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Organosilicon ion-exchange and complexing adsorbents

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Abstract. Data on the ion-exchange and complexing organosilicon adsorbents published during the last 10 – 12 years, including the results of systematic research of the authors, are summarized and analyzed. The following types of substances are considered: silicas with covalently grafted modifiers, silicas and aluminosilicates with non-covalently grafted modifiers and carbofunctional polyorganylsilsesquioxanes prepared by polycondensation of appropriate organosilicon monomers. Adsorbents of these types find extensive practical use, in particular, as analytical reagents for determination of metals in natural and artificial specimens, agents for isolation of valuable elements from industrial wastes and agents for removal of especially hazardous components from wastes and effluents. The bibliography includes 109 references.

I. Introduction

Silicates (such as zeolite, vermiculite) and both natural (for instance, siliceous clay or siliceous argillite) and artificial (silica gel, silochromes, fumed silica, porous glass, *etc.*) silicas are well known sorption materials. They do not swell in aqueous or organic media and exhibit high chemical and hydrolytic stability and mechanical strength, thus being attractive materials.[1,2] At present, a rather large series of silicon-containing adsorbents have been prepared on the basis of silica and products of its modification. Particularly, silicon-containing enterosorbents[3] (intestinal adsorbents) like polysorb (sillard, silix), which is a highly dispersed silica with 10 – 12 nm pores, and hydrogels of methylsilicic acid such as enterosgel and sorbogel have acquired a great importance in recent years. The scope of application of these adsorbents is very wide ranging from elimination of radionuclides and toxins from the body to removal of various pollutants and necrotic epidermal cells from skin in cosmetology.

The goal to improve the efficiency and selectivity of silicas as sorbents led to the development of innovative silicon-containing adsorbents. It was possible because of the presence of hydroxyl groups on the silica surface. The presence of these groups was assumed by A V Kiselev, a professor of the Moscow State University, back in 1936.[4] In 1950, this hypothesis was confirmed experimentally by Kiselev himself and independently by Swiss scientist Deuel and co-workers[5] considering the interaction of silica gel with methanol and clay minerals with compounds like propylene oxide. This opened up the possibility of developing new organosilicon materials, including organosilicon adsorbents, by covalent and non-covalent modification of silicas. These sorbents include supramolecular structures of the host – guest type, and particularly, a large number of adsorbents obtained by non-covalent immobilization of organic compounds on the silica surface.[6]

At present, another area of the chemistry of silicon-containing sorption materials is under active development; this is creation of highly selective adsorbents on the basis of polymeric systems structurally adjustable to the target sorbate at the nanolevel, *i.e.*, so-called imprinted polymers, which are produced by the method of molecular imprinting.[7] To prepare these adsorbents, silicas are often used as a matrix, whereas organosilicon compounds of the general formula X_3SiR [X = Hal, OR′ or OC(O)R′, where R is a carbofunctional organic substituent] serve as binding agents.

The present review is aimed at generalization of the latest data concerning the silicon-containing sorption materials representing ion exchangers and complex-forming agents. The results obtained by the authors of the review

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in this field of applied organosilicon chemistry before 1998 were considered in earlier reviews.[8,9]

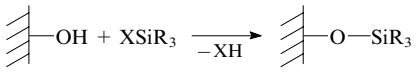
The organosilicon adsorbents that are prepared by methods based on the use of anchoring compounds, which chemically link ion exchanges and complexing agents to the silica surface, or on immobilization on this surface of reactive organosilicon monomers of the general formula X_3SiRY [X = Hal, OR′ or OC(O)R′, R is divalent hydrocarbon moiety, Y is carbofunctional substituents capable to ion exchange or complexation], were surveyed in a monograph [10] under the general name 'covalently modified silicas.' Silicas with adsorbed complexing and ion exchange reagents,[10] which are retained on the substrate due to electrostatic, donor-acceptor, hydrophobic and some other interactions with the surface groups of silicas, form another group of adsorbents, which also includes supramolecular adsorbents. Xerogels of silicic acid modified with analytical reagents [10] were also ascribed to this group. This modification consists in binding of an analytical reagent by the silica network structure formed during the preparation of silica by hydrolysis of tetraethoxy- or tetramethoxysilane in the presence of this reagent (sol–gel method).[11–13] Unfortunately, the monograph [10] does not consider one more large class of organosilicon adsorbents, which has been comprehensively and thoroughly studied by the authors of the present review. Those are three-dimensional polyorganylsilsesquioxanes containing carbofunctional ionogenic and complexing moieties in organic substituents. The method for their synthesis is extremely simple and consists in hydrolytic polycondensation or copolymerization of the carbofunctional organosilicon monomers.[8,9] We obtained a large number of such monomers in the course of our fundamental studies of carbofunctional organic silicon derivatives.

II. Adsorbents based on covalently modified silicas

A widely used method of the synthesis of organosilicon adsorbents is chemical immobilization of compounds containing ionogenic and complexing groups on the silica surface. Usually, the modifiers, or anchoring compounds, used for further assembling of the adsorbent, are described as X_3SiR, where X = Hal, OR′ or OC(O)R′, R is a carbofunctional organic substituent.

The mechanism of modification of silica is described in monographs [10,14] and review.[15] It is based on the interaction of functional groups at the silicon atom with surface hydroxyls of silica (Scheme 1).

Scheme 1



X = Hal, OR, OAc

The formed Si—O—Si siloxane bonds ensure the stability of these silicas with covalently grafted groups.

Various covalently modified silicas containing functional groups that are of interest as analytical reagents for preconcentration and determination of metals are considered in detail in a monograph,[10] and their use as reagents in spectrophotometric analysis is mentioned in a review.[15]

Silica gels modified with organosilicon monomers containing thiol or disulfide groups have found wide application for adsorptive preconcentration, identification and recovery of metals. Silica gel modified by thiol groups (**1**) was obtained by immobilization of mercaptopropyl(triethoxy)silane on the surface. Silica gel modified by disulfide groups (**2**) was prepared by oxidation of silica gel **1** containing mercaptopropyl groups [$(CH_2)_3SH$] by elemental iodine. Silica gels **1** and **2** extract palladium(II) from hydrochloric acid solutions in the HCl concentration range from 6 M to dilute solutions with pH 4 with the distribution ratio of $10^4–10^5$ cm^3 g^{-1} (Refs 16–18). These silica gels were used to develop combined adsorption/photometric and adsorption/atomic absorption procedures for determination of palladium. The detection limit for palladium is 0.1 μg per 0.1 g of the adsorbent. The $(10^4–10^5)$-fold amounts of alkaline earth metal ions, Al^{III}, Co^{II}, Ni^{II}, Pb^{II} ions or (10–100)-fold amounts of other transition metals do not interfere with the determination of palladium.

It is noteworthy that the selectivity of determination of palladium in the presence of hydrated ions of other metals is more than 100 times higher with silica gel **2** than with silica gel **1** having grafted $(CH_2)_3SH$ groups. It is because during complexation, thiol groups participate in the side reactions of reduction of concomitant elements to lower oxidation states. Conversely, disulfide groups do not participate in the redox processes that interfere with complexation.

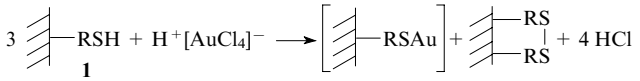
Modified silica gels **1** and **2** also exhibit high and specific sorption activity towards osmium. On the basis of silica gel **1**, a method for determination of Os^{VIII} in hydrochloric and sulfuric acid solutions with acidities in the range from 6 M HCl or 4 M H_2SO_4 to pH 4 was developed.[19] The time it takes for the sorption equilibrium to be established in the static mode is 2–3 min, the phase distribution coefficient is 1×10^5 cm^3 g^{-1}, and the relative detection limit for osmium is 0.03 μg ml^{-1}. This approach is suitable for quantitative preconcentration and recovery of Os^{VIII} from highly dilute solutions in the dynamic mode.[19]

A method for Os^{VIII} recovery or gas-phase determination [20] and a method for Os^{VI} separation and separate determination in the presence of Os^{IV} (Ref. 21) are also based on the use of silica gel **1**. The distinctive features of sorption separation of osmium in different oxidation states (IV, VI, VIII) by modified silica gels **1** and **2** were reported.[22] It was suggested based on the results that the reaction of osmium with sulfur-containing ligands grafted on the silica gel surface gives first a coordination compound of osmium in one of the highest oxidation states (Os^{VI}). Then osmium is reduced to Os^{IV} and further to Os^{II} within the coordination compound if an adsorbent with thiol groups is used. A similar conclusion was made by the same authors from the studies of the recovery of osmium in different oxidation states by sorption on silicas with grafted thiourea derivatives.[23]

Organosilicon adsorbent **1** containing thiol groups was also used for low-temperature sorption of gold for subsequent luminescence determination.[24] The adsorbent was prepared by immobilization of mercaptopropyl(triethoxy)-silane on silica gel for column chromatography (Merck, fraction of 0.06–0.16 mm, specific surface area ~500 m^2 g^{-1}, average pore diameter 6 nm). The concentration of SH groups grafted on the surface was determined by thiolometric and iodometric back titration to be 0.87 ± 0.03 mmol g^{-1}. The sorption determination of gold(III) was carried out in hydrochloric acid solutions with acidity in the range from 6 M HCl to neutral medium (pH = 8).[24]

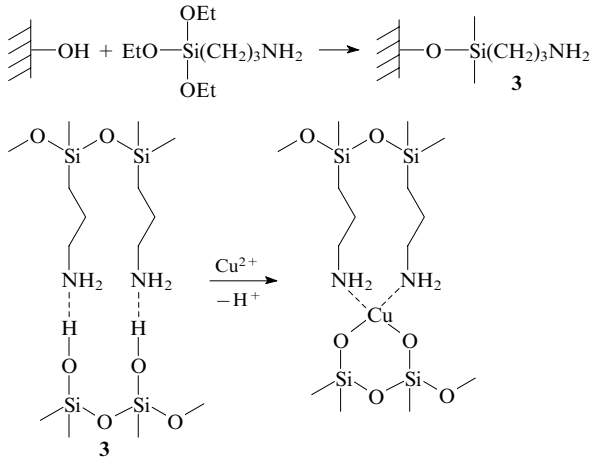
Since luminescence is usually inherent in gold(I) compounds,[25] it was supposed that gold(III) is reduced in the course of adsorption by the adsorbent thiol groups to the monovalent state (Scheme 2).

Scheme 2



Silica gels modified with 3-chloro- and 3-aminopropyl(triethoxy)silanes were used both as adsorbents and as precursors for synthesis of new sorption materials.[26] Particularly, silica modified with 3-aminopropyl(triethoxy)silane (**3**) proved to be a highly effective adsorbent for the Cu^{2+} and Zn^{2+} ions. Cobalt(II) and nickel(II) are poorly adsorbed on this material. The amino groups and residual silanol groups are responsible for binding of metal ions by this adsorbent (Scheme 3).†

Scheme 3



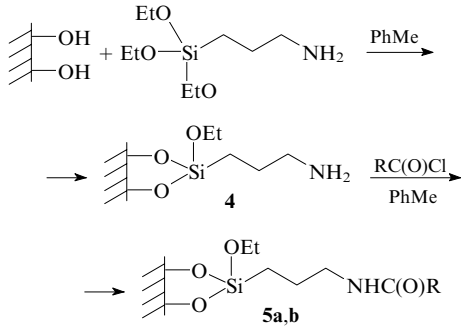
Silica gel chemically modified with 3-chloropropyl(triethoxy)silane is a less efficient adsorbent for these metals because only silanol groups of the adsorbent are able to react with the metal ions in this case.

A series of organosilicon adsorbents (**4**, **5a**,**b**) containing carbofunctional amino or amide groups were prepared by chemisorption of 3-aminopropyltriethoxysilane on silica gel followed by the reaction of the product with RC(O)Cl (R = Pr^i, Ph) (Scheme 4).[27]

Silica gels **4** and **5** were tested as adsorbents of uranium. Their sorption activity decreases depending on the substituent in the series $NH_2 \gg NHC(O)Ph \approx NHC(O)Pr^i$. The sorption capacity with respect to uranium of the most efficient adsorbent **4** is 54 mg g^{-1} at pH = 7. This adsorbent recovers 65% of uranium from solutions in the presence of sodium ions in the ratio $U : Na = 1 : 10^4$. Therefore, uranium can be extracted with adsorbent **4** from neutral media and concentrated solutions of sodium carbonate.

† As a rule, the modifying organosilicon reagent forms only one bond with the substrate surface. The other alkoxy groups also do not remain intact since they undergo intermolecular condensation, resulting in the formation of siloxane coating chemically bonded to the substrate. In this review, this situation is depicted by the bonds at Si atom without substituent (see, for instance, adsorbent **3**). If the authors of the cited studies suppose that the condensation is not complete, alkoxy groups remain preserved at Si atoms (for example, in the formulas of adsorbents **4** and **5**).

Scheme 4



R = Pr^i (**a**), Ph (**b**)

Silica gel with immobilized imine diacetate groups was applied in the flow-injection photometric determination of trace amounts of copper in natural waters.[28]

Silica gel with similar protonated groups of iminodiacetic acid was utilized to determine alkaline earth metals in HCl solutions by ion chromatography.[29] By using this sorbent in combination with chelating agents, it was possible to determine, particularly, trace amounts of Ca^{2+} and Mg^{2+} in a physiological saline solution of NaCl and in a laboratory solution of KCl.

Mixed matrix membranes with a zeolite chemically modified with 3-aminopropyl(dimethyl)ethoxysilane were used for separation of gas mixtures of nitrogen with oxygen and carbon monoxide.[30]

Silica gel chemically modified with 3-aminopropyl(triethoxy)silane was used for extraction and preconcentration of copper, cadmium and chromium from sea water with subsequent determination by atomic absorption spectrometry.[31] The elements can be quantified at pH = 5, they are desorbed into 2.0 M HCl to 96%–98%. The detection limits are 6.6, 7.5 and 6.0 mg $litre^{-1}$ for Cu, Cd and Cr, respectively.

The anion exchange behaviour of silicas (aerosil, silica gel, silochrome) modified with (3-aminopropyl)triethoxysilane was studied by conductometric titration in relation to HCl adsorption.[32] It was established that adsorbents synthesized from porous silicas (silica gel, silochrome) can adsorb the acid from aqueous solutions.

Diasorb-130, a silica with grafted iminodiacetate groups, was applied for test determination of copper(II). Colour reactions of Cu^{II} adsorbed on this modified silica with 4-(pyridin-2-ylazenyl)resorcinol (PAR) and 7-[(2-hydroxy-3,5-dinitrophenyl)azenyl]-8-hydroxynaphthalene-1,6-disulfonic acid (picramine-epsilon) was studied by diffusion reflectance spectroscopy.[33]

Silochrome C-80‡ chemically modified with *N*-allyl-*N*′-propylthiocarbamide (**6**) was used to determine palladium(II).[34] The limit of palladium(II) detection for sorption followed by photometric determination was 1 mg per 0.1 g of silica **6** or 1.5 mg ml^{-1}. Another method for palladium determination includes sorption preconcentration of Pd^{II} with modified silica **6**, elution of adsorbed Pd^{II} with solutions of thiourea in hydrochloric acid and determination in the eluate by atomic absorption spectrometry. Both methods were used to determine the content of palladium in

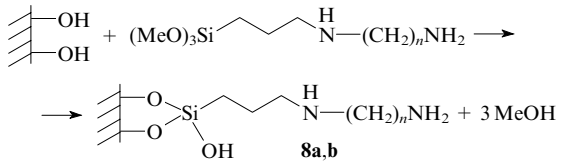
‡ The specific surface area (*S*) is indicated in the designations of silochromes; for instance, C-80 means $S \approx 80$ m^2 g^{-1}.

copper-nickel ores and products of their industrial processing.[34]

Silicas chemically modified with *N*-allyl- (**7a**), *N*-phenyl- (**7b**) and *N*-benzoyl-*N*′-propylcarbamides (**7c**) have been recommended for sorption determination of gold(III).[35] Silochrome C-80 (fraction of 0.1–0.2 mm with pore diameter of ~50 nm) served as a matrix. According to elemental analysis, the surface concentration of grafted groups was 0.12, 0.11 and 0.10 mmol g^{-1} for adsorbents **7a**, **7b** and **7c**, respectively. The method for sorption determination of gold(III) includes adsorption of metals by silica **7**, heat treatment of samples saturated with the sorbate to reduce Au^{III} to Au^0 and subsequent determination of gold by diffusion reflectance spectroscopy. The detection limit for gold is 1 μg per 0.1 mg of the adsorbent. Gold can be determined in the presence of (10^4-10^5)-fold amount of nonferrous metals (cobalt, nickel, copper, chromium, zinc) and iron.

Adsorption of Cu^{II}, Pb^{II} and Fe^{III} on silica modified by 7-amino-4-azaheptyl- and 10-amino-4-azadecyl(trimethoxy)silanes [adsorbents AAH Si (**8a**) and AAD Si (**8b**), respectively] was described.[36] Organosilicon precursors of these adsorbents were synthesized by reactions of sodium 3-aminopropylamide and sodium 6-aminohexylamide with trimethoxy(3-chloropropyl)silane, respectively (Scheme 5). The starting silica (Merck, 0.2–0.5 mm fraction) was initially activated by heating at 150 °C in vacuum for 5 h. The amount of precursor molecules immobilized on silica gel was 0.7 and 0.5 mmol g^{-1} for adsorbents **8a** and **8b**, respectively.

Scheme 5



n = 3 (**a**), 6 (**b**)

Adsorbents **8a**,**b** have specific surface area of 270 ± 20 and 240 ± 20 m^2 g^{-1} and degree of dispersion of 109 and 117 nm, respectively.

The optimum pH for adsorption is 6.0 for Cu^{II} and Pb^{II} and 4.0 for Fe^{III} and duration of the contact with the sorbates is 180 min. Modified silica gel **8b** proved to be more efficient.

Silica gels functionalized by organic groups are usually preferred as sorbents because they do not swell and are structurally stable. Indeed, it was established[36] that the immobilized organic groups are retained in adsorbents **8a**,**b** even after heating up to 300 °C. However, the reaction scheme proposed by the authors does not disclose completely the structure of the obtained sorption materials. Particularly, it is not clear whether silanol groups remain in their structure, and if not, what are their subsequent transformations.

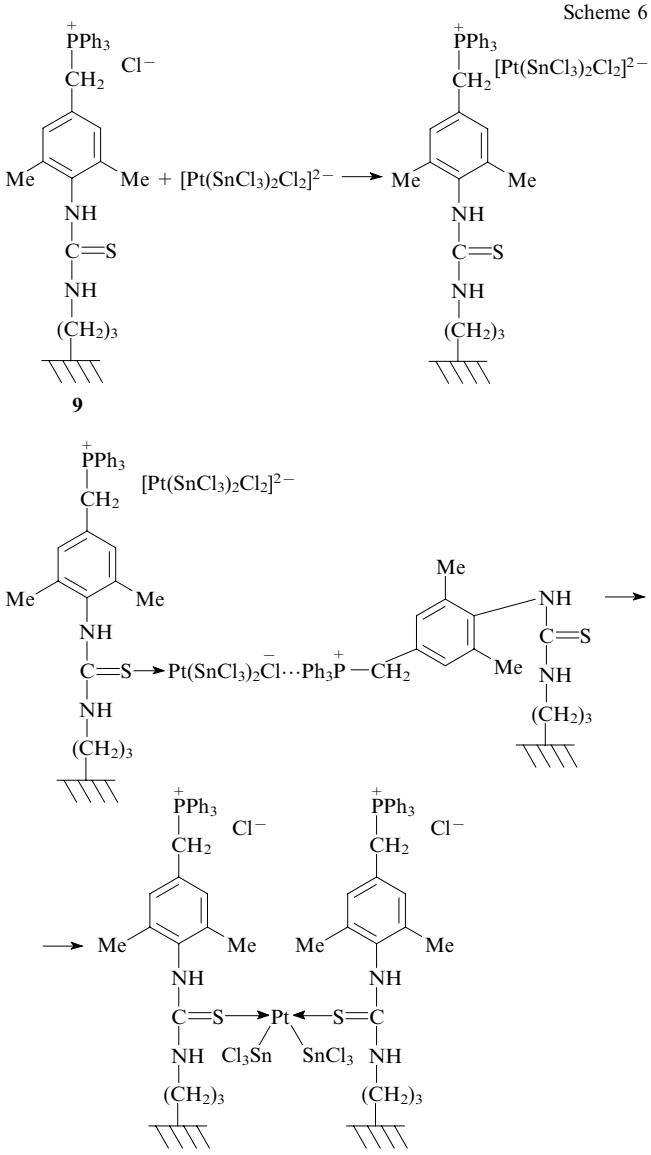
Silica gel with covalently grafted 4-(pyridin-2-ylazenyl)-resorcinol was prepared in one step by the Mannich reaction.[37] At pH 6.8–7, it quantitatively adsorbs some toxic metal ions such as Pb^{II}, Cd^{II} and Ni^{II}. This adsorbent is promising for solid-phase preconcentration of heavy metals in the analyses of various natural specimens.

Modified silica gels containing two types of groups differing in their reactions with metals are of special interest as adsorbents. Particularly, chemical immobilization of *N*-cyanoethylaminopropyl(triethoxy)silane on the silica surface resulted in production of a new complexing adsorbent.[38]

The sorption of palladium and platinum by silica gel **9** with grafted *N*-(2,6-dimethyl-4-triphenylphosphinomethyl)-phenyl-*N*′-propylthiocarbamide groups (adsorbent PS-C) from aqueous solutions was studied.[39] Silochrome C-80 (0.1–0.2 mm fraction) was used as the starting material for the synthesis of this adsorbent. According to elemental analysis, the concentration of the groups grafted on this adsorbent was 0.08–0.12 mmol g^{-1}.

Adsorbent **9** has sorption centres of two types, *viz.* thiocarbamide moieties NHC(S)NH and phosphorus-containing groups $P^+Ph_3Cl^-$, which are capable of both complexation and ion exchange with metals. The interaction of PS-C with Pd^{II} includes complexation, whereas the reaction with Pt^{II} and Pt^{IV} includes both complexation and ion exchange. On the basis of studies of diffusion reflectance spectra and luminescence intensity, it was found that adsorption of platinum is accompanied by some rearrangements that occur on the adsorbent surface

Scheme 6



and finally lead to complexation of the metal with the thiocarbamide group; furthermore sorption of Pt^{IV} is accompanied by reduction to Pt^{II}.

Rearrangements on the PS-C sorbent surface were also detected in sorption of dichlorobis(trichlorostannate)palladium(II) and -platinum(II) (Scheme 6).[40] Green complex of palladium(II) and yellow complex of platinum(II), *cis*-$Pt(SnCl_3)_2Cl_2]^{2-}$, were studied as sorbates.

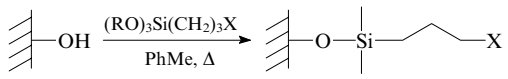
Some features of the reaction of PS-C with these complexes were elucidated from diffusion reflectance spectroscopy data and from comparison with the adsorption of these complexes on silica gel chemically modified with *N*-(2,6-dimethyl-4-triphenylphosphinomethyl)phenyl-*N*′-propylcarbamide groups (adsorbent TFFS, **10**),[40] which is a typical anion exchanger with respect to anionic complexes of platinum metals. The change in the spectral characteristics of PS-C with the adsorbed complex is related to the rearrangement occurring on the adsorbent surface (see Scheme 6).

The rearrangement is accompanied by the change in the mechanism of interaction with the sorbate from anion exchanging to complexation and results in coordination of a transition metal atom to the sulfur atom of the thocarbamide moiety of PS-C (**9**). Adsorption of palladium(II) and platinum(II,IV) halide complexes proceeds analogously.[39]

Modified silica gel **10** (TFFS) proved to be a very efficient sorbent for a Co^{II} complex with nitroso R salt. A sorption/spectrometric procedure for cobalt determination in aqueous phases and alloys with the use of TFFS was developed.[41]

A series of new organosilicon adsorbents containing thiazolidine (**11**), thiazole (**12**), imidazoledithiocarboxylate (**13**), propanethiol (**14**) and pyridine (**15**) moieties were obtained by means of surface assembly.[42] The synthesis of adsorbents **11**–**15** consisted in initial chemical modification of silica gel (Kieselgel 100, 63–200 μm fraction), which was activated for 12 h at 200 °C with organosilicon monomers of general formula $(RO)_3Si(CH_2)_3X$ (Scheme 7).

Scheme 7



R = Me, Et; X = NH_2, Cl, OCH_2(CHCH$_2$O-cyclo)

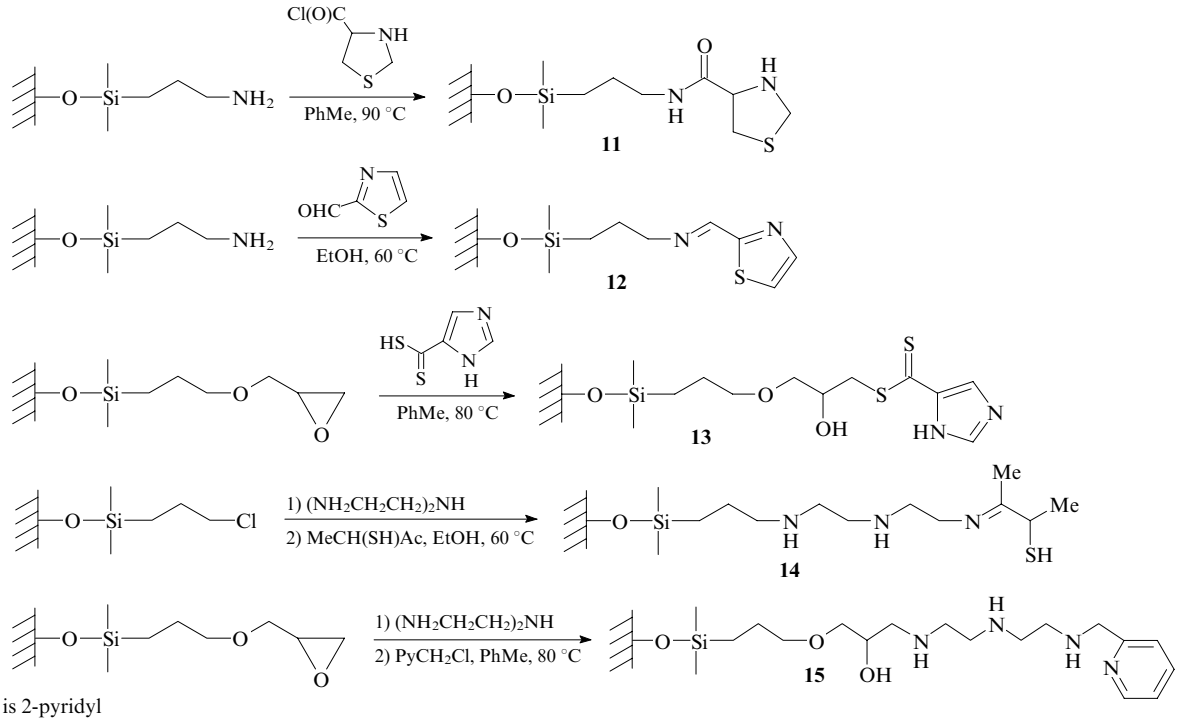
Chemically modified silica gels obtained in this way were made to react with desired reagents (Scheme 8).

According to the elemental analysis, the surface concentrations of functional groups grafted on the silica gel surface were 780, 690, 550, 160 and 390 mmol kg^{-1} for adsorbents **11**, **12**, **13**, **14** and **15**, respectively. Modified silica gels **11**–**15** were studied as adsorbents for Pb^{II} and Cd^{II}, and the utility of modification of silica gel for increasing its efficiency as a metal adsorbent was clearly demonstrated. The highest sorption activity with respect to the studied metals was exhibited by adsorbents **13** and **15**.

The synthesis of hybrid adsorbent **16** containing chitosan (Scheme 9)[43] represents an example of multistep assembly of a sorption layer on the silica gel surface. The first step of the assembly includes modification of the silica gel with 3-aminopropyl(trimethoxy)silane. Thus obtained Sil-NH_2 is treated with glutaraldehyde, then the hybrid material Sil-Glut reacts with chitosan dissolved in 0.8% acetic acid. Then, the resulting Sil-Quit reacts again with glutaraldehyde to induce binding of some of the amino groups of grafted chitosan (see Scheme 9).

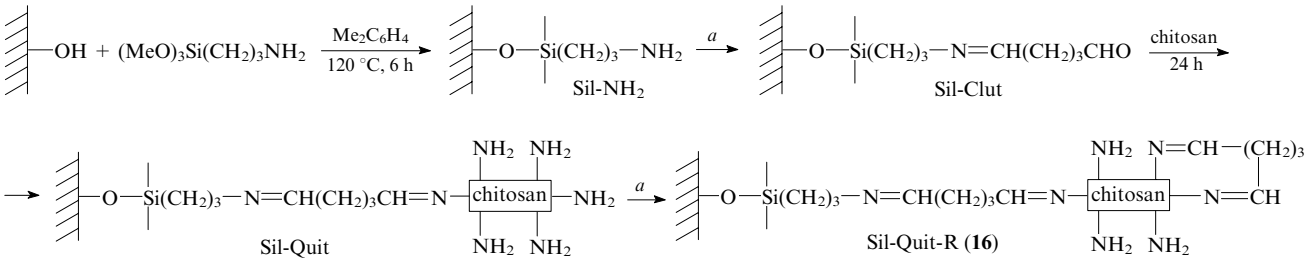
According to thermogravimetric analysis data, the finally obtained hybrid material Sil-Quit-R (**16**) starts to lose mass at 30–150 °C due to adsorbed water. The major changes in the adsorbent structure occur at 430 °C. The specific surface area of adsorbent **16** is 8 $m^2 g^{-1}$, this value is substantially smaller than that of non-modified silica gel (Merck, dispersion is 70–230 nm/the specific surface area is

Scheme 8



Py is 2-pyridyl

Scheme 9

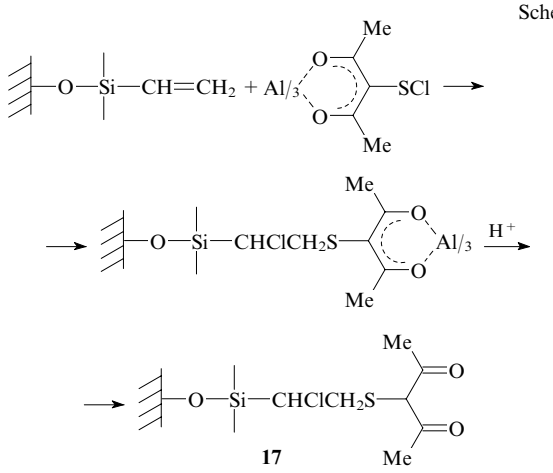


(*a*) $OHC(CH_2)_3CHO$, rt, 2 h

395 $m^2\ g^{-1}$); however, this was to be expected. The surface concentration of chitosan on Sil-Quit-R (**16**) is 20.2 ± 0.5 mg g^{-1}. Adsorbent **16** containing amino groups was studied as an anion exhanger with respect to dyes Reactive Yellow GR and Reactive Red RB having ionogenic groups SO_3Na.

The chemical surface assembly method was used to prepare adsorbents **17** containing complexing β-diketonate groups.[44] Natural zeolites from Far East, *viz*., tuffs from Chuguevsky (Primorye) and Lyugovsky and Chekhovsky (Sakhalin) deposits, were used as matrices (Scheme 10).

Scheme 10

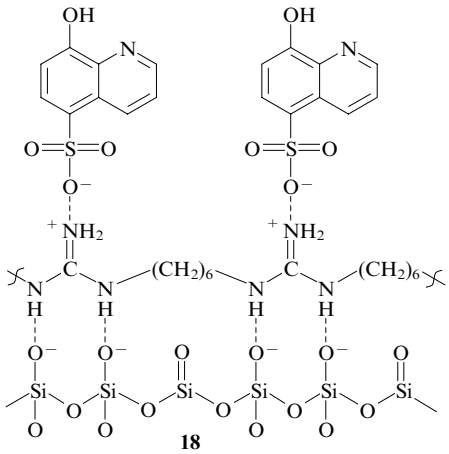


The same paper reports the synthesis of ion exchangers by modification of zeolites with ferricyanide complexes of metals (iron, zinc, copper).[44] The zeolites modified with copper and iron ferricyanide complexes were used to separate peptides and to isolate alkaline phosphatase. It was established that these ion exchangers can be utilized in the affinity chromatography of proteins. The zeolite modified with the iron ferricyanide complex has the largest separating activity.

III. Adsorbents based on non-covalently modified silicas and aluminosilicates

Although almost any reagent can be chemically immobilized on the silica surface either by means of direct chemical reaction or with the use of auxiliary reagents, *i.e*., by the chemical assembly, the adsorbents obtained in this way have a number of drawbacks. Those are multistep synthesis, irregularity in the distribution of functional ionogenic or complexing groups on the surface, and hence poor reproducibility of sorption properties. Therefore in inorganic analysis, the sorption materials obtained by non-covalent modification of silica are considered as preferable. The reagents used to modify the silica are held by electrostatic, donor-acceptor, and other non-covalent interactions. A wide overview of sorption materials with reagents non-covalently immobilized on silica (silica gel) and capable of ion exchange or complexation is given in monographs.[10,14]

Besides, supramolecular sorbents with silica as a matrix have found application in analysis.[45,46] Polyhexamethylene guanidine was proposed to create supramolecular structures on silica surfaces; some of its amino groups react with the surface silanol groups and other amino groups react with a complexing reagent.



Particularly, features of sorption preconcentration of metal ions by silica modified with polyhexamethylene guanidine and 8-hydroxyquinoline-5-sulfonic acid (**18**) were studied.[46] Adsorbent **18** quantitatively recovers Cu^{II}, Zn^{II}, Co^{II}, Ni^{II}, Cd^{II}, Fe^{III} and Al^{III} from solutions with pH 4–7 and Mn^{II} from solutions with pH 5.5–7.0 in the static mode. In the dynamic mode at pH 5, group preconcentration of these elements occurs. Owing to good reproducibility of the analysis, adsorbent **18** was used for sorption followed by atomic emission determination of metals in low-mineralized natural waters. The use of this adsorbent or silica modified only by polyhexamethylene guanidine is very profitable because it gives a possibility to perform metal preconcentration in the field and, hence, to transport a small mass of sorbent rather than a large quantity of water to a stationary chemical laboratory.

The same authors proposed adsorbents based on some inorganic oxides including SiO_2 (silica gel) sequentially modified with polyhexamethylene guanidine and 3,3′-(1,10-phenanthroline-4,7-diyl)bis(benzenesulfonic acid) (adsorbent **19**) for iron sorption coupled with photometric determination.[47] This adsorbent extracted iron(II) from solutions

with pH 4–8 with the 98%–99% recovery, the time of reaching the sorption equilibrium being 5 min. The procedure of sorption coupled with photometric determination using adsorbent **19** is suitable to quantify iron(II) with the detection limit of 0.02–0.05 μg per g of the adsorbent. This method was used to determine iron in natural waters.

The supramolecular assembly based on silica gel 60 (Merck, 200–230 nm fraction, specific surface area 270 $m^2\ g^{-1}$, pore diameter 12 nm), polyhexamethylene guanidine and nitroso R salt was proposed as an adsorbent for palladium(II) and cobalt(II) from aqueous solutions.[48]

Silica gel modified with salicylaldoxime was proposed as a sorption material for preconcentration, recovery and detection of zinc ions in the aqueous phase. The maximum sorption of the metal is observed at pH 5.5. Alkali and alkaline earth metals and ammonia do not affect the adsorption of zinc.[49]

The adsorbents obtained by non-covalent modification of silochromes C-60 and C-120 and enterosgel with 8-hydroxyquinoline, 5,7-dibromo-8-hydroxyquinoline and 8-hydroxyquinoline-5-sulfonic acid were reported.[50, 51] Silochrome C-60 modified with 8-hydroxyquinoline[52] efficiently adsorbs zinc at pH 7.1 and a contact time of 30 min having capacity of 60 μmol g^{-1}. The yellow-green fluorescence of the sorbate occurs upon UV irradiation of the loaded adsorbent. The method of sorption coupled with fluorimetric determination of zinc is suitable to determine 5–50 μg of Zn^{II} in the presence of Cu^{II}, Cd^{II}, Pb^{II}, Bi^{III}, Fe^{III}. This method was applied to quantify zinc in river and waste waters.

To purify water from petroleum products, an adsorbent was developed comprising the aluminosilicates vermiculite and perlite, which were modified with lignosulfate with addition of potassium and (or) sodium silicate and then thermally treated in a flow of gases formed after burning of hydrocarbon fuels (natural gas, diesel fuel, fuel oil).[53] The advantage of the modified aluminosilicates consists in the increase (up to 2.5-fold) of their sorption capacity with respect to the spilled, emulsified or dissolved petroleum products.

Silica gel modified with dithizone (**20**) was prepared and used as a solid-phase extraction agent for trace amounts of copper from intricate mixtures for subsequent detection by flame atomic absorption spectrometry.[54] The dynamic sorption capacity of modified silica gel **20** with respect to Cu^{2+} is 0.76 mg g^{-1}. The practical use of this adsorbent is related to preconcentration of copper present in trace amounts in water of different origin (sea, river, atmospheric and tap water, snow).

Silica surface-modified with n-propyl-1,4-diazoniabicyclo[2.2.2]octane chloride turned out an excellent complexing adsorbent for copper(II) chloride.[55]

Silica doped with rhodamin B isothiocyanate was obtained by microemulsion method.[56] Then complexes of Fe^{III} with bis-picolylamine were grafted on the surface of particles of this silica.[56] The resulting nanoparticles were spherically shaped and had the average diameter of 74 nm. They represented multi-functional nanoparticles that combined the anticancer activity and fluorescence behaviour, thus being simultaneously a therapeutic agent and a means for imaging.

Chitosan and chitosan combined with ferricyanide complexes of metals were used for surface modification of aluminosilcates, *viz.*, zeolite and vermiculite.[57, 58] The use of chitosan for modification of the surface of the natural absorbents is related to its valuable properties such as the ability to form fibres, films, and the capability of complexing and ion exchange.

Using a zeolite from the Chuguevsky deposit (Primorsky Territory), it was established that the optimum content of chitosan (obtained from the king crab carapace) attained upon modification is 3%–4%.[58] A series of adsorbents were obtained on the basis of the Chuguevsky zeolites by modification with either chitosan or chitosan in combination with ferricyanide complexes; their sorption activity with respect to acidic and basic dyes and Cu^{II} and Fe^{III} ions was explored. The obtained data clearly demonstrate that the use of modifiers makes it possible to increase several-fold the sorption activity of natural adsorbents such as zeolites. Since the zeolite surface is mildly acidic due to the presence of silanol groups, it has low sorption activity with respect to acidic dyes. The modification of the zeolite surface with chitosan containing amino groups affords organic-mineral adsorbent with neutral surface pH. By virtue of this, the sorption capacity of thus modified adsorbents with respect to acidic dyes such as bromophenol blue is 9 times higher than that of the starting zeolite (28%–29% and 3%, respectively). At the same time, the chitosan film structure does not impede the penetration of molecules of basic dyes like brilliant green towards the acidic surface of the zeolite (the degree of sorption of the basic dye on the zeolite is 89%, while that on the zeolite modified with chitosan is 90%–92%). The degree of sorption of the investigated heavy metals on the zeolite modified with chitosan is 3.5 times higher than that on the starting zeolite.

A nanosized sorbent comprising magnetite nanoparticles coated by siloxane and obtained by treating magnetite with tetraethoxysilane was modified with *N*-cetylpyridinium bromide and used for adsorption and determination of traces of Cu^{II}, Ni^{II}, Co^{II}, Cd^{II}, Pb^{II} and Mn^{II} in natural water samples.[59] The limits of detection of the listed elements with the use of this adsorbent were 4.7, 9.1, 9.5, 2.3, 7.4 and 15.3 ng $litre^{-1}$, respectively.

IV. Carbofunctional polyorganylsilsesquioxanes

Hydrolytic polycondensation and copolycondensation of carbofunctional organosilicon monomers of general formula $YRSiX_3$ or $Y(RSiX_3)_2$ [Y is ionogenic or complexing group; X = Cl, OR′, OC(O)R′, NR'_2 (R′ = Me, Et); R is divalent hydrocarbon moiety] is the simplest method for synthesis of carbofunctional organosilicon polymers with the cross-linked three-dimentional structure (silsesquioxanes). Very often, tetraethoxysilane (TEOS) is also introduced in this process. The thus obtained polymers are efficient ion exchangers and complexing agents being the subjects of several reviews.[8, 9, 60, 61]

Particularly, the products of copolycondensation of teraethoxysilane with 3-chloro- and 3-aminopropyl(triethoxy)silanes and their derivatives were prepared and studied, along with chemically modified silica gel, as adsorbents for copper, zinc, cobalt and nickel.[26] Adsorbent **21** containing the $N(CH_2CO_2Na)_2$ group was prepared by the reaction of sodium iminodiacetate with the product of copolycondensation of teraethoxysilane with 3-chloropropyl(triethoxy)silanes in DMSO in the presence of sodium iodide (Scheme 11).

Scheme 11

$$[(SiO_2)_2SiO_{1.5}(CH_2)_3Cl]_n + n\,HN(CH_2CO_2Na)_2 \xrightarrow[-HCl]{NaI} [(SiO_2)_2SiO_{1.5}(CH_2)_3N(CH_2CO_2Na)_2]_n$$

21

Organosilicon adsorbent **22** containing the $N[(CH_2)_2CO_2H]_2$ group was synthesized analogously. In this case, the reaction proceeds without sodium iodide.

Similar adsorbents were prepared in the reaction between the product of copolycondensation of tetraethoxysilane with 3-aminopropyl(triethoxy)silane and acrylic acid or by the surface assembly of these components on silica gel (Scheme 12).[26, 62]

Scheme 12

$$[(SiO_2)_2SiO_{1.5}(CH_2)_3NH_2]_n + n\,H_2C{=}CHCO_2H \longrightarrow \{(SiO_2)_2SiO_{1.5}(CH_2)_3N[(CH_2)_2CO_2H]_2\}_n$$

22

$$\equiv SiOH \xrightarrow[2)\ H_2C{=}CHCO_2H]{1)\ (EtO)_3Si(CH_2)_3NH_2} \equiv SiO(CH_2)_3N[(CH_2)_2CO_2H]_2$$

22′

Adsorbent **23** containing a phenylaminopropionic acid residue was synthesized by the reaction of the product of copolycondensation of tetraethoxysilane with (3-chloropropyl)triethoxysilane and ethyl β-phenylaminopropanoate in the presence of sodium iodide without a solvent (Scheme 13).[26]

Scheme 13

$$(SiO_2)_2SiO_{1.5}(CH_2)_3Cl + PhNH(CH_2)_2CO_2Et \longrightarrow [(SiO_2)_2SiO_{1.5}(CH_2)_3N(Ph)CH_2CH_2CO_2Et]_n \longrightarrow [(SiO_2)_2SiO_{1.5}(CH_2)_3N(Ph)CH_2CH_2CO_2H]_n$$

23

Adsorbents **21**–**23** containing the $N(CH_2)_nCO_2H$ groups (n = 1, 2)[26, 62] exhibit both an enhanced sorption activity towards copper, zinc, cobalt and nickel ions and selectivity towards the Cu^{2+} ions. The largest sorption capacity and selectivity were observed for adsorbents **22** and **22′**, which contain the $N[(CH_2)_2CO_2H]_2$ group. Adsorbent **23** with the $PhN(CH_2)_2CO_2H$ group is also highly selective towards the listed metals.

An efficient sorption of metals from aqueous solutions of MCl_2 salts (M = Cu^{2+}, Ni^{2+}, Co^{2+}, Pb^{2+}, Hg^{2+}) was found for adsorbent **24** prepared§ by hydrolytic copolycondensation of tetraethoxysilane with the product of reaction of ethylene sulfide with (3-aminopropyl)triethoxysilane (Scheme 14).[63]

The sorption capacity of product **24** towards Cu, Ni, Co, Pb and Hg ions is 1.66, 1.44, 1.26, 1.90 and 8.51 mmol g^{-1}, respectively. Adsorbent **24** was not only highly efficient with respect to mercury owing to the presence of sulfur in two groups (sulfide and thiol) but was also able to bind mercury ions selectively in aqueous media in the presence of other listed cations.

§ Some authors[63–65] consider TEOS as a precursor of SiO_2 (silica), *i.e.*, the substrate to which carbofunctional organosilicon monomers are bound; therefore, adsorbents **24** and **25** (Schemes 14–16) are depicted with the substrate rather than by molecular formulas.

Scheme 14

$$(MeO)_3Si(CH_2)_3NH_2 + 2\,H_2C\text{—}CH_2 \longrightarrow (MeO)_3Si(CH_2)_3NH(CH_2)_2S(CH_2)_2SH \xrightarrow[NH_4OH,\ H_2O-EtOH]{Si(OEt)_4} \equiv SiO(CH_2)_3NH(CH_2)_2S(CH_2)_2SH$$

24

Unfortunately, no data confirming the structure of adsorbent **24** are given in the cited study. It is not clear whether methoxy substituents are retained at the silicon atoms of the obtained sorption material. If yes, it is not clear how the authors were able to obtain a stably operating adsorbent, especially in aqueous media.

Porous organosilicon adsorbent **25** with chemically immobilized iminodiacetic acid was synthesized by interaction of the product of tetraethoxysilane–3-(iodopropyl)trimethoxysilane copolycondensation[64] with diethyl iminodiacetate (Scheme 15).

Scheme 15

$$(MeO)_3Si(CH_2)_3I + 2\,Si(OEt)_4 \xrightarrow[H_2O-MeOH]{HCl} \equiv SiO(CH_2)_3I \xrightarrow[Et_3N]{HN(CH_2CO_2Et)_2} \equiv SiO(CH_2)_3N(CH_2CO_2Et)_2 \xrightarrow{HCl} \equiv SiO(CH_2)_3N(CH_2CO_2H)_2$$

25

The sorption activity of polymer **25** with respect to doubly and triply charged ions Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+} was studied. A distinctive feature of this polymer is the ability to be hydrolyzed in acidic media with the release of diethyl iminodiacetate; therefore, this polymer should rather be considered as an extractant but not as adsorbent of these elements. It decomposes in strongly acidic or basic media with the Si—O—Si bond cleavage.

Afterwards, adsorbent **25** was synthesized in a different way, in particular, by hydrolytic copolycondensation of tetraethoxysilane and the product of reaction of (3-aminopropyl)trimethoxysilane with ethyl chloroacetate in an HCl solution (Scheme 16).[65]

Scheme 16

$$(MeO)_3Si(CH_2)_3NH_2 + ClCH_2CO_2Et \xrightarrow[-HCl]{Et_3N} (MeO)_3Si(CH_2)_3N(CH_2CO_2Et)_2 \xrightarrow[MeOH]{Si(EtO)_4\ (2\ equiv),\ HCl-H_2O} \equiv SiO(CH_2)_3N(CH_2CO_2Et)_2 \xrightarrow{HCl} \mathbf{25}$$

Adsorbent **25** prepared in this way forms 1 : 1 (metal : ligand) complexes with Ni^{2+} and Cu^{2+} ions.

A broad range of adsorbents were reported by the authors of the cited studies[64, 65] in a review.[66] The adsorbents were synthesized like adsorbent **25** either by hydrolytic copolycondensation of $Si(OR)_4$ with carbofunctional organosilicon monomers $(RO)_3Si(CH_2)_3X$ (R = Me, Et; X = NH_2, Cl, I) followed by the reaction of formed poly-

organylsilsesquioxanes with organic reagents (similarly to Scheme 15) or by copolycondensation of $Si(OR)_4$ with organosilicon monomers prepared by interaction of $(RO)_3Si(CH_2)_3X$ with organic compounds (by analogy with Scheme 16). These adsorbents are recommended to recover, preconcentrate and determine di- and trivalent metal ions such as zinc, copper, iron, cobalt, nickel, manganese.

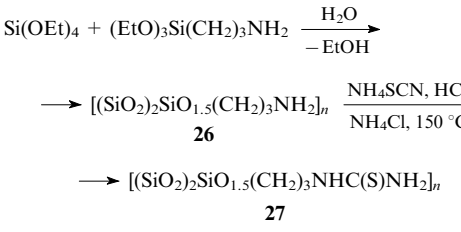
The cross-linked polysiloxane obtained by polycondensation of 3-(trimethoxysilyl)propyl methacrylate with *N*-(2-aminoethyl)-3-aminopropyl(trimethoxy)silane was used as the active phase of a potentiometric sensor for anion detection.[67] The use of this polysiloxane as an anion exchanger made it possible to design sensors for the NO_3^-, Cl^-, HCO_3^-, $H_2PO_4^-$, F^-, CH_3COO^-, SO_4^{2-} anions present in concentrations of $3\times10^{-5}-10^{-1}$ mol litre^{-1}.

The effect of the ratio of TEOS and 3-mercaptopropyl(trimethoxy)silane on the sorption activity of the products of their copolycondensation was investigated.[68] If the $Si(EtO)_4:(MeO)_3Si(CH_2)_3SH$ ratio was changed from 1:1 to 5:1, the concentration of sulfanylpropyl groups in the xerogels decreased from 5.0 to 1.9 mmol g^{-1}, whereas the specific surface area of xerogels increased from 13 to 631 m^2 g^{-1}.

The products of copolycondensation of TEOS and trimethoxy(3-sulfanylpropyl)silane (in different ratios) proved to be efficient adsorbents of mercury from aqueous media.[69–71] Copolycondensation of these monomers was carried out in the presence of a structuring agent, *viz*., the polyethylene oxide–polypropylene oxide–polyethylene oxide triblock copolymer described as PEO_{20} $PPO_{70}PEO_{20}$. The possibility of desorption of mercury was studied.[70] The desorption could be carried out only on treatment with chemical compounds that form stable complexes with Hg^{II}, *e.g*., thiocyanate or thiourea.

Cross-linked polysiloxane **26** (APPS) containing carbofunctional amino group was prepared by hydrolytic copolycondensation of tetraethoxysilane with (3-aminopropyl)-triethoxysilane.[72] Polysiloxane **26** reacted with ammonium thiocyanate to give organosilicon adsorbent **27** (PSMT) containing thiocarbamide groups (Scheme 17).

Scheme 17

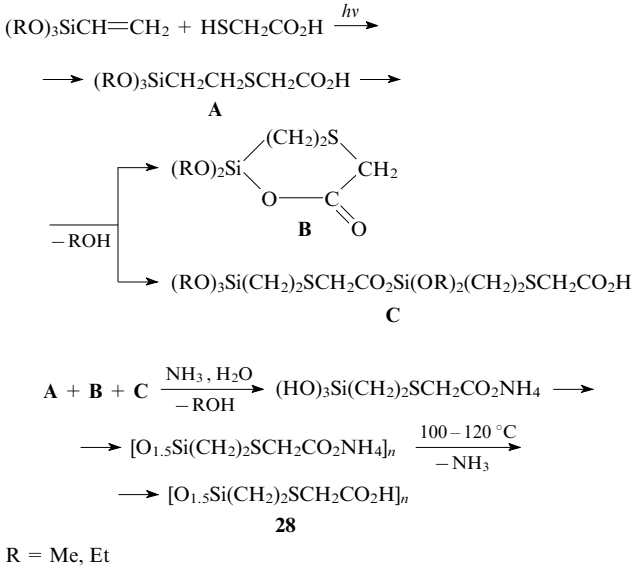


Adsorbent **26** efficiently collects Pb^{II} and is capable of separating Cu^{II} and Zn^{II} from Co^{II} and Ni^{II}, while PSMT (**27**) adsorbs Bi^{III} from 0.1–2 M HCl solutions, Pt^{IV} at pH 2 and Pb^{II} at pH > 3. Doubly charged Co, Ni, Cu and Zn may be adsorbed by **27** from alkaline solutions.[72] A high sorption activity with respect to Cu^{II}, Zn^{II}, Co^{II} and Ni^{II} was also shown by the xerogel obtained from teraethoxysilane, (3-aminopropyl)triethoxysilane and vinylpyridine.[73]

New hybrid organic-inorganic adsorbents containing 3-aminopropionate chelating group were synthesized by copolycondensation of tetraethoxysilane with (3-aminopropyl)triethoxysilane and a series of modifying agents such as $MeSi(OEt)_3$, $EtSi(OEt)_3$, $Ti(OEt)_4$, $AlONO_3$, $ZrOCl_2$ followed by carboxyethylation with acrylic acid.[74–76] Carboxyethylation of the organic-inorganic materials obtained in the first step of the synthesis that contain amino groups furnished *N*-mono- and *N*,*N*-dicarboxyethylated derivatives. The sorption properties of these hybrid adsorbents were studied by the example of Co^{II}, Ni^{II}, Cu^{II} and Zn^{II} ions. The sorption capacity of hybrid materials containing dicarboxyethyl groups is substantially larger than that of adsorbents with amino groups. All the obtained adsorbents exhibit significant selectivity towards copper ions. In the presence of Cu^{II} ions, the cations of Ni^{II} and Co^{II} are not virtually adsorbed. Only adsorption of the Zn^{II} ions can compete with that of the copper ions. Among studied adsorbents, most promising is the product described as $[SiO_2SiO_{1.5}(CH_2)_3N(CH_2CH_2CO_2H)_2]_n$ (an analogue of adsorbent **22**).

The sorption activity of the organosilicon polymer obtained from *S*-trialkoxysilylethyl derivatives of thioglycolic acid, which are formed in the photochemical reaction of vinyltriethoxysilane with $HSCH_2CO_2H$ (Scheme 18), was studied in detail.[77]

Scheme 18



The product of hydrolytic polycondensation of a mixture of organosilicon monomers **A**–**C** in a 5 M solution of ammonium hydroxide, a polymer with salt-like structure, was heat treated (100–120 °C) to remove ammonia and form the polymeric structure with free acid groups (polymer **28**, PSK-3).

Polymer PSK-3 (**28**) was studied as a sorbent of silver(I) from 0.5–5.0 M thiosulfate or nitric acid solutions and also of gold(III), platinum(IV) and palladium(II) from 0.5–5.0 M solutions of hydrochloric acid. The metals under study exist in these media as Ag^+, $[Ag(S_2O_3)_2]^{3-}$, $[AuCl_4]^-$, $[PtCl_6]^{2-}$, $[PdCl_4]^{2-}$ (Refs 78 and 79).

It is noteworthy that PSK-3 operates as a cation exchanger with respect to silver. Silver(I) is adsorbed more efficiently from nitric acid solutions than from thiosulfate solutions. It is because in thiosulfate solution, silver exists initially as complex anions that undergo stepwise dissociation to Ag^+ (Scheme 19).

Scheme 19

$$[Ag(S_2O_3)_2]^{3-} \rightleftharpoons S_2O_3^{2-} + [AgS_2O_3]^-$$
$$[AgS_2O_3]^- \rightleftharpoons Ag^+ + S_2O_3^{2-}$$

The adsorption of other noble metals that exist in the form of complex chlorometallate anions under these conditions and possibly the $[Ag(S_2O_3)]^{3-}$ anion proceeds according to the anion exchange mechanism. The anion exchange ability of polymer **28** is due to the ability of its functional group to exist in the betaine form (Scheme 20).

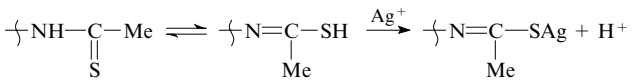
Scheme 20

$$RSCH_2CO_2H \longrightarrow \overset{+}{R}SHCH_2CO_2^- \xrightarrow{H^+} \overset{+}{R}SHCH_2CO_2H \xrightarrow{[AuCl_4]^-} \overset{+}{R}SHCH_2CO_2H\cdot[AuCl_4]^-$$

R = $O_{1.5}Si(CH_2)_2$

The adsorbent that was obtained by hydrolytic polycondensation of *N*-(3-triethoxysilylpropyl)thioacetamide acts as a cation exchanger when reacts with silver ions owing to the thiol–thione tautomerism of its thioacetamide groups (Scheme 21).[80]

Scheme 21



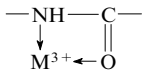
The functionalized polysilsesquioxanes $[O_{1.5}Si(CH_2)_3.NHC(O)Me]_n$ (**29**) and $\{1,2\text{-}[O_{1.5}Si(CH_2)_3NHC(O)]_2C_6H_4\}_n$ (**30**),[81,82] which proved earlier to adsorb noble metals (gold, platinum, palladium) were found to be effective sorbents of lanthanides (Table 1).[83] The choice of lanthanides as sorbates was dictated by the simultaneous presence of nitrogen and oxygen atoms in carbofunctional groups of adsorbents **29** and **30**, which represent the most preferable coordination centres for lanthanide ions.[84]

Table 1. Recovery of lanthanides (as trivalent ions) by polymers **29** and **30**.[a]

Lanthanide	Degree of recovery (%)	
	29	**30**
La	97.5	69.5
Ce	97.0	67.5
Pr	96.0	67.0
Nd	95.3	66.3
Sm	53.8	53.3
Eu	61.3	62.0
Gd	70.5	70.0
Tb	67.8	67.0
Dy	68.0	62.5
Ho	62.0	59.3
Er	73.8	72.0
Tm	81.3	80.3
Yb	85.0	90.0
Lu	90.5	98.3

[a] The starting sorbate concentration is 4 mg litre^{-1}, the solution volume is 50 ml, the mass of the adsorbent is 50 mg, the sorption time is 30 min.

When lanthanide adsorption was studied, the tetrad effect was vividly manifested. This effect, first described in the 1960s–1970s [85,86] is quite weak when lanthanides react with complexing reagents in solutions. One can assume that such a clear manifestation of the tetrad effect in the reaction of lanthanides with these organosilicon adsorbents is due to the transfer of complexation to the solid phase. The adsorption proceeds according to the complexation mechanism due to chelation of lanthanide ions by the amide groups of adsorbents **29** and **30**.



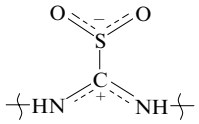
Even more vivid manifestation of the tetrad effect is observed in the lanthanide sorption by organosilicon adsorbent **31**, which contains dioxothocarbamide carbofunctional groups.[87] Functionalized polysilsesquioxane $[O_{1.5}Si(CH_2)_3NHC(SO_2)NH(CH_2)_3SiO_{1.5}]_n$ (**31**) was synthesized [88] from *N*,*N*′-bis(3-triethoxysilylpropyl)thiocarbamide using the oxidative hydrolytic polycondensation method developed earlier (Scheme 22).[8]

Scheme 22

$$[(EtO)_3Si(CH_2)_3NH]_2C{=}S \xrightarrow[-EtOH,\ -H_2O]{H_2O_2,\ H_2O} [O_{1.5}Si(CH_2)_3NHC(SO_2)NH(CH_2)_3SiO_{1.5}]_n$$

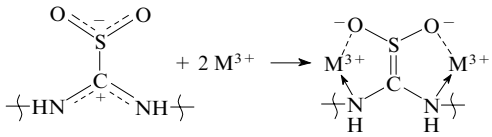
31

A distinctive feature of polymer **31** is the zwitter-ionic structure of its carbofunctional group $\text{-}NHC(SO_2)NH\text{-}$.



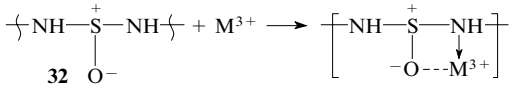
According to the IR data [decrease in intensity of the 1695 cm^{-1} absorption band ($\nu_{C=N}$) and appearance of the band in the 1350–1370 cm^{-1} region typical of $\nu_{C=S}$], this group loses its zwitter-ionic structure after adsorption of lanthanides.[87] According to the potentiometric data, the lanthanide sorption does not change the concentration of hydrogen or hydroxide ions in the solution. This suggests that the sorption of lanthanides proceeds according to the ion-coordination mechanism (Scheme 23).

Scheme 23



A similar mechanism of lanthanide sorption is involved in the case of the organosilicon polymer $[O_{1.5}Si(CH_2)_3.NHS(O)NH(CH_2)_3SiO_{1.5}]$ (**32**) (Scheme 24).[87]

Scheme 24



32

Synthesis and some properties of polymer **32** and also synthesis and properties of analogous polysilsesquioxane $[O_{1.5}Si(CH_2)_3NHS(O_2)NH(CH_2)_3SiO_{1.5}]$ (**33**), which was

studied as an adsorbent of lanthanides,[86] were reported earlier.[89] Polymer **33** shows quite high sorption activity only towards late lanthanides starting from erbium. This opens up the possibility of selective extraction of erbium, thulium, ytterbium and lutetium in the presence of lanthanides of the cerium subgroup.[90]

Due to the zwitter-ionic structure of its carbofunctional group [$-(NH)C(SO_2)NH-$], polymer **31** behaves as an ampholyte with respect to V^V, Mo^{VI}, W^{VI}, Th^{IV} and U^{VI}. It efficiently adsorbs both cationic (VO_2^+, MoO_2^{2+}, Th^{4+}, UO_2^{2+}, UO_2OH^+, $ThOH^{3+}$) and anionic (VO_4^{2-}, MoO_4^{2-}, WO_4^{2-}) forms of these elements.[91–93]

Adsorbents **34a**,**b** were prepared[94] by the reaction of polymer **31** with ammonia and methylamine (Scheme 25, a formula unit is shown). They contain a guanidine group and exhibit quite high sorption activity towards Ag^I (the static sorption capacity is >4 mmo g^{-1}).

Scheme 25

$$[O_{1.5}Si(CH_2)_3NH]_2CSO_2 \xrightarrow{RNH_2} \underset{\mathbf{31}}{} \longrightarrow \underset{\mathbf{34a,b}}{[O_{1.5}Si(CH_2)_3NH]_2C{=}NR} + 2\,H^+ + SO_2^{2-}$$

R = H (**a**), Me (**b**)

Organosilicon adsorbents with the carbofunctional guanidine groups were also prepared by hydrolytic polycondensation of organosilicon monomers **35a**,**b** of the general formula $(EtO)_3Si(CH_2)_3NHC(=NH)NHR$ [R = H (**a**), $(CH_2)_3$ $Si(OEt)_3$ (**b**)].[95] The starting monomers were synthesized by interaction of guanidine carbonate with 3-aminopropyl(triethoxy)silane at the 1 : 1 or 1 : 2 reactant molar ratio (Scheme 26).

Scheme 26

$$[(H_2N)_2C{=}NH]_2\cdot H_2CO_3 + (EtO)_3Si(CH_2)_3NH_2 \longrightarrow$$

$$\xrightarrow[-NH_3,\,CO_2,\,H_2O]{1:1} \underset{\mathbf{35a}}{H_2NC(=NH)NH(CH_2)_3Si(OEt)_3}$$

$$\xrightarrow[-2\,NH_3,\,CO_2,\,H_2O]{1:2} \underset{\mathbf{35b}}{NH{=}C[NH(CH_2)_3Si(OEt)_3]_2}$$

Organosilicon polymers of the general formulas $[O_{1.5}Si(CH_2)_3NHC(=NH)NH_2)]_n$ and $\{SiO_2[O_{1.5}Si(CH_2)_3.$ $.NH]_2C(=NH)\}_n$ obtained by hydrolytic polycondensation of monomer **35a** or copolycondensation of monomer **35b** with teraethoxysilane were tested as adsorbents of noble metals, *viz*., gold(III), rhodium(III), palladium(II) and platinum(IV). The metals were adsorbed from 1–5 M solutions of HCl. The sorption mechanism is anion exchange in view of the existence of the sorbates in the form of complex chlorometallate anions in such media (an example is presented in Scheme 27).

Scheme 27

$$RNH_2 + HCl \longrightarrow RNH_2\cdot HCl \xrightarrow{H_2[PtCl_6]} \longrightarrow (RNH_3)_2[PtCl_6]^{2-} + 2\,HCl$$

R = $O_{1.5}Si(CH_2)_3NHC(=NH)$

Polymer **36** was prepared by hydrolytic polycondensation of the organosilicon monomer *N*-(3-(triethoxysilylpropyl)-*N′*-acetylthiocarbamide with tetraethoxysilane (Scheme 28).[96]

Scheme 28

$$(EtO)_3Si(CH_2)_3NHC(S)NHC(O)Me + Si(EtO)_4 \xrightarrow[-EtOH]{H_2O} \longrightarrow \underset{\mathbf{36}}{\{SiO_2[O_{1.5}Si(CH_2)_3NHC(S)NHC(O)Me]_2\}_n}$$

This polymer was examined as an adsorbent of noble metals (silver, gold, rhodium, palladium, platinum) from solutions of nitric and hydrochloric acids.

Characteristic features of adsorbent **36** are the high rate of sorption equilibration in the static mode (3–5 min for any of the metals studied except for rhodium) and the capability of efficient uptake of Au^{III} cyanide complexes from mildly acidic, neutral and alkaline solutions. For instance, gold is adsorbed from solutions with pH 4, 6, 8 and 10 when present in the amount of 50 mg litre^{-1} together with 400 mg litre^{-1} of KCN to 85%, 88%, 90% and 92%, respectively.

In terms of sorption capacity, this sorbent resembles the previously described organosilicon sorbent PSTM-3 of the formula $\{[O_{1.5}Si(CH_2)_3NH]_2C(S)\}_n$ (**37**).[8,9] However, unlike **37**, adsorbent **36** is a stronger redoxite with respect to gold(III). With the overall sorption capacity with respect to Au^{III} being 694 mg g^{-1}, only 200 mg g^{-1} is detected in the matrix of adsorbent **36**. The rest of gold is recovered from the solution as free metal. By analogy with the behaviour of adsorbent **37**,[97] this phenomenon can be explained, taking into account the thiol – thione tautomerism of the thiocarbamide moiety (Scheme 29).

Scheme 29

$$\text{NH–C(S)–NH} \rightleftharpoons \text{NH–C(SH)=N} \xrightarrow{[AuCl_4]^-}$$

$$\longrightarrow \text{NH–C(=N)–S–S–C(=N)–NH} + AuCl_2^- + 2\,Cl^- + 2\,H^+$$

$$\text{NH–C(SH)=N} + 2\,AuCl_2^- \longrightarrow$$

$$\longrightarrow \text{NH–C(=N)–S–S–C(=N)–NH} + 2\,Au^0 + 4\,Cl^- + 2\,H^+$$

The thiol – thione tautomerism also determines the cation exchange mechanism of sorption of the silver ions by polymer **36**. In this case, however, the complexing mechanism cannot be ruled out either (Scheme 30).

Scheme 30

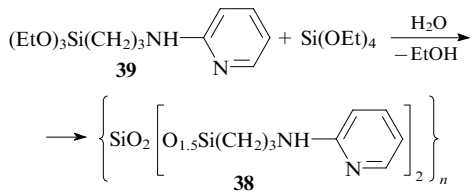
$$\text{NH–C(=S)–NH} + AgNO_3 \longrightarrow \text{NH–C(=S}\rightarrow Ag^+\text{)–NH}$$

An analogous mechanism of complexation also operates when **36** adsorbs platinum, palladium and rhodium, although reduction of the metals to lower oxidation states is not observed even in the case of platinum(IV), which is prone to lower the oxidation state.

Adsorbent **37** (PSTM-3) formed the basis of a procedure comprising sorption and atomic emission determination of gold, palladium and platinum in rocks and ores, which was implemented in the practice of analytical services of geological prospecting companies.[98] The limits of quantitative determination are 0.001 g t^{-1} for gold and palladium and 0.01 g t^{-1} for platinum.

Adsorbent **38**, an efficient sorbent of noble metals (gold, rhodium, palladium, platinum), was synthesized by hydrolytic copolycondensation of tetraethoxysilane and 2-[*N*-(3-triethoxysilyl)propylamino]pyridine (**39**) (Scheme 31).[99]

Scheme 31



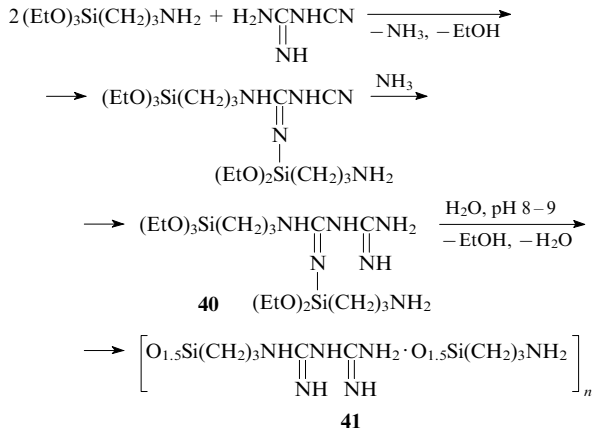
These elements were sorbed from the 0.5 M solutions of hydrochloric acid. The static sorption capacities (mg g^{-1}) and phase distribution coefficients (cm^3 g^{-1}, shown in parentheses) for gold, rhodium, palladium and platinum are 134 (4.3×10^3), 110 (1.3×10^3), 124 (2.8×10^3) and 141 (5.4×10^3), respectively. The obtained data indicate that adsorbent **38** can be used to preconcentrate these elements from solutions containing them in trace amounts. The sorption of these elements proceeds according to the anion exchange mechanism because these noble metals exist in this medium in the form of chloro- or chloro-aqua complexes.[78]

The fact that adsorbent **38** does not adsorb silver and copper from acidic media, where they exist as cations, corroborates that this adsorbent is a cation exchanger.

The sorption activity of some homopolymers based on monomers **35a** and **39**, the products of hydrolytic copolycondensation of these monomers with teraethoxysilane and the natural zeolite Shivyrtuin modified by these monomers was studied.[100] All of the listed products exhibit good sorption activity towards noble metals (gold, rhodium, palladium, platinum), which is not inferior to the activity of known nitrogen-containing organic ion exchangers and complexing agents.[101]

The organosilicon monomer 1-*N*-[3-(triethoxysilylpropyl]-2-*N*-[(3-aminopropyl)diethoxysilyl]biguanidine (**40**) was synthesized [102] by analogy with organic compounds of similar structure,[103] the specific character of its formation being related to the acidity of dicyandiamide.[104] Hydrolysis of monomer **40** gave product **41** of polycondensation of 3-(triethoxysilyl)propylamine and 1-[*N*-(3-triethoxysilylpropyl]biguanidine, which were formed upon hydrolytic cleavage of both Si–OC and Si–N bond in the monomer (Scheme 32).

Scheme 32

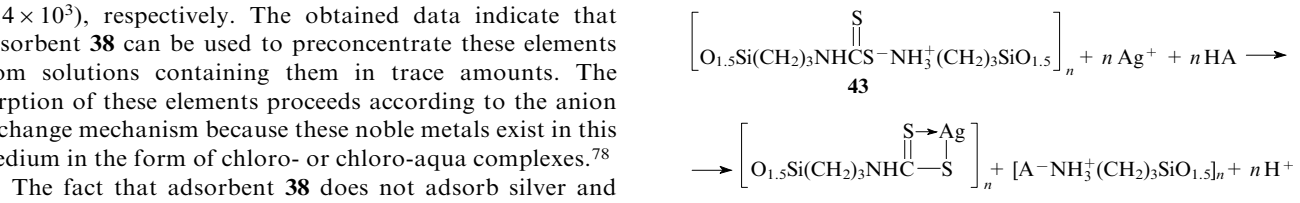


Product **41** proved to be a very efficient adsorbent of Ag^{I}.[102]

The syntheses of the products of hydrolysis of *N*-3-(triethoxysilyl)propylammonium *N*-3-(triethoxysilyl)propylthiocarbamate (**42**) (adsorbent **43**) and copolycondensation of tetraethoxysilane with 1,3-bis(3-triethoxysilylpropyl)iminoguanidine (**44**) (adsorbent **45**; consisting of the elementary units $SiO_2\{NH{=}CNH[NH(CH_2)_3SiO_{1.5}]_2\}$) were reported.[105, 106] Similarly to starting monomer **42**, adsorbent **43** has a salt-like structure.

The activity of adsorbents **43** and **45** was studied with respect to the noble metals (silver, gold, rhodium, palladium and platinum) and mercury. The sorption of these metals by adsorbent **43** from acid media follows an ion-coordination mechanism with allowance for the changes of the thiocarbamate moiety (Scheme 33). It is indicated by minor (less than 5%–10%) desorption of these metals on treatment with nitric or hydrochloric acid.

Scheme 33



Adsorbent **43** is very efficient with respect to silver and mercury as these elements tend to be complexed with sulfur-containing ligands. The values of the static sorption capacity (SSC) for polymers **43** and **45** are presented in Table 2.

Table 2. Sorption activity of organosilicon polymers **43** and **45**.[a]

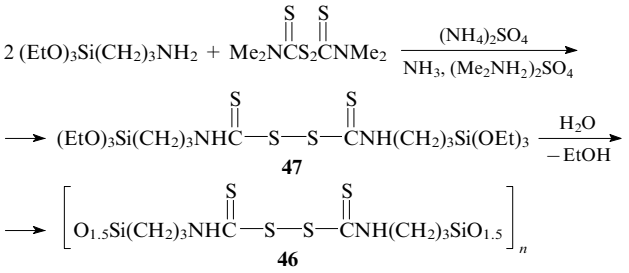
Polymer	SSC /mg g^{-1}					
	Ag^{I}	Au^{III}	Pd^{II}	Rh^{II}	Pt^{IV}	Hg^{II}
43	180	330	100	34	102	440
45	520	54	90	162	120	330

[a] The medium is 3 M HNO_3 for Ag^{I} and Hg^{II} or 3 M HCl for Au^{III}, Pt^{IV}, Pd^{II}, Rh^{III}, As^{V}, Cd^{II}, Co^{II}, Ni^{II}, Cu^{II}; the mass of the adsorbent is 50 mg; the time of the contact of the sorbent with the sorbate solution is 3 h.

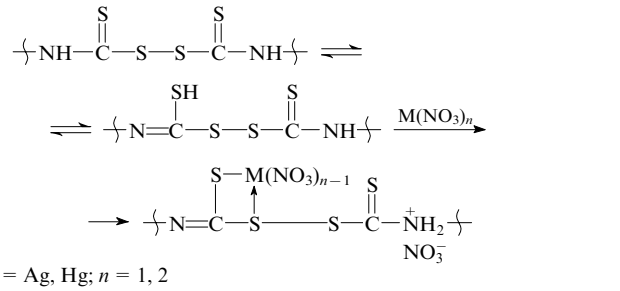
Organosilicon adsorbent **46** containing carbofunctional thiuram disulfide group was synthesized by hydrolytic polycondensation of *N*,*N*′-bis(3-triethoypropyl)thiuram disulfide (**47**), which was obtained by condensation of aminopropyl(triethoxy)silane and tetramethylthiuram disulfide (Scheme 34).[107]

The sorption activity of sorbent **46** was studied with respect to the noble metals (Ag^{I}, Au^{III}, Rh^{II}, Pd^{II}, Pt^{IV}) and some toxic heavy elements (As^{V}, Co^{II}, Ni^{II}, Cu^{II}, Cd^{II}, Hg^{II}). A comparison of the SSC values of adsorbent **46** towards these elements with its theoretical total sorption capacity (TSC), which is 2.7 or 5.4 μm g^{-1} provided that all functional groups of the adsorbent participate in the sorption and form 1 : 1 or 1 : 2 complexes (Table 3), made it possible to divide the sorbates into two groups. The first group includes Cd^{II}, Ag^{I}, As^{V}, Hg^{II} and Ni^{II}, whose sorption giving 1 : 1 complexes is 58%–79% of the theoret-

Scheme 34



Scheme 35



M = Ag, Hg; n = 1, 2

Table 3. Sorption activity of adsorbent **46**.[a]

Sorbate	SSC /m g^{-1}	SSC/TSC (%)
Ag^{I}	2.22	82.35
Hg^{II}	1.75	64.80
Au^{III}	0.18	7.14
Pt^{IV}	0.17	6.45
Pd^{II}	0.20	7.55
Rh^{III}	0.37	13.84
As^{V}	1.85	68.81
Cd^{II}	2.65	97.35
Co^{II}	0.64	23.89
Ni^{II}	1.58	58.55
Cu^{II}	5.00	184.97 (1 : 1)
		92.75 (1 : 2)

[a] Ag^{I} and Hg^{II} are recovered from 3 M HNO_3, the other sorbates are extracted from 3 M HCl; the sorption time is 3 h.

ical value. The second group includes Au^{III}, Rh^{II}, Pd^{II} and Pt^{IV}, whose sorption under the same conditions varies within 6%–14%. A special place among the sorbates is occuppied by Cu^{II}, which forms 1 : 2 complexes with participation of almost all functional groups of the adsorbent (SSC = 98%).

The sorption of Ag^{I} and Hg^{II} by adsorbent **46** proceeds according to the ion-coordination cation-exchange mechanism owing to thiol–thione rearrangement of the thiuram disulfide group to give S,S-chelate complexes (Scheme 35).

The sorption of Au^{III}, Rh^{III}, Pd^{II} and Pt^{IV} follows the ion-coordination mechanism but with formation of the N,S-chelates in view of the fact that the anions present in the complexes act as sorbates.

Table 4. Colour of adsorbents **41**, **43**, **45** and **47** after the a 3-h contact with solutions containing metal ions.[a]

Metal	Polymer colouring			
	41	**43**	**45**	**47**
Ag^{I}	beige	primrose	grey	grey-green
Au^{III}	bright yellow	orange	vinous	yellow
Pd^{II}	brown	brown	orange	orange-brown
Rh^{III}	–	pink	red	yellow
Pt^{IV}	pale yellow	beige	yellow	yellow
Hg^{II}	–	bright yellow	decoloura-tion[b]	–
Cu^{II}	–	–	–	brown
Co^{II}	–	–	–	light green

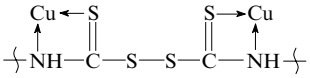
[a] The medium is 3 M HNO_3 in the case of Ag^{I} and Hg^{II}; 3 M HCl in the case of Au^{III}, Pt^{IV}, Pd^{II}, Rh^{III}, As^{V}, Cd^{II}, Co^{II}, Ni^{II}, Cu^{II} ; the adsorbent mass is 50 mg.
[b] The free adsorbent is pinkish.

Table 5. Colour of the paper with immobilized monomers[a] **40**, **42**, **46** after the contact with metal salts solutions during 10 min.[b]

Paper-immobilized monomer	Metal	Metal concentration /g litre^{-1}			
		0.1	0.5	0.8	1.0
40	Au^{III}	brown	brown	–	orange-brown
	Rh^{III}	–	pink	–	bright pink
42	Hg^{II}	decolouration	decolouration	decolouration	decolouration
	Pd^{II}	pale orange	pale orange	orange	brown
	Au^{III}	pale orange	pale orange	orange	orange
	Hg^{II}	decolouration	decolouration	decolouration	decolouration
46	Pt^{IV}	yellow	yellow	yellow	yellow
	Au^{III}	pale yellow	yellow	orange	brown
	Pd^{II}	orange	orange	orange	dark orange
	Rh^{III}	pale pink	pink	pink	red
	Ag^{I}	green	gray-green	gray	gray
	Cu^{II}	brown	brown	brown	brown

[a] The 40% solutions of the starting monomers in diethyl ether were used for modification. [b] The paper with immobilized monomers has yellowish or pinkish colour.

When Cu^{II} reacts with adsorbent **46**, the N,S-chelate complex is formed, but in this case, the coordination mechanism operates.



A distinctive feature of both monomeric and polymeric organosilicon derivatives of dithiocarbamic acid (monomer **42**, adsorbent **43**), biguanidine (monomer **40**, adsorbent **41**), iminoguanidine (monomer **44**, adsorbent **45**) and thiuram disulfide (monomer **46**, adsorbent **47**) is the colour change upon interaction with the metals (metallochromism).[105, 106] This discovery led to the development of test systems of new generation, *viz*., powder systems in the case of adsorbents and indicator paper in the case of monomers, which are easily immobilized on any substrate (Tables 4 and 5).

These organosilicon test systems provide an exceptionally simple way to the development of new chemical test methods based on them. The importance of test methods is ever increasing. They are widely used in analytical practice in environmental, industrial, clinical and forensic fields, ensuring quickness, simplicity and low cost of qualitative, semi-quantitative and quantitative determination of certain components, including those especially hazardous to human health, in various natural and man-made specimens.[11, 108, 109]

V. Conclusion

The above data convincingly demonstrate that organosilicon ion-exchange and complexing adsorbents are now finding the widest practical application. They are efficient analytical reagents used to determine metals in natural and man-made specimens, reagents for recovery of especially valuable elements from industrial wastes and sewages and for purification of the wastes and effluents from highly toxic and highly dangerous impurities. There are three types of sorption materials. First, silicas that are chemically modified by compounds containing functional ionogenic and complexing groups. Second, silicas with adsorbed analytical reagents or silicic acid xerogels obtained by the sol – gel method from tetramethoxy- or tetraethoxysilanes in the presence of such reagents. And finally, the third group includes adsorbents obtained by hydrolytic polycondensation and copolycondensation of carbofunctional organosilicon monomers and representing carbofunctional organosilicon polymers with the silsesquioxane structure.

The disadvantage of the adsorbents of the first type consists in their multi-step syntheses caused by the necessity of using anchoring reagents or the surface assembly method and the uncontrollable concentration of grafted functional groups on their surface. The multi-step assembly of the hybrid adsorbent containing chitosan moieties[43] represents an example of such a synthesis.

According to an opinion expressed in monographs,[10, 14] adsorbents of the second type are most acceptable for analytical applications. Indeed, due to their accessibility, sorption materials of this type are used to preconcentrate metals as the first step of many physicochemical methods for metal quantification. However, the stability of such sorption materials with reagents being physically adsorbed on the silica surface and capable of ion exchange and complexation and reproducibility of their synthesis are problematic.

The adsorbents that represent products of hydrolytic polycondensation or copolycondensation of organosilicon monomers of the general formula X_3SiRY or $(X_3SiR)_2Y$ [X = Cl, OR′, C(O)OR′, NR'_2 (R′ = Me, Et); R is a divalent hydrocarbon moiety, Y is an iogenic or complexing group], *i.e*., carbofunctional polyorganylsilsesquioxanes, are easily prepared and their composition and properties are well reproducible. The three-dimensional cross-linked silsesquioxane structure of these adsorbents ensures their high thermal stability and resistance to corrosive acidic media, while the silsesquioxane matrix does not affect the specific reactivity of their carbofunctional substituents. For instance, the capability of thiocarbamide for thiol – thione tautomerism is retained in its polymeric organosilicon derivatives such as adsorbents **36**[96] and **37**[97] and determines their amphoteric and redoxite properties.

An important new area of the application of carbofunctional polyorganylsilsesquioxanes and the starting organosilicon monomers is the development of test systems of new generation.

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