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Dedicated to Academician Yu.A. Zolotov in the year of his 90th birthday

Specific Features of Complexation on the Surface of Modified Silica Sorbents: Sorption and Complexation Chromatography of Metals

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Abstract—The results of studying the complexation of a number of metal ions on the surface of silica chemically modified by various functional analytical groups are systematized in the review. Examples of the influence of the matrix of sorbents (silica) on the thermodynamic and kinetic parameters of surface complexation reactions with metals are presented. Specific features of using finely dispersed silicas with complexing functional groups in high performance complexation metal ion chromatography are considered.

Keywords: silica, sorbent, complexation, sorption, chromatography

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INTRODUCTION

Sorption concentrating remains to be one of the demanded and efficient methods for sample preparation in chemical analysis. This method of concentrating was brought to the forefront due to high concentrating coefficients of substances, a possibility of automation, and a broad assortment of produced sorbents. Among numerous sorbents the sorbents based on silica (quartz, silica gel, glass, and others) attract rapt attention. A possibility of varying structural characteristics (specific surface area, pore diameter and volume, particle size and shape) in broad ranges, good chemical stability and mechanical strength, and a low cost provided a wide propagation of silicas in diverse adsorption and chromatographic processes. A distinctive feature of silica is a possibility of chemical modification of the surface by various organic compounds in order to obtain new sorption materials with the required selectivity to certain groups of sorbates or to particular sorbates. It should be mentioned that the priority in the area of chemical modification of the silica surface belongs to Russian scientists A.V. Kiselev and K.D. Shcherbakova who published the article (submitted to publication on November 15, 1949) in which methylation (esterification) of silanol groups was used to change the adsorption activity [1].

Chemical modification is widely used for the preparation of various selective adsorbents for sorption concentrating and chromatography. It turned out that the use of silica sorbents with covalently immobilized complexing functional groups is among the most efficient methods for the selective extraction and chromatographic separation of metals. The development of this topic in our country (as well as many other scientific trends in the field of analytical chemistry) was initiated in 1978 by Yu.A. Zolotov who noticed a huge potential of this class of sorbents for concentrating microquantitites of metals [2]. The starting point for the development of this trend should be considered to be the pioneer works [3, 4] published in 1975 by Prof. D.E. Leyden (University of Denver, Colorado, USA), who was a good acquaintance of Yu.A. Zolotov. The first domestic work on studying the sorption properties of complexing chemically modified silica (CMS) was published by V.M. Ivanov and coauthors in 1979 [5].

The subsequent studies in the field of synthesis, structure, and properties of the surface compounds demonstrated perspectives of applying silicas chemically modified by organic compounds as sorbents for the extraction of various microcomponents from solutions. At the Chair of Analytical Chemistry of the Moscow State University, the studies of the sorption concentrating of metals were carried out in the research groups under the leadership of V.M. Ivanov, V.I. Fadeeva, L.N. Simonova, and others. The early works on the synthesis and application of diverse CMSs, including complexing silicas, are considered in reviews of coworkers of the Moscow State University [6, 7]. The present article is the first retrospective review of scientific works of coworkers of the Moscow

State University in the area of studying the properties of complexing chemically modified silicas.

Silicas chemically modified by organic compounds combine the properties of a matrix and an immobilized reagent-modifier and thus represent new materials with the properties differed from those of the starting compounds. The sorbent surface can significantly change the properties of the immobilized reagents and affect the processes that occur in the surface layer of the sorbent. The following effects can be distinguished among the main factors affecting the complexation on the silica surface:

(1) limited mobility of the ligands (L) immobilized on the surface impedes the formation of complexes with metals (M) of the composition ML and ML_2;

(2) residual (after modification) silanol groups on the surface affect the acid-base properties of the immobilized ligands and, correspondingly, relative stability constants of the complexes;

(3) residual silanol groups can coordinate and change configurations of immobilized ligands and can also coordinate some metal ions;

(4) properties of the ligands depend on the method of immobilization on the silica surface, and the spacer can affect the sorption properties of the sorbent and participate in the coordination of metals;

(5) owing to steric hindrances, the porous structure of the sorbents affects the surface concentration of the grafted ligands and ability of metals to interact with several ligands in micropores and mesopores;

(6) surfaces of the sorbent and matrix are energetically nonuniform, which affects the confidence interval of the calculated and measured values of stability and dissociation constants of the ligands.

When new complexing sorbents for metal ion extraction were prepared, researchers start, as a rule, from the data on complexation in homogeneous systems assuming that the ligand capable of forming a complex with a metal ion in an aqueous solution would retain this capability being immobilized on the support surface. In several cases, this analogy is valid even at the quantitative level, which allows one to predict sorption characteristics of sorbents from the data on complexation in aqueous solutions. However, the revealed analogies predominantly concern the sorption of relatively simple metal ions, such as copper(II), zinc(II), etc. [8].

The pattern can sharply become more complicated on going to the metals characterized by a variety of ionic forms in a solution. In this work, we present examples for specific features of complexation on the surface of the silica sorbents and changes in the complexation ability of the ligands upon their immobilization on the support surface. The structures and properties of the sorbents, including specific surface area (S_{sp}), pore diameter (D_{pore}), particle size (d_{P}), and concentration of grafted functional groups (C_{fg}), are listed in Table 1.

The silicas chemically modified by various reagents containing the following functional analytical groups were studied:

(i) O,O-ligands including sorbents with grafted acetylacetonate groups (CMS-AA) and silica-based carboxyl cation-exchange resins;

(ii) N,N-ligands including aminopropyl (CMS-A), ethylenediamine (CMS-EDA), diethylenetriamine (CMS-DETA), tetraethylenepentamine (CMS-TEPA), and pyridyl (CMS-Pyr) ligands;

(iii) N,O-ligands including groups of hydroxamic acid (CMS-HA), amidoxime (CMS-AO), and iminodiacetic acid (CMS-IDA);

(iv) N,S-ligands including covalently immobilized 2,5-dimercapto-1,3,4-thiadiazole or Bismuthol I (CMS-Bis);

(v) P,O-ligands including propylphosphonic (CMS-PrPA) and phenylphosphonic (CMS-PPA) acids; and

(vi) more complicated ligands, for instance, N,O,S-ligand (*N*-benzoyl-*N*-propylthiourea) [9] and N,O,P-ligand (aminomethylphosphonic acid) (CMS-AMP) [10].

SORPTION OF METAL IONS ON SILICAS CHEMICALLY MODIFIED BY REAGENTS WITH AMIDOXIME AND HYDROXAMIC ACID GROUPS

The main factor affecting metal ion sorption on the complexing sorbents is the acidity of the aqueous phase predetermining both the ionic state of the metal and the form in which the functional analytical groups of the sorbent exist. A comparison of the results on the sorption of vanadium(V), molybdenum(VI), and tungsten(VI) on the CMS-AO and CMS-HA sorbents with the published data on the state of these ions in solutions in the pH range of maximum sorption allows the authors to conclude that these metals are sorbed in the form of oxo cations [11–13].

The characteristic feature of the sorbents considered is the protonation of functional analytical groups. This explains a decrease in sorption in acidic media and the fact that on the sorbent with HA groups manifesting weak basic properties metal ions are extracted in more acidic media compared to the sorbent containing AO groups. Metal ions are sorbed due to complexation with the grafted ligands, which is confirmed by the coloration of the sorbents in violet and yellow for the sorption of vanadium and molybdenum, respectively, whereas the tungsten complexes are colorless. The spectral characteristics of the complexes formed on the surface remain unchanged when the acidity of the solution is varied in a range of 2 M HCl (pH 5), indicating that their compositions are constant under the conditions used.

Table 1. Structure and properties of the complexing CMS

R in sorbent structure $=(SiO_2)-O-Si-R$	Designation	S_{sp}, m^2/g	D_{pore}, nm	d_P, μm	C_{fg}, mmol/g
$-(CH_2)_3NH_2$	CMS-A	120	40	100–200	0.70
$-(CH_2)_3NHCH_2CH_2NH_2$	CMS-EDA	120	40	100–200	0.40
$-(CH_2)_3(NHCH_2CH_2)_2NH_2$	CMS-DETA	120	40	100–200	0.2
$-(CH_2)_3(NHCH_2CH_2)_4NH_2$	CMS-TEPA	120	40	100–200	0.3
		300[a]	10	10.0	0.28
$-(CH_2)_2CO(NHOH)$	CMS-HA	120	35	100–200	0.2
$-(CH_2)_3CNH(NHOH)$	CMS-AO	80	50	100–200	0.35
		570[a]	60	6.0	0.56
$-(CH_2)_3N(CH_2COOH)$	CMS-IDA	80	50	60–200	0.15
$-(CH_2)_3OCH_2CH(OH)CH_2N(CH_2COOH)$	CMS-HIDA	330[a]	11	5.0	0.21
$-(CH_2)_3P(O)(OH)_2$	CMS-PrPA	80	50	160–250	0.13
$-(CH_2)_2C_6H_4P(O)(OH)_2$	CMS-PPA	80	50	160–250	0.16
$-(CH_2)_3OCH_2CH(OH)CH_2NHCH_2P(O)(OH)_2$	CMS-AMP	360[a]	10	3.0	0.45[b]
$-(CH_2)_4C_6H_5N$	CMS-Pyr	120	35	100–200	
$-(CH_2)_3C_2HN_2S_3$ (Bismuthol I)	CMS-Bis	80	50	100–200	0.05
$-(CH_2)_3CH(COOCH_3)_2$	CMS-AA	120	35	100–200	

[a] Sorbents for the use in HPCIC.

[b] Total concentration of primary amino groups and AMP groups.

The IR spectra of the samples of the CMS-HA sorbent treated with solutions containing metal ions exhibit a decrease in the intensity of the band at 1630 cm^{-1} corresponding to stretching vibrations of the C=O group of hydroxamic acid and the appearance of a new band at 1520 cm^{-1}. This possibly indicates the coordination of the metal ions with the donor oxygen atoms and chelate formation [12]. In the case of the CMS-AO sorbent, the treatment of the metal ions with the solution does not almost shift the stretching vibration band of the C=N groups of amidoxime, which can be related to a low strength of the coordination bond between the metal ion and this group. An analysis of the sorption dependence of the acidity of the medium shows that the metals considered form 1 : 1 complexes on the sorbent surface.

The complexation of the studied metal ions with ligands of a similar structure in aqueous solutions was studied in comparison. It is found that vanadium(V) and molybdenum(VI) with acetohydroxamic acid form an uncolored complex compound (λ_{max} = 225 nm). No complexes are formed with acetamidoxime in a wide acidity range (2 M HCl, pH 13) and in a broad range of ratios of the reacting components (from 1 : 1 to 1 : 1000), whereas these metal ions form colored complexes on the surface of the CMS-HA and CMS-AO sorbents [14].

One of possible explanations is the participation of residual silanol groups of the sorbent in chelate formation. However, the spectral characteristics of the complexes on the sorbent in which the silanol groups are blocked by trimethylchlorosilane remained unchanged, which excludes the involvement of silanol groups in complexation. Another mechanism of the influence of the support on the spectral characteristics and stability of the complexes formed on the surface is possible. It is known that the colored complexes formed by vanadium(V) with aromatic hydroxamic acids and amidoximes are complexes with the ligand-to-metal charge transfer. In the case of the sorbents considered, the role of this electron donor can be performed by the silica matrix exhibiting the $(p-d)\pi$-conjugation effect in the chain of Si–O bonds of the sorbent matrix.

This assumption can indirectly be confirmed by the data on the complexation of copper(II) with grafted groups of the CMS-AO sorbent and acetamidoxime in an aqueous solution. It is shown that the complete analogy of complexation in homogeneous and heterogeneous systems is observed for copper(II) ions that are not characterized by the formation of charge-transfer complexes. Either 1 : 1 complex (λ_{max} = 700 nm), or 1 : 2 complex (λ_{max} = 650 nm) is formed depending on the pH of the solution and the metal to ligand ratio of the components both in an aqueous solution and on the CMS-AO sorbent surface [15].

The CMS-HA sorbent was also successfully applied for the sorption of zirconium, thorium, and scandium forming stable complex compounds with hydroxamic acids in aqueous solutions [16]. Zirconium is established to be sorbed in a strongly acidic range reaching a maximum value in 1 M HCl, and scandium and thorium are sorbed at pH >2, which is consistent with the behavior of these metals in aqueous solutions.

SORPTION OF TRANSITION METALS ON SILICA CHEMICALLY MODIFIED BY THE REAGENT WITH IMINODIACETIC ACID GROUPS

One of the first studied sorbents was CMS-IDA, since its monomeric analog, iminodiacetic acid (IDA), forms stable complexes with a wide scope of metals and the sorbent based on IDA can be applied for both group concentrating and selective extraction of some metals [17–19].

It should be mentioned that the sorption behavior of transition metals correlates with the stability of their complexes with IDA in an aqueous solution: the higher the stability constant of the complex, for example, of the iron and copper complexes, the more acidic the medium in which the maximum sorption range is observed. At the present time, the CMS-IDA sorbent is produced by the domestic company BioKhimMak ST under trade name Diapak IDK, including the form of concentrating cartridges.

Metal sorption on CMS-IDA is characterized by a high mass exchange rate, which makes it possible to perform extraction in the dynamic mode at a high rate of passing solutions (to 10 mL/min) and to use the sorbent in flow methods of analysis. For instance, the sorption atomic absorption method was used for the determination of transition metals in milk products [20].

FORMATION OF HETEROLIGAND COMPLEXES ON THE SURFACE OF CHEMICALLY MODIFIED SILICAS

A rigid silica matrix and a low concentration of grafted functional analytical groups favor the predominant formation of 1 : 1 complexes of the ML composition.

This induces a possibility of their further target conversion to heteroligand complexes with an intensive color or luminescence. The participation of such organic reagents that can form colored complexes on the surface in complexation was used for the direct determination of metal ions on the sorbent surface using diffuse reflectance spectroscopy.

It was found that the treatment of the CMS-AO sorbent samples containing molybdenum(VI) or tungsten(VI) ions with a solution of Pyrocatechol Violet (PCV) was followed by the formation on the sorbent surface of compounds colored in intensive blue (λ_{max} = 650–660 nm), whereas the reagent itself sorbed on CMS-AO is yellow-colored (λ_{max} = 420 nm) and the binary molybdenum complex with PCV is violet-colored (λ_{max} = 560 nm). The optimum conditions for the formation of a heteroligand compound were found: pH 3–5 and a twofold excess of PCV over the metal content on the sorbent [21].

The authors assumed an analogy of the complexation on the sorbent surface and in Mo(VI)–W(VI)–PCV–cationic surfactant systems where the regions of the silica sorbent surface containing protonated amidoxime groups behave similarly to micelles of cationic surfactants. Unlike the amidoxime sorbent, the silica surface with grafted hydroxamic acid groups, which are not protonated in the pH range, demonstrates the formation of a compound with the spectral characteristics identical to those of the binary Mo–PCV complex in aqueous solutions (λ_{max} = 560 nm). This conclusion is confirmed by the fact that the compounds with similar characteristics are also formed on the surface of other CMS, whose functional groups include the nitrogen atom able to protonation [22].

It seems probable that the coordination sphere of the metal contains only one ligand in the case of formation of heteroligand Mo(VI) and W(VI) complexes on the sorbent surface involving PCV. Since the coordination number of the studied metal ions is not so high (6–8) and the complexes are formed by oxo cations, it seems difficult for the second ligand to enter the coordination sphere of the metal.

The formation of the europium complex with functional groups of silica chemically modified by iminodiacetic acid groups and β-diketones was observed for the metals with high coordination numbers, such as rare-earth elements. It is found that the inner coordination sphere of europium forming the complex with the groups of the sorbent on the silica surface contains β-diketone as the second ligand. This is accompanied by the sensitized luminescence of europium where excitation occurs in the organic moiety of the complex (β-diketone) and the europium ion is the emitting center [23]. A similar effect is also observed when an antibiotic, for example, tetracycline, is used as the second ligand [24].

SORPTION OF PLATINUM METALS AND GOLD BY CHEMICALLY MODIFIED SILICAS

The sorbents, whose functional groups contain amine groups, were used for the sorption extraction of platinum metals. The sorption of Ru(IV), Os(VIII), Rh(III), Ir(IV), Pd(II), and Pt(IV) on the silica chemically modified by propylamine groups (CMS-A) was studied [25]. The order of sorption affinity in highly acidic media was found to be as follows: Rh(III) ≈ Ir(IV) ⩾ Ru(IV) ≈ Pt(IV) ≈ Pd(II) > Os(VIII), and at pH > 1 Ir(IV) ≈ Pt(IV) ≈ Pd(II) ⩾ Ru(IV) > Rh(III) > Os(VIII). The sorption of platinum metals can proceed via two mechanisms: ion-exchange mechanism and insertion mechanism where the nitrogen atom enters the inner coordination sphere of the metal, which is especially characteristic of primary amines. In highly acidic media where platinum metal ions exist predominantly as anionic chloride complexes and the CMS-A sorbent exists in the completely protonated form, the sorption proceeds via the anion-exchange mechanism. The degree of protonation of the sorbent groups is minimal in the weakly acidic or neutral regions, and then the sorbent represents a complexing macroligand. Platinum, iridium, and palladium ions exhibit the highest affinity to complexation with primary amines, whereas rhodium, ruthenium, and osmium ions form less stable complexes, which is consistent with the order of the sorption affinity of the CMS-A sorbent to the metal ions listed. A distinctive feature of sorption on the silica sorbent is an anomalously high rate of sorption equilibration of 2–5 min at 20°C, whereas for many analogous organopolymeric sorbents the process usually takes 0.5–2 h at 90–100°C. This effect is explained by the catalytic effect of the matrix of the sorbent (silica).

The effect was studied in more detail for the formation of the ruthenium(II) and osmium(II) complexes with 1,10-phenanthroline (1,10-Phen), which are usually synthesized by the reduction of the corresponding oxo- and hydroxohalide complexes in the presence of 1,10-Phen. The complexes are formed in the solution under rather drastic conditions: at 100°C for 2–3 h. It was established for ruthenium as an example that the application of silica chemically modified by the reagent containing sulfo groups accelerated the formation of the phenanthrolinate complexes upon the sorption of ruthenium from solutions in the presence of 1,10-Phen compared to the formation of these complexes in the solution [26]. The same regularity was established for osmium [27]. The detailed study of this process by diffuse reflectance spectroscopy, luminescence, and X-ray photoelectron spectroscopy showed the formation of the phenanthrolinate complexes of different compositions at room temperature: bis- and tris(1,10-Phen)metal(II,III) [28]. The quantitative yield of the tris(1,10-Phen)metal(II) complexes is observed at 100°C within 2 min in the case of ruthenium and within 30 min in the case of osmium, which is significantly faster than the complexation in a solution.

Interesting results were obtained for the sorption of gold(III) in the form of tetrachloroaurate by the silica sorbents with the grafted complexing groups of propylamine (CMS-A), ethylenediamine (CMS-EDA), diethylenetriamine (CMS-DETA), and tetraethylenepentamine (CMS-TEPA) and anion-exchange trimethylpropylammonium groups. At pH < 1 the sorption is characterized by the formation of surface complexes of various composition with amino groups of the sorbents depending on the denticity of the ligands. As the pH increases in the range from 1.0 to 3.5, the consecutive hydrolysis of tetrachloroaurate appreciably affects the sorption, which results in the appearance of alternating maxima and minima on the sorption curve [29]. The reliability of the unusual sorption curves is doubtless, since the degree of extraction of gold was monitored for tetrachloroaurate labeled by radioactive isotopes ^{195}Au and ^{198}Au. Interestingly, a plateau with a high degree of sorption of gold is observed in this pH range for the sorbent with trimethylpropylammonium groups. The further increase in pH results in a decrease in sorption due to the formation of the insoluble species $Au(OH)_3$ [29]. The quantitative desorption of gold from the CMS studied is possible when using aqueous solutions of 0.1 M thiourea and 2 M potassium thiocyanate, or a 3 M solution of pyridine [30].

It should be mentioned that since 1980 the CMS-A sorbent was produced in industry with the commercial name LIK-21 (Reakhim), and at present its analog has the commercial name Diapak Amin and is produced by BioKhimMak ST.

CHEMICALLY MODIFIED SILICAS CONTAINING GROUPS OF PHOSPHONIC ACIDS

Scandium and elements of the titanium subgroup form stable complexes with O,O-containing ligands, for example, phosphonic acids. These metals were extracted from aqueous solutions by the silica-based sorbents chemically modified by groups of the phos-

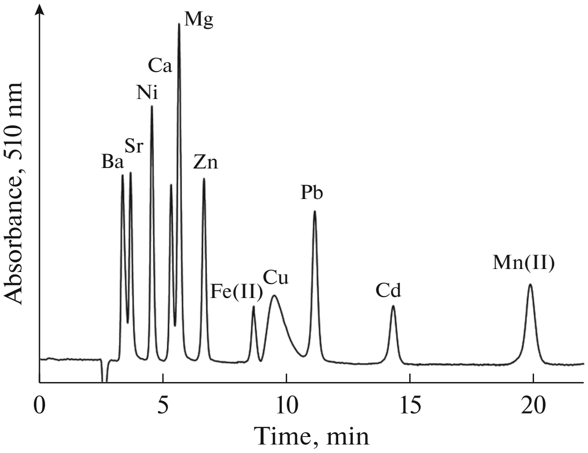

Fig. 1. Separation of the model mixture of alkaline-earth and transition metals on the column 150 × 4.0 mm packed with the CMS-AMP sorbent. Eluent: 5 mM nitric acid with 0.8 M potassium nitrate. Photometric detection with the post-column reaction with 4-(2-pyridylazo)resorcinol. Adapted from [41].

phonic acids: phenylphosphonic (CMS-PPA) and propylphosphonic (CMS-PrPA) acids [31].

A distinctive feature of these sorbents is a high selectivity to the studied metals in acidic media, which is especially important for such readily hydrolyzed elements.

The influence of the structure of the radical of the grafted functional analytical group on the character of sorption of scandium and titanium subgroup elements was studied. It is found that the replacement of the PPA group by PrPA substantially changes the selectivity of the sorbents. It is shown that the CMS-PPA sorbent has a high affinity to all metals studied and is recommended for group extraction, and a more selective sorbent CMS-PrPA should be used for intragroup separation.

Thus, the studied properties of the grafted ligands on the silica surface indicate their ability to sorb metal ions via the complexation mechanism, which predetermines a high efficiency of sorption systems and makes it possible to develop new methods for concentrating metal ions. An additional information about the use of the complexing CMS can be found in the reviews [32, 33] and monographs [34, 35].

CHELATION ION CHROMATOGRAPHY OF METAL IONS

Silicas chemically modified by complexing groups can be used as stationary phases for the separation of metal ions by high performance chelation ion chromatography (HPCIC) [34, 36]. The surfaces of the predominant majority of complexing CMS contain charged functional groups, such as negatively charged groups of hydroxyiminodiacetic acid (CMS-HIDA), phosphonic acid (CMS-PrPA, CMS-PPA), and aminophosphonic acid (CMS-AMP) or positively charged amino groups (CMS-A, CMS-EDA, CMS-TEPA) and, hence, the resulting retention of metals is determined by the sum of electrostatic and coordination interactions. It should be mentioned that the selectivity of simple cation-exchange interactions is usually orthogonal to the selectivity of complexation and, therefore, the complexation mechanism on the CMS surface is an efficient tool for changing and optimization of the separation selectivity. The suppression of electrostatic interactions is usually required for the exclusively complexation mechanism of separation to occur, and the suppression is achieved by the generation of a high electrolyte concentration in the eluent, for instance, of alkaline metal nitrates or perchlorates. For instance, the affinity of lanthanide cations to the sulfocation-exchange resin in nitric acid solutions increases monotonically from La^{3+} to Lu^{3+}, but the complete reverse of selectivity is observed for the complexing cation-exchange resin based on CMS-HIDA in nitric acid solutions with the addition of potassium nitrate to a concentration of 1 mol/L, which made it possible for the first time to separate completely 14 lanthanides and yttrium in the isocratic regime [37] but for the complexing cation-exchange resin CMS-HIDA in solutions of nitric acid.

An important advantage of complexation chromatography is a possibility of a priori evaluating the separation selectivity if the stability constants of the separated metal complexes are known. This makes it possible to prepare sorbents for the selective separation of metals or groups of metals. For instance, CMS-AO with amidoxime groups manifested a high selectivity to UO_2^{2+} [38], CMS-AMP is highly selective to Mn^{2+} [39], and CMS-HIDA exhibits a high selectivity to Al^{3+} and Fe^{3+} [40].

As a whole, complexation is commonly accepted to be considered as a kinetically slower chromatographic process than the classical cationic exchange. For this

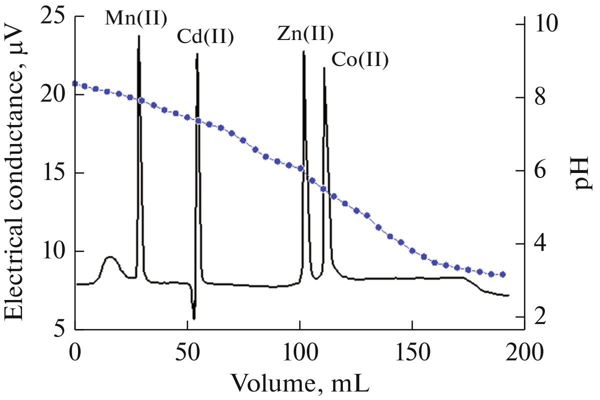

Fig. 2. Chromatofocusing of the model mixture of metals. Column 250 × 4.6 mm with CMS-TEPA initially equilibrated at pH 8 with a 4 mM solution of histidine. Eluent: Polybuffer 74 diluted by 50 times, flow rate 1 mL/min. Adapted from [45].

reason, it is considered that the efficiency of separation in complexation chromatography should be lower than that in ion chromatography. However, complexing cation-exchange resins, i.e., sorbents with acidic functional groups, interact with metal cations in two stages. At the first stage, acidic groups of the sorbent rather rapidly coordinate cations of separated metals according to the electrostatic attraction and then coordination binding of the metal cations into a surface complex occurs. Highly efficient and selective metal separations are achieved due to such a two-step interaction. An example of this separation [41] for CMS-AMP is shown in Fig. 1. A distinctive kinetics of the interaction of the metal ions with iminodiacetate functional groups is also shown for the chromatographic use of monolithic porous silica columns with covalently immobilized IDA for efficient metal separation at elevated eluent rates [42].

Highly selective metal separations can be obtained for CMS with basic complexing groups. For example, a possibility of using the CMS-AO sorbent for the separation of a number of transition metals was shown. A solution of sodium citrate forming complexes of various stability with the metals was used as the eluent. Thus, Ni(II), Cu(II), Fe(III), and Mo(VI), for example, were separated, and the order of elution of the metals coincides with the stability of the metal complexes with amidoximes [38, 43]. For the sorbents with the basic groups, the separation efficiency is somewhat lower because of the electrostatic repulsion of protonated functional groups and likely charged metal cations.

As mentioned above, many complexing CMS bear groups capable of dissociating in aqueous solutions. If a ligand with several groups having different values of pK_a is immobilized on the CMS surface, this sorbent would possess the properties of a polybuffer ion-exchange resin in a wide range of pH. For example, CMS-TEPA with immobilized tetraethylenepentamine has the following set of pK: 9.9, 9.1, 7.9, 4.3, and 2.7 and is characterized by the buffer ability in a wide pH range from 3 to 9 [44]. This polybuffer ability of ligands can provide the formation of linear descending gradients of pH. In this case, metal concentrating and separation occur due to the gradual destruction of surface metal complexes and their elution when passing an acidic polyampholyte eluent through the column initially equilibrated at a sufficiently high pH corresponding to the quantitative adsorption of the metals [45, 46]. Owing to the pH gradient, the surface complexes decompose in accord with the stability constants and the separated metals are eluted from the column as very narrow peaks (Fig. 2). Therefore, this variant of complexation chromatography was named chromatofocusing of transition metals by analogy to chromatofocusing of proteins.

A practically important feature of complexation is a weak dependence of the stability constants on the ionic strength, which extends practical possibilities of the method for the separation and determination of metals in matrices with a complicated composition. For example, CMS-HIDA can be used for the chromatographic determination of trace amounts of metals in brines [42] and sea water [47, 48] and of magnesium and strontium in calcium carbonate [49] and calcite matrices of sea microorganisms [50] and molluscs [51]. The generalized information on the sorption of various metals by the complexing CMS is presented in Table 2.

To conclude, the synthesis of new complexing sorbents and study of their properties and possibilities of application for the sorption concentrating and chromatographic separation of various metals are extensively developed areas in our country. The use of chemically modified silicas with complexing groups makes it possible to solve a broad range of practically important problems in the areas of chemical analysis, chemical technology, and heterogeneous catalysis. The geography of this topic extended appreciably within the last years. In addition to the Moscow State

Table 2. Sorption of metals by the complexing CMS

Sorbent	Metals	Sorption medium	References
CMS-A	Pt(IV), Pd(II), Ir(IV), Cu, Zn, Co, Ni	Chloride, 2 M HCl, pH 6.0; nitrite; sulfate pH 1.0–3.0	[52–54]
	Os(IV)	Chloride 1 M HCl, pH 2.7	[55]
	Ru(IV), Rh(III), Pd(II), Os(VIII), Ir(IV), Pt(IV), Au(III)	Chloride 5 M HCl, pH 9.0	[25, 29]
	Sc(III), Th(IV), Hf(IV), Zr(IV), Fe(III)	Chloride 0.7 M HCl, pH 9.0 and sulfate in the presence of salicylhydroxamic acid	[56–58]
	Ag(I), Pd(II), Cu(II)	Nitrate 0.1–4.0 M	[59]
CMS-EDA	Pt(IV), Pd(II), Ir(IV), Cu, Fe(III), Zn, Co, Ni, Mn(II)	Chloride 2 M HCl, pH 8.5	[52]
	Au(III)	Chloride 1 M HCl, pH 3.0	[25, 29]
CMS-DETA	Au(III)	Chloride 1 M HCl, pH 3.0	[25, 29, 30]
CMS-TEPA	Au(III)	Chloride 1 M HCl, pH 3.0	[25, 29]
CMS-HA	Zr(IV), Hf(IV), W(VI), Mo(VI), Th(IV), Al, Co, Ni, Sc(III), Y, La, V(V), Fe(III)	Chloride 4 M HCl, pH 8.0	[12, 14, 16]
CMS-AO	W(VI), Mo(VI), V(V), Fe(III), Cu	Chloride 2 M HCl, pH 7.0	[11, 14, 21]
	V(V), Cu	Nitric pH 1.85–6.55	[13, 15]
CMS-IDA	Ti(IV)	Sulfate pH 1.0–7.0 in the presence of H_2O_2	[60]
	Eu(III)	Chloride pH 3.0–8.0	[23]
	Fe(III), Cu, Pb, Al, Ni, Zn, Fe(II), Mn(II), Ti(IV), U(VI), Ce(III), Y(III), Sn(II)	Chloride pH 0.8–7.5	[61]
	Sn(IV)	Chloride pH 0.5–2.0	[62]
	V(IV), V(V), Mo(VI)	Chloride pH 1.0–6.0	[19]
	Hg(II), Cd(II)	Acetate 1 M HCl, pH 6.3	[63]
CMS-PrPA	Ti(IV), Zr(IV), Hf(IV), Sc(III), Fe(III)	Chloride 4 M HCl, pH 5.0	[31]
CMS-PPA	Ti(IV), Zr(IV), Th(IV), Hf(IV), Sc(III), Fe(III)	Chloride 4 M HCl, pH 5.0	[31, 64]
CMS-AA	Cu(II), Ni(II), Ni(II), Zn(II)	Nitrate pH 4.0–8.0	[65]
CMS-Pyr	Ru(II)	Chloride pH 2.0–9.2	[26]
		in the presence of 1,10-phenantroline	
	Sc(III)	Chloride 0.7 M HCl, pH 9.0	[58]
CMS-Bis	Hg(II), Fe(III), Pb, Cu, Ni, Co, Zn	Nitric, 10 M, pH 10	[66]
	Hg(II), CH_3Hg^+, $C_3H_7Hg^+$, $C_6H_5Hg^+$	Nitric, pH 1–7	[67]

University, active studies in this field are performed in research groups guided by M.G. Voronkov (Favorsky Institute of Chemistry, Irkutsk), V.N. Losev (Research Engineering Center Kristall), L.K Neudachina (Ural Federal University), and Z.A. Temerdashev (Kuban State University), as well as in other research centers of the country.

CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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