIP-Ph	102.56

The infrared spectra of coatings on glass plates were recorded directly as ATR-FTIR (Fig. 3). The most abundant absorption peaks match for all obtained spectra; they correspond to characteristic bands of PDMS, interpreted according to the book and article [17, 18]. Particularly, there are sharp band at 2960 cm^{-1}, corresponding to asymmetrical C-H stretching vibrations of Si-CH_3 groups, the bands at 1412 and 1258 cm^{-1} (asymmetrical and symmetrical deformational H-C-H vibrations of Si-CH_3), the most intense band near 1010 cm^{-1} with a shoulder at 1078 cm^{-1} (asymmetrical Si-O-Si and Si-O-R stretchings) and a band of Si-C stretchings near 780 cm^{-1}. Absence of the wide band of O-H stretchings in the 4000–3000 cm^{-1} range, that was observed for the spectra obtained by ATR-FTIR spectra and by FTIR of coating sample compressed with KBr (Fig. 3 *d*), indicate negligible quantity of the Si-OH groups in the coatings.

There is a sharp band at 924 cm^{-1} in the spectra of all coatings that contained TIP in sol mixture. According to the book [17], this band corresponds to Ti-O-Si stretchings, revealing presence of covalently bonded titanium.



a *b*

c *d*

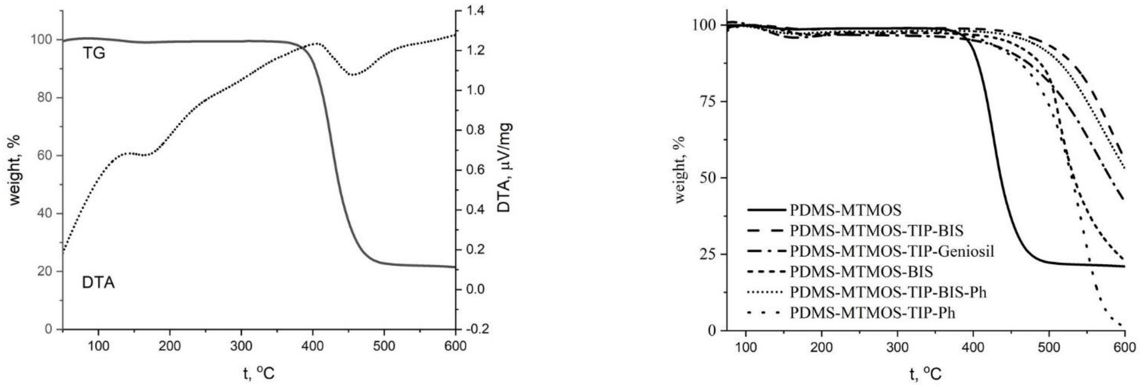
Fig. 3. ATR-FTIR spectra of PDMS-based coatings *a*) PDMS-MTMOS-BIS, *b*) PDMS-MTMOS-TIP-Ph, *c*) PDMS-MTMOS-TIP-BIS *d*) FTIR spectra of PDMS-MTMOS-TIP-Ph in KBr

To be coupled with gas chromatography determination the materials should be stable throughout the thermal desorption process. While PDMS chromatography columns must withstand continuous heating in the oven up to 250 °C without decomposition, the PDMS coating is subjected to short-term heating in the injector, usually at a steady temperature in the range of 200–300 °C. It should be noted that this takes place in an inert atmosphere of helium carrier gas.

Based on literature data [19, 20], the thermal stability of PDMS-based materials is dependent on strength of the bonds (Si-O bond might have dissociation energy in the range 100–120 kcal/mol, whereas C-C, C-O, $C_{(aromatic)}$-C have corresponding energies around 80–100 kcal/mol), but due to flexibility of the -$[Si\text{-}O]_x$- chain segments, they are prone to intramolecular redistribution reaction.

According to the literature [19, 20], in the presence of air, PDMS undergoes thermo-oxidative degradation, forming pure silica, CO, H_2O, CH_2O, CO_2, but in an inert atmosphere at high temperatures, the degradation products are volatile low-molecular cyclic oligomers. From the obtained thermograms in the inert atmosphere (Ar) up to 600 °C (Fig. 4), we can assume that when the temperature rises to 100–150 °C moisture is lost from the sample, and with a further rise in temperature to 350–550 °C, a significant change in the mass of polymer films is observed.

It was expected that addition of TIP (that results in formation of Ti-O-Si and Ti-O-Ti bonds within material) should increase thermal stability, as for example in PDMS/SiO_2/TiO_2 composites (prepared by solvent-free sol-gel technique by Alexandru M. *et al.*) the partial replacement of SiO_2 with TiO_2 increased thermal stability [21]. Based on the results (Table 3), we can assume that introduction of TIP and BIS increases the thermal stability, and the addition of phenyltriethoxysilane, on the contrary, reduces it, but the exact proof of this assumption would require additional research. Although all coatings demonstrate resistance up to 350–450 °C, it is important to remember that such coatings are intended for repeated use so PDMS-MTMOS-TIP-BIS and PDMS-MTMOS-TIP-Geniosil are of the most interest as for later research to be used with gas chromatography.



a *b*

Fig. 4. Study of thermogravimetric properties: *a*) Thermogravimetric (TG) and Differential Thermal Analysis (DTA) curves for PDMS-MTMOS coating, *b*) TG curves for obtained coatings

Table 3. Temperature of the stage and coating weight (in %) results by TG

Coating type	100 °C	200 °C	300 °C	350 °C	400 °C	450 °C	500 °C	550 °C
PDMS-MTMOS	99.8	98.8	98.8	98.8	91.8	36.8	22.2	21.5
PDMS-MTMOS-TIP-BIS	99.9	98.9	98.9	98.9	98.8	97.6	93.3	81.1
PDMS-MTMOS-TIP-Geniosil	100.0	96.6	96.6	96.3	95.0	91.0	81.3	63.5
PDMS-MTMOS-BIS	100.0	97.3	97.3	97.3	96.8	94.1	82.9	39.3
PDMS-MTMOS-TIP-BIS-Ph	99.7	98.0	98.0	98.0	97.9	96.5	90.8	75.0
PDMS-MTMOS-TIP-Ph	99.8	97.6	97.6	97.6	96.1	89.9	73.6	26.9

After the sorption of analytes onto the coating, it is necessary to subsequently desorb the substances. It can be thermal desorption in the injector of a gas chromatograph, or desorption (elution) with organic solvents for liquid chromatography or spectrophotometry. The scheme of the procedure is shown in Fig. 5. To achieve this, it is important for coating to be compatible with solvents. The solvents should be selected to ensure that sorption onto the coating is the most efficient when using solvent 1 and that complete elution is achieved with solvent 2. That said, the coating must withstand solvent without destruction. There should be no dissolving of coating. Moreover, organic polymers are known to swell in nonpolar solvents, so it is common for PDMS coating to swell and undergo destruction in nonpolar solvents as hexane.

The swelling degree of coating materials in acetonitrile and hexane was determined by division of coating mass after the swelling by coating mass at the beginning of the experiment (Fig. 6). Although PDMS coating without other precursors demonstrated the lowest degree of swelling, and even showed the decrease of swelling in hexane with time, apparently it was a result of fast destruction of the coating and its weight loss during the experiment. Although sometimes swelling might increase sorption and there are methods that include step of pre-saturation of PDMS coating with organic solvent vapors, when to comes to direct contact with solvents the swelling should be avoided. As can be seen from Fig. 6., coating PDMS-MTMOS-TIP-BIS-Ph demonstrated the lowest swelling degree.

The sorption properties will vary depending on the selected analyte and sorption conditions. The dependence of the sorption of Sudan I by PDMS-TIP-BIS and PDMS-TIP-BIS-Ph coatings from ethyl acetate solutions and desorption with acetonitrile has been studied. The dependences are shown in Fig. 7. The dependency might be considered as sorption isotherm for Sudan I, however it might be not quite correct to refer to this curve as adsorption isotherm, because some part of sorption process can be referred to as absorption or gel sorption, especially considering light swelling occurring in nonpolar solvent that changes the coating size and volume. The initial section of the curve is straight line, so the coatings have linear dependence for Sudan I sorption in solutions within low concentration range (approximately up to 0.01 M). The isotherm curve is limited by the solubility of Sudan I in ethyl acetate. The achieved sorption values are suitable for the determination of low concentrations of analytes in the analysis of impurities and contaminants, rather than the main components.

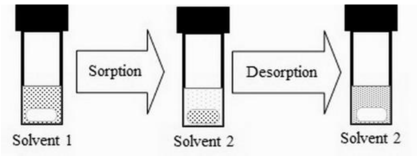
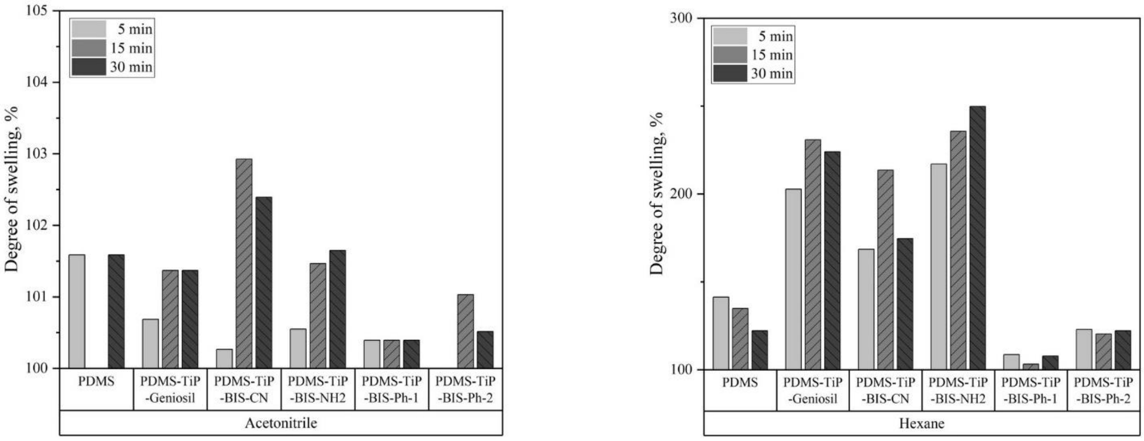


Fig. 5. Schematic representation of stir-bar extraction



a *b*

Fig. 6. Coatings swelling degree after submerging of stir bars in solvent for 5, 15 and 30 min in *a*) acetonitrile, *b*) hexane

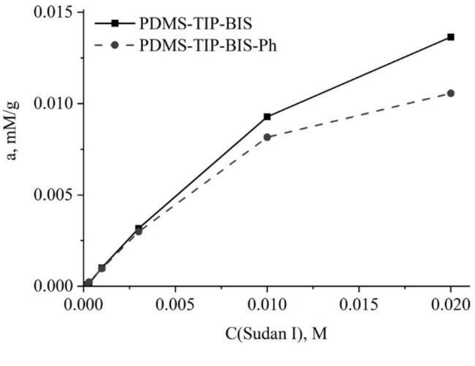


Fig. 7. Dependence of quantity of Sudan I (mM) sorbed per gram of coating on Sudan I concentration in ethyl acetate (sorption isotherm for Sudan I)

CONCLUSIONS

The preparation of PDMS coatings was conducted by sol-gel method. ATR-IR spectra of coatings were close to pure PDMS spectra, and confirmed the presence of Ti (with covalent bonds -Si-O-Ti-) in coatings by peak at 924 cm^{-1} and absence of an abundance of OH-groups. All of the coatings were hydrophobic with water contact angles ranging from 99.7 to 105.6 and stable up to 350–425 °C. The stability of PDMS-MTMOS-TIP-BIS and PDMS-MTMOS-TIP-Geniosil coatings at 425 °C might indicate their potential application in gas chromatography. Coatings were checked for Sudan I sorption and showed a linear dependence for Sudan I sorption in solutions within low concentration range. The PDMS-MTMOS-TIP-BIS-Ph coating might be used in nonpolar solvents if careful observation of its stability is ensured. The observed qualities of the coatings suggest that they can be further used in the development of analytical determination methods at sample preparation stage with further gas or liquid chromatography.

Вплив складу суміші компонентів золю на формування кремнійорганічних покриттів на скляних підкладках

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У роботі синтезовані гібридні кремнійорганічні покриття на скляних підкладках з використанням сумішей активного полімеру PDMS з OH-кінцевими групами і одного або декількох прекурсорів, а саме метилтриметоксисилану, біс(3-триметоксісилілпропіл) аміну, фенілтриметоксісилану, ціанопропілтриметоксісилану, амінопропілтриетоксісилану) у присутності модифікаторів (поліетиленгліколю, органічних розчинників), каталізатора трифтороцтової кислоти. Метою роботи було отримання нових сорбційних матеріалів для вилучення неполярних і напівполярних аналітів, наприклад, карбонільних сполук у формі ПФБГА-дериватів, азобарвників, фталатів, інших, і очистки зразків зі складною матрицею з наступним газохроматографічним визначенням. Перевагами отриманих сорбційних покриттів є ефективне відокремлення мікрокількостей цільових сполук неполярної та напівполярної природи від полярних сполук, які присутні у водних зразках у достатньо високих концентраціях.

В роботі описано синтез кремнійорганічних покриттів різного складу, об'ємне співвідношення активного полімера, прекурсорів, деактивуючого агента, каталізатора, модифікаторів. Покриття наносили на скляні підкладки двома методами: спін-коатингу та діп-коатингу (занурення). Часом нанесення було ускладнене через нерівномірний розподіл золю, коли суміш розчинів була надто в'язкою або вимагала тривалого часу сушіння. Біс(3-триметоксісилілпропіл) амін та N-(2-аміноетил)-3-амінопропілтриетоксісилан виявилися ефективними зшиваючими агентами з близькими властивостями отриманих покриттів, додавання даних прекурсорів значно покращило характеристики отриманих покриттів. Показано, що суміші, що містять PDMS з OH-кінцевими групами, утворюють товсті покриття (до 325 мкм) без тріщин в присутності більшості досліджених прекурсорів, а додавання ізопропоксиду титану покращує термічну стабільність і призводить до утворення більш рівномірного покриття у випадку підкладок складної форми (скляної мішалки).

Були отримані ІЧ-спектри досліджених покриттів, більшість смуг спектра є характеристичними для незвязаного полімера ПДМС, як підтвердження присутності ковалентно зв'язаного титану в покриттях, було виявлено пік при 924 см$^{-1}$. Усі покриття гідрофобні, для порівняння були виміряні кути контакту з водою, які становили від 99.7 до 105.6. Термогравіметричний аналіз (ТГ і ДТА) був проведений для перевірки термостабільності покриттів для подальшого використання в твердофазній мікроекстракції з газовою хроматографією, і було показано, що покриття можуть витримувати нагрівання до 350–425 °С.

Для сорбції в аналітичних кількісних методах необхідно використовувати однорідні, рівномірні, міцні, менш схильні до набухання, відтворювані в синтезі та при сорбції покриття. Синтезовані нами покриття є ефективними для подальшого використання в хімічному аналізі для очищення зразків від заважаючих компонентів або для попереднього концентрування аналітів. Покриття мають достатню стабільність для використання в гібридних методах аналізу.

***Ключові слова**: золь-гель синтез, сорбція, мікроекстракція, пробопідготовка, покриття, тонкі плівки, полідиметилсилоксан, спектрофотометрія*

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