

DESIGN OF FUNCTIONALIZED POLYSILOXANES: SYNTHESIS AND STUDY ON SULFUR-CONTAINING XEROGELS WITH MONO- AND BIFUNCTIONAL SURFACE LAYER

Yu.L. Zub¹, I.V. Melnyk¹, A.A. Chuiko¹, D.Cauzzi², and G.Predieri²

¹*Institute of Surface Chemistry, National Academy of Sciences,
Gen. Naumov Str. 17, 03680 Kyiv-164, UKRAINE*

²*Dipartimento di Chimica Generale ed Inorganica, Chimica Analitica, Chimica Fisica,
Università di Parma, Parco Area delle Scienze, 17/A, 43100 Parma, ITALY*

Abstract

Urea- and thiourea-containing trialkoxysilanes were prepared with a high yield and purity. By sol-gel processing of these precursors the new functionalized xerogels were synthesized and characterized by FTIR, elemental analysis, thermal analysis and adsorption method. Mono- and bifunctionalized xerogels were easily prepared by mixing of precursors in the desired ratios together with tetraethyl orthosilicate. Obtained functional polysiloxanes are perspective materials for metal sorption and hybrid catalysis applications.

Introduction

Sulfur-containing functional groups anchored to the surface of different matrices possess as a rule good selectivity in the sorption of analytically important metals. Significant effort has been made to obtain and investigate sorbents of this class [1-3]. Silicas of different nature obtained by several methods are often used as support for surface modification. Seldom in this case the concentration of sulfur-containing groups on the surface is higher than 0.5 mmol/g [2, 3]. For instance, by using the method of "surface assembly" to obtain grafted sulfur-containing heterocycle ligands, the concentration of such groups on the silica surface was 2-10 times lower respect to the above-mentioned value. In other words, the sorption capacity of such materials with respect to metal ions was not high ([4] and references therein). Moreover side reaction of modifying reagents with surface silanol groups are possible, which lead to the formation of hydrolytically unstable species.

Therefore it is not surprising that sol-gel method was proposed as an alternative approach to obtain sulfur-containing sorbents [5]. Many trifunctional silanes of the type $(RO)_3SiR'$ (R – alkyl, and R' – sulfur-containing group) can be prepared for the realization of this method. Voronkov and collaborators have prepared a number of compounds of such type and obtained different sulfur-containing xerogels [1, 5]. These sorbents showed high efficiency in the sorption of Ag(I), Hg(II), Au(III) and platinum groups metals. This synthesis is performed in one-pot route using hydrolysis of appropriate trifunctional silanes, usually in basic medium (water or water/dioxane). This, in principle, can lead to partial hydrolysis of C=S bond. Besides, the specific surface areas of such sorbents were relatively low.

By using sol-gel method, it is easy to vary composition and structure-adsorption characteristics. In order to use this method we prepared by simple synthesis different sulfur-containing trifunctional silanes and, for comparison, their oxygen-containing analogues. By the sol-gel approach we also prepared a number of xerogels with a bifunctional surface layer in a simple way.

Experimental

1. Materials and analytical equipment.

All organic reagents were pure commercial products (Aldrich and Fluka): *n*-propylamine (99%); *n*-dipropylamine (99%); 2-aminobenzothiazole, ABTA (97%); *n*-propylisothiocyanate (98%); phenylisocyanate (98%); phenylisothiocyanate (98%); 3-(triethoxysilyl)propylisocyanate, TEPIC (>95%); 3-aminopropyltriethoxysilane, APTES (99%), *N*-[3-(trimethoxysilyl)propyl]ethylenediamine, TMPED (97%); tetraethoxysilane, TEOS (99%).

The solvents were reagents grade and were dried and distilled by standard techniques before use. All manipulations of reagents containing the trimethoxy- or triethoxysilyl group (before the sol-gel process) were carried out under dry nitrogen by means of standard Schlenk-tube techniques.

Elemental analyses (C, N, H, S) were performed with a Carlo Erba EA 1108 automated analyzer. Thermal analysis was performed in the range 20-800°C with a heating rate of 5°C min⁻¹ in an air stream using Perkin-Elmer Thermal System. IR spectra were recorded on a Nicolet NEXUS FTIR spectrometer using thin films or KBr disks. ¹H NMR spectra were obtained with a Bruker AC-300 instrument. Mass spectra were recorded on a Finnigan SSQ 710 mass spectrometer. Energy dispersive X-ray (EDX) microanalyses and scanning electron microscopy (SEM) images were obtained by the electron microscopy microanalyses system JEOL 6400 EDS.

BET surface areas [6] were measured using a Micromeritics 2200 equipment from nitrogen adsorption at the temperature of liquid nitrogen, after degassing the samples in a nitrogen stream at 423K for about 1 h.

2. Preparation of trialkoxysilanes.

2.1. (EtO)₃Si(CH₂)₃NCS

The synthesis of this compound was performed following to the published method with minor changes [7]. *n*-Hexane instead of diethyl ether was used to extract the liquid isothiocyanate that was subsequently obtained as the yellow oil, by filtering the suspension and evaporating the hexane under vacuum.

2.2. [(EtO)₃Si(CH₂)₃NH]₂C=O (I).

In a 100 ml Schlenk flask 0.025 mol of APTES was dissolved under nitrogen in 10 ml of dry hexane and cooled using an ice-bath. 0.025 mol of TEPIC in 10 ml of hexane were added dropwise with stirring. A white precipitate was formed after 5 min. The suspension was kept for 30 min in an ice-bath, filtered, washed with 10 ml of cold hexane and dried in vacuum. From the filtrate an additional portion of white product can be obtained. Total yield is quantitative. Melting point: 63-65°C. Elemental analysis (calcd for C₁₉H₄₄N₂O₇Si₂): C, 48.25 (48.60); H, 9.86 (9.46); N, 5.94 (6.00); Si, 11.41 (12.00). ¹H NMR (CDCl₃, δ/ppm): 0.62 (m, SiCH₂), 1.21 (t, CH₃), 1.61 (m, CH₂), 3.14 (m, CH₂N), 3.80 (q, CH₂O), 4.50 (m, NH). MS, m/z (%): 498(35), 470(72), 468(45), 424(100), 422(85), 245(18), 219(15), 174(15). IR, cm⁻¹: 3336 vs (very strong) (νNH), 2975 vs, 2928 vs, 2885 vs (νCH), 1620 vs (νCO), 1596 vs (ν_{as}NCN, B band), 1289 m (medium) (ν_sNCN+νNH, C band), 1104 vs, 1076 vs (νSiO).

2.3. [(EtO)₃Si(CH₂)₃NH]₂C=S (II).

0.025 M of (EtO)₃Si(CH₂)₃NCS was dissolved under nitrogen in 10 ml of dry hexane and added to solution of 0.025 M of APTES in 10 ml of hexane. The solution was allowed to react for 1 h with stirring and then heated for 1 h at 60°C. After cooling and evaporating the hexane under vacuum the light-yellow oil distilled in vacuum. Yield was 95%. ¹H NMR (CDCl₃, δ/ppm): 0.64 (m, SiCH₂), 1.21 (t, CH₃), 1.71 (m, CH₂), 3.42 (m, CH₂N), 3.80 (q, CH₂O), 6.0 (m, NH). MS, m/z (%): 498(35), 470(72), 468(45), 424(100), 422(85), 245(18),

219(15), 174(15). IR, cm^{-1} : 3272 m, br (νNH), 2976 vs, 2928 vs, 2886 vs (νCH), 1554 vs ($\nu_{\text{as}}\text{NCN}$, B band), 1295 m, 1268 w (weak) ($\nu_{\text{s}}\text{NCN}+\nu\text{NH}$, C band), 1103 vs, 1079 vs (νSiO).
2.4. $(\text{EtO})_3\text{Si}(\text{CH}_2)_3\text{NHC}(\text{O})\text{NHC}_3\text{H}_7\text{-n}$ (III).

In a 100 ml Schlenk flask 0.030 mol of *n*-propylamine was dissolved under nitrogen in 10 ml of hexane and cooled using an ice-bath. 0.025 M of TEPIC in 10 ml of hexane was added dropwise with stirring. An exothermic reaction took place. The solution was stirred for 15 min at ice-bath temperature and then for 3 h at room temperature. A white waxy product was obtained after the solvent was completely evaporated under vacuum. Yield is quantitative. Elemental analysis (calcd for $\text{C}_{13}\text{H}_{30}\text{N}_2\text{O}_4\text{Si}$): C, 46.63 (50.95); H, 10.32 (9.87); N, 9.73 (9.14). ^1H NMR (CDCl_3 , δ/ppm): 0.55 (m, SiCH_2), 0.83 (m, $\text{CH}_3(\text{CH}_2)_2\text{N}$), 1.14 (t, CH_3), 1.40 (m, $\text{CH}_3\text{CH}_2\text{CH}_2\text{N}$), 1.51 (m, CH_2), 3.00-3.10 (m, CH_2N), 3.74 (q, CH_2O), 5.31 (m, NHC_3H_7), 5.37 (m, NHC_3H_6). MS, m/z (%): 335(8), 306(12), 265(6), 261(100), 245(6), 220(5), 202(8), 163(12). IR, cm^{-1} : 3344 vs (νNH), 2974 vs, 2928 vs, 2880 vs (νCH), 1630 vs (νCO), 1579 vs, br (bright) ($\nu_{\text{as}}\text{NCN}$, B band), 1278m, 1262m ($\nu_{\text{s}}\text{NCN}+\nu\text{NH}$, C band), 1103 vs, 1079vs (νSiO).

2.5. $(\text{EtO})_3\text{Si}(\text{CH}_2)_3\text{NHC}(\text{S})\text{NHC}_3\text{H}_7\text{-n}$ (IV).

In a 100 ml Schlenk flask 0.025 mol of APTES was dissolved under nitrogen in 30 ml of ethanol. To this solution, 0.025 M of *n*- $\text{C}_3\text{H}_7\text{NCS}$ dissolved in 10 ml ethanol was added with stirring. An exothermal reaction took place. The resulting solution was boiled for 1 h. After cooling, the solvent was completely evaporated under vacuum. By staying some time in vacuum the clear transparent oil transformed into a white waxy solid. Yield was quantitative. Elemental analysis (calcd for $\text{C}_{13}\text{H}_{30}\text{N}_2\text{O}_3\text{SSi}$): N, 8.41 (8.68); S, 9.47 (9.94). ^1H NMR (CDCl_3 , δ/ppm): 0.55 (m, SiCH_2), 0.84 (m, $\text{CH}_3(\text{CH}_2)_2\text{N}$), 1.11 (t, CH_3), 1.51 (m, $\text{CH}_3\text{CH}_2\text{CH}_2\text{N}$), 1.60 (m, CH_2), 3.00-3.33 (m, CH_2N), 3.71 (q, CH_2O), 6.20 (br s, NHC_3H_7), 6.30 (br s, NHC_3H_6). MS, m/z (%): 325(8), 324(30), 333(85), 322(100), 277(16), 163(20). IR, cm^{-1} : 3267 vs, br (νNH), 2973 vs, 2928 vs, 2885 vs (νCH), 1556 vs, br ($\nu_{\text{as}}\text{NCN}$, B band), 1294 m, 1268 m ($\nu_{\text{s}}\text{NCN}+\nu\text{NH}$, C band), 1103 vs, 1079 vs (νSiO).

2.6. $(\text{EtO})_3\text{Si}(\text{CH}_2)_3\text{NHC}(\text{O})\text{NHC}_6\text{H}_5$ (V).

0.025 M $\text{C}_6\text{H}_5\text{NCO}$ was added dropwise under nitrogen to a solution of 0.025 M of APTES in 15 ml ethanol with stirring. An exothermic reaction took place. The solution was allowed to react for 30 min and then the solvent was completely evaporated under vacuum. The transparent oil formed and after staying in vacuum gave a white solid. Yield is quantitative. M.P. is 44-46°C. Elemental analysis (calcd for $\text{C}_{16}\text{H}_{28}\text{N}_2\text{O}_4\text{Si}$): C, 56.71 (56.44); H, 8.53 (8.29); N, 8.16 (8.23). ^1H NMR (CDCl_3 , δ/ppm): 0.62 (m, SiCH_2), 1.20 (t, CH_3), 1.62 (m, CH_2), 3.20 (m, CH_2N), 3.79 (q, CH_2O), 5.34 (m, NH), 6.95 (br s, NHC_6H_5), 7.00-7.05, 7.23-7.30 (m, C_6H_5). MS, m/z (%): 542(75), 503(20), 370(72), 341(100), 324(46), 295(100), 293(43), 202(42), 93 (20). IR, cm^{-1} : 3351 vs, br, 3310 s (strong) (νNH), 3077 w, 3039 w (νCH arom), 2971 vs, 2924 vs, 2883 vs (νCH aliph), 1644 vs (νCO), 1559 vs, br ($\nu_{\text{as}}\text{NCN}$, B band), 1237 m ($\nu_{\text{s}}\text{NCN}+\nu\text{NH}$, C band), 1108 vs, 1079 vs, br (νSiO).

2.7. $(\text{EtO})_3\text{Si}(\text{CH}_2)_3\text{NHC}(\text{S})\text{NHC}_6\text{H}_5$ (VI).

The synthesis of this compound was performed following to the published method [8] from APTES and $\text{C}_6\text{H}_5\text{NCS}$. Under staying in vacuum the product was obtained as a pale-yellow viscous liquid, giving satisfactory spectroscopic data. ^1H NMR (CDCl_3 , δ/ppm): 0.58 (m, SiCH_2), 1.16 (t, CH_3), 1.68 (m, CH_2), 3.61 (m, CH_2N), 3.71 (q, CH_2O), 6.24 (br s, NH), 7.18-7.28, 7.37-7.42 (m, C_6H_5), 8.02 (br s, NHC_6H_5). MS, m/z (%): 356(100), 311(32), 218(10), 176(16), 163(30), 152(12), 135(15), 93(10). IR, cm^{-1} : 3275 s, br, 3212 sh (shoulder), br (νNH), 3062 w, 3039 w (νCH arom), 2975 vs, 2926 vs, 2887 vs (νCH aliph), 1537 vs ($\nu_{\text{as}}\text{NCN}$, B band), 1242 m ($\nu_{\text{s}}\text{NCN}+\nu\text{NH}$, C band), 1103 vs, 1079 vs, br (νSiO).

2.8. (EtO)₃Si(CH₂)₃NHC(O)NHCNSC₆H₄ (VII).

In a 100 ml Schlenk flask 0.025 mol of ABTA was dissolved under nitrogen in 30 ml of CH₃CN. To this light yellow-green solution 0.025 mol of TEPIC was added dropwise with stirring. The resulting solution was refluxed for 2 h. After cooling the solvent was completely evaporated under vacuum. The residue was dissolved in 10 ml of warm ethanol and filtered. The filtrate was evaporated under vacuum yielding a light-green solid in 90% yield. M.P. is 79-81°C. Elemental analysis (calcd for C₁₇H₂₇N₃O₄SSi): C, 50.91(51.39); H, 6.62(6.8); N, 10.49(10.58); S, 8.14(8.06); Si, 7.54(7.05). ¹H NMR (CDCl₃, δ/ppm): 0.70 (m, SiCH₂), 1.22 (t, CH₃), 1.73 (m, CH₂), 3.37 (m, CH₂N), 3.82 (q, CH₂O), 7.19-7.24, 7.34-7.40, 7.69-7.73 (m, C₆H₅), 11.14 (br s, NH). MS, m/z (%): 426(16), 398(100), 353(25), 351(48), 247(8), 222(18), 202(8), 176(10), 150(37). IR, cm⁻¹: 3325 vs, br (νNH), 3056 w (νCH arom), 2976 vs, 2929 vs, 2889 vs (νCH aliph), 1700 vs, br (νCO), 1540 vs, br (ν_{as}NCN, B band), 1272 m, 1251 m (ν_sNCN+νNH, C band), 1103 vs, 1079 vs (νSiO).

3. Preparations of xerogels.

3.1. SiO₂/[SiO_{3/2}(CH₂)₃NH]₂C=O (2 : 1) (MI).

0.025 mol of APTES was dissolved under nitrogen in 10 ml of ethanol and to this solution 0.025 mol of TEPIC in 10 ml of ethanol was added dropwise under stirring. An exothermal reaction took place. After 30 min the resulting solution was cooled using an ice-bath and added of a solution of 0.0278 g NH₄F in 2.48 ml (0.1375 mol) of water. After stirring for some seconds, 0.05 mol of the cold TEOS was added to this solution. After reaching homogeneity the clear resulting solution was left to reach room temperature. Gelation occurred in less that 10 min, giving a slight opalescent gel. After 24 h the gel was crushed and dried under vacuum at 60/70/80°C, for 2 h at each temperature. Then it was crushed again, washed with 500 ml of water and dried under vacuum at 70/80/90°C for 2 h at each temperature. 10.9 g of white solid were obtained.

3.2. SiO₂/[SiO_{3/2}(CH₂)₃NH]₂C=O (4 : 1) (MID).

This xerogel was obtained by the same method of 3.1 with the following changes: 0.0125 mol of APTES was dissolved in 10 ml of ethanol and to this solution 0.0125 mol of TEPIC in 5 ml of ethanol was added; 0.0189 g NH₄F in 2.14 ml (0.1188 mol) of water was used; xerogel was washed with 500 ml of water. Yield was 6.5 g.

3.3. SiO₂/[SiO_{3/2}(CH₂)₃NH]₂C=S (4 : 1) (MIID).

0.025 mol of APTES was dissolved under nitrogen in 20 ml of ethanol and to this solution 0.025 mol of [(EtO)₃Si(CH₂)₃NH]₂C=S (obtained in 2.3) in 20 ml of ethanol was added dropwise under stirring. After 30 min stirring the reaction mixture was heated for 1 h at 60°C and only after that it was cooled using an ice-bath and added of a solution of 0.0278 g NH₄F in 4.28 ml (0.2375 mol) of water. After stirring some seconds, 0.10 mol of the cold TEOS was added to this solution. After reaching homogeneity the clear resulting solution was left to reach room temperature. Gelation occurred in less that 50 min, giving a slight opalescent gel. After 24 h the gel was crushed and dried under vacuum at 60/70/80°C, for 2 h at each temperature. Then it was crushed again, washed with 1000 ml of water and dried under vacuum at 60/70/80°C for 2 h at each temperature. 13.5 g of light-yellow solid was obtained.

3.4. SiO₂/SiO_{3/2}(CH₂)₃NHC(O)NHC₃H_{7-n} (2 : 1) (MIII).

0.025 mol (EtO)₃Si(CH₂)₃NHC(O)NHC₃H_{7-n} (obtained in 2.4) was dissolved in 20 ml ethanol and cooled with an ice-bath. To this solution, 0.0278 g of NH₄F dissolved in 2.48 ml of water was added and after some seconds of stirring, in which the solution stayed clear, 0.05 mol of cold TEOS was added with stirring. Gelation occurred in less than 5 min. After 24 h the gel was crushed and dried under vacuum at 60/70/80°C (for 2 h at each temperature).

Then it was crushed again, washed with 500 ml of water and dried under vacuum at 70/80/90°C (for 2 h at each temperature). Yield of white product was 7.9 g.

3.5. $\text{SiO}_2/\text{SiO}_{3/2}(\text{CH}_2)_3\text{NHC}(\text{O})\text{NHC}_3\text{H}_7\text{-n}$ (4 : 1) (MIID).

This xerogel was obtained using the method described in 3.4 with the following changes: trifunctional silane was dissolved in 30 ml ethanol; the water amount was 4.28 ml (0.2375 mol), and TEOS amount was 0.10 mol; xerogel was washed with 1000 ml of water. Yield was 10.7 g.

3.6. $\text{SiO}_2/\text{SiO}_{3/2}(\text{CH}_2)_3\text{NHC}(\text{O})\text{NHC}_3\text{H}_7\text{-n}/\text{SiO}_{3/2}(\text{CH}_2)_3\text{NH}_2$ (4 : 1 : 1) (BIII).

0.025 mol of $(\text{EtO})_3\text{Si}(\text{CH}_2)_3\text{NHC}(\text{O})\text{NHC}_3\text{H}_7\text{-n}$ (obtained in 2.4) was dissolved in 20 ml ethanol and cooled with an ice-bath. A second solution of TEOS/APTES (0.10/0.025 mol) was prepared and cooled. 4.95 ml of water was added to the first solution and after several second the second was added to the mixture. A milk-white gel was obtained in 20 min. After 24 h it was crushed and dried in vacuum at 60/70/80°C (for 2 h at each temperature). Then it was crushed again, washed with 1000 ml of water and dried under vacuum at 80/90/105°C (for 2 h at each temperature). Yield of white product was 10.5 g.

3.7. $\text{SiO}_2/\text{SiO}_{3/2}(\text{CH}_2)_3\text{NHC}(\text{S})\text{NHC}_3\text{H}_7\text{-n}$ (2 : 1) (MIV).

0.025 mol of $(\text{EtO})_3\text{Si}(\text{CH}_2)_3\text{NHC}(\text{S})\text{NHC}_3\text{H}_7\text{-n}$ (obtained in 2.5) was dissolved in 20 ml ethanol and cooled using an ice-bath. The preparation followed to the one reported in 3.4. Gelation occurred in less than 10 min. Yield of slightly yellow solid was 8.2 g.

3.8. $\text{SiO}_2/\text{SiO}_{3/2}(\text{CH}_2)_3\text{NHC}(\text{S})\text{NHC}_3\text{H}_7\text{-n}$ (4 : 1) (MIVD).

It was obtained by method described in 3.5 with the following changes: trifunctional silane was dissolved in 30 ml of ethanol, the water amount was 4.28 ml (0.2375 mol), and TEOS quantity was 0.10 mol; aging time was 48 h. Yield was 11.4 g.

3.9. $\text{SiO}_2/\text{SiO}_{3/2}(\text{CH}_2)_3\text{NHC}(\text{S})\text{NHC}_3\text{H}_7\text{-n}/\text{SiO}_{3/2}(\text{CH}_2)_3\text{NH}_2$ (4 : 1 : 1) (BIV).

This xerogel was obtained according to 3.6 with the following changes: 30 ml of ethanol was used. Yield of white product was 12.2 g.

3.10. $\text{SiO}_2/\text{SiO}_{3/2}(\text{CH}_2)_3\text{NHC}(\text{O})\text{NHC}_3\text{H}_7\text{-n}/\text{SiO}_{3/2}(\text{CH}_2)_3\text{NHC}(\text{S})\text{NHC}_3\text{H}_7\text{-n}$ (4:1:1) (BIII/IV).

0.025 mol $(\text{EtO})_3\text{Si}(\text{CH}_2)_3\text{NHC}(\text{O})\text{NHC}_3\text{H}_7\text{-n}$ (obtained in 2.4) was dissolved in 20 ml of ethanol and added to a solution of 0.025 mol of $(\text{EtO})_3\text{Si}(\text{CH}_2)_3\text{NHC}(\text{S})\text{NHC}_3\text{H}_7\text{-n}$ (obtained in 2.5) in 20 ml of ethanol. The resulting solution was cooled and was added of a solution of 0.0278 NH_4F in 4.95 ml (0.275 mol) of water. After obtaining solution homogeneity 0.10 mol of cold TEOS was added to that solution with stirring. Gelation occurred in 12 min. After 24 h the gel was crushed and dried in vacuum at 60/70/80°C (for 2 h at each temperature). Then it was crushed again, washed with 1000 ml of water and dried under vacuum at 70/80/90°C (for 2 h at each temperature). Yield of slight-yellow product was 16.2 g.

3.11. $\text{SiO}_2/\text{SiO}_{3/2}(\text{CH}_2)_3\text{NHC}(\text{S})\text{NHC}_6\text{H}_5$ (2 : 1) (MVI).

0.025 mol of $(\text{EtO})_3\text{Si}(\text{CH}_2)_3\text{NHC}(\text{S})\text{NHC}_6\text{H}_5$ (obtained in 2.7) was dissolved in 20 ml of ethanol and cooled using an ice-bath. Then the synthesis was performed according to 3.4. Gelation occurred in 5 min. Yield was 8.7 g.

3.12. $\text{SiO}_2/\text{SiO}_{3/2}(\text{CH}_2)_3\text{NHC}(\text{S})\text{NHC}_6\text{H}_5$ (4 : 1) (MVID).

0.025 mol of $(\text{EtO})_3\text{Si}(\text{CH}_2)_3\text{NHC}(\text{S})\text{NHC}_6\text{H}_5$ (obtained in 2.7) was dissolved in 30 ml of ethanol and cooled using an ice-bath. Then the synthesis was performed according to 3.5. Gelation occurred in 5 min. Yield of white product was 12.1 g.

3.13. $\text{SiO}_2/\text{SiO}_{3/2}(\text{CH}_2)_3\text{NHC}(\text{S})\text{NHC}_6\text{H}_5$ (8 : 1) (MVID').

0.025 mol of $(\text{EtO})_3\text{Si}(\text{CH}_2)_3\text{NHC}(\text{S})\text{NHC}_6\text{H}_5$ (obtained in 2.7) was dissolved in 40 ml of ethanol and cooled using an ice-bath. Then the synthesis was performed according to 3.12 with the following changes: the water amount was 7.88 ml (0.4375 mol), and TEOS quantity was 0.20 mol. Gelation occurred in 10 min. Yield of slight-yellow product was 19.6 g.

3.14. $\text{SiO}_2/\text{SiO}_{3/2}(\text{CH}_2)_3\text{NHC}(\text{S})\text{NHC}_6\text{H}_5/\text{SiO}_{3/2}(\text{CH}_2)_3\text{NH}_2$ (4 : 1 : 1) (BVI).

The synthesis of this xerogel was performed like in 3.6 with the following changes: 30 ml of ethanol was used. Gelation occurred in 15 min. Yield of white product was 15.0 g.

3.15. $\text{SiO}_2/\text{SiO}_{3/2}(\text{CH}_2)_3\text{NHC}(\text{O})\text{NHC}_6\text{H}_5/\text{SiO}_{3/2}(\text{CH}_2)_3\text{NHC}(\text{S})\text{NHC}_6\text{H}_5$ (4 : 1 : 1) (BV/VI).

0.025 mol of $(\text{EtO})_3\text{Si}(\text{CH}_2)_3\text{NHC}(\text{O})\text{NHC}_6\text{H}_5$ (obtained in 2.6) was dissolved in 20 ml of ethanol and mixed with a solution of 0.025 mol of $(\text{EtO})_3\text{Si}(\text{CH}_2)_3\text{NHC}(\text{S})\text{NHC}_6\text{H}_5$ (obtained in 2.7) in 20 ml of ethanol. The resulting solution was cooled with an ice-bath and then added of a solution of 0.0278 g of NH_4F in 4.95 ml of water. After obtaining solution homogeneity, 0.10 mol of the cold TEOS were added to the previous solution. Gelation occurred in less than 7 min. After 24 h the gel was crushed and dried in vacuum at 60/70/80°C (for 2 h at each temperature). Then it was crushed again, washed with 1000 ml of water and dried under vacuum at 70/80/90°C (for 2 h at each temperature). Yield of slightly-yellow product was 18.3 g.

3.16. $\text{SiO}_2/\text{SiO}_{3/2}(\text{CH}_2)_3\text{NHC}(\text{O})\text{NHCNSC}_6\text{H}_4$ (2 : 1) (MVII).

The solution of 0.025 mol of the initial trifunctional silane was obtained according to 2.8. The residue obtained after complete evaporation of CH_3CN was dissolved in 40 ml of warm ethanol, filtered and cooled in an ice-bath. Then it was added of a solution of 0.0278 g of NH_4F in 2.48 ml of water. After 10-15 sec 0.05 mol of cold TEOS was added to the previous solution. Gelation occurred in 15 min. After 24 h the gel was crushed and dried in vacuum at 60/70/80°C (for 2 h at each temperature). Then it was crushed again, washed with 500 ml of water and dried under vacuum in the same conditions. Yield of slightly-green product was 10.2 g.

3.17. $\text{SiO}_2/\text{SiO}_{3/2}(\text{CH}_2)_3\text{NHC}(\text{O})\text{NHCNSC}_6\text{H}_4$ (4 : 1) (MVIID).

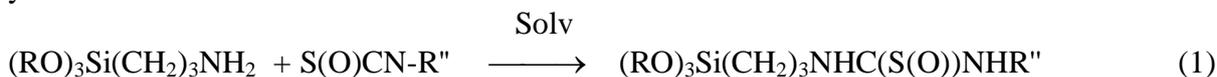
This xerogel was obtained according to 3.16 with the following changes: 4.28 ml (0.2375 mol) of water and 0.10 mol of TEOS were used; the xerogel was washed using 1000 ml of water; the second drying was performed at 70/80/90°C (2 h at each temperature). Yield was 13.0 g.

3.18. $\text{SiO}_2/\text{SiO}_{3/2}(\text{CH}_2)_3\text{NHC}(\text{O})\text{NHCNSC}_6\text{H}_4/\text{SiO}_{3/2}(\text{CH}_2)_3\text{NH}(\text{CH}_2)_2\text{NH}_2$ (4 : 1 : 1) (BVII).

This xerogel was obtained according to 3.16 with the following changes in method: the catalyst was not used; the water amount was 4.95 ml (0.275 mol); TEOS was previously mixed with TMPED (0.10/0.025 M). Gelation occurred in less than 20 min. The second drying was performed at 70/80/90°C (2 h at each temperature). Yield was 17.2 g.

Results and discussion

For the synthesis of trialkoxysilanes with oxygen- and sulfur-containing functional groups we used the well-known reaction of primary amines with isothiocyanates (see Scheme 1). This reaction as a rule does not show the formation of by-products, often goes at room temperature and allows one to obtain a wide spectra of trifunctional silanes with high yield.



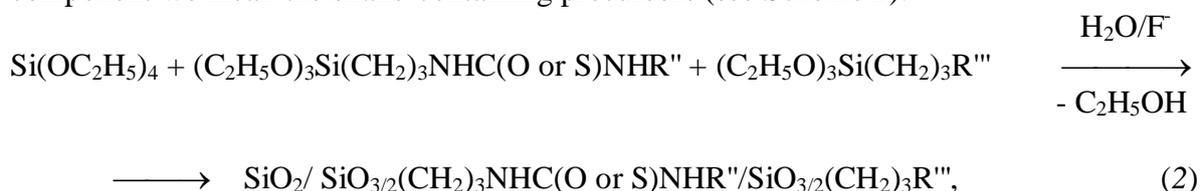
Thus we obtained triethoxysilanes which contain R'' radicals such as *n*-C₃H₇ (O I; S II); C₆H₅ (O III; S IV); (CH₂)₃Si(OC₂H₅)₃ (O V; S VI); CNSC₆H₄ (O VII). It should be noted that V and VI were synthesized earlier [9-12] using the transamination reaction. In this case V was obtained as an oil with 12.2 % yield. Using the reaction (1), independently from the solvent (*n*-hexane or benzene), it crystallizes as a white solid (melting point 61-63°C) in quantitative yield. Spectral characteristics of this product are consistent with those described in [12] except the NH position in ¹H NMR spectrum; for the crystalline product this signal is shifted to strong fields (an analogous situation is observed for substance IV, ¹H NMR spectrum of which was described in [8]). A single strong band in the

range 3000-4000 cm⁻¹ was identified in the IR spectrum of this substance, which is attributed to ν(NH). After drying in vacuum, this substance does not dissolve well in alcohols, benzene, etc. The product is air and moisture stable. Also substance IV was earlier described as an oil [8] and a solid product [13]. However our goal consisted in obtaining triethoxysilanes precursors for sol-gel synthesis that, as a rule, did not need special purification. Their purity according to spectral data was quite satisfactory for the further use. At the same time it should be said that most triethoxysilanes can form oils, because they contain traces of solvents, for example ethanol, which can be seen in ¹H NMR spectra. However in our case that was not a problem because they were prepared in ethanol, which is the solvent used for the further gels obtaining.

All the precursors used in this work have been characterized by IR spectroscopy due to their intense and typical functional-group absorption bands. NHC(O)NHR" groups show a strong, narrow ν(NH) absorption band in the range 3200-3400 cm⁻¹. In the case of NHC(S)NHR" groups the ν(NH) band is broader and less intense. Secondly, in the range 1500-1700 cm⁻¹ we observe the ν_{as}(NCN) and ν(CO) absorption bands [14, 15]. In the case of S-containing silanes, the ν_{as}(NCN) is a single broad band (also in the case of different groups on the nitrogen atoms). For the O-containing silanes we observe two strong and narrow absorption bands.

In the ¹H NMR spectra of the synthesized precursors, the NH-groups absorption is present at low field (>4.5 ppm). In the case of symmetrical (thio)urea (V and IV substances) the two NH have the same chemical shifts, in the case of (thio)urea with substituents of different nature (I – IV substances) there are two signals. For VII substance despite of the different nature of the substituents only one broad signal is observed at about 11.0 ppm, probably because of exchange processes.

All the obtained precursors were used in the synthesis of gels. By the reaction of hydrolytic co-condensation, we prepared two- and three-component xerogels, where by component we mean the silane-containing precursors (see Scheme 2):



where R'' = *n*-C₃H₇; C₆H₅; (CH₂)₃Si(OC₂H₅)₃; CNSC₆H₄ and R''' = -NH₂ or -NH(CH₂)₂NH₂. As a solvent, ethanol was used and NH₄F as a catalyst. The ratio F/Si was usually 1/100 or less. The amount of water was one half of the one needed for complete hydrolysis of all ethoxy groups [16].

The gels obtained have opalescent, which is characteristic for the sol-gel process in basic or nucleophilic medium. After ageing (usually for 24 h) the gels were crushed, dried in vacuum, crushed again, washed with water and dried again at vacuum. The drying conditions for sulfur-containing gels were softer than in other cases. Elemental analysis (C, H, N, S) data for the obtained xerogels are given in Table 1.

The synthesized xerogels can be divided into two groups related with the composition of their surface layer; xerogels with monofunctionalized (M) and bifunctionalized (B) surface layers. Xerogels M are hydrophobic and possess a small value of specific surface area (S_{sp}) when TEOS/trifunctional silane ratio was 2:1. Therefore xerogels with higher TEOS/trifunctional silane ratio (4 : 1; MD xerogels) were prepared and they show hydrophilic properties. Also xerogels with a bifunctional surface layer (B), displayed hydrophilic character of their surface.

All the xerogels were obtained as light powdery materials, which, as a rule, are easily suspended in air. Sometimes sulfur-containing xerogels possess a pale-yellow color. In Fig. 1 SEM pictures are shown. They are typical for such xerogels and indicate that they consist of particles of different size with sharp edges, with finely dispersed small grains.

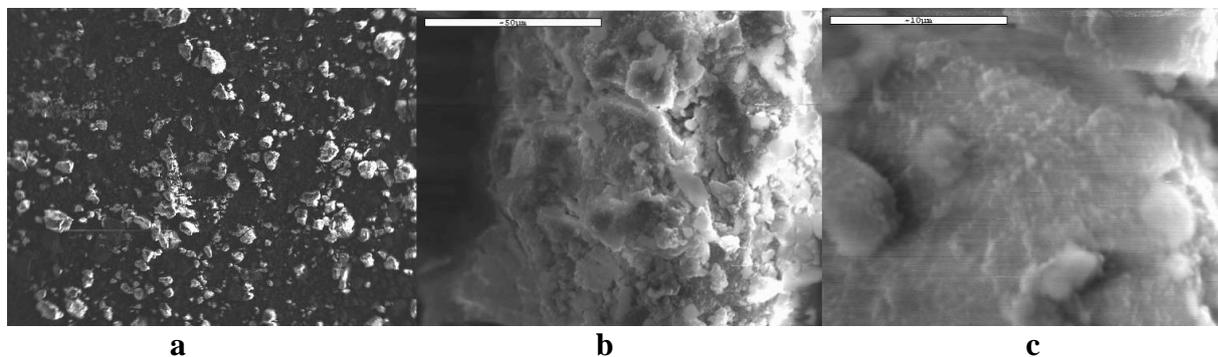


Fig. 1. Scanning electron micrograph for the sample BIV: 25x (a); 1100x (b) and 5500x (c)

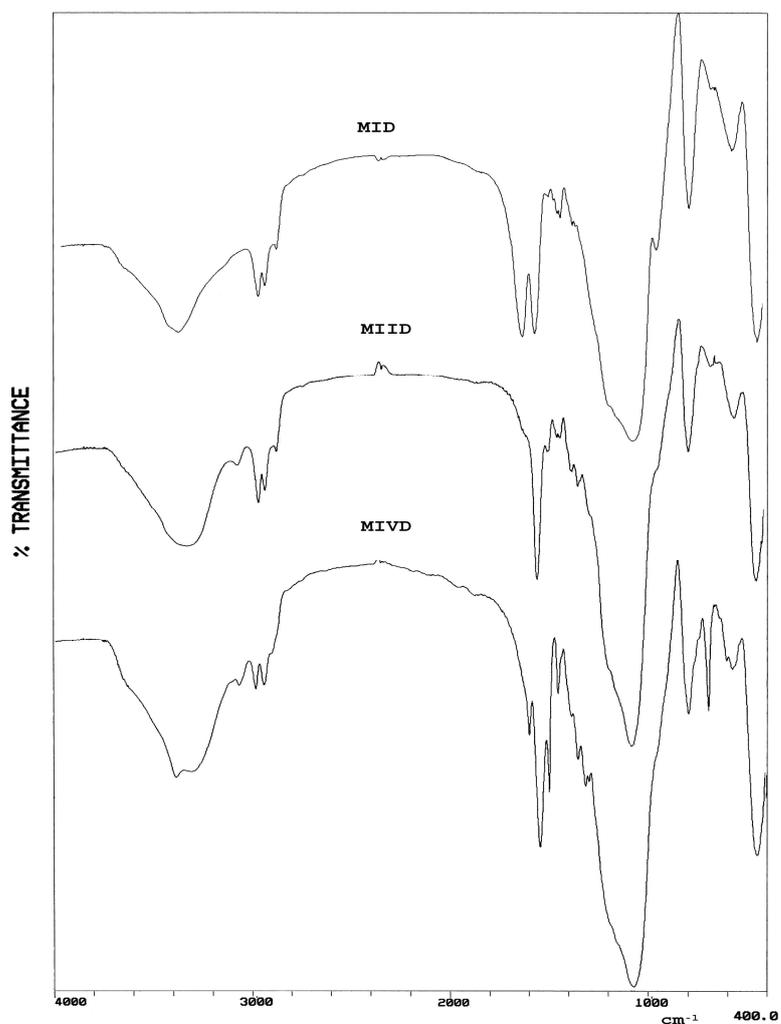


Fig. 2. IR spectra of MID; MIID; MIVD.

Table 1. Elemental analysis data and specific surface area of the obtained xerogels.

Xerogels abbreviations	Composition of reacting mixture and ratio of components	Elemental analysis data (wt.%)				C/N/S ratio	¹ C _{f.g.} mmol g ⁻¹	S _{sp.} m ² g ⁻¹
		C	H	N	S			
MI	TEOS/I (2:1)	24.74	5.02	7.54	-	7.6/2.0/-	2.9	<1
MID	TEOS/I (4:1)	18.53	3.37	5.16	-	8.4/2.0/-	1.9	
BI	TEOS/I/APTES (4:1:1)	14.93	3.26	5.31	-	9.8/3.0/-	1.3	
MII	TEOS/II (2:1)	24.64	4.68	7.49	9.19	7.1/1.9/1.0	3.2	
MIID	TEOS/II (4:1)	20.60	3.75	5.89	9.44	5.8/1.4/1.0	3.3	189
BII	TEOS/II/APTES (4:1:1)	18.96	4.01	6.33	2.67	19.0/5.4/1.0	0.9	109
BI/II	TEOS/I/II (4:1:1)	25.49	5.13	7.64	4.38	15.5/4.0/1.0	1.4	
MIV	TEOS/IV (2:1)	31.31	4.03	6.82	8.37	10.1/1.9/1.0	2.2	<1
MIVD	TEOS/IV (4:1)	24.64	3.15	5.21	6.51	10.1/1.8/1.0	2.9	175
MVID'	TEOS/IV (8:1)	17.22	2.23	3.38	1.96	23.5/3.9/1.0	0.6	276
BIV	TEOS/IV/APTES (4:1:1)	25.24	3.48	6.53	6.11	11.0/2.4/1.0	2.0	70
BIII/IV	TEOS/III/IV (4:1:1)	32.85	4.22	6.94	5.13	17.1/3.1/1.0	1.7	
MV	TEOS/V (2:1)	26.74	5.39	5.83	-	10.7/2.0/-	2.2	<1
MVD	TEOS/V (4:1)	14.44	3.38	4.53	-	7.4/2.0/-	1.7	
MVID	TEOS/VI (4:1)	15.67	3.65	4.41	7.02	6.0/1.4/1.0	2.4	
MVII	TEOS/VII (2:1)	32.03	3.43	9.03	7.16	11.9/2.9/1.0	2.4	
MVIID	TEOS/VII (4:1)	25.14	2.76	6.92	7.36	9.1/2.2/1.0	2.5	
BVII	TEOS/VII/TMPED(4:1:1)	27.58	4.36	9.65	5.61	13.2/3.9/1.0	1.9	

¹Concentration of functional group in mmol g⁻¹ (from elemental analysis data).

Table 2. Main absorption bands in IR spectra of synthesized xerogels (cm⁻¹) and their assignment.

Xerogel	v(NH)+v(OH)	v(CH)	v(CO)	v _{as} (NCN)	v(SiO)
MI	3373	2870, 2936, 2969	1636	1574	1072, 1134
MID	3380, 3440	2876, 2936, 2976	1639	1574	1077, 1164
BI	3303, 3362	2880, 2939, 2965	1639	1574	1059, 1144
MII	3283	2874, 2933, 2965	-	1559	1074, 1141
MIID	3327	2880, 2936, 2968	-	1558	1079, 1162
BII	3289, 3357	2877, 2939, 2965	-	1559	1064, 1141
BI/II	3323	2876, 2933, 2970	1653	1535	1070, 1125
MIV	3258	2873, 2932, 2965	-	1540	1128
MIVD	3301, 3383	2894, 2936, 2980	-	1543	1077, 1164
MVID'	3385	2896, 2941, 2992	-	1550	1075, 1160
BIV	3272	2879, 2933, 2965	-	1540	1070, 1145
BIII/IV	3316, 3385	2885, 2943, 2992	1665	1546	1051, 1133
MV	3371	2975, 2933, 2891	1652	1570	1074, 1102
MVD	3415	2895, 2933, 2985	1660	1580	1068
MVID	3384	2896, 2925, 2978	-	1567	1072
MVII	3267, 3360	2882, 2937, 2972	1683	1539	1070, 1130
MVIID	3271, 3365	2880, 2940, 2977	1684	1539	1075, 1140
BVII	3290, 3368	2880, 2940, 2980	1706	1548	1048, 1133

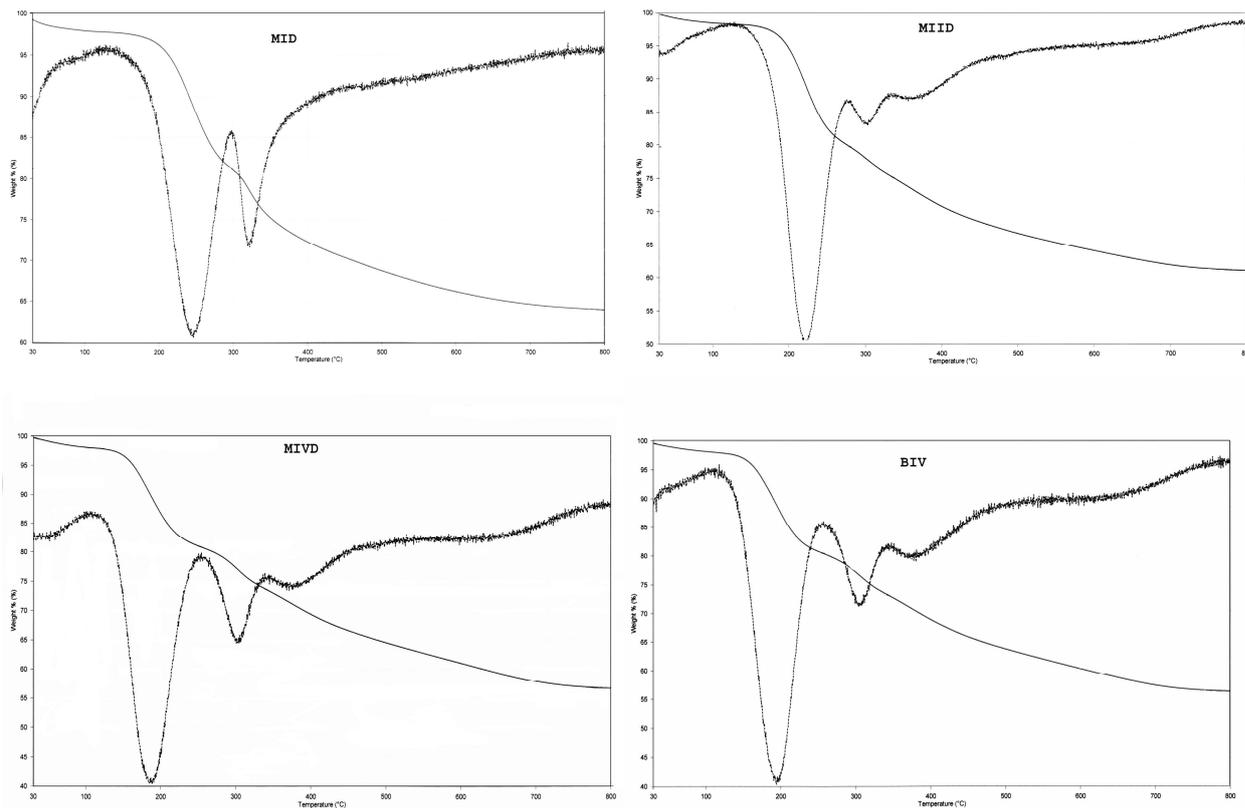


Fig. 3. Thermograms of MID, MIID, MIVD and BIV.

C : N : S ratio, calculated using elemental analysis data (Table 1), indicates that all the functional groups are incorporated on the surface of the xerogels. Their presence is confirmed by IR spectroscopy data. Table 2 shows the positions of main absorption bands, which were found in IR spectra and their assignment. The strong absorption bands in the range $1500-1700\text{ cm}^{-1}$ were useful for identification. IR spectra of all the xerogels show in the range $1000-1180\text{ cm}^{-1}$ the strongest absorption band (which usually compares with a shoulder on the left side of the band). The appearance of this band is typical of three-dimensional siloxane skeleton [17]. Fig. 2 shows IR spectra for some synthesized xerogels.

Xerogels, prepared from precursors with O-containing functional groups, display, as expected, more high thermal stability as compared with appropriate S-containing substances. In Fig. 3 some examples of thermograms are shown.

In Table 1 values of S_{sp} are represented. As expected, 2 : 1 system shows a low or very low specific surface area. S_{sp} is higher for 4 : 1 : 1 ternary and 4 : 1 binary systems. The highest value of S_{sp} is found for the 8 : 1 system.

Conclusions

By simple reaction new xerogel precursors were prepared and obtained in satisfactory yield and purity. By using these precursors in the sol-gel process we could obtain surface-functionalized xerogel with the desired silicon/function ratio and relative composition. Their properties will be investigated in the field of metal-sorption and metal hybrid catalysis, trying to relate them to their surface composition and structure.

Acknowledgement

Financial support for Yu.L. Zub by CNR-NATO is gratefully acknowledged.

References

1. Voronkov M.G., Vlasova N.N., and Pozhidaev Yu.N. Organosilicon ion-exchange and complexing adsorbents // *Appl. Organomet. Chem.* – 2000. – V.14. – P.287-303.
2. Zaitsev V.N. *Complexing Silicas: Synthesis, Structure of Bonded Layer and Surface Chemistry* - Khar'kov: Folio, 1997. – 240 p. (in Russian).
Kholin Yu.V. and Zaitsev V.N. Complexes on a Surface of Chemically Modified Silicas. – Khar'kov: Folio, 1997. – 136 p. (in Russian).
3. Trokhymchuk A.K. and Yanovs'ka E.C. Complexation of Pt(IV) at the surface of silica with sulfur-containing ligands immobilized at silica // *Ukr. Khim. Zh.* – 2000. – V.66, N4. – P. 67-71.
4. Voronkov M.G., Vlasova N.N., and Pozhidaev Yu.N. Organosilicon ion-exchange and complexing adsorbents // *Zh. Prikl. Khimii.* – 1996. – V.69, N5. – P.705-7183.
5. Brunauer J.S., Emmet P.H., and Teller E. Adsorption of gases in multimolecular layers // *J. Amer. Chem. Soc.* – 1938. – V.60. – P.309-319.
6. Yamamoto T., Sugiyama S., Akimoto K., and Hayashi K. One-pot synthesis of isothiocyanates from primary amines synthesis using cyanamide // *Org. Prep. Proc. Int.* – 1982. – V.24. – P.364-369.
7. Ferrari C., Predieri G., Tiripicchio A., and Costa M. Anchoring metal species on a thiourea-functionalized silica xerogel. In situ production of colloidal palladium particles // *Chem. Mater.* – 1992. – V.4. – P.243-245.
8. Gilkey J.U. and Kraenke R.E. Bis-silylureas and their copolymers // *Patent of USA N3208971.* – 1965.
9. Vlasova N.N., Pestunovich A.E., and Voronkov M.G. N,N'-Bis(3-trialkoxysilylpropyl)- and N,N'-bis(3-trialkoxysilylpropyl) of thiourea // *Izv. AN SSSR. Ser. Khim.* – 1979. – N9 – P.2105- 2107.
10. N,N'-Bis(3-silatranylpropyl)-Derivate von Harnstoff und Thioharnstoff / M.G.Voronkov, A.E.Pestunovich, T.I.Kositsyna, B.Z.Sterenber, T.A.Pusechkina, N.N.Vlasova // *Z. Chem.* – 1983. – Bd. 23, N7. – S. 248 – 249.
11. Voronkov M.G., Pestunovich A.E., Kositsina E.I., Shterenberg B.Z., Pushechkina T.A., and Vlasova N.N. N,N'-Bis(3-silatranylpropyl)derivatives of urea and thiourea // *Zh. Obshchei Khimii.* – 1984. – V.54, N5. – P.1098-1102.
12. Baigozhin A. Reaction 3-aminopropyltriethoxysilane with allyl- and phenylisothiocyanates // *Zh. Obshchei Khimii.* – 1972. – V.43, N6. – P.1408.
13. Lin-Vien D., Colthup N.B., Fateley W.G., and Grassely J.G. *The Handbook of Infrared and Raman Characteristic Frequencies of Organic Molecules.* – San Diego, CA: Academic Press, 1991. – 504 p.
14. Jensen K.A. and Nielsen P.H. Infrared spectra of thioamides and selenoamides // *Acta Chem. Scand.* – 1966. - V.20. – P.597-629.
15. Zub Yu.L. and Parish R.V. Fuctionalized Polysiloxane Sorbents: Preparation, Structure, Properties and Use // *Stud. Surf. Sci. Catal.* – 1996. V.99. – P. 285-299.
16. Finn L.P. and Slinyakova I.B. Structure and thermal degradation of polyorganosiloxane xerogels as shown by IR-spectra // *Kolloid. Zh.* – 1975. – V.37, N4. - P.723-729.