

Chelating Sorbents in Inorganic Chemical Analysis

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This review is concerned with the preparation, characterization and the applications of new chelating sorbents in the separation, concentration and determination of trace metals from different complex samples.

INTRODUCTION

Accurate analysis of various complex samples (natural and waste waters, geological, biological and industrial materials, substances of high purity), especially at trace levels, is one of the most difficult and complicated analytical tasks.

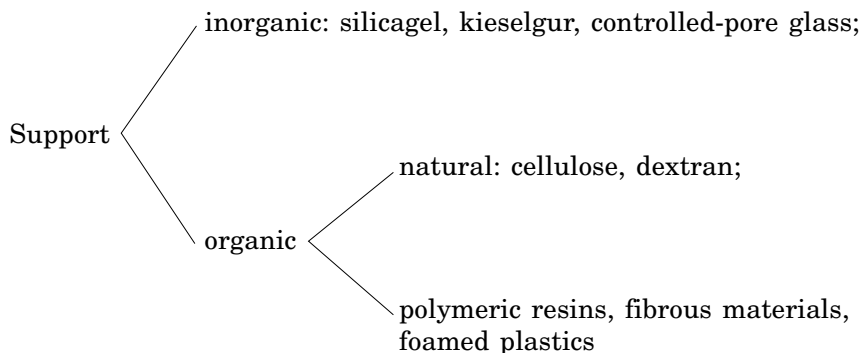
The rapid development of electronic instrumentation has created powerful analytical tools for trace element determination. At the same time, matrix effects (which can give erroneous results) and the extent of separation chemistry in instrumental methods have become evident.¹

In the last years, the importance of separation and concentration techniques involving chelating sorbents in the trace analysis has risen substantially. Pre-treatment of an aqueous sample by the sorption technique not only increases the ion concentration to a detectable level but also eliminates matrix effects. The use of chelating sorbents can provide a concentration factor up to several hundred folds, better separation of interferent ions, high efficiency and rate of process, and the possibility of combining with different determination methods.²⁻⁵

A chelating sorbent essentially consists of two components: the chelate forming functional group and the polymeric matrix or the support; the properties of both components determine the features and the applications of the respective material.

If the selectivity of the sorbents is determined mainly by the chelating group (the nature of the functional group and / or donor atom able to form complexes with metal ions), other analytical properties of the sorbents, namely the capacity, kinetic features, mechanical and chemical strength and regeneration depend on the polymeric matrix.

Different polymeric materials used for chelating groups immobilization can be ordered as follows:



In the present paper, aspects concerning the preparation, properties and applications in inorganic analysis of new chelating sorbents are reviewed.

METHODS OF PREPARATION

Incorporation of complexing (more often chelating) functional groups into polymeric support can be accomplished by three methods:⁶

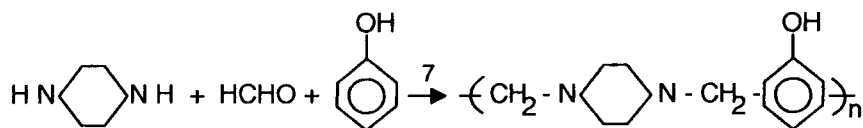
- by formation of a chemical covalent bond between the organic reagent and support (chelating sorbents with grafted groups);
- by formation of an ionic bond between the chelating reagent and the functional group of an ion exchange resin (modified resins);
- by impregnation and physical adsorption of the organic reagent on support (impregnated sorbents).

Chelating Sorbents with Grafted Groups

Chelating sorbents with grafted groups can be synthesized either by direct polycondensation or polymerization of monomers containing chelating groups, or by chemical transformation of a preformed polymer.

The polycondensation method is based on the capacity of some monomeric organic ligands to react with aldehydes, forming polymeric sorbents.

Sometimes, cross-linking agents (phenol, resorcinol) are used. Preparation of a copper selective polymer by the reaction of phenol, formaldehyde and piperazine⁷ is shown in Scheme 1 as an example.



Scheme 1

In the same way, chelating resins based on 8-hydroxy-quinoline,⁸ imino-diacetic acid,⁹ macrocyclic ligands,¹⁰ derivatives of hydroxy acetophenones¹¹ have been synthesized.

Heteroatoms can be directly incorporated into the composition of a polymer chain. For example, a polymeric thioether $(-\text{CH}_2-\text{S}-)_n$ (complexing sorbent with heterogenous chain), specific for platinum metals,¹² has been prepared by condensation of formaldehyde with hydrogen sulphide in alkaline medium. Also, polymeric tertiary amines¹³ and polymers containing N and S have been synthesized.¹⁴

Although the polycondensation method is extensively used because of its simplicity, condensation polymers have a poor chemical and mechanical stability.

Polymerisation of vinylic derivatives containing chelating groups is less used due to the difficulties connected with the synthesis of starting substances; complexing properties of polyvinylpyridine sorbents have been observed.¹⁵

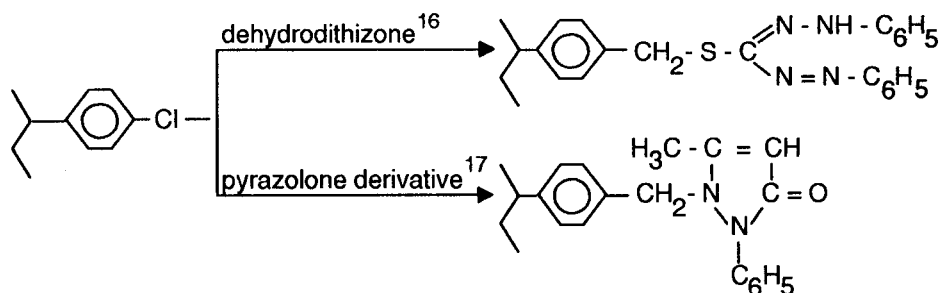
The main synthesis method of chelating sorbents proves to be the incorporation of an active functional group into polymeric matrix by »reactions on polymers« (the grafting procedure). Usually, reactive groups (chloromethyl, epoxy, amino) able to interact with complexing reagents are incorporated into organic polymeric supports as shown in Scheme 2.

In this way, chelating sorbents with high capacity and selective retention properties containing functional groups of dithizone,¹⁶ methylphenylpyrazolone,¹⁷ chromotropic acid derivative,²⁰ poly-hydroxyanthraquinones²¹ have been prepared starting from linear low molecular polystyrene.

Sorbents with a three-dimensional structure have a better stability in aggressive medium and can be easily regenerated and are thus used for sorption under dynamic conditions.

The sorbents with macroporous structure have a superior capacity and kinetic properties. Thus, cross-linked polystyrene chelating resins with

phosphino and/or phosphono groups²², *N*-phenylhydroxamate,²³ thioglycolate,²⁴ quinaldinamide,²⁵ acetoacetanilide,²⁶ or benzoylacetanilide,²⁷ trithiocarbonate and dithiocarbamate,¹⁸ aminopyrazolone,²⁸ aminopolyacetic acids²⁹ or 8-hydroxyquinoline^{19,30} moieties have been synthesized.



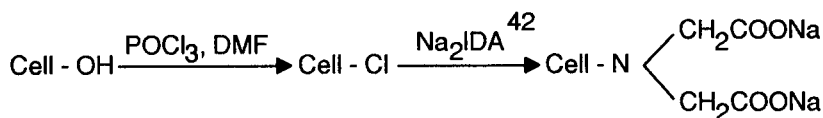
Scheme 2

Also, different organic synthetic cross-linked polymers with covalent binding of ligands, have been used lately. Thus, chelating resin containing aminomethylphosphonic acid groups from methyl methacrylate-divinylbenzene copolymer³¹ or resin poly [*N*-(2-aminoethyl)]acrylamide³² have been prepared. By the introduction of formazane derivatives (with acidic groups $-\text{COOH}$, $-\text{OH}$, $-\text{AsO}_3\text{H}_2$) in polyacroleine,³³ as well as by modification of polyallylamine with acrylic or phosphorous acid,³⁴ new chelating resins have been obtained. Chelating sorbents with functional groups aminocarboxylate, dithiocarbamate or aminophosphate³⁵ have been synthesized by chemical modification of polyethylenimine and polyhexamethyleneguanidine. Bonding of imidazole groups³⁶ or 8-hydroxyquinoline³⁷ to glycidyl methacrylate gel has been carried. Resins containing amidoxime groups have been prepared from various copolymers of acrylonitrile and cross-linking agents.³⁸ Also, by chemical transformation of poly (vinyl chloride), chelating resins with diethylentriamine³⁹ or thiopropionamide⁴⁰ groups have been obtained.

Among the naturally organic matrices, cellulose is the most extensively used support for grafting of suitable functional groups because of its typical properties: availability and low price, mechanical strength, high porosity, hydrophilicity and chemical reactivity in functionalizations.⁴¹

The chelating sorbents based on chemically modified cellulose have been synthesized using different »reactions on polymers«, as shown in scheme 3.⁴²

Thus, cellulose sorbents with bonded groups of iminodiacetic acid,^{42,43} acetoacetamide,⁴⁴ 8-hydroxyquinoline,⁴⁵ mercapto groups,⁴⁶ aminoalkyl groups,⁴⁷ pyridylazoresorcinol,⁴⁸ azopyrocatechine⁴⁹ have been obtained.



Scheme 3

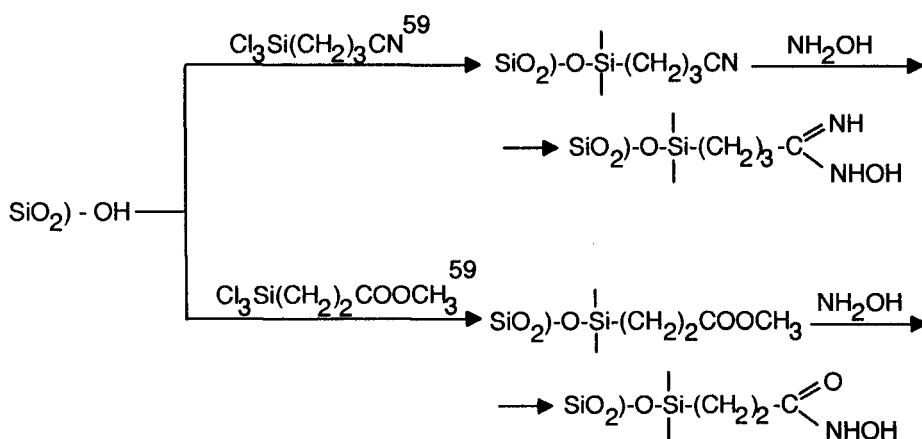
Similar products have been prepared from cyanuric acid derivatives of cross-linked dextrans. Thus, sorbents of Sephadex type with chelating groups diethylaminoethyl⁵⁰ or methylphenyl-pyrazolone⁵¹ are singled out.

Fibrous chelating sorbents (cellulosic and synthetic) characterized by a large surface area, high flow-rate through the column and excellent kinetic properties are superior to granular sorbents.

A few examples of fibrous sorbents with chelating groups immobilized by covalent bonds are: poly(acrylamidrazone-hydrazide lacmoid) chelating fibres,⁵² acrylonitrile amidoxime fibres,⁵³ fibrous sorbent Thiopan-13 (polyacrylonitrile) containing mercaptobenzthiazole groups,⁵⁴ fibrous sorbent PP-PAK (polypropylene-polyacrylic acid) with carboxylic groups,⁵⁵ polyacryloacyliso-thiourea chelating fibres⁵⁶ and polystyrene-polypropylene fibrous exchangers with aminopolyacetic groups.⁵⁷

A new type of chelating sorbent has been prepared from fibrous materials which holds very fine particles (up to several μm) of chelating sorbents.⁵⁸

In the same way, chelating sorbents with functional groups immobilized by covalent bonds on inorganic polymers, usually silica, have been synthesized by chemical transformation of the matrix, as follows:⁵⁹



Scheme 4

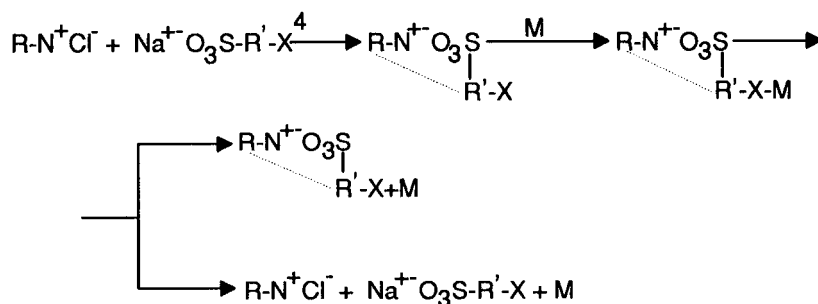
Thus, chelating sorbents containing hydroxamic acid and amidoxime groups,⁵⁹ ethylenediaminetetraacetic acid,⁶⁰ mercapto groups,⁶¹ 8-hydroxyquinoline,⁶² 3-(1-imidazolyl)propyl groups,⁶³ amino crown-ethers,⁶⁴ pyrazolone derivative⁶⁵ have been obtained. Although inorganic supports have high mechanical strength, thermal and chemical stability, chelating sorbents based on inorganic matrix have a poor degree of functionalization and relatively low sorptive capacity.⁶⁶

Ion Exchangers Modified with Chelating Reagents

The disadvantages of chelating sorbents with grafted functional groups, determined by synthesis difficulty, such as: low reversibility of sorption-desorption processes and, sometimes, unsatisfactory kinetic features can be eliminated by »sorption« of organic reagents on ion exchangers.

In this case, the polymer matrix is represented by a conventional ionic resin that keeps its properties (porosity, swelling, granulation). The resin is equilibrated with solutions of chelate, forming reagents that must be organic molecules with a strongly dissociated, anionic (for example sulfonic) or cationic (quaternary nitrogen) group. By different analytical methods (infrared spectroscopy, potentiometric titration of released chloride) it was established that »sorption« (immobilization) of these reagents on ion-exchange resins take place by an ion-exchange mechanism, but also interactions between the exchanger matrix and condensed rings of the organic reagent has a remarkable importance.^{67,68}

Preparation and regeneration of an anion-exchange resin loaded with a chelating reagent are shown in scheme 5, where X is the functional group of chelating reagent, M-sorbed species and ...-physical interaction.



Scheme 5

Thus, several chelate forming reagents: thoron,⁶⁹ sulfosalicylic acid,⁷⁰ 8-hydroxyquinolin-5-sulfonic acid,⁷¹ Eriochrome Black T,⁷² sulfonated azo-

dyes,⁷³ bismuthiol II-sulfonic acid,⁷⁴ SPADNS,⁷⁵ pyrocatechol violet⁷⁶ have been immobilized on anionic resins.

Very recently, a new support – fibrous poly-acrylonitrile loaded during the process of forming with a fine-grained ion exchanger – which immobilizes the chelating reagents (xylenol-orange,⁷⁷ arsenazo I,⁷⁸ 1-(2-pyridylazo)-2-naphthol,⁷⁹ *p*-nitrosodiethylaniline⁸⁰) has been proposed.

Impregnated Sorbents

A simple and rapid technique of chelating sorbent preparation is based on »the mechanical impregnation« of the inert matrix with complexing reagents. For this reason, the support is treated with the solution of the complexing reagent in an organic solvent, which is then removed by filtration or evaporation. Sometimes, the inert support is utilized for direct sorption (noncovalent binding) of the metal-complexes of analytical reagent.

Among the organic materials used as support, foamed plastics and especially flexible open-cell polyurethane foams are singled out.⁸¹ Examples of chelating reagents physically immobilized on polyurethane foams are: biacetylmonooxime,⁸² dithizone,⁸³ diethylammonium-diethyldithiocarbamate,⁸⁴ 5,7-dichloro-8-hydroxyquinoline,⁸⁵ etc.

The use of nonionic polymeric adsorbents as inert matrix, for instance Amberlite XAD-2 impregnated with pyrocatechol violet⁸⁶ or 1,10-phenanthroline,⁸⁷ as well as of cellulose impregnated with β -hydroxyoximes⁸⁸ or of poly(vinylchloride) membrane containing bathophenanthroline⁸⁹ is mentioned. Metal chelates (with ammonium pyrrolidinedithiocarbamate⁹⁰ or 8-hydroxyquinoline⁹¹) have also been adsorbed on Amberlite XAD.

Chelating sorbents with 2-mercaptobenzthiazole,⁹² hydrazones,⁹³ diaza-18-crown-6 and octaethylporphyrine,⁹⁴ 1-(2-pyridylazo)-2-naphthol,⁹⁵ 8-hydroxy-quinoline⁹⁶ have been prepared by mechanical impregnation of the silica support.

PHYSICO-CHEMICAL PROPERTIES

Information about the stability of fixed functional groups and quantitative characteristics of their interaction with ions from the solutions is very useful for the optimization of the retention process of metallic cations on complexing sorbents.

Mechanical and chemical stability of chelating sorbents depends on the synthesis method and matrix nature.^{2,4,6,19} Thus, condensation polymers can undergo hydrolytic and cleavage reactions and have poor chemical and mechanical stability. Linear addition polymers are unstable in acid and alkaline medium or in the presence of organic solvents. Cross-linked polymers

with hydrophobic matrix are preferred because of their high chemical stability and mechanical strength. Also, chelating sorbents with a silica matrix have a high mechanical and thermal stability and good chemical resistance in organic solvents and mineral acids.

The sorption capacity of chelating sorbents determined by the content of immobilized functional groups is, generally, lower than that of conventional ion exchangers. It varies within sufficiently large limits ($< 0.1 \div > 1 \text{ mmol g}^{-1}$) depending on the matrix nature and synthesis conditions of the sorbent. High capacities have been found for the chelating resins prepared by polymerization or polycondensation and for polystyrene-based resins. The sorption capacity of inorganic chelating sorbents depends on the surface area of the support and is lower than that of analogous organic polymers.⁶⁶ The sorption capacity for different ions changes with the ionic strength and pH of the solution;^{97,98} pH of quantitative sorption decreases in the presence of organic solvents.⁹⁹

The acid-base properties of chelating resins are characterized by dissociation constants of functional groups (K_a). The $\text{p}K_a$ values calculated from the potentiometric titration studies for different chelating resins are in good agreement with those of the corresponding low molecular-weight analogues.⁹⁷ The smaller dissociation constants of the amino groups bonded on silica gel are explained by the interaction of fixed amino groups with residual hydroxylic groups of the surface.¹⁰⁰ Acidic properties of the 8-hydroxyquinoline groups do not change by immobilization on controlled-pore glass.¹⁰¹

Correlations between the structure of chelating resins, acid-base properties and pH of the sorption of metal ions were established.

The heterogeneous protonation equilibria of chelating resins have been studied by Liu *et al.*,^{4,102} who proposed a scheme of protonation process and a general equation of the equilibria, taking into account the electrolyte used to adjust the ionic strength.

The property of chelating sorbent to react with metallic ions under certain favourable conditions is determined by the nature of functional groups and/or donor atom (O, N, S) capable of forming chelate rings. Selectivity of suitable specific functional groups fixed into the polymeric matrix has been explained on the basis of the concept of strong and weak acids and bases.⁵ Functional groups in chelating sorbents usually act as bases: oxygen-containing functional groups have strong, sulphur-containing groups have weak and nitrogen-containing groups have an intermediate character.

Equilibria for the complex formation of chelating sorbents towards some metal ions have been studied by several authors.^{68,97,98,102-105} The series of stability for metal complexes on chelating sorbents and in solutions (in free state) are similar but the values of stability constants of complexes formed by metal ions with macromolecular and low molecular-weight functional

ligands are not completely analogous. This is caused by the polymeric structure of the matrix,¹⁰⁶ some steric and geometrical factors, interaction with polymeric matrix,¹⁰⁷ and possible modification of the sorbent monofunctionality. Sorption selectivity for cations by cyclic polyether (crown ether) carboxylic acid resins is controlled by the relationship between the crown ether and metal ion diameters.¹⁰ For the inorganic chelating sorbents, the difference in the stability of immobilized and free complexes have been explained by changes in the electrical potential of matrix surface.¹⁰⁸

Different physico-chemical methods such as potentiometric titration,¹⁰⁵ infrared spectroscopy,^{27,38,102,109} diffuse reflectance electronic spectra,^{98,110} thermogravimetry,¹⁰⁹ fluorescence spectroscopy,¹⁰⁸ *etc.*, were used to characterize chelating sorbents and their metal complexes.

In addition, in order to maintain the selectivity, a reasonable time of establishment of the sorption equilibrium is very important for the application of chelating sorbents. Kinetic characteristics of chelating sorbents depend on the nature and properties of polymeric matrix (cross-linking degree). Generally, the sorption rate is slower than that of ion exchange and is controlled either by a particle-diffusion mechanism or by a second-order chemical complexation reaction.^{111,112} Measurement of the sorption rate under the conditions of diffusion through the particle as the rate-determining process proves the effect of the functional group concentration and of the sorbent structure on its kinetic properties.

Functional groups of chelating sorbents and the formed chelates have larger dimensions than the functional groups of classical exchangers and can hinder the diffusion of ions into the centre of the sorbent particle.

The time of establishing the sorption equilibrium varies from a few minutes to hours. Polystyrene-based sorbents exhibit poor kinetic properties because of the hydrophobic nature of the matrix.

The sorbents with the best kinetic characteristics are those based on typically hydrophilic matrices, such as cellulose¹¹¹ or macroporous methacrylate copolymers.^{19,37} Also, chelating sorbents based on fibrous materials¹¹² or silica gel¹¹³ are characterized by good kinetic properties determined by the macroporous structure of the support, large surface area and total accessibility of the functional groups (without steric hindrance).

APPLICATIONS IN INORGANIC ANALYSIS

The selective sorption of certain elements in the presence of others, based on different stability of complexes formed with functional groups of the sorbents, has led to the use of these materials for selective concentration and separation of inorganic ions from different natural and industrial materials.

Choice of the effective sorbent, optimum sorption conditions (medium acidity, temperature, the presence of masking agents) and concentration techniques (batch, sorptive filter or column chromatography) is determined by the analyzed systems (volume and composition of solution, microelement content, concentration of macrocomponents), as well as by the method of determination of elements in the concentrate.

After sorptive concentration or separation, elements can be determined either directly in the sorbent phase, its decomposition residue, eluent solution after desorption, or the effluent after the solution has been passed through the sorbent. The sorptive methods of concentration with subsequent determination of elements directly in the sorbent phase, which decrease the work time and impurity sources, have gained special importance.

Examples of some chelating sorbents used for the concentration and determination of inorganic elements from various samples are shown in the Tables I–VI.

TABLE I
Concentration and separation of some microelements on chelating resins with grafted groups

	Support and functional group	Sorbed elements	Sample	Analysis method	References
1	Polycarboxylic resin with polyether units	Alkali-metal cations	aqueous solutions	IC	114
2	Polycondensation resins-8-hydroxyquinoline	Pb (II) Separations Pb (II)-Cu (II), Zn (II)	aqueous solutions	AAS	115
3	Crown ether polymer [Poly (DB-18-C-6)]	U (VI)	HCl medium	spectrophotometry	116
4	PS chromotropic acid derivative	Nb (V)	silicate rocks	spectrophotometry	20
5	»POLYORGS« (PS, PS / DVB-heterocyclic amines, amidoxime)	Ag (I), Au (III), Platinic metals	various materials	AAS AES XRF	117
6	Chelex 100 (PS/DVB-IDA)	V (V) Fe (III), Cu (II), Mn (II), Ni (II), Co (II), Cd (II)	sea water phosphoric acid	ICP-AES AAS	118 119
7	PS/DVB-picolinamide	Hg (II)	natural and waste waters	AAS	120

TABLE I Cont.

	Support and functional group	Sorbed elements	Sample	Analysis method	References
8	PS/DVB-trithiocarbonate, dithiocarbamate	Pb (II), Cu (II), Ni (II), Co (II)	aqueous solutions	AAS	18
9	PS/DVB-N-benzoyl-phenylhydroxylamine	Separation Zr (IV)-Hf (IV)	aqueous solutions	spectrophotometry	121
10	Poly (hydroxamic acid) resin	Cr (III)	multi-component mixtures	AAS	122
11	Poly (acrylamidoxime) resin	Cu (II), Co (II), Zn (II), Cd (II)	sea water	NAA, AAS	123
		U (VI)	sea water	spectrophotometry	124
12	Poly (dithiocarbamate) resin	Cd (II), Pb (II)	fresh water	AAS	125
13	Poly (vinylthiopropionamide)	Noble metals	sample solutions	ICP-AES	40
14	Poly (vinylphosphoramidic acid)	Dy (III), Ho (III), Er (III), Yb (III)	waste water	ICP-AES	126
15	Poly (vinylbenzotetraazo-1,4,8,11-cyclotetradecane)	Mg (II)	sea water	ETAAS	127
16	Vinyl polymer gel-8-hydroxyquinoline	Mn (II)	sea water	spectrophotometry	128
17	Vinyl polymer (TSK) gel-8-hydroxyquinoline	Fe (III)	aqueous solutions	chemiluminescence	129
18	Glycol methacrylate-8-hydroxyquinoline, thiol or salicyl groups	Pd (II), Cu (II)	aqueous solutions		130
19	Methacrylic acid/DVB-thioacetamide	Cu (II)	synthetic mixtures, alloy sample		131

TABLE II

Concentration and separation of some microelements on celluloses with grafted groups

	Support and functional group	Sorbed elements	Sample	Analysis method	References
1	Cellulose-aminoalkyl groups	Cu (II), Mn (II), Co (II), Ni (II)	aqueous solutions	AAS	47
2	Ethylcellulose-iminodiacetate	Co (II), Cd (II), Pb (II), U (VI), Mn (II)	natural waters	AAS ICP-AES	132
3	Cellex-P (cellulose phosphate)	Cu (II), Ni (II), Mn (II), Cd (II), Zn (II)	natural waters	AAS	133
		Separation: Au (III)-Platines	amine solutions	AAS	134
4	Cellulose phosphate	Cu (II), Pb (II)	alcoholic drinks	AAS	135
		Separation: Al (III)-Ga (III)- In (III)-Tl (III)	aqueous solutions	spectro- photometry	136
5	Spherical cellulose OSTORB DTTA (-diethylenetriaminetetra- acetate)	Separation: Cu (II)-Zn (II)-Mg (II)	solutions of aminoacids		137
6	OSTORB DTTA, OSTORB OXIN	Cu (II)	aqueous solutions	AAS	138
7	Cellulose-1-(2'-hydroxy- phenylazo)-2-naphthol (Hyphan)	Bi (III), Cd (II), Cu (II), Fe (III), Mg (II), Ni (II), Zn (II), Mn (II)	pure gallium	ICP-AES	139
		Ag (I), Au (III), Pd (II), Pt (IV)	aqueous solutions	ETAAS	140
8	Paper filter-2-hydroxy- propyliminodiacetate (EXPAPIER)	Mn (II), Fe (III), Cu (II), Zn (II), Ca (II), Sr (II)	natural waters	XRF	141

TABLE III
 Concentration and separation of some microelements on fibrous chelating sorbents with grafted groups

	Support and functional group	Sorbed ions	Sample	Analysis method	References
1	Cotton (fibres or fabrics)-sulfhydryl groups	CH_3Hg^+	natural waters	CGC	46
2	Fibrous cellulose-diethylenetriamine-tetraacetate	Heavy metals	sea water	ICP-AES	142
3	PAN fibres-acyliso thiourea	Au (III), Pd (II), Ru (III)	real samples	ICP-AES	56
4	PAN unwoven filter-amidoxime (POLYORGS-VII-M)	Cu (II), Ni (II), Zn (II), Cr (III)	waste waters	XRF	143
5	PAN fibres-mercaptobenzthiazole (Thiopan-13)	Cr (III), Ni (II), V (V), Zn (II), Cd (II), Co (II)	low mineralized waters	AES	144
6	PAN fibres-polyethylenepolyamine	Mo (VI), W (VI), V (V), As (III), Cr (III)	natural waters	AES AAS XRF	145
7	PAN fibres-amino groups	Cr (VI), Cr (III)	natural waters		146
8	PS-PAN fibres-sulfhydryl groups	Pt (IV), Pd (II), Rh (III), Ir (IV), Ru (IV)	aqueous solutions	AES	147
9	PP-PAA fibres-carboxyl groups	Bi (III), Ti (IV), Zr (IV)	acidic solutions		55

TABLE IV

Concentration and separation of some microelements on inorganic support with grafted chelating groups

	Support and functional group	Sorbed elements	Sample	Analysis method	References
1	Silica gel-8-hydroxyquinoline	Heavy metals	sea water	ICP-MS	148
2	Silica gel-propyl-hydroxamic acid, propylamidoxime	Mo (VI), W (VI)	aqueous solutions	DRS	149
3	Silica gel- γ -amino propyltriethoxysilane	Au (III), Pt (IV), Pd (II)	aqueous solutions		150
4	Silica gel-thiamacrocycles	Au (III), Pd (II)	industrial waters	ICP-AES	151
5	Silica gel-thiourea derivatives	Pd (II) Separation Pd (II)-Nonferrous	aqueous solutions	spectro-photometry	152
6	Silica gel- <i>N,N,N',N'</i> -tetra (2-aminoethyl) ethylenediamine	Co (II), Ni (II), Cu (II), Zn (II), Cd (II), Pb (II)	natural waters	spectro-photometry	153
7	Kieselgur and Silica gel-3-methyl-1-phenyl-5-pyrazolone	Cu (II), Mn (II), Cd (II), Pd (II)	aqueous solutions		65
8	CPG-ethylenediamine-tetraacetic acid	Al (III)	natural waters	AAS	154
9	CPG-5 (phenyl-azo-8-hydroxyquinoline)	Ca (II)	aqueous solutions	AAS	155

TABLE V

Concentration and determination of some microelements on ion exchangers modified with chelating reagents

	Support and chelating reagent	Sorbed elements	Sample	Analysis method	References
1	Amberlyst A-26-thoron	Fe (III)	aqueous solutions	potentiometry	156
2	Amberlyst A-27-bathocuproinedisulfonic acid	Cu (II)	natural waters	ETAAS	157
3	KU-2 x 8-Dye Basic Blue K	Pb (II)	acidic solutions	SPS	158
4	Dowex 1 x 8-4-(2-pyridylazo) resorcinol	Co (II)	beers, drugs, waters	SPS	159
5	Sephadex QAE A-25-5-bromosalicylhydroxamic acid	V (V)	petroleum crudes, waters	SPS	160
6	Paper-pyperazinium polyelectrolyte-7-iodo-8-hydroxyquinoline-5-sulfonic acid	Fe (II), Fe (III)	aqueous solutions of heavy metals	ASV	161
7	PAN fibres-KU-2-4-phenolazo-3-aminorodanine	Hg (II)	natural and waste waters	DRS	162
8	PAN fibres-KU-2-KSCN, DMG, NaDDC	Fe (III), Ni (II), Cu (II)	waters	DRS	163
9	Fabric of phosphate cellulose-1(2-pyridylazo)-2-naphtol	Co (II)	natural waters	DRS	164

TABLE VI

Concentration and determination of some microelements on inert supports impregnated with chelating reagents

	Support and chelating reagent	Sorbed elements	Sample	Analysis method	References
1	PUF-phenylhydrazide	Mo (VI)	aqueous solutions	visual colorimetry	165
2	PUF-diphenyldithiocarbazon	Hg (II)	aqueous solutions	SPS	166
3	PUF-salicylhydroxamic acid	V (V)	glass, ceramic raw materials	spectrophotometry	167
4	Non-polar PS/DVB Amberlite XAD-2-8-hydroxyquinoline	Cd (II), Cu (II), Fe (III), Mn (II), Ni (II), Zn (II)	Antarctic sea water	ICP-AES	168
		Cu (II), Co (II), Hg (II), V (V), Zn (II)	aqueous solutions	NAA	169
5	PS/DVB neutral resin xylenol orange	Zn (II), Pb (II), Ni (II), Cu (II)	coastal sea water	HPLC	170
6	XAD-type resins-8-(benzenesulfonamido)-quinoline	Zn (II), Cd (II)	very dilute solutions	fluorescence	171
7	Silica gel-1-(2-pyridylazo-2-naphtol)	Co (II)	tap water	DRS	172
8	Silasorb-aluminon	Cu (II)	food stuffs	DRS	173
9	Silica gel-aza analog of dibenzo-18-crown-6	Co (II), Zn (II), Cu (II), Ni (II)	alloys, waters	AAS	174
10	Silica gel-1-nitroso-2-naphtol	Co (II)	flow analytical systems	spectrophotometry	175

Abbreviations: AAS – atomic absorption spectrometry; AES – atomic emission spectrometry; ASV – anodic stripping voltametry; CGC – capillary gas chromatography; DRS – diffuse reflectance spectrometry; ETAAS – electrothermal atomic absorption spectrometry; HPLC – high-performance liquid chromatography; IC – ion chromatography; ICP-AES – inductively coupled plasma atomic emission spectrometry; ICP-MS – inductively coupled plasma mass spectrometry; NAA – neutron activation analysis; SPS – solid phase spectrophotometry; XRF-X – ray fluorescence; CPG – controlled – pore glass; PS – polystyrene; PUF – polyurethane foam; PAN – polyacrylonitrile; PP – polypropylene; PAA – polyacrylic acid; DMG – dimethylglyoxime; NaDDC – sodium diethyldithiocarbamate; IDA – iminodiacetic acid.

CONCLUSION

Among the techniques applied to the pre-treatment of samples, the procedures based on chelating sorbents have gained special importance in analysis of complex matrices.

New chelating sorbents – macromolecular compounds with chelating groups – have been prepared by covalent immobilization of desired groups, also by some special, noncovalent methods.

The choice of the effective sorbent in the analytical method is made taking into consideration the nature of functional group, the proper features of the support as well as the characteristics of the sample solution (its pH, metals to be removed, the presence of other cations or anions which might interfere with the process).

Applications of chelating sorbents in chemical analyses are determined by high selectivity and efficiency of the concentration of trace elements from complex samples, process simplicity and rapidity, possibility of combining with different determination methods, especially with those allowing the analysis of samples in solid state.

Preconcentration with chelating sorbents improves the sensitivity and reliability of the determination of elements in a wide variety of samples including natural and waste waters, geological, biological and industrial materials.

Chelating sorbents can play an important role in solving environmental problems, decontaminating aqueous systems and recovering toxic trace metals.

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SAŽETAK**Kelatirajući sorbensi u anorganskoj kemijskoj analizi**

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Ovaj pregledni rad odnosi se uglavnom na pripravu, određivanje svojstava i primjenu novih kelatirajućih sorbensa pri separiranju, koncentriranju i određivanju tragova metala u različitim kompliciranim uzorcima, npr. u prirodnim i otpadnim vodama, geološkim, biološkim i industrijskim materijalima, supstancijama visoke čistoće.