Synthesis and sorption properties of new hybrid chelating sorbents with β-alanine functional groups

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A series of γ-aminopropylsilylated sorbents was obtained from different oxide supports (silica gels, silica fillers, macroporous glasses, alumina) and by the direct synthesis (hydrolytic polycondensation of tetraalkoxysilanes with γ-aminopropyltriethoxysilane). The highest degree of immobilization was achieved for silicas, while the most convenient solvent was methanol. Sorbents with β-alanine functional groups were obtained by the subsequent reaction with acrylic acid. The degree of β-carboxyethylation was 1.3—1.9, and the highest content of functional groups (ν_{COOH} = 3.23 mmol g^{-1}) was achieved for carboxyethylated xero gel synthesized by the copolycondensation of tetraethoxysilane with γ-aminopropyltriethoxysilane. The sorbents containing β-alanine possess a higher selectivity of Cu^{2+} ion sorption than the initial γ-aminopropylsilylated sorbents.

Key words: chelating sorbents, β-alanine, polysiloxane, γ-aminopropyltriethoxysilane.

Chelating sorbents are used for concentrating and separation of metals from natural and waste waters as well as geological, biological, and industrial objects for analytical and technological purposes. Sorbents based on organic polymers and hybrid sorbents with an inorganic support, whose surface contains organic functional groups, can be used as chelating sorbents. In design of such materials, the decisive role belongs to a successful combination of the properties of the matrix and chelating group. The most commonly used chelating groups for the modification of various organic and inorganic polymeric matrices are complexones containing glycine moiety.[1] The chelating sorbents with β-alanine functional groups are virtually unstudied. It has previously been found that *N*-alkylated[2,3] and, to a greater extent, *N*-arylated[3—6] β-aminopropionic acids are highly selective with respect to Cu^{2+}. They form less stable complexes with transition metal ions than their glycinate analogs do; however, their ability to differentiate metal ions having similar properties is higher.[6] Therefore, the introduction of β-alanine groups into sorbents should provide, in our opinion, the creation of materials with a higher selectivity of sorption of Cu^{2+} ions.

Various oxide sorbents (silicas, aluminas, titanias, zirconias, and others) are used as inorganic supports. Among them, silica gels have found the widest use due to mechanical strength, developed surface, and porosity.[7] Modified sorbents possess chemical properties of a grafted compound along with mechanical and hydrodynamic properties of silica gel, which enables the preparation of non-swelling and thermally and radiation stable sorbents.

In addition to the modification of prepared supports, the direct synthesis of modified sorbents from various silicon alkoxides by the sol-gel method has widely been used in the recent time.[8]

The purpose of this work is the development of new hybrid chelating sorbents by the covalent modification of different oxide supports with β-alanine functional groups, direct synthesis of sorbents of this type, and study of their selectivity with respect to transition metal ions.

Results and Discussion

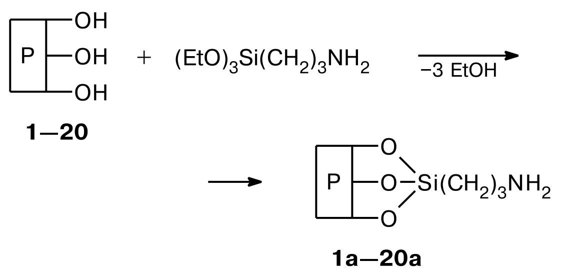
γ-Aminopropylsilylation of supports. The first stage of modification of the sorbent surface was carried out by silylation with γ-aminopropyltriethoxysilane (APTES, trade mark AGM-9), which is presented in Scheme 1 (grafted sorbents).

To choose a support providing the maximum specific content of amino groups, modification with APTES was carried out for silica gels **1—7**, silica fillers **8—10**, macroporous glasses **11—16**, and alumina samples **17—20**. Some characteristics of the initial supports and γ-aminopropylsilylation products (**1a—20a**) are presented in Table 1.

Before modification, sorbents were activated with hydrochloric acid (alumina was activated with acetic acid), and water was used during modification. The proton ex-

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 12, pp. 2620—2625, December, 2004.

Scheme 1



change capacity (PEC), which characterizes the number of amino groups accessible for protonation, was determined by reverse acid-base titration.

As follows from the data in Table 1, for γ-aminopropylsilylated silica gels **1a—7a**, silica fillers **8a** and **9a**, and Aerosil **10a**, the PEC value increases with a decrease in the particle size, that is, with an increase in the surface area. In the case of modified macroporous glasses **11a—16a** and alumina samples **17a—20a**, the PEC values within each group are close and almost independent of the particle size. In the two latter cases, the degree of immobilization is probably determined by a limited number of reactive groups on the support surface. As a whole, it should be mentioned that the highest degree of immobilization is achieved for silica gels.

Supports are usually activated before modification. Activation is considered to be necessary, because the support surface can contain either salt residues of the ≡SiONa type or bridging groups ≡SiOSi≡ along with hydroxyl groups. To remove salts and hydrolyze "bridges" if any, a support is treated with aqueous solutions of inorganic (HCl, H_2SO_4, HNO_3) or, more rarely, organic (acetic, propionic, trichloroacetic, trifluoroacetic) acids.[9] From this point of view, activation of sorbents is a necessary stage of successful immobilization. However, in some studies (see, *e.g.*, Ref. 10), commercial silica gels were used as received, and the degree of immobilization of products was rather high. To answer the question whether support activation is necessary or not, we modified both activated and non-activated samples. The results presented in Table 1 show that activation is not a necessary procedure for sorbents of laboratory design (**6**, **20**), while activation is necessary for industrial sorbents (sample **10**).

Immobilization of APTES can be carried out in different solvents. For example, the study[11] of the reaction of APTES with silica gel in water or toluene showed the preference of water. Another approach is also known: preliminary hydrolysis of APTES and treatment of a support with the resulting polymer.[12] The hydrolysis is carried out, as a rule, in aqueous methanol, where its rate is maximum. The interaction of Al_2O_3 with APTES was studied in several works.[13,14] We studied the influence of the solvent nature on the degree of immobilization for support samples **6**, **10**, **14**, and **20** demonstrating the highest degree of modification (PEC) in aqueous solutions. The obtained data are compared in Table 2.

The results of elemental analysis (see Table 2) show that all samples contain non-hydrolyzed OEt groups. Since

Table 1. Some characteristics of initial supports **1—20** and products of their γ-aminopropylsilylation **1a—20a**

Support	Trade mark of initial support	Particle size/mm	Sample	PEC/mmol g^{-1}
1	Silochrom SKh-2	0.2—0.3	**1a**	0.50
2	Silica gel for TLC	0.10—0.35	**2a**	0.81
3	Coarse-size silica gel for TLC	0.08—0.20	**3a**	1.16
4	Merck	0.07—0.23	**4a**	1.33
5	SILPEARL	0.07—0.15	**5a**	1.36
6	Silica gel for TLC (Czechoslovakia)	0.005—0.042	**6a**	1.53 (1.50*)
7	Silica gel for TLC (Czechoslovakia)	0.007	**7a**	1.42
8	Silica filler BS-50	45**	**8a**	0.48
9	Silica filler BS-100	100**	**9a**	0.69
10	Rosil 175	140**	**10a**	1.06 (0.83*)
11	MPS-200	0.10—0.15	**11a**	0.47
12	MPS-250 gkh	0.18—0.26	**12a**	0.59
13	MPS-700 gkh	0.15—0.20	**13a**	0.67
14	MPS-700 gkh	<0.1	**14a**	0.68
15	MPS-1150 gkh	0.14—0.25	**15a**	0.64
16	MPS-2000 gkh	0.18—0.26	**16a**	0.42
17	Al_2O_3 Voelm DO	0.15—0.22	**17a**	0.57
18	Al_2O_3 Brockmann activity II	0.05—0.15	**18a**	0.42
19	Al_2O_3 neutral for chromatography	0.04—0.250	**19a**	0.54
20	Al_2O_3 neutral for TLC 5—40	0.005—0.040	**20a**	0.59 (0.60*)

* The reaction was carried out without preliminary activation of the surface.

** Specific surface/m^2 g^{-1}.

Table 2. Characteristics of γ-aminopropylsilylated supports modified in different solvents

Solvent	Sample	Found (%)			$n_{\mathrm{OEt/N}}$*	ν_{N}**	PEC
		C	H	N		mmol g^{-1}	
Water	**6a**	6.33	1.93	1.53	0.92	1.09	1.53
	10a	3.95	1.38	1.39	0.16	0.99	1.06
	14a	3.89	0.99	1.38	0.15	0.97	0.68
	20a	—	—	—	—	—	0.59
Toluene	**6b**	8.04	2.12	2.12	0.72	1.51	1.63
	10b	10.73	2.73	2.95	0.62	2.11	1.80
	14b	9.81	2.45	3.13	0.33	2.23	1.62
	20b	5.80	1.99	1.42	0.89	1.01	0.86
Methanol	**6c**	4.21	1.55	1.52	0.11	1.09	1.05 (1.65***)
	10c	5.18	1.65	1.85	0.16	1.32	1.00
	14c	2.51	0.55	0.79	0.37	0.56	0.61
	20c	5.06	2.03	1.57	0.40	1.12	0.98

* The molar fraction of OEt groups is $n_{\mathrm{OEt/N}} = [(\omega_{\mathrm{C}}/\omega_{\mathrm{N}})(M_{\mathrm{N}}/M_{\mathrm{C}}) - 3]/2$.

** The amount of nitrogen in 1 g of the sorbent is $\nu_{\mathrm{N}} = 10\omega_{\mathrm{N}}/M_{\mathrm{N}}$ (mmol g^{-1}).

*** For a doubled amount of the methanol hydrolyzate.

the carbon content can vary for different degrees of hydrolysis of the OEt groups, the nitrogen content is an especially important parameter. The amount of amino groups in the samples, as a whole, is somewhat greater than the titrated amount, because not all groups are accessible for protonation.

The greatest coverage of the support surface is observed in toluene for the most part of samples. This agrees with the published data[15] on the modification of porous glasses with APTES. It is established[15] that a monolayer of an immobilizing agent is formed in an aqueous solution, whereas a multilayer coating is formed in toluene. It is shown[16] that for the monolayer silica gel coating the limiting concentration of aminopropyl groups is 1.02 mmol g^{-1}, and each fragment occupies 64 Å^2 of the surface area of the support. Thus, comparison of our results and published data suggests that a monolayer coating of the APTES support is formed in both water and methanol, while several layers are formed in toluene.

The method of immobilization in water is most economical (1.2 moles of APTES are needed to graft 1 mole of γ-aminopropylsilane). The method of immobilization in methanol is somewhat less economical (1.9 moles). The maximum consumption of APTES (even if the regeneration of its portion after distillation of a mother liquid is taken into account) is observed in toluene. The method of immobilization in methanol is most experimentally convenient due to a high solvolysis (hydrolysis) rate of alkoxysilanes. The degree of immobilization can be increased by using a doubled amount of a methanol hydrolyzate (see Table 2, sample **6c**). Thus, taking into account all factors, we can assert that the methanol treatment of silica gel is preferential.

Synthesis of APTES-based polysilicate sorbents by the sol-gel method. The method is based on the interaction of a sol of one component with another component to form a gel, whose processing affords the desired substrate.[17] Another variant of the sol-gel method applied for syntheses of silica gels modified by organic reagents[18] is the hydrolysis of tetraalkoxysilanes in an aqueous or aqueous-alcohol medium in the presence of a linked organic reagent to form a gel followed by drying of the latter: preparation of a "dry gel" (xero gel). In our case, this variant can be carried out through the copolycondensation of tetraalkoxysilanes with APTES.[19]

It is known[20] that silica sol reacts with APTES, and the product is used for covering capron threads; the use of this reaction to prepare modified supports is not described. Therefore, we studied the interaction of silica sol with APTES at different ratios of components, and the obtained results are presented in Table 3.

The highest yield (in addition to one of the highest capacity values) is observed for sample **21c** at a silica sol to APTES ratio of 5 : 1. However, the PEC of the sorbent is low, and this method seems less preferential compared to immobilization on silica gel.

Table 3. Sorbents obtained from silica sol and APTES

Sample	Silica sol : APTES*	m**/g	PEC /mmol g^{-1}
21a	5 : 0.3	0.238	0.44
21b	5 : 0.5	0.811	0.51
21c	5 : 1.0	1.049	0.50
21d	5 : 1.5	0.736	0.50
21e	5 : 2.0	0.418	0.32

* Volume ratio.

** Weight of the product.

Table 4. Characteristics of sorbents obtained by the copolycondensation of tetraalkoxysilanes with APTES

Sample	Silane	*t**/min	Found (%)			ν_N /mmol g^{-1}
			C	H	N	
22a	$Si(OMe)_4$	**	11.63	3.62	4.55	3.25
22b	$Si(OEt)_4$	1.5	16.56	3.92	5.20	3.71
22c	$Si(OPr)_4$	4	10.57	3.56	4.10	2.93

* Duration of the reaction.

** Instantly.

Different tetraalkoxysilanes (Scheme 2) can be used for copolycondensation with APTES. The ratio of components silane : APTES = 2 : 1 was recommended earlier[19], because this provides the maximum exchange capacity of the resulting xero gel. The characteristics of polymeric sorbents **22a—c** are presented in Table 4.

Scheme 2

$$2n\ Si(OR)_4 + n\ (EtO)_3Si(CH_2)_3NH_2 \xrightarrow[-ROH,\ EtOH]{H_2O}$$

$$\longrightarrow [(SiO_2)_2SiO_{1.5}(CH_2)_3NH_2]_n$$

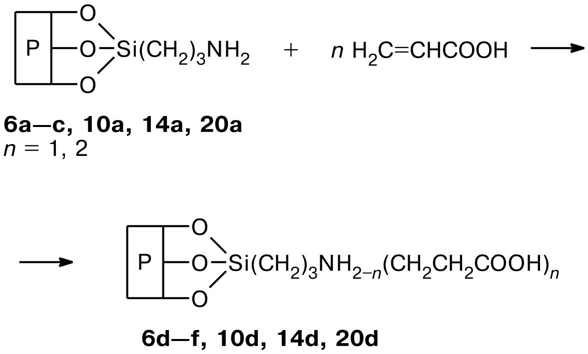
22a—c

R = Me (**a**), Et (**b**), Pr (**c**)

The reaction occurs most rapidly when tetramethoxysilane is used; however, the high rate of the process results in nonuniform gel formation with stirring and, as a consequence, heterogeneity of the product. The reaction with tetrapropoxysilane occurs slowly; therefore, tetraethoxysilane (TES) was chosen for further studies. At the same time, the data presented demonstrate that this variant of sol-gel method makes it possible to synthesize a sorbent with the maximum content of functional groups. The results obtained are comparable with the published data[19]: the PEC for the copolymer of TES with APTES is threefold higher than that for the modified silica gel (3.05 and 1.05 mmol g^{-1}, respectively).

β-Carboxyethylation of γ-aminopropylsilylated supports. Propionate groups were introduced into the sorbent structures by the aza-Michael reaction: addition of acrylic acid to the prepared aminosilicate sorbents (Scheme 3).

Scheme 3



The best (by PEC) samples of each group of the γ-aminopropylsilylated supports were carboxyethylated (Table 5).

As can be seen from the data in Table 5, all samples are characterized by the very high (although not maximum) degree of β-carboxyethylation (DS > 1.3), and the highest specific content of carboxyl groups was achieved for the carboxyethylation of xero gel **22b**. For silica gel **6**, we attempted to combine γ-aminopropylsilylation followed by β-carboxyethylation in the same reaction flask in an aqueous medium (see Table 5, sample **6g**). In this case, the amount of carboxyl groups is comparable with that obtained for sample **6f**, which was immobilized with APTES in methanol.

Thermogravimetry. The weight loss curves for aminopolysiloxane and its β-carboxyethylated derivative are pre-

Table 5. Characteristics of β-carboxyethylated sorbents

Sample	Initial substrate	Found (%)			DS*	ν_N	ν_{COOH}**
		C	H	N		mmol g^{-1}	
6d	**6a**	7.59	1.65	1.25	1.36	0.89	1.21
6e	**6b**	7.68	1.57	1.16	1.57	0.83	1.26
6f	**6c**	8.71	1.69	1.34	1.53	0.96	1.47
6g	**6**	8.26	1.75	1.15	1.79	0.82	1.47
10d	**10a**	4.33	1.24	0.72	1.36	0.51	0.69
14d	**14a**	2.20	0.57	0.30	1.91	0.21	0.40
22d	**22b**	17.98	3.66	2.50	1.79	1.80	3.23

* The degree of substitution (of β-carboxyethylation) DS = $[(\omega_C/\omega_N)(M_N/M_C) - 3]/3$ was calculated ignoring a possible presence of OEt groups.

** $\nu_{COOH} = \nu_N \cdot DS$ characterizes the overall amount of carboxyl groups in 1 g of the sorbent.

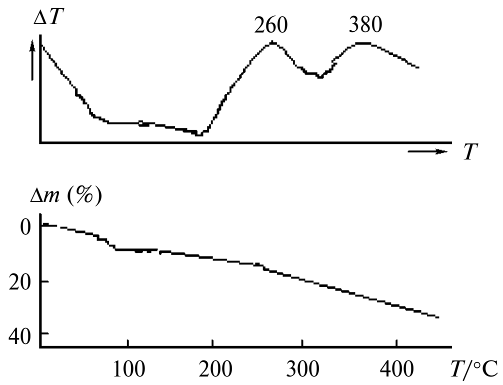


Fig. 1. Thermograms of aminopolysiloxane **22b**.

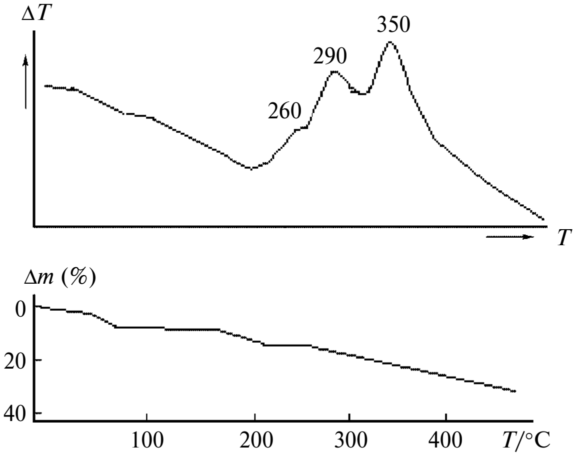


Fig. 2. Thermogram of sample **22d**.

sented in Figs 1 and 2. Both curves demonstrate the appearance of weight losses at temperatures below 100 °C corresponding to adsorbed water losses (~5%).

For the initial γ-aminopropylsilylated polymer (see Fig. 1), a weight loss (*i.e.*, elimination of the aminopropyl group) begins at ~200 °C and reaches a maximum rate at 260 °C. The decomposition proceeds *via* two stages, and the second maximum is observed at 380 °C. The total weight losses (below 450 °C) correspond to 24% (according to the elemental analysis data, to ~26%).

For the β-carboxyethylated polymer (see Fig. 2), the aminopropyl group is also eliminated first (at 260 °C); however, further this process is accompanied by the elimination of the carboxyethyl groups (DTA peaks at 290 and 350 °C), and the process becomes more exothermic. The total weight losses (below 450 °C) correspond to 40% (according to the elemental analysis data, ~30%). A remarkable real increase in the weight losses over the calculated values (which is, unambiguously, a result of a greater exothermicity of the process) indicates a partial silicon loss during decomposition.

It should be mentioned, as a whole, that the thermal stability of the resulting sorbents is not high.

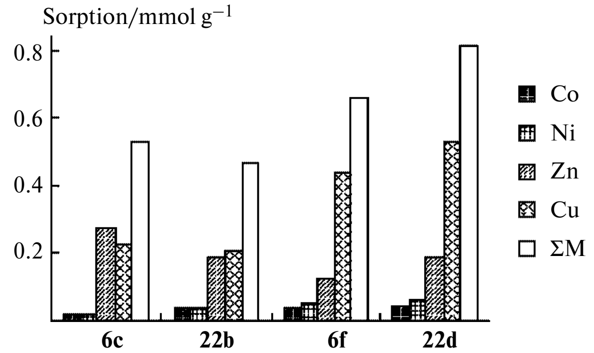


Fig. 3. Results of sorption of transition metal ions. Conditions of sorption: $[M^{2+}] = 0.025$ mol L^{-1}, $V = 25$ mL, sorbent weight 0.3 g, pH 6.3, 20 °C.

Sorption of transition metal ions. The results of sorption of Cu^{2+}, Zn^{2+}, Co^{2+}, and Ni^{2+} ions, when they are simultaneously present in solution, by the sorbents with the highest PEC are presented in Fig. 3.

For sorbents **6c** and **22b** containing only primary amino groups, the Cu^{2+} and Zn^{2+} ions are sorbed approximately equally, whereas Co^{2+} and Ni^{2+} are sorbed insignificantly. According to a change in the sorption selectivity, the cations can be arranged in the following series: $Co^{2+} \approx Ni^{2+} \ll Cu^{2+} \approx Zn^{2+}$.

The carboxyethylated samples (**6f**, **22d**) exhibit an increase in both the total sorption of metal ions and selectivity with respect to Cu^{2+} ions (see Fig. 3). The sorption series $Co^{2+} \approx Ni^{2+} \ll Cu^{2+} > Zn^{2+}$ corresponds to the known Irwing—Williams series for O,N-ligands. The highest capacity with respect to Cu^{2+} ions is observed for sample **22d**: β-carboxyethylated aminopolysiloxane obtained by the copolycondensation of TES and APTES.

Experimental

Diffuse reflectance IR spectra were recorded on a Perkin—Elmer Spectrum-One spectrometer. The C,H,N-analyses were carried out on a Perkin—Elmer automated analyzer. Thermograms were obtained on a MOM OD-102 derivatograph. The content of metals (Co, Ni, Cu, Zn) in sorbents was determined by atomic emission spectroscopy on an Optima 4300 DV spectrometer, and the relative error of analysis did not exceed 10%. The pH values were measured on an I-130M ionomer with glass (ELS-43-07) and silver/silver chloride (EVL-1M3.1) electrodes.

Activation of silica gels. A support (10 g) was poured with 20% HCl (10 mL), and the mixture was refluxed for 4 h. A precipitate was separated by decantation, washed with water for 4—6 times to pH ~7, and dried at 150 °C to a constant weight.

Activation of alumina. A mixture of Al_2O_3 (10 g) and 10% AcOH (70 mL) was refluxed for 1 h. A precipitate was washed with water to pH ~7 and dried at 400 °C to a constant weight.

Modification of supports in water. Preparation of sorbents 1a—20a. A solution of APTES (2 mL) in water (40 mL) was stored for 1 h at room temperature (~20 °C), then a support (5 g) was added, and the mixture was stirred for 1 h. A precipitate was filtered off, washed with water (3×20 mL), and dried at 120 °C to a constant weight. IR spectrum of **6a**, ν/cm^{-1}: 3370 (NH_2).

Modification of supports in toluene. Preparation of sorbents 6b, 10b, 14b, and 20b. A mixture of a support (2 g), APTES (12 mL), and anhydrous toluene (20 mL) was refluxed for 24 h. A precipitate was filtered off, washed successively with toluene (3×20 mL) and ethanol (3×20 mL), and dried at 120 °C to a constant weight. IR, ν/cm^{-1}: **6b**, 3366 (NH_2); **10b**, 3367 (NH_2); **14b**, 3354 (NH_2); **20b**, 3455 (NH_2).

Modification of supports in aqueous methanol. Preparation of sorbents 6c, 10c, 14c, and 20c. A mixture of APTES (0.7 mL), methanol (0.6 mL), and water (0.06 mL) was stored for 4 h at room temperature (~20 °C). Then methanol (4 mL) and a support (2 g) were added, and the mixture was stored in air for 2.5 h and dried at 120 °C to a constant weight. IR spectrum of **6c**, ν/cm^{-1}: 3292 (NH_2).

Preparation of sorbents 21a—e by the sol-gel method. Mixtures of silica sol (SiO_2, 255 g L^{-1}; Na_2O, 2.02 g L^{-1}) and APTES in ratios of 5 : 0.3, 5 : 0.5, 5 : 1.0, 5 : 1.5, and 5 : 2.0 (vol/vol, mL) were stored for 30 min. The resulting gel was dried at 100 °C, powdered, and washed with water to pH ~7, decanting a finely dispersed part with water. A precipitate was filtered off and dried at 100 °C to a constant weight.

Preparation of xero gels 22a—c. A mixture of tetraalkoxysilane (Alk = Me, Et, Pr) (0.28 mol) and water (13.2 mL) was stored in a water bath for 5 min, then APTES (33 mL, 0.14 mol) was added, and the mixture was stirred until homogenation was achieved. After several minutes, the gel was formed and dried for 24 h in air and for 2 h at 100 °C. The resulting substrate was powdered, washed with water to pH ~7, and dried again at 100 °C to a constant weight. IR spectrum of **22b**, ν/cm^{-1}: 3347, 3290 (NH_2).

β-Carboxyethylation of γ-aminopropylsilylated supports. Preparation of sorbents 6d—f, 10d, 14d, and 22d. A sorbent (2.1 mmol, calculated to the content of amino groups) was added to a solution containing acrylic acid (0.6 mL, 4.2 mmol) and water (8 mL). The mixture was refluxed for 10 h. The sorbent was filtered off, washed with water to pH ~7, and dried at 100 °C to a constant weight. IR, ν/cm^{-1}: **6d**, 1713, 1577 (C=O); **22d**, 1722, 1567 (C=O).

One-pot synthesis of sorbent 6g. A mixture of silica gel (3 g), APTES (1.4 mL, 0.006 mol), and distilled water (20 mL) was kept for 1 h. Then acrylic acid (1.7 mL, 0.024 mol) was added, and the mixture was refluxed for 8 h. The product was washed with water to the neutral reaction and dried at 100 °C to a constant weight. IR, ν/cm^{-1}: 1718, 1583 (C=O).

Study of the selectivity of extraction of metal transition ions. In a volumetric 250-mL flask, $Co(AcO)_2 \cdot 4H_2O$ (1.557 g), $Zn(AcO)_2 \cdot 2H_2O$ (1.372 g), $Ni(AcO)_2 \cdot 4H_2O$ (1.555 g), $Cu(AcO)_2 \cdot H_2O$ (1.248 g), and NH_4AcO (1.9 g) were dissolved to obtain a solution with concentrations of M^{2+} and NH_4AcO of 0.025 and 0.1 mol L^{-1}, respectively, and pH 6.3. A sorbent (0.3 g) was added to the resulting solution (25 mL), and the mixture was stirred and left for 24 h. The sorbent was filtered off and dried at 100 °C for 5 h. The content of metal ions was determined by atomic emission spectroscopy.

The authors thank O. V. Koryakova (Institute of Organic Synthesis, Ural Branch of the Russian Academy of Sciences) for recording diffuse reflectance IR spectra.

This work was financially supported by the Ministry of Science and Education of the Russian Federation (Scientific Program "Universities of Russia," Grant UR.05.01.007) and the Ural Research and Educational Center for Advanced Materials (Grant REC-005) supported by the Ministry of Science and Education of the Russian Federation and the U.S. Civilian Research and Development Foundation (CRDF, Grant EK-005-X1).

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Received January 19, 2004;
in revised form April 20, 2004