






# Modification conditions of poly-3-(2-aminoethylamino)propylsilsesquioxane with sulfur-containing groups as an instrument for influencing silver(I) sorption from multicomponent solutions

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## Abstract

The effect of modification conditions of poly-3-(2-aminoethylamino)propylsilsesquioxane with ammonium thiocyanate was studied. The possibility of varying the sorption properties of materials due to the formation of dithiobiuret or thiourea groups on the sorbent surface under certain conditions was established. The synthesized sorbents have high selectivity for silver(I) at pH from 0 to 8. The use of thiourea sulfuric acid solutions as a desorbent allows for a total desorption rate of up to 90%. An isochronous study of the stability of the sorption properties of modified polysilsesquioxanes was carried out for the first time: the sorption properties are preserved for 5 years. Modified poly-3-(2-aminoethylamino)propylsilsesquioxanes can be used for the selective and quantitative extraction of silver(I).

## Key findings

- Modification conditions make it possible to vary the selective properties of the sorbent.
- The synthesized sorbents exhibit selective properties in a wide pH range from 0 to 8.
- The degree of desorption is 90%.
- The synthesized sorbents retain their properties for 5 years.

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## 1. Introduction

Many original articles are devoted to the sorption concentration of silver [1–3]. The relevance of developing methods for extracting silver is explained by the need to process secondary raw materials containing it (metal scrap, electronic waste, printed circuit boards). In comparison with the

development of ore deposits, recycling of secondary raw materials is characterized by low energy costs, produces a minimal amount of waste, and allows the disposal of various types of electronic waste [4–6]. Sorption provides efficient and cost-effective removal of metal ions among a variety of extraction methods [7]. Sulfur-containing ligands are characterized by the greatest affinity for silver(I). For

## Accompanying information

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### Supplementary information

Supplementary materials: [▶ READ](#)

Transparent peer review: [▶ READ](#)

### Sustainable Development Goals



example, the study [8] shows that the degree of silver extraction from nitrate solutions increases with increasing the number of donor sulfur atoms in one ligand molecule.

Currently, sorbents with a matrix modified with thiourea groups have a leading place among sorption materials for the sorption of silver(I) [9–10]. The main method for producing sorption materials is polymer-analogous transformations using commercially available polymers. The sorption properties of polymer organic membranes often deteriorate due to hard modification conditions. So the use of inorganic membranes in some cases is much more rational due to their high chemical and radiation resistance [12]. Another advantage of matrices of this type is their swelling resistance and mechanical strength, which allows them to be used in high-performance liquid chromatography [13]. Polysilsesquioxane is a promising matrix for the production of sorbents, since it provides high stability and high porosity of the sorbent [14]. In addition, methods for the synthesis of polysilsesquioxanes are simple and reproducible, and allow one to vary the physicochemical and structural adsorption characteristics of the sorption material [15].

Polysilsesquioxane is an organosilicon hybrid material consisting of a siloxane network with functional organic groups covalently bonded to silicon atoms. Over the past 10 years, the field of sorbents based on polysilsesquioxane synthesis has been actively developing. Table S1 (Supplementary) shows sorbents that exhibit selective properties to silver(I).

Since sulfur atoms have unpaired pair of electrons, according to the theory of hard and soft acids and bases, they are soft bases. This contributes to their interaction with soft acids, which include silver(I), even in highly acidic environments, which is a great advantage in practical application. However, in order to use sorbents based on polysilsesquioxane to concentrate silver ions from electronic waste, it is necessary to evaluate the selectivity of the sorbent to silver(I) from multicomponent solutions, which has been studied only in a few works.

The sorption properties of thiocarbamoylated poly-3-aminopropylsilsesquioxane were previously investigated [16]. It was established that this sorbent exhibits selectivity for silver(I), but calcium(II), iron(III) and copper(II) have a certain interfering effect on its sorption. It is assumed that the selective properties of this sorbent can be improved by introducing an ethylamine spacer between the thiourea group and the propyl radical due to an increase in the stability of the complex formed in the sorbent phase when it becomes possible to form an additional chelate ring involving donor nitrogen atoms. For example, proved that the introduction of an additional donor nitrogen atom and an ethyl fragment into the structure of surface groups has a significant effect on the sorption properties of the material. Takagi et al. [17] found that amine centers inhibit the diffusion of aqueous cationic pollutants when using aminopropyl radicals on a matrix. In order to weaken interactions around amine centers without losing the high density of

absorption centers, the authors proposed a method of mixing 3-aminopropyl and N-(aminoethyl)-3-aminopropyl groups. The work [18] established that polysilsesquioxane xerogels with ethyl spacer in the matrix structure have better structural adsorption characteristics than the corresponding polysiloxanes. The authors claim that the presence of ethyl spacer in the sorbent frame increases the stability of the sorbent.

The purpose of this work was to study the influence of the modification conditions of poly-3-(2-aminoethylamino)propylsilsesquioxane on its sorption properties silver during its sorption from multicomponent systems. In the future, the results obtained will be useful for the sorption concentration of silver ions from electronic waste, as well as in the synthesis of sorption materials with established properties.

## 2. Experimental Section

### 2.1. Reagents

AgNO<sub>3</sub>, Mg(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, Ca(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, Pb(NO<sub>3</sub>)<sub>2</sub>, Cd(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O, Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, Mn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O, Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, Fe(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O, NH<sub>4</sub>SCN, thiourea (c.p.); HNO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub>, CH<sub>3</sub>COOH, NH<sub>3</sub>·H<sub>2</sub>O (h.p.); N-(2-aminoethyl-3-aminopropyl) trimethoxysilane from AlfaAesar (98%, USA), tetraethoxysilane from AlfaAesar (98%, USA), ethanol from Constanta-Pharm M (95%, Russia).

### 2.2. Equipment

Deionized water was obtained using a Milli-Q Academic high purification system (Millipore, USA). The concentration of metal ions in solutions before and after sorption was determined by flame atomic absorption spectrometry using a Solaar M6 spectrometer (Thermo Scientific, USA). The acidity of solutions was controlled using an I 160MI ion meter with an ESK 10601/7 combined glass electrode (Measuring equipment, Russia). Mixing of the solutions was carried out using a RITM-01 magnetic stirrer (Measuring equipment, Russia). Accurate weighed amounts of reagents were selected using an Acculab analytical balance (Sartorius, Germany). The IR spectrum of the synthesized samples was obtained using an IR Fourier spectrometer with an attenuated total reflection attachment (Thermo Scientific, USA). Differential thermal analysis was carried out using a TGA/DSC 1 derivatograph (Mettler Toledo) at a heating rate of 10 °C/min in flowing air (60 cm<sup>3</sup>/min). The mass fraction of elements C, H and N was determined using an elemental analyzer CHN, model PE2400, series II (Perkin Elmer Instruments, USA) according to the corresponding measurement methods (Appendix). Micrographs of the sorbent were acquired using a SEM scanning electron microscope (ZEISS, Germany). The specific surface area values were obtained using Get 210–2019: State Primary Standard of Units of Specific Adsorption of Gases, Specific Surface Area of Pores, Specific Volume of Pores, Dimension of Pores, Open

Porosity, and Coefficient of Gas Permeability of Solid Substances and Fabricated Materials.

### 2.3. Synthesis of PS1

24.96 g (0.12 mol) of tetraethoxysilane and 11.40 g (0.06 mol) of N-(2-aminoethyl-3-aminopropyl)trimethoxysilane were mixed using a magnetic stirrer, and 5.94 g (0.33 mol) of water was added to the water-ice mixture while cooling. The mixture was left for 12 hours, ground and dried at 100 °C for 24 hours. The obtained gel was washed with water and dried again at 100 °C to constant weight. PS1 product weight is 12.87 g.

### 2.4. Synthesis of PS1-D1, PS1-D2, PS1-D3

PS1 was thoroughly ground with ammonium thiocyanate (see Table 1). The mixture was kept for 2 h s at a temperature of 150 °C, cooled, and washed with water and ethanol. The product was dried to constant weight at room temperature.

### 2.5. Synthesis of PS1-D4, PS1-D5

2.00 g (5.70 mmol) of PS1 was uniformly impregnated in 0.65 cm<sup>3</sup> (11.40 mmol) of water (PS1-D4) or acetic acid (PS1-D5) and thoroughly ground with 1.30 g (17.10 mmol) of ammonium thiocyanate. The mixture was kept for 2 hours at a temperature of 150 °C, cooled and washed with water 10 times in portions of 40 cm<sup>3</sup> and once with ethanol in portions of 40 cm<sup>3</sup>. The precipitate was dried to constant weight at room temperature. The product was additionally washed 6 times with water in portions of 50 cm<sup>3</sup> and dried to constant weight at room temperature. PS1-D4 product weight is 1.51 g; PS1-D5 product weight is 1.25 g.

### 2.6. Preparation of model solutions

Solutions containing metal ions ( $C_{mMe} = 1 \cdot 10^{-4}$  mol/dm<sup>3</sup>;  $C_{mMe} = 4 \cdot 10^{-4}$  mol/dm<sup>3</sup>) were prepared by dissolving the corresponding salts in deionized water. The acidity of the medium was created using nitric acid (up to pH 2) and ammonium acetate buffer solution (pH from 3 to 10). Pb<sup>2+</sup> и Fe<sup>3+</sup> were not introduced into solutions with a pH above 7 to prevent the formation of poorly soluble compounds due to hydrolysis.

### 2.7. Static sorption investigation

50.0 cm<sup>3</sup> of a standardized test solution ( $C_{mMe} = 1 \cdot 10^{-4}$  mol/dm<sup>3</sup>) containing the metal salts under study was added to a sample of sorbent weighing 0.0100 g (grain diameter ( $d_{grain}$ ) less than 0.071 mm); the systems

were left with periodic stirring for 24 hours and then filtered. The concentration of components was determined, and the amount of sorbed metal ions per unit mass of sorbent ( $a$ , mmol/g) was calculated by the Equation 1:

$$a = \frac{V \cdot (C_0 - C)}{g \cdot M}, \quad (1)$$

where  $C_0$  and  $C$  are the concentration of the metal ion in the solution before and after sorption, respectively, mg/dm<sup>3</sup>;  $V$  is the volume of solution, dm<sup>3</sup>;  $g$  is the mass of the sorbent, g;  $M$  is the molar mass of the metal, g/mol.

The values of the selectivity factors were determined as the ratio of the corresponding distribution coefficients of metal ions between the solution and the sorbent. Determination of the concentration of metal ions with their joint presence in solutions before and after sorption was carried out using a Solaar M6 Atomic Absorption Spectrometer (AAS). Each experiment was repeated three times and the average of the three is reported. For the results of sorption in static condition, the error is less than 8%.

### 2.8. Dynamic sorption investigation

A sorbent weighing 0.1000 g ( $0.071 \text{ mm} < d_{grain} < 0.100 \text{ mm}$ ) was placed in a concentrating cartridge with a diameter of 0.5 cm. A standardized test solution was passed through the cartridge at a certain rate ( $C_{Ag+} = 1 \cdot 10^{-4}$  mol/dm<sup>3</sup>;  $C_{mMe} = 8 \cdot 10^{-4}$  mol/dm<sup>3</sup>). The filtrate was selected in portions of 15.0 cm<sup>3</sup> at the outlet of the cartridge, and the concentration of metal ions was determined. For the results of sorption in the dynamic condition, the error is less than 5%.

### 2.9. Methodology for isochronous study of the stability of sorption properties of modified polysilsesquioxanes

Samples of synthesized polysilsesquioxanes were separated into two parts. One of these (part 1) was stored at room temperature, the other (part 2) was stored at 120 °C in an oven for five hours. The sample was then removed from the oven. After cooling the sorbent, sorption was carried out in a static mode using a standardized test solution with pH 1.5 ( $C_{mMe} = 1 \cdot 10^{-4}$  mol/dm<sup>3</sup>). The remaining part of the sorption material was again placed in the oven at a given temperature and kept for five hours; this procedure was repeated 9 times.

**Table 1** Modification conditions of poly-3-(2-aminoethylamino)propylsilsesquioxane.

Sorbent	Reagent weights		Washing		Product weight, g
	Amount of PS1	Amount of ammonium thiocyanate	Water (1st stage)	Ethanol (2nd stage)	
PS1-D1	3.50 g (9.92 mmol)	1.51 g (19.80 mmol)	The dried precipitate was washed 6 times in portions of 35 cm <sup>3</sup>	1 time in portions of 35 cm <sup>3</sup>	4.64
PS1-D2	10.00 g (27.80 mmol)	8.46 g (111.10 mmol)	The dried precipitate was washed 9 times in portions of 100 cm <sup>3</sup>	1 time in portions of 100 cm <sup>3</sup>	13.52
PS1-D3	8.00 g (22.80 mmol)	5.20 g (68.40 mmol)	The dried precipitate was washed 11 times in portions of 100 cm <sup>3</sup>	1 time in portions of 100 cm <sup>3</sup>	8.27

The first part of the sorbent was stored for two years, and sorption was carried out periodically in a static mode using a standardized test solution with pH 1.5.

The duration of the stability study  $\tau$  at fixed storage temperatures is estimated by the Equation 2

$$\tau = \frac{T}{2^{\frac{t_1 - t_0}{10}}}, \quad (2)$$

where  $T$  is the expected shelf life of the material, h;  $t_0$ ,  $t_1$  are the storage temperature of the material and the storage temperature during accelerated aging, °C.

### 3. Results and Discussion

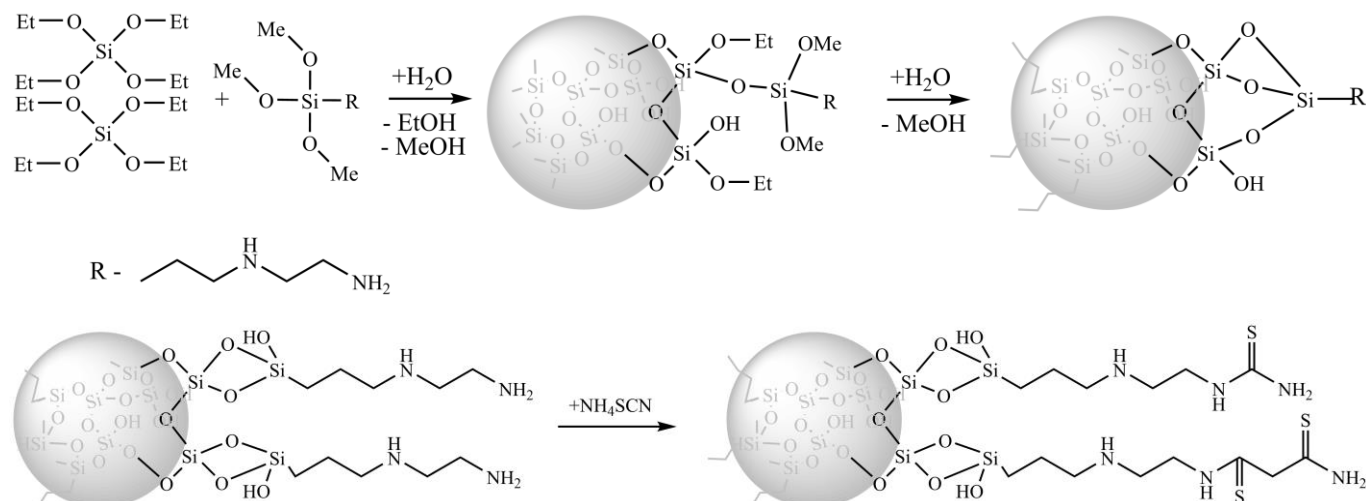
#### 3.1. Research object and its synthesis

A series of modified polysilsesquioxanes was obtained by functionalizing the hydrolytic polycondensation product of tetraethoxysilane with N-(2-aminoethyl-3-aminopropyl)trimethoxysilane in the presence of ammonium thiocyanate, as illustrated in Figure 1. The synthesis conditions for the sorbents are summarized in Table 1. Hydrolytic copolycondensation of tetraethoxysilane with N-(2-aminoethyl-3-aminopropyl)trimethoxysilane in the presence of water resulted in the formation of a polysilsesquioxane framework bearing aminoethylaminopropyl groups on the surface. At the stage of polysilsesquioxane network formation, the aminoethylaminopropyl groups are introduced predominantly onto the particle surface due to differences in the hydrolysis rates of the silane precursors [19]. All

obtained sorbents are fine powders composed of non-spherical particles with colors ranging from light yellow to bright orange.

Figure S1 (Supplementary) and Table 3 show the IR spectra of poly-3-(2-aminoethylamino)propylsilsesquioxane before and after its modification. The bands in the range of 440–1300  $\text{cm}^{-1}$  are present in all samples and correspond to the deformation vibrations of the Si–O bond, symmetric stretching vibrations of the Si–O bond, characteristic bands of the polysilsesquioxane framework of the matrix, stretching vibrations of the Si–OH bond, stretching vibrations of the Si–O–Si bond [20, 21]. Although these bands are preserved in all sorbents, which indicates the preservation of the polysilsesquioxane structure of the matrix, the shifts and changes in the band intensity in the samples after modification are observed. This confirms minor changes in the structure of silsesquioxanes and an increase in the number of hydroxyl groups on the surface of the matrix. Also, in the PS1-D5 sample, broadening of the bands at 557  $\text{cm}^{-1}$  and 691  $\text{cm}^{-1}$  is observed, which is explained by slight destruction of the structure in an acidic medium.

The broadening of the band corresponding to the Si–O–Si stretching vibrations is due to its overlap with the characteristic absorption band of the C=S bond at 1143  $\text{cm}^{-1}$ , which is consistent with the incorporation of thiourea groups. The appearance of the band at 2052–2057  $\text{cm}^{-1}$  is attributed to the equilibrium isomerization of thiourea groups to thiocyanate fragments.



**Figure 1** Scheme for the synthesis of thiocarbamoylated poly-3-(2-aminoethylamino)propylsilsesquioxane.

**Table 2** Results of elemental analysis of poly-3-(2-aminoethylamino)propylsilsesquioxane samples before and after modification.

Sorbent	Theoretical mass fraction of element, %					Elemental analysis data, %				
	C	H	N	Si	S	C	H	N	Si	S
PS1	17.68	4.27	7.94	31.63	-	17.67	4.24	7.94	31.63	-
PS1-D1	17.65	3.52	10.23	24.69	11.43	17.70	3.54	10.26	24.90	11.46
PS1-D2	16.55	4.11	10.62	24.04	11.04	16.53	4.11	10.62	24.04	11.05
PS1-D3	20.42	3.65	10.96	26.74	11.10	20.67	4.21	11.20	27.33	11.34
PS1-D4	19.06	4.01	12.11	22.91	12.78	19.09	4.18	12.14	22.96	12.81
PS1-D5	20.25	4.47	10.89	23.25	10.19	20.19	4.22	10.86	23.19	10.16

**Table 3** IR spectra data of poly-3-(2-aminoethylamino)propylsilsesquioxane samples before and after modification.

Assignment	PS1	PS1-D1	PS1-D2	PS1-D3	PS1-D4	PS1-D5
st (-OH)						
			~3500–2750 m.br			
st (N-H)	3367 w.	3289 w.	3293 w.	3289 w.	3300 w.	3305 w.
st (N-H)	3285 w.	3189 w.	3188 w.	3185 w.	3176 w.	3185 w.
st (C-H)	2935 w.	2943 w.	2957 w.	2934 w.	2934 w.	3076 w.
as (C-H)	2879 w.	2885 w.	2809 w.	2788 w.	2810 w.	2924 w.
st (SCN <sup>-</sup> )		2052 s.	2052 s.	2055 s.	2056 s.	2057 s.
$\delta$ as (NH <sub>3</sub> <sup>+</sup> )	1652 w.	1668 sh.	1669 sh.	1664 sh.	1664 sh.	
st (C-N)		1615 w.	1613 m.	1614 m.	1614 m.	1617 m.
$\delta$ (N-H)	1598 sh.	1557 w.		1552 w.	1554 w.	1556 w.
st (C-N)		1517 w.	1520 w.	1520 w.	1521 w.	
$\delta$ (C-H)	1460 w.br.	1455 w.	1464 m.	1453 m.	1450 m.	1452 m.
$\delta$ (C-H)	1412 v.w.	1410 sh.	1413 sh.	1410 sh.	1413 sh.	
r (NH <sub>2</sub> )	1354 v.w.	1354 m.	1359 m.	1354 m.	1357 m.	1369 m.
st (C=S)	1143 sh.	1143 sh.	1143 sh.	1143 sh.	1143 sh.	1143 sh.
st (Si-O-Si)	1037 v.s.br.	1046 v.s.br.	1060 s.br.	1069 v.s.br.	1080 v.s.br.	1077 v.s.br.
st (Si-OH)	945 sh.	954 sh.	957 sh.	946 sh.	946 sh.	949 m.
sy (Si-O)	783 m.	791 m.	792 m.	794 m.	793 m.	795 m.
		694 sh.	692 w.	693 w.	692 w.	690 w.
$\gamma$ (Si-O-Si)	568 w.br.	562 w.br.	566 w.br.	558 w. br.	544 w.br.	557 w.br.
$\delta$ (Si-O)	447 s.	444 s.	453 s.	460 s.	449 s.	447 s.

Note: w. = weak, m. =medium, s. = strong, v. = very, sh. = shoulder, br. = broad.

Thus, this band does not indicate the presence of free ammonium thiocyanate but rather confirms the existence of -C(S)-NH<sub>2</sub>-containing moieties in the polysilsesquioxane structure, which arise from the isomerization of thiourea units [22].

The absorption band at 1652–1669 cm<sup>-1</sup> corresponds to the asymmetric deformation vibrations of NH<sub>3</sub><sup>+</sup> ions formed in small quantities on the surface. Shifts and changes in the intensity of the absorption bands corresponding to symmetric and asymmetric stretching vibrations and asymmetric deformation vibrations of the C-H bonds confirm the formation of propylene and ethylene groups on the matrix [23].

The shift in the absorption bands of stretching vibrations of amino groups at 3367 cm<sup>-1</sup> and 3285 cm<sup>-1</sup> indicates a change in amino groups from aminoethyl to more electron-saturated amine-containing groups during the modification process. The appearance of absorption bands in the products PS1-D1–PS1-D5 at 1614–1617 cm<sup>-1</sup> and 1517–1520 cm<sup>-1</sup> corresponding to various amine and thioamide groups, and a change in the ratio of these bands in the products indicates the formation of thiourea and dithiobiuret groups [23]. The permamency of the band at 1552–1557 cm<sup>-1</sup> corresponding to N-H vibrations in

the spectra before and after modification of PS1 indicates the interaction of ammonium thiocyanate with the primary amino group.

Based on the results of elemental analysis of the samples (Table 2), the proportions of sulfur-containing groups formed on the sorbents as well as the total concentration of sulfur-containing groups (Table 4) were calculated. Differences in the results of elemental analysis and theoretical values are explained by sorption of water and carbon dioxide on the surface of the samples.

An increase in the fraction of the inorganic matrix by 14.2–18.4% relative to aminoethylaminopropyl polysilsesquioxane is recorded from the ratio of the polysilsesquioxane matrix to the organic radical (Z) in samples PS1-D1–PS1-D3 obtained under solid-phase synthesis conditions. These changes are possible due to the thermal remove of aminoethylaminopropyl groups weakly bound to the surface during prolonged heating (2 hours) at a temperature of 150 °C under conditions of solid-phase modification with ammonium thiocyanate. Losses of the organic component are practically not observed in samples PS1-D4, PS1-D5 obtained using an aqueous medium.

**Table 4** Characteristics of samples of thiocarbamoylated poly-3-(2-aminoethylamino)propylsilsesquioxanes.

Sorbent	Proportion of thiourea groups (X), %	Proportion of dithiobiuret groups (Y), %	Ratio (SiO <sub>1/5</sub> ):R (Z)	Total concentration of sulfur-containing groups, mmol/g	Specific surface area, m <sup>2</sup> /g
PS1-D1	9.4	90.6	4.7	1.88	1.84
PS1-D2	33.4	66.6	4.1	2.07	1.32
PS1-D3	41.4	58.6	4.4	2.23	0.97
PS1-D4	29.0	71.0	3.5	2.34	0.95
PS1-D5	61.8	38.2	3.6	2.29	0.94

The formation of predominantly dithiobiuret groups with equimolar loadings of nitrogen and ammonium thiocyanate is explained by the greater reactivity of the primary amino group as well as a steric factor that hinders interaction with the aminopropyl group. An increase in the proportion of thiourea groups when using excess thiocyanate is possible due to the competing reaction of isomerization of excess ammonium thiocyanate into thiourea with its subsequent thermal decomposition [24].

There were no significant differences in the process of thermal decomposition of samples PS1 and PS1-D1 according to thermogravimetric and differential thermal analysis (Figure 2), which confirms the stability of the inorganic matrix after modification of the organic component. Primary weight loss (about 5%) occurs in the range of 30–115 °C for both samples; this is explained by the desorption of carbon dioxide and water from the surface of the matrix. The main destruction takes place in the range of 225–550 °C, followed by complete decomposition at 550–700 °C, which corresponds to the decomposition of aminoethylaminopropyl fragments and sintering of the matrix. The destruction of the PS1-D1 sample in the range of 225–550 °C occurs with a greater mass loss in several steps, which indicates a different structure of organic radicals on the surface of the sorbent.

To characterize the textural properties of sorbents, their micrographs were obtained at different magnifications, and the specific surface area values were determined (Table 4). Micrographs of the PS1-D1 sample are shown in Figure 3.

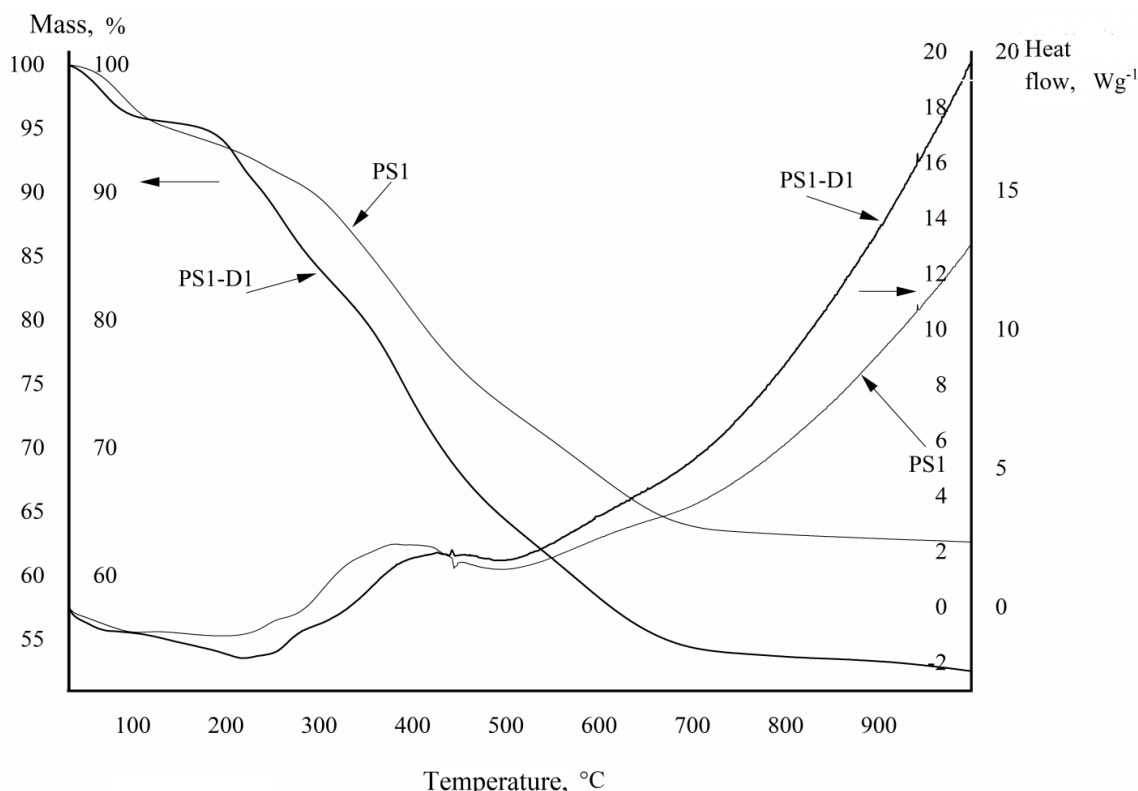
It was found that the sorbent particles are irregular in shape. The materials are non-porous and have a relatively

small specific surface area (Table 4). According to the literature data [25] this should contribute to the sorption of silver(I).

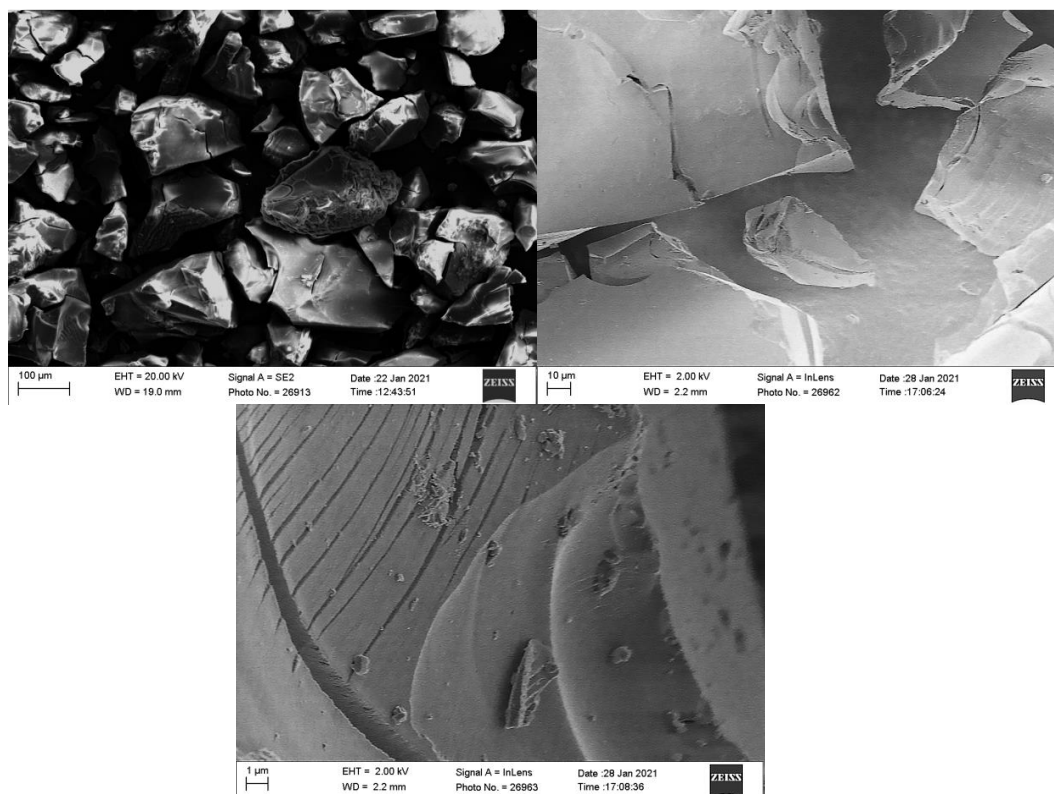
Based on IR spectroscopy, thermogravimetric and elemental analysis data, the structure of the sorbents was proposed (see Figure 4).

Sorption materials based on melamine-formaldehyde-thiourea resin [26] for the sorption of palladium(II) and hyperbranched polyacrylonitrile [27] for the sorption of gold(III) modified with thiourea fragments with a total concentration of functional groups from 1 to 3.28 mmol/g are known in literature. A high degree of modification in the above works could be achieved due to the use of materials with a hyperbranched structure, which include resins, since the contact area of the modifier reagent with the surface of the material increases. In addition, there is a high probability of embedding a modifier into the internal structure of the sorbent, which will complicate the possibility of sorption.

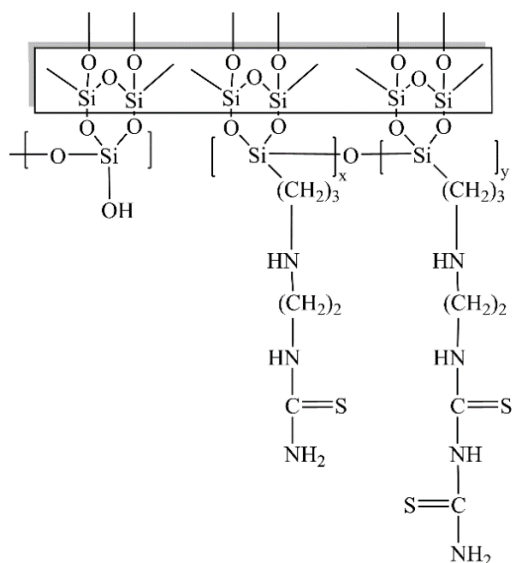
Combining the “sol-gel” method with subsequent modification makes it possible to obtain organic-inorganic sorbents in which the concentration of grafted sulfur-containing groups is currently considered to be quite high. The great advantage of this method for producing sorption materials is the ability to vary the concentration of modifier groups, since it determines the sorption capacity of the resulting sorbent. The use of the sol-gel technique in the synthesis of the intermediate product PS1 leads to the production of a material with a highly developed surface, which ensures a high concentration of thio-containing fragments in the final product.



**Figure 2** Thermograms of poly-3-(2-aminoethyl amino)propyl silsesquioxane before and after modification.



**Figure 3** Micrographs of the PS1-D1 sample.



**Figure 4** Functional groups on the surface of thiocarbamoylated poly-3-(2-aminoethylamino)propylsilsesquioxane.

### 3.2. Study of the selective properties of sorbents under static conditions



The mass fraction of silver in printed circuit boards and electronic waste is estimated to be around 0.008–0.035% and 0.2%, respectively [28–30]. Other metals included in the recyclable materials (copper, nickel, cobalt, cadmium, zinc, etc.) are present in excess or in equimolar quantities and in some cases have a significant interfering effect in the process of silver concentration [9, 31]. Therefore, the study of the selective properties of the synthesized sorbents in relation to  $\text{Ag}^+$  was carried out by sorption from a solution

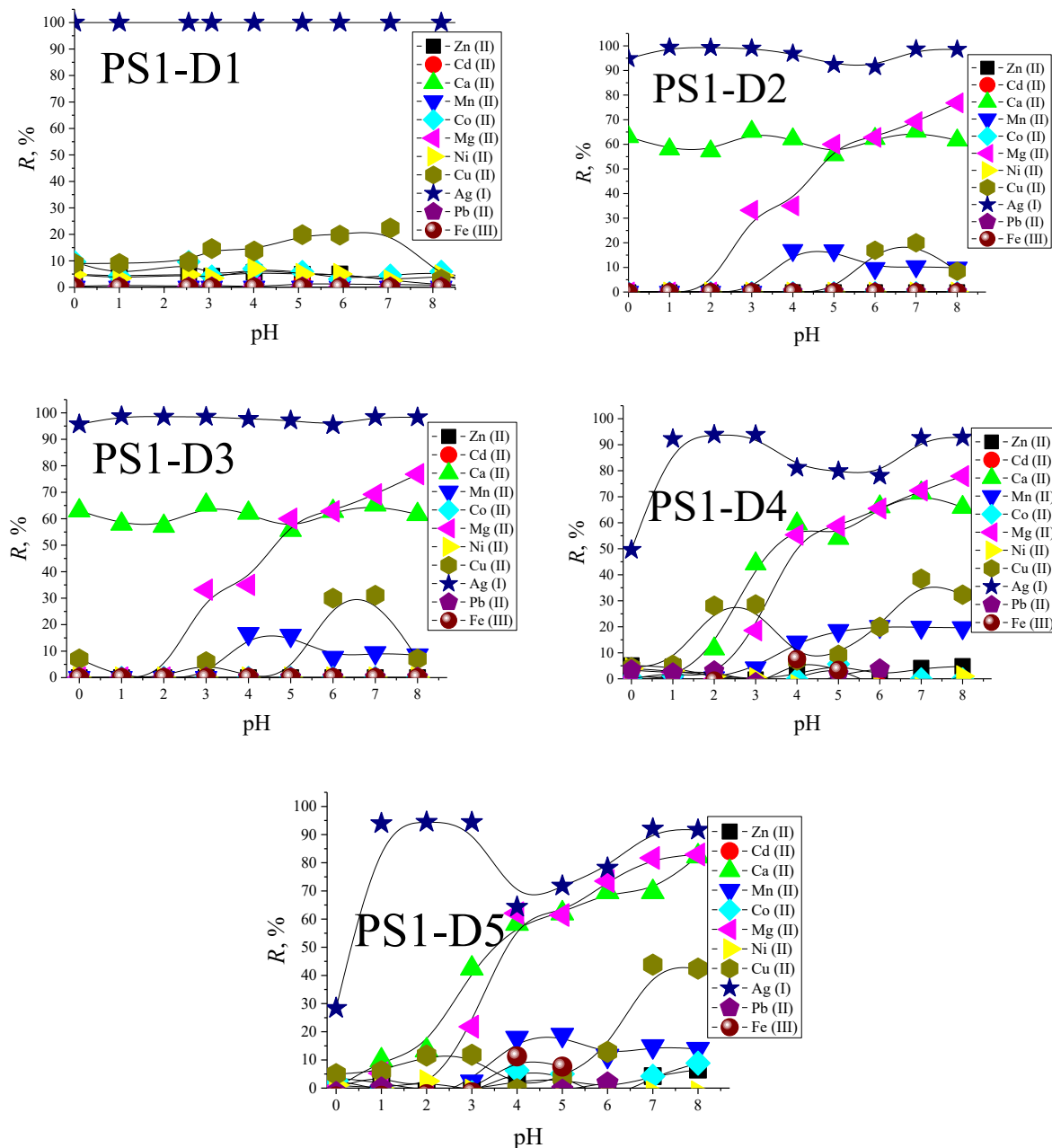
containing  $\text{Fe}^{3+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Zn}^{2+}$ . This composition of the model solutions was selected based on the composition of commercially available radio components from which silver extraction can potentially be realized(I) (Table 5).

The obtained dependences of the sorption of metal ions on the pH value of the model solution to sorbents are presented in Figure 5.

All the synthesized sorbents extract silver(I). The highest values of the degree of extraction (90% or more) of this ion are observed in the pH range from 0 to 8 for sorbents PS1-D1, PS1-D2 and PS1-D3. Quantitative extraction on these sorbents is realized in a narrower pH range from 3 to 7 with an increase in the concentration of silver(I) to  $4 \cdot 10^{-4} \text{ mol/dm}^3$  against the background of accompanying metal ions ( $C_{\text{mMe}} = 1 \cdot 10^{-4} \text{ mol/dm}^3$ ).

**Table 5** Composition of some radio components containing silver.

Object	Appearance of the radio component	Metal	Mass fraction of metal, %
Contact from the switch (relay)		Ag	32
		Cu	52
		Pb	10
		Mn, Fe, Co, Ni	<3
Capacitors		Ag	2.5
		Cu	54
		Pb	30
		Fe, Co, Ca	<1



**Figure 5** Effect of the pH of the solution on the sorption of metal ions on sorbents.  $g_{\text{sorbent}} = 0.0100 \text{ g}$ ;  $V_{\text{model solution}} = 0.05 \text{ dm}^3$ ,  $d_{\text{grain}} < 0.071 \text{ mm}$ ;  $C_{\text{mMe}} = 1 \cdot 10^{-4} \text{ mol/dm}^3$ .

The selective properties of sorbents are largely determined by the ratio of the amounts of thiourea and dithiobiuret groups, and, consequently, by the synthesis conditions. Thus, sorbents PS1-D3 and PS1-D2 with similar contents of thiourea and dithiobiuret groups (Table 4) are characterized by similar dependences of the sorption of metal ions on pH (Figure 5). These materials, in addition to silver(I), are capable of sorbing calcium(II) and magnesium(II) (extraction degree 30–70%) in a wide pH range. However, the sorption of these ions on PS1-D2 and PS1-D3 does not lead to a decrease in the sorption of silver(I), which means that the sorption centers in the case of calcium(II) and magnesium(II) are –OH groups. There is a slight uptake of manganese(II) and copper(II) at pH 4–8 (the degree of extraction does not exceed 15%) for sorbents PS1-D2 and PS1-D3, which also indicates the presence of free sulfur-containing

groups that begin to sorb manganese and copper ions in absence of silver ions and with insignificant influence of protons. Thus, polysilsesquioxane modified with thiol groups is also capable to extracting manganese(II) and mercury(II) in a weakly acid medium [32]. Sorption of copper(II) does not occur in an acid medium, which can be explained by the lower stability of thiourea complexes of copper compared to thiourea complexes of silver.

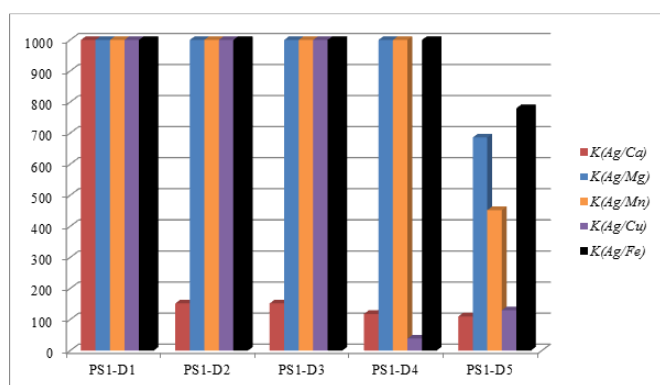
Some general patterns can be identified in the behavior of sorbents PS1-D4 and PS1-D5, the modification of which was carried out by prior soaking PS1 in water or acetic acid, respectively. These materials are characterized, on the one hand, by a slight decrease in the sorption of silver(I) at pH > 3 up to 65%, and on the other, by an increase in the sorption of copper(II).

The highest content of dithiobiuret groups (90%) is characterized by PS1-D1 obtained by solid-phase modification with an aminopolymer to modifier ratio of 1:2. This sorbent provides quantitative and highly selective sorption of silver(I) over a wide pH range. PS1-D1 extracts copper(II) ions, but the degree of their extraction does not exceed 22% at pH 5-7.

Figure 6 shows the selectivity coefficients for the sorption of silver(I) by the studied sorbents. Thus, the most selective sorbent with respect to silver(I) is PS1-D1, the synthesis of which involves solid-phase modification at a "modifier to aminopolymer" ratio of 1:2. When the amount of modifier increases against the background of a constant amount of amino polymer, the selective properties of the sorbent sharply decrease, and the modification in the presence of weak Bronsted acids negatively affects both the selective properties and the degree of silver(I) extraction.

Thus modified polysilsesquioxanes are characterized by greater sorption selectivity compared to poly(N-thiocarbamoyl-3-aminopropylsilsesquioxanes) in this work [33]. The increase in the selectivity of silver(I) sorption can be associated, firstly, with the presence of dithiobiuret groups on the surface of the sorbents under study, and secondly, with less steric hindrance during complex formation due to the presence of an ethylamine spacer in the sorbents.

The high selectivity of the studied materials (especially PS1-D1) can be explained as follows: according to the Pearson classification, silver belongs to the so-called "soft acids". Therefore, it exhibits affinity for ligands representing "soft bases" (sulfur-containing ligands). Thus, the coordination of silver with donor sulfur atoms in the composition of the sorbent functional groups is most likely. If there is a significant predominance of dithiobiuret groups in the composition of the material and their sufficiently dense distribution along the polymer chain, it becomes possible to form complexes with 4 sulfur atoms (2 atoms each of neighboring dithiobiuret groups). The formation of such a complex (with a silver coordination number of 4) makes it difficult for functional groups to interact with ions of other metals, which leads to increased sorption selectivity compared with sorbents with a lower content of dithiobiuret groups.



**Figure 6** Values of selectivity coefficients of synthesized sorbents. pH = 2,  $g_{\text{sorbent}} = 0.0100$  g;  $d_{\text{grain}} < 0.071$  mm;  $C_{\text{mMe}} = 1 \cdot 10^{-4}$  mol/dm<sup>3</sup>.

It was found that the introduction of an aminopropyl linker into the structure of polysilsesquioxane promotes the formation of mono and disubstituted thiourea groups on the sorbent surface, and the presence of an aminoethylaminopropyl linker promotes dithiobiuretic and thiourea groups. Both types of functional groups exhibit high affinity for noble metal ions, but sorbents with dithiobiuretic groups have the highest sorption capacity.

In the experiment, a sharp darkening of the sorbent was observed after sorption in a static mode at pH > 4 after two days of keeping the sorbent in a model solution. In the literature, this phenomenon is attributed to the reduction of Ag<sup>+</sup> to the metallic state or the formation of Ag<sub>2</sub>S on the surface of the sorbent [34].

It was established that maximum silver recovery is achieved over a wide acidity range. However, for further research, we selected the pH 1-2 range. The use of such a pH value for sorption is preferable not only from the point of view of a high degree of silver extraction, but also from the point of view of high selectivity of sorption (absence of interfering influence from base metal ions). The acidity of solutions obtained by dissolving real objects (including secondary raw materials) often corresponds to a pH of 1.0-2.0. Sorption at these acidity values eliminates the need to add additional reagents after the sample is dissolved. Therefore, a pH value of 1.5, which excludes the occurrence of redox processes with the participation of silver(I) and corresponds to the high selectivity of sorption of these ions, was selected for further studies of the properties of sorbents in a dynamic investigation.

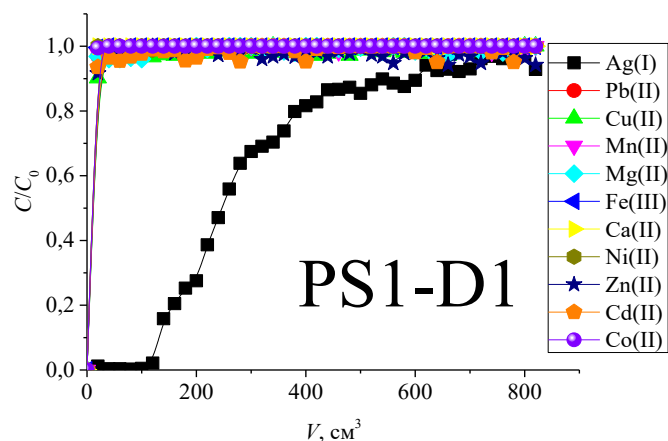
In most previously published works the effect of accompanying metal ions on silver(I) sorption was not studied (Table S2, Supplementary).

### 3.3. Sorption in dynamic investigation

According to literature data [35], the dynamic version of sorption is most often realized at a solution transmission rate through the sorbent layer of 2-15 cm<sup>3</sup>/min; this rate directly affects the efficiency of the sorption process. A low transmission rate promotes a higher degree of extraction of components from the mixture, but a decrease in the rate increases the time required for sorption. A solution transmission rate of 2 cm<sup>3</sup>/min was chosen to obtain dynamic output curves for the sorption of metal ions by the studied sorbents at pH 1.5.

It was not possible to obtain the output sorption curves for sorbents PS1-D4 and PS1-D5, since the diameter of the sorbent particles is smaller than the pore diameter of the filter, which leads to clogging of the cartridge filter after passing the first portion of the solution and the passage of sorbent particles through the cellulose membrane.

Figure 7 shows the output sorption curves of metal ions PS1-D1. The dependences obtained for sorbents PS1-D2 and PS1-D3 have a similar form. Sorption of base metal ions in the dynamic mode is not realized. This indicates the high affinity of the synthesized sorbents for silver(I), which suggests the selective extraction of silver ions from a multi-component solution.



**Figure 7** Output sorption curves of metal ions on samples PS1-D1, PS1-D2, PS1-D3. pH = 1.5;  $C_{\text{Me}} = 1 \cdot 10^{-4}$  mol/dm<sup>3</sup>;  $g_{\text{sorbent}} = 0.1000$  g;  $0.071 < d_{\text{grain}} < 0.1$  mm; solution transmission rate – 2 cm<sup>3</sup>/min.

Quantitative extraction of silver ions is observed in the initial section of the output curves of silver(I) sorption (Figure 7). The calculated values of the dynamic capacity before breakthrough and the total dynamic capacity of the sorbents for silver(I) are given in Table 6.

The dependence of the change in the sorption properties of sorbents on the ratios of reagents during modification has been established based on the results obtained. An increase in the total dynamic sorption capacity occurs with an increase in the amount of modifier, while the dynamic sorption capacity before breakthrough decreases, which can be explained by the interaction of silver ions with various types of surface sulfur-containing groups. It is possible that the formation of the complex in the case of dithiobiuret groups occurs faster, as evidenced by the high value of the dynamic sorption capacity before breakthrough for PS1-D1, in which the proportion of dithiobiuret groups is about 90%. The capacity to breakthrough also decreases with a decrease in the proportion of dithiobiuret groups, while with an increase in the total concentration of sulfur-containing groups; the value of the total dynamic sorption capacity increases.

Sorbents PS1-D1, PS1-D2, and PS1-D3 allow quantitative extraction of silver(I) at pH 1.5 and can be recommended for developing methods for selective and quantitative extraction from multicomponent solutions.

Comparison of the kind of sorption in static and dynamic investigations makes it possible to find the following differences: in the cases of PS1-D2 and PS1-D3 (Figure 5), calcium ions are extracted in addition to silver ions in the static mode, since an equilibrium is established between the components of the solution and the sorbent in static mode due to the long phase contact time.

The absence of sorption of silver ions in a dynamic investigation confirms the higher affinity of the grafted sulfur-containing groups to the noble metal ion and the high rate of interaction of ions with them, because of which the selective extraction of silver ions from multicomponent solutions is realized.

**Table 6** Dynamic sorption capacities of sorbents.

Sorbent	Dynamic sorption capacity before breakthrough, mmol/g	Total dynamic sorption capacity, mmol/g
PS1-D1	0.120	0.170
PS1-D2	0.070	0.185
PS1-D3	0.056	0.244

### 3.4. Effect of solution transmission rate and excess of accompanying metal ions on the sorption of silver(I)

Sample PS1-D1, characterized by the highest selectivity of sorption under static conditions, was selected for further optimization of the conditions for the selective extraction of silver on sorbents. The influence of the solution transmission rate and the excess amount of accompanying metal ions on the sorption of silver was studied (Figure S1, Supplementary). When the transmission rate is increased to 4 cm<sup>3</sup>/min, silver ions are extracted quantitatively; the sorption capacity of PS1-D1 decreases with these changes, but the decrease in its value does not exceed 10%. When the solution flow rate is increased to 6 cm<sup>3</sup>/min, silver is not extracted quantitatively.

An increase in the concentration of accompanying metal ions to  $8 \cdot 10^{-4}$  mol/dm<sup>3</sup> does not affect the sorption of silver(I).

The results obtained allowed determining the permissible rate limit for transmitting the solution through the cartridge at which selective quantitative extraction of silver ions is realized: up to and including 4 cm<sup>3</sup>/min.

### 3.5. Desorption

Desorption of metal ions from the surface of polysilsesquioxane PS1-D1 was carried out immediately after the sorption stage in a dynamic mode. A prerequisite for choosing the composition of eluents was the presence of low-molecular ligands capable of binding silver ions into stable complexes. These include thiourea and thiocyanate ion [36, 37]. Cyanide ion is excluded from this list of ligands due to its toxicity. Eluents of one group (containing the same ligand) were transmitted through the sorbent sequentially one after another. The composition of the eluents and the results of the desorption study are given in Table 7.

It was found that the use of sulfuric acid solutions of ammonium thiocyanate as eluents does not provide quantitative desorption of silver(I): the total value of the degree of desorption after the transmission of three solutions with increasing concentrations of ammonium thiocyanate is 41%.

The total degree of desorption of silver(I) after transmitting through three sulfate solutions of thiourea reaches 90% (Table 7). However, establishing the feasibility of reusing the sorbent requires further research. Possible ways to increase the degree of desorption include altering the concentration gradient during desorption (varying the concentration of acid and thiourea) and performing desorption under heating.

**Table 7** Degree of desorption of silver ions by thiourea and thiocyanate solutions from the surface of the PS1-D1 sorbent ( $V_{\text{solution}} = 20.0 \text{ cm}^3$ , transmission rate:  $1 \text{ cm}^3/\text{min}$ ).

Composition of the solution	Desorption degree, %	Total desorption degree, %
H <sub>2</sub> SO <sub>4</sub> (1 mol/dm <sup>3</sup> )	3	90
Thiourea (0.5 %) in H <sub>2</sub> SO <sub>4</sub> (1 mol/dm <sup>3</sup> )	75	
Thiourea (5.0 %) in H <sub>2</sub> SO <sub>4</sub> (1 mol/dm <sup>3</sup> )	12	41
Ammonium thiocyanate (0.5 %) in H <sub>2</sub> SO <sub>4</sub> (1 mol/dm <sup>3</sup> )	10	
Ammonium thiocyanate (1.0 %) in H <sub>2</sub> SO <sub>4</sub> (1 mol/dm <sup>3</sup> )	23	
Ammonium thiocyanate (5.0 %) in H <sub>2</sub> SO <sub>4</sub> (1 mol/dm <sup>3</sup> )	8	

After desorption of silver under the described conditions, repeated sorption of metal ions from multicomponent solutions was carried out under selected conditions for two cycles (sorption-desorption). The resulting dynamic output sorption curves are shown in Figure S2 (Supplementary). When sorption is repeated after using sulfuric acid solutions of thiourea or ammonium thiocyanate as eluents, the extraction of silver(I) PS1-D1 is no longer quantitative. In this case, the extraction degree of silver(I) after desorption is higher provided that thiocyanate solutions are used for regeneration. Thus, it is necessary to optimize the composition of the regenerant or the conditions for the dynamic concentration of silver(I) on the sorbent after desorption to ensure the possibility of repeated use of the sorbent.

### 3.6. Isochronous stability study of PS1-D1

An important property of sorption materials from a practical point of view is their stability over time, since in some cases isomerization of surface organic functional groups may occur with possible subsequent decomposition, which will lead to a degeneration in the sorption properties of sorbents.

A literature review revealed a lack of studies on the stability of modified polysilsesquioxanes over time. In order to assess the influence of the sorbent storage time on the stability of its sorption properties, a repeated experiment was carried out in static investigation on the PS1-D1 sorbent after its storage at room temperature in a sealed bottle without access to sunlight for 2 years. It was found that the sorption properties of PS1-D1 did not change as a result of storage for two years, which indicates the high stability of sorption materials with the polysilsesquioxane matrix.

The “accelerated aging method” was used as an alternative and more rapid technique for studying the stability of PS1-D1. After the first five hours of heating the sorbent, the smell of thiourea emanated from the furnace, suggesting the possible subsequent deterioration in the extraction of silver ions. However, no such deterioration was observed. The Figure 4S show that the values of the extraction degree

of silver(I) depending on the aging time change within the error limits of the sorption experiment. The experimental results suggest that the PS1-D1 sorbent extracts up to 5% of associated metal ions, while the extraction of silver varies from 96 to 99%, which further demonstrates the affinity of thio-containing groups of the materials for silver ions.

## 4. Limitations

The main disadvantages and limitations of the studied sorbents are: the relatively low specific surface area of the sorbents ( $\leq 1.84 \text{ m}^2/\text{g}$ ), which could limit overall capacity; incomplete (90%) and non-quantitative desorption, which leads to performance degradation over reuse cycles; the inability to use PS1-D4 and PS1-D5 in dynamic mode due to particle size and filter clogging; and the potential for redox reactions and sorbent darkening at higher pH levels, which restricts the operational pH range.

The following can be formulated as further directions for research: selection of eluents to ensure quantitative desorption, which will allow the development of new methods for the extraction and concentration of noble metal ions using the studied sorbents; the use of the studied sorbents for the concentration of noble metal ions from secondary raw materials; study of the sorption behavior of modified polysilsesquioxanes in the presence of ions of other noble or precious metals.

## 5. Conclusions

The use of the sol-gel method in the synthesis of sorbents with subsequent functionalization of the surface of the resulting aminopolymer with sulfur-containing groups made it possible to obtain a modified polysilsesquioxane, which is characterized by a high degree of functionalization among representatives of organosilicon sorbents. It was shown that the synthesized material belongs to the group of highly selective sorbents with respect to the sorption of silver(I). The possibility of reusing modified polysilsesquioxane in a dynamic investigation of sorption has been revealed, and the prospects for its use for concentrating silver ions from multicomponent solutions have been established. When studying the sorption of silver ions using synthesized samples, the most selective and quantitative extraction of silver ions was achieved at pH from 1 to 2. Sample PS1-D1 selectively extracts silver ions over the entire pH range studied. An increase in the proportion of thiocyanate during synthesis does not lead to an increase in the concentration of grafted sulfur-containing groups. When using an excess of ammonium thiocyanate for modifying amino groups, the proportion of dithiobiuret groups decreases from 90% to (71–38)%, depending on the reaction medium and the ratio of reagents. All the synthesized sorbents show an affinity for silver(I) regardless of the modification conditions. The maximum extraction of sorbed ions in the dynamic sorption mode was 90 % (eluent - thiourea sulfuric acid solutions).

An isochronous study of the stability of the sorption properties of modified polysilsesquioxanes was carried out for the first time. They retain their sorption properties for 5 years. The results of the work allow asserting the possibility of using the studied sorbents in practice. Modified poly-3-(2-aminoethylamino)propylsilsesquioxane can be employed for selective and quantitative extraction of silver(I).

### Supplementary materials

This manuscript contains supplementary materials, which are available on the corresponding online page.

### Data availability statement

Date will be made available on request.

### Author contributions

Conceptualization: M.E.A., P.Yu.S., O.V.A., P.A.V., N.L.K.

Data curation: M.E.A., O.V.A.

Formal Analysis: M.E.A., P.Yu.S., O.V.A., P.A.V., N.L.K.

Investigation: M.E.A., O.V.A.

Methodology: M.E.A., P.Yu.S., O.V.A., P.A.V., N.L.K.

Project administration: M.E.A., P.Yu.S., P.A.V., N.L.K.

Supervision: P.Yu.S., P.A.V., N.L.K.

Validation: M.E.A.

Visualization: M.E.A., O.V.A.

Writing – original draft: M.E.A., O.V.A.

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### Conflict of interest

The authors declare no conflict of interest.

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